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Program and Abstracts

2017

Atomic, Molecular, and Optical Sciences
Research PI Meeting

Gaithersburg Marriott Washingtonian Center
Gaithersburg, Maryland
October 22–24, 2017

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
Office of Science
U.S. Department of Energy

Cover Graphics: The input for the Wordle (<http://www.wordle.net>) cover art is based on the titles of the abstracts for this year's meeting. The font is "Beryllium".

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FOREWARD

This volume summarizes the 37th annual Research Meeting of the Atomic, Molecular and Optical Sciences (AMOS) Program sponsored by the U. S. Department of Energy (DOE), Office of Basic Energy Sciences (BES), and comprises descriptions of the current research sponsored by the AMOS program. The participants of this meeting include the DOE laboratory and university principal investigators (PIs) within the BES AMOS Program. The purpose is to facilitate scientific interchange among the PIs and to promote a sense of program identity.

The BES/AMOS program is vigorous and innovative, and enjoys strong support within the Department of Energy. This is due entirely to our scientists, the outstanding research they perform, and the relevance of this research to DOE missions. The AMOS community continues to explore new scientific frontiers relevant to the DOE mission and the strategic challenges facing our nation and the world.

We are deeply indebted to the members of the scientific community who have contributed their valuable time toward the review of proposals and programs, either by mail review of grant applications, panel reviews, or on-site reviews of our multi-PI programs. These thorough and thoughtful reviews are central to the continued vitality of the AMOS program.

We are privileged to serve in the management of this research program. In performing these tasks, we learn from the achievements and share the excitement of the research of the scientists and students whose work is summarized in the abstracts published on the following pages.

Many thanks to the staff of the Oak Ridge Institute for Science and Education (ORISE), in particular Connie Lansdon and Tim Ledford, and to the Gaithersburg Marriott Washingtonian Center for assisting with the meeting. We also thank Diane Marceau and Gwen Johnson in the Chemical Sciences, Geosciences, and Biosciences Division for their indispensable behind-the-scenes efforts in support of the BES/AMOS program.

Finally, we welcome Bruce Garrett, who started as the new Director for the Chemical Sciences, Geosciences, and Biosciences Division approximately 11 months ago; Bruce will kick off the meeting on Monday morning with news from our Division.

Thomas B. Settersten
Jeffrey L. Krause
Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
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US Department of Energy

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Agenda

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2017 Atomic, Molecular and Optical Sciences Research PI Meeting

Office of Basic Energy Sciences

U. S. Department of Energy

Gaithersburg Marriott Washingtonian Center, Gaithersburg, Maryland

October 22–24, 2017

Sunday, October 22

3:00 – 6:00 pm **** Registration ****
**** Dinner (on your own) ****

Monday, October 23

7:30 am **** Breakfast (Salon A-B) ****

All presentations are in Salon C-E

8:00 am *Welcome and Introductory Remarks*
Thomas B. Settersten, AMOS Program Manager

8:10 am *BES/CSGB Update and Outlook*
Bruce C. Garrett, CSGB Division Director

Session I Chair: **Louis F. DiMauro**, Ohio State University

8:30 am *Dynamics in Complex Systems Probed by Ultrafast Inner-Shell Spectroscopy and Coherent X-Ray Diffraction*
Oliver Gessner, Lawrence Berkeley National Laboratory

9:00 am *Time-Resolved Two Color X-Ray Pump/ X-Ray Probe Photoelectron Spectroscopy*
Gilles Doumy, Argonne National Laboratory

9:30 am *Dynamics from Noisy Data with Extreme Timing Uncertainty*
Abbas Ourmazd, University of Wisconsin

10:00 am **** Break ****

Session II Chair: **Peter M. Weber**, Brown University

10:30 am *Imaging Ultrafast Molecular Motion*
Philip H. Bucksbaum, SLAC National Accelerator Laboratory

11:00 am *Nonlinear Materials Spectroscopies Probed by Ultrafast X-Ray Beams*
Keith A. Nelson, MIT

11:30 am *Monitoring and Imaging of Elementary Molecular Events by Ultrafast Nonlinear X-Ray Spectroscopy*
Shaul Mukamel, University of California, Irvine

12:00 pm ***** Lunch (Salon A-B) *****

Session III *Discussion: Opportunities in Ultrafast XFEL Science*

1:00 pm

2:30 pm ***** Free/Discussion Time *****

Session IV Chair: **Arvinder Sandhu**, University of Arizona

4:00 pm *Hard X-Ray Spectroscopy for Tracking Optically Driven Molecular Dynamics*
Anne Marie March, Argonne National Laboratory

4:30 pm *Control of Molecular Dynamics: Algorithms for Design, Analysis and Implementation*
Herschel A. Rabitz, Princeton University

5:00 pm *Imaging Ultrafast Molecular Dynamics with Coincident Momentum Spectroscopy*
Artem Rudenko, Kansas State University

5:30 pm *Bright Soft X-Ray Beams for Probing and Imaging Materials at the Nanoscale*
Jorge J. Rocca, Colorado State University

6:00 pm ***** Dinner (on your own) *****

Tuesday, October 25

7:30 am ***** Breakfast (Salon A-B) *****

Session V Chair: **Adi Natan**, SLAC National Accelerator Laboratory

8:00 am *Controlling the Polarization State of High Harmonics, and Applications in Molecular and Materials Science*
Henry C. Kapteyn, University of Colorado

8:30 am *Time-Resolved Photoemission Spectroscopy of Helium Atoms and Complex Targets*
Uwe Thumm, Kansas State University

9:00 am *Atoms and Ions Interacting with Particles and Fields*
Francis Robicheaux, Purdue University

9:30 am *Atomic and Molecular Physics in Strong Fields*
Shih-I Chu, University of Kansas

10:00 am ***** Break *****

Session VI Chair: **Kenneth Lopata**, Louisiana State University

10:30 am *Strong-Field Physics in Dense Media*
Shambhu Ghimire, SLAC National Accelerator Laboratory

11:00 am *Femtosecond and Attosecond Processes in Condensed Matter*
Mark I. Stockman, Georgia State University

11:30 am *Electron Dynamics on the Nanoscale*
Tony F. Heinz, SLAC National Accelerator Laboratory

12:00 pm ***** Lunch (Salon A-B) *****

Session VII Chair: **Guillaume M. Laurent**, Auburn University

1:00 pm *The Correlated Electronic Ionization Continuum in Molecular Attosecond Spectroscopy and High Harmonic Generation*
Robert R. Lucchese, Lawrence Berkeley National Laboratory

1:30 pm *Manipulating and Probing Ultrafast Atomic and Molecular Dynamics*
Robert R. Jones, University of Virginia

2:00 pm *Ionization-Driven Attosecond Charge Migration*
Kenneth J. Schafer, Louisiana State University

2:30 pm *Closing Remarks and Discussion*
Thomas B. Settersten, BES/DOE

3:00 pm ***** Adjourn *****

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Laboratory Research Summaries
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AMO Physics at Argonne National Laboratory

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1 Overview

The Argonne AMO physics program is focused on exploring the frontiers of x-ray physics and laying the foundation for ultrafast x-ray applications in other scientific domains. We take unique advantage of the existing and upcoming accelerator-based light sources, primarily the Advanced Photon Source (APS) Synchrotron at Argonne and the Linac Coherent Light Source (LCLS) x-ray free-electron laser (XFEL) at SLAC. Our experimental efforts are typically based on optical/x-ray and x-ray/x-ray pump/probe approaches. The experimental work is supported and complemented by theoretical developments, often taking advantage of massively parallel codes developed for the MIRA supercomputer at the Argonne Leadership Computing Facility (ALCF).

The program is structured in three subtasks that complement each other. The first subtask aims at a quantitative and predictive understanding of x-ray interactions with matter in the high-intensity limit and exploring new approaches enabled by the most intense femtosecond x-ray pulses. For the investigation of the fundamental ionization dynamics in intense x-ray pulses we are moving our focus from simple atomic and small molecular systems to larger samples with nanometer-sized dimensions. Single-shot imaging of single particles allows us to gain unique insight into non-equilibrium electronic and nuclear dynamics in nanometer-sized samples with femtosecond time and nanometer spatial resolution. Ultrafast hard x-ray scattering is used to investigate the effects of massive parallel excitation and the correlated nuclear response in small finite systems.

In the second subtask we utilize inner-shell excitations to follow the flow of energy in molecular systems. We take unique advantage of the short time structure of x-ray pulses from free-electron laser sources and explore inner-shell spectroscopy and processes in the time domain. We pursue x-ray pump approaches to create localized electronic excitations and subsequently probe them at specific sites and develop theoretical tools to describe such experiments. Further, we explore non-linear spectroscopy techniques for the new operational modes of free-electron laser sources.

The third task is focused on developing instrumentation and methods to measure electronic and geometric changes of photo-excited processes in chemically relevant systems with MHz repetition rate at the APS and future light sources. We develop new spectroscopic approaches for molecules in solution based on polychromatic excitation, increasing the measurement efficiency by orders of magnitude. Our studies include transition-metal-centered molecular complexes and nanoparticles whose photo-induced transitions are important to understand in order to develop solar fuels and other applications. We develop advanced multi pulse pump x-ray-probe techniques to measure, and ultimately guide, the complex electronic and structural dynamics of solvated molecules. In earlier work we have demonstrated that holographic optical tweezers can trap and position individual par-

ticles in solution with the stability and precision required for Bragg coherent diffraction imaging at a synchrotron beamline. In cooperation with the broad community of users of time-resolved x rays, we are contributing to plans for beamlines and end station upgrades at APS.

2 X-ray Physics at the Intensity Frontier

2.1 Fundamental processes in atoms, molecules, and clusters

P. J. Ho, C. Bostedt, L. Young, S. H. Southworth, C. Knight,¹ A. Rudenko,² D. Rolles,² , S.-K. Son,³ R. Santra³ and other collaborators

Project Scope: The unprecedented intensity of XFELs allows us to explore a new frontier of light-matter interactions. In the high-intensity x-ray regime, where the single-photon saturation fluence is exceeded, early experiments at LCLS established that multiphoton x-ray ionization via sequential single photon absorption is the dominant interaction [44] but that “hidden” inner-shell resonances [45] and the atomic environment [46] can vastly alter the inner shell ionization dynamics. We aim at an predictive understanding of the ionization dynamics in intense x-ray pulses through a combined experimental and theoretical approach.

Recent Progress: In the past year, we have furthered our understanding of intense x-ray interactions with matter in increasingly complex systems, moving our focus from atoms to molecules and clusters. We have developed a Monte-Carlo rate equation (MCRE) approach [1], which systematically incorporates bound-bound resonances to model multiphoton ionization dynamics induced by high-fluence, high-intensity XFEL pulses. We showed that these resonances are responsible for ionization far beyond the sequential single photon absorption limit and are central to a quantitative understanding of atomic ionization dynamics in XFEL pulses. We have investigated multiphoton ionization dynamics for Kr and Xe atoms in XFEL pulses for a variety of conditions and compared as well as quantified the effects of bandwidth, pulse duration, pulse fluence and photon energy [1]. This comprehensive computational investigation reveals that resonant transitions can be critically important, and the resulting ionization dynamics with narrow and broadband x-ray pulses can be drastically different.

Recent experiments in the hard x-ray regime, in collaboration with the group at Kansas State University, showed that the femtosecond response of small polyatomic molecules containing an heavy atom can lead to extreme molecular charging [15]. The ionization of a molecule is considerably enhanced compared to that of an individual heavy atom with the same absorption cross-section. This enhancement is driven by ultrafast charge transfer within the molecule, which refills the core holes that are created in the heavy atom, providing further electrons for inner-shell ionization and resulting in the emission of more than 50 electrons during the X-ray pulse. Our results demonstrate that efficient modelling of X-ray-driven processes in complex systems at ultrahigh intensities is feasible.

The response of x-ray induced dynamics of atoms in clusters is drastically different from those in isolated atoms and small molecules. The nanometer sized systems exhibit a much richer and more complex dynamics, in which electron trapping, collective charge transfer processes and electron-ion recombination as well as secondary ionization play an important role. To describe these systems theoretically, we added to our comprehensive atomic codes [1, 48] classical molecular dynamics (MC/MD) methods allowing us to track electron and ion dynamics over on ultrafast timescales in complex systems[14]. In a recent study we investigated the inner-shell fluorescence emission of isolated Ar atoms and Ar atoms in the cluster environment, see Fig. 1.

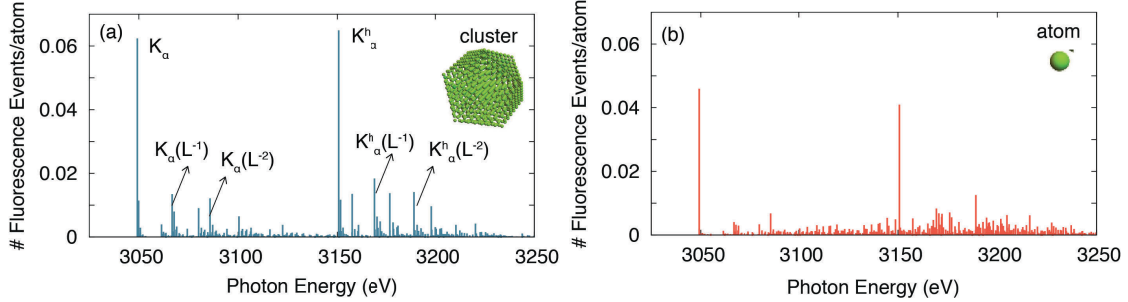


Figure 1: Fluorescence spectrum of an Ar cluster (left) and isolated Ar atoms exposed to an intense 2-fs, 5-keV x-ray pulse with 10^{12} photons/ μm^2 [14]. The cluster spectrum exhibits a much richer structure due to additional recombination processes.

We found that the Ar cluster fluorescence spectrum in the high-intensity pulse (10^{22} W/cm²) is very different from the Ar atom spectrum, as shown in Fig. 1. Most notably, the Ar cluster spectrum depicts stronger fluorescence lines for K_α and K_α^h . Moreover, their satellites ($K_\alpha(L^{-1})$, $K_\alpha^h(L^{-1})$ and others), which are negligible in the atomic spectrum, become very pronounced in the Ar cluster spectrum. Our analysis shows that recombination processes are an important contribution to these fluorescence features, in which recombination processes enable additional pathways to reach the required electronic configurations for fluorescence transitions.

Future Plans: An ongoing effort is to use our MC/MD method to study intense x-ray induced dynamics of homogeneous as well as heterogeneous clusters with larger sizes and heavier (Xe) elements under realistic experimental pulse conditions. Xe is of particular interest as it has been the system of choice for ultrafast x-ray scattering experiments. However, it is difficult to model due to the many involved electronic states and possible transitions. Further, we plan to explore the foundation of ultrafast imaging of catalytic relevant nanoparticles and core-shell systems. Understanding x-ray induced electron and nuclear dynamics in these heterogeneous particles is important as they typically contain mixtures of high- and low-Z elements. Therefore these particles have inherent localized x-ray ionization hot spots.

2.2 Ultrafast imaging of clusters and nanoparticles

M. Bucher, P. J. Ho, G. Doumy, A. Al-Haddad, L. Young, C. Bostedt, T. Gorkhover,⁴ O. Gessner,⁵ A. Vilesov,⁶ T. Fennel,⁷ A. Rudenko,² M. Kling,⁸ D. Rupp,⁹ T. Möller,⁹ J. Hajdu,¹⁰ F. Maja,¹⁰ and other collaborators

Project Scope: Single-shot imaging with intense x-ray pulses from XFELs opens the opportunity to probe the non-equilibrium electronic and nuclear dynamics in nanometer-sized samples with femtosecond time and nanometer spatial resolution. We combine experiments and theory to investigate the correlation between x-ray ionization and ultrafast imaging with single-pulse, optical pump / x-ray probe as well as x-ray pump / x-ray probe approaches.

Recent Progress: Over the past years we have developed experimental methods for ultrafast imaging as well as coincident imaging and spectroscopy of nanometer-sized clusters [12, 49, 50] and superfluid helium droplets [2, 10, 16, 47]. We have performed the first femtosecond time-resolved

coherent x-ray diffractive imaging experiment at LCLS, following the evolution of individual xenon clusters with 15-30 nm radii after exposure to near-infrared laser pump pulses [6]. Here we found that the clusters expand starting with the outer layers akin to a surface melt-off that leaves a distinct finger print in the diffraction pattern. These experiments were followed by imaging the ignition and expansion of doped helium droplets in intense optical fields which revealed interesting anisotropic droplet expansion on long time scales.

A novel x-ray pump x-ray probe scheme was used to investigate charge transfer processes in heavily doped He nanodroplets [51]. Such systems are of interest to potentially control the x-ray induced electronic and structural damage during ultrafast x-ray imaging. The idea is to embed the sample in a sacrificial layers, e.g. a He droplet, that can replenish the sample with electrons and suppress Coulombic expansion. We used superfluid He droplets as a host matrix for Xe clusters in order to investigate ultrafast charge transfer processes from the strongly absorbing Xe core to the He shell. The ultrafast scattering information from these systems indicated a rapid charge transfer from the He shell to the strongly x-ray absorbing Xe core structure. For Xe clusters embedded in He droplets the x-ray contrast from the core was maintained over a long delay window up to 900 femtoseconds indicating strongly reduced x-ray radiation damage. Simultaneously recorded time-of-flight ion spectra showed a delay-dependent kinetic energy release from the shell ions supporting the hypothesis of efficient charge transfer mechanisms inside the nanoplasma.

The experimental efforts were complemented by our Monte-Carlo/Molecular Dynamics calculations to understand the x-ray induced dynamics and ultimate limitations in the ultrafast imaging process. In a follow-up study we focused on the effect of non-resonant and resonant excitations of sucrose clusters in the water window and compared the results with experimental data by performing large scale MC/MD calculations with systems up to 216,000 sucrose molecules and for a range of relevant pulse parameters on Mira. We found that there is an important role of resonant excitation (RE) in the molecular scattering response in the water window as shown in Fig. 2. In particular, $1s \rightarrow 2p$ RE cycling enabled in the oxygen atom/ion provide additional ionization pathways which lead to substantial reduction in scattering power of sugar clusters for photon energies just below the oxygen K-edge.

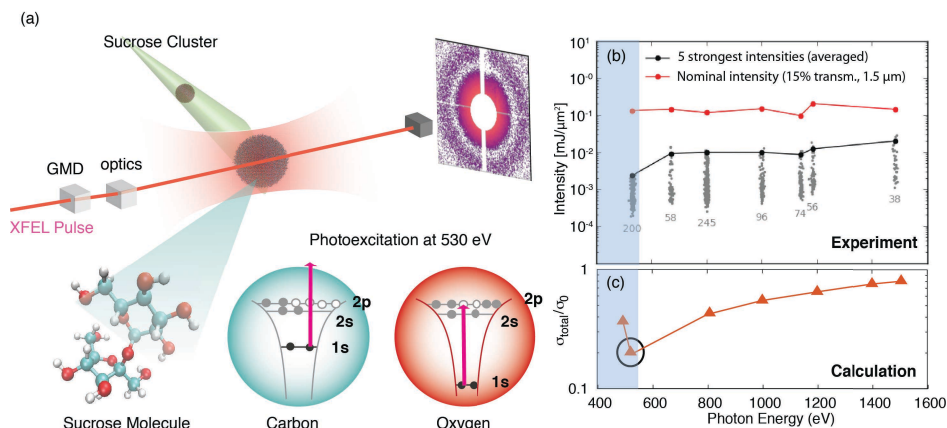


Figure 2: (a) XFEL single-particle imaging of sucrose cluster. (b) Experimental measured signal with cluster diameters in the range of 40 to 50 nm. (c) Calculated scattering signals for 50-nm sucrose cluster. The shaded area indicates the water window. At 530 eV, direct one-photon K-shell ionization in oxygen atom is energetically forbidden.

The theoretical work underlines the importance of electronic structure and transitions on the

ultrafast imaging process. In a complementary experimental study on electronic redistribution during the imaging process we recorded scattering images of xenon clusters with intense extreme ultraviolet radiation in the vicinity of the Xe 4d ionization threshold. The data showed the emergence of a transient electronic core-shell structure within the otherwise homogeneous sample. In the future such resonant scattering approaches may enable imaging of ultrafast electron dynamics on their natural time scale.

Another set of experiments is aimed at maintaining phase information in imaging experiments. A common problem in imaging is that the phase information is lost during the measurement. Iterative phasing can reconstruct objects from their diffraction patterns alone, but it requires solving a non-convex high-dimensional minimization. Holography provides a way to immediately obtain an image of the sample. This imaging could subsequently also be used as the starting point for the iterative algorithm. We developed a method to obtain in-flight X-ray Fourier holograms of biological test particles using single Xe clusters as reference scatterers in the gas phase. Our experiments showed that we could recover asymmetric shape projections via a simple two-dimensional inverse Fourier transformation. Our new in-flight holography method has the potential to significantly reduce the complexity of structure determination and can be used as a tool for single shot imaging of nanometer-sized objects in the gas phase.

Future Plans: Our ongoing and future efforts are targeted at understanding the x-ray induced electron dynamics during the ultrafast imaging process. Experimentally we will investigate the resonant and non-resonant imaging process on time scales of the Auger decay. Theoretically we will continue to develop and use our Monte-Carlo/Molecular Dynamics calculations to study the correlation between atomic ionization, electronic resonances, and the imaging process and expand these efforts to collective effects such as charge migration in core-shell systems.

2.3 Ultrafast scattering with atomic resolution

P. J. Ho, M. Bucher, Y. Kumagai, L. Young, C. Bostedt, C. Knight,¹ M. Tegze,¹¹ G. Faigel,¹¹ K. Nagaya,¹² H. Fukuzawa,¹³ K. Ueda¹³ and other collaborators

Project Scope: Ultrafast hard x-ray scattering yields information about the atomic structure with Ångstrom resolution, in contrast to imaging approaches that yield information about the particle shape and envelope. We have pioneered hard x-ray scattering experiments with nanometer-sized atomic clusters. Our interest in these studies are the impact of ultrafast parallel ionization on the nuclear dynamics and attainable resolution from single-shot experiments in the highest intensity regime.

Recent Progress: Electronic excitation is closely coupled to nuclear response and structural changes. For any sample in strong fields, the ionization and electron redistribution within the sample leads to strong changes in its interatomic potential energy landscape. In finite, nanoscale systems these sudden changes can lead to a strong structural response that is competing with the nanoparticle expansion and disintegration dynamics. The internal atomic arrangement of small nanoparticles can be investigated with few femtosecond, hard x-ray bursts from XFELs with Ångstrom resolution. In a first x-ray pump/x-ray probe experiment, single large van der Waals clusters were isochorically heated to a massively ionized state with an intense 10-fs x-ray pump pulse and the structural evolution of the sample was probed with a second x-ray pulse [7]. The data showed systematic contraction of the cluster within 80 fs and indications for rapid electronic damage within 10 fs after the pump pulse. The unexpected and fast compression of the cluster is currently not understood

and so far attributed to the massive electronic excitation inducing a collective change in bond character. This process is thought to lead to an x-ray induced “metallization” of the van-der-Waals cluster resulting in a transient bond contraction prior to Coulomb expansion.

In order to gain insight into the surprising cluster compression upon massive parallel ionization, we are complementing the x-ray pump / x-ray probe experiments with optical laser pump approaches. In contrast to x-ray ionization, strong optical fields couple to the electrons in the outer valence levels. Tuning the laser intensity allows us to control the degree of ionization and electron mobility in the cluster, yielding deeper insight into the light induced nuclear disorder as well as transient bond contraction mechanism in strongly excited nanoscale systems.

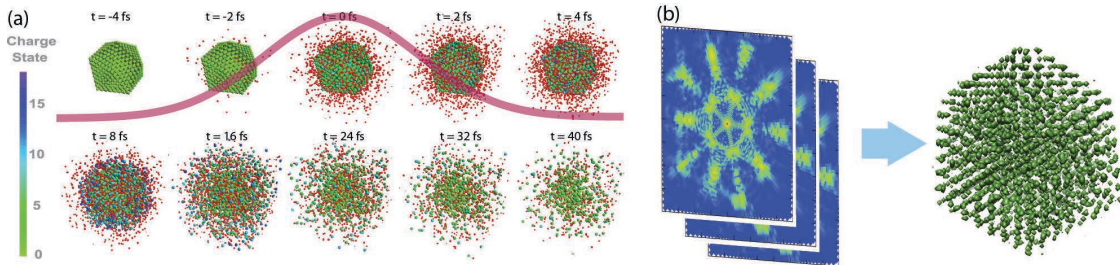


Figure 3: (a) An intense 2-fs XFEL pulse with 10^{14} photons/ μm^2 transforms the exposed Ar cluster into a highly excited and dynamically changing transient, including nuclear motion in femtoseconds. (b) The obtained diffraction patterns are used to successfully reconstruct the cluster structure with resolution reaching 2\AA .

Theoretically we address the possibility of 3D-imaging of inorganic nanoclusters with atomic resolution with our MC/MD method [13] using Ar clusters as prototypes. The goal is to understand the required pulse parameters and x-ray intensities for such experiments. We found that including both, the electron and nuclear dynamics is critical even on the femtosecond level because the timescale of nuclear motion is comparable to the x-ray pulse duration in a highly ionized cluster (c.f. Fig. 3). Phase retrieval analysis of the scattering patterns showed that recovery of the original structure is possible with 3\AA resolution for particles of 11-nm diameter (Fig. 3) despite the presence of the backgrounds from both the Compton and free-electron scattering.

Future Plans: We aim at clarifying the impact of massively parallel ionization and the nuclear response in nanometer sized samples. For that purpose we advance our experimental approaches in optical/x-ray as well as x-ray/x-ray pump/probe techniques with the goal of obtaining single-particle pre-pump and probe information. The previous experiments only recorded the probe information. Simultaneously we expand our theoretical efforts to include changes in the overall potential energy landscape upon x-ray ionization in order to investigate the relationship between massive ionization and lattice response in and to predict pulse conditions for obtaining atomic resolution in small, nanometer-sized systems.

3 Ultrafast Inner-Shell Induced Molecular Dynamics

3.1 Time-resolved innershell spectroscopy

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Project Scope: Inner-shell spectroscopy yields element and even site specific electronic information. Exploring inner-shell processes in the time domain allows us to follow electronic excitations, or more generally the flow of energy, over a molecule. We pursue x-ray/x-ray pump/probe approaches to create localized electronic excitations and subsequently probe them at specific sites. We develop theoretical tools to describe and interpret the experiments. These efforts are complemented by optical/x-ray pump/probe experiments.

Recent Progress: Our first experiments utilized ion spectroscopy to study the x-ray induced fragmentation of XeF₂ molecules [20]. Here, an x-ray photon from the pump pulse was absorbed by a Xe 3d electron and triggered a decay process in which several Auger electrons were ejected, and the molecule dissociated into atomic Xe and F ions. After a delay between 4-54 fs, an x-ray photon from the probe pulse was absorbed by one of the emerging F ions and increased its charge state. The separated ions were detected in coincidence with an ion momentum imaging spectrometer and the pathways leading to fragmentation products were identified. A theoretical model was developed to describe the ionization and fragmentation mechanisms.

Building on the first experiments we also investigated the ionization and fragmentation dynamics of N₂ molecules [21]. Compared to XeF₂, N₂ has a simpler electronic structure and is more accessible for theoretical modeling. The first x-ray photon produces a core-hole state that dominantly decays by an Auger process leaving two holes in the valence shell. A manifold of two-hole states of N₂²⁺ are produced, out of which some are dissociative (leading to N⁺-N⁺ separated ions) while others are quasibound (producing long-lived N₂²⁺ ions). While the nuclear wave packets evolve on the N₂²⁺ potential curves, an x-ray photon from the probe pulse is absorbed and projects the ions onto the N⁺-N³⁺ breakup channel. With our quantum mechanical model accounting for K-shell ionization, Auger decay, and the time evolution of the nuclear wave packets, we could explain the time-dependent features in the measured kinetic energy release distributions from the dissociative states and the contributions of quasibound states.

A focal point of our efforts during the past year was the development of time-resolved photoemission techniques utilizing the x-ray/x-ray pump/probe approach. Photoemission responds instantly to changes in the electronic environment as compared to Auger, fluorescence, and ion spectroscopies that are all ultimately limited by the core-hole lifetime. Our first experiments were targeted at investigating the electronic to nuclear relaxation in CO, a simple hetero-nuclear molecule. The pump pulse was tuned to resonantly excite the O 1s electron and trigger Auger decay and dissociation of the molecular ion. The second pulse dominantly photoionized the C 1s electron and its energy spectrum was recorded as a function of time delay. The time-dependent energy shifts in C 1s spectrum are sensitive to the transient chemical environment and yield information about the time evolution of the core-excited molecule.

In support of the experiments we developed a time-dependent Schrödinger equation approach for molecular core-hole dynamics [27]. With our formalism we can follow electronic relaxation during Auger decay and nuclear relaxation processes on their natural femtosecond time scales. Our theoretical time-dependent approach is flexible but also fully integrated in a quantum chemistry code in order to calculate the required electronic and nuclear properties. We will be able to calculate

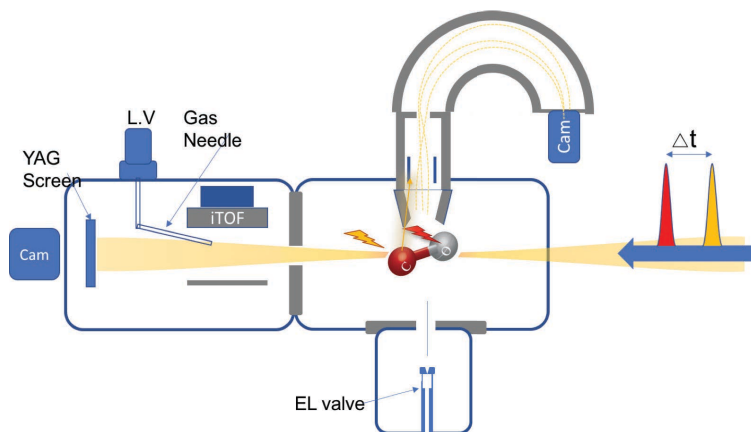


Figure 4: Schematic of the time-resolved photoemission experiment.

the continuum orbitals and the corresponding transition elements involving those orbitals, such as Auger or photoionization transitions, as we have already demonstrated for the atomic case [23].

Complementing our x-ray/x-ray pump/probe efforts we have participated in *K*-edge absorption spectroscopy to study the $\pi\pi^*/n\pi^*$ internal conversion of optically excited chromophores [25] and utilized Auger spectroscopy to observe ultrafast x-ray induced fragmentation processes [26].

Future Plans: We are actively pursuing the time-resolved photoelectron and Auger-electron emission approach at free-electron laser sources. In addition to analyzing the recent data, we are developing ideas to use the x-ray/x-ray pump/probe approach in complex molecular systems, such as metallo-porphyrin complexes, to investigate charge dynamics over the whole complex as a function of chemical bridging. Future free-electron laser capabilities with higher repetition rates and shorter pulses will allow us to investigate charge migration, transfer, and separation processes with unprecedented time and spatial (site-specific) resolution.

3.2 Site-selective photochemistry of core-excited molecules / Electron ion coincidence studies

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Project Scope: Earlier work in our group investigated the femtosecond molecular response to site-specific inner-shell excitation in simple diatomic systems with x-ray pump/x-ray probe techniques. Here we extend this theme to more complex molecules, where an initially localized inner-shell hole can be created in several distinct chemical environments.

Recent Progress: For low *Z*-elements the decay of the hole is dominated by Auger decay to form two valence holes, which may remain localized and lead to preferential bond breakage around the initial hole site. For non-resonant excitation, the degree of selectivity is governed by the competition between double hole transfer and Coulomb explosion, the former of which can be induced on femtosecond timescales by small nuclear displacements [52]. Site selective photochemistry was first observed in early synchrotron radiation studies [53], where excitation into near-edge resonance features was shown to create fragmentation localized to the atom initially excited. Subsequent

studies using non-resonant excitation to investigate elemental specificity highlighted the key role of internal energy in small molecules [54]. Site-specificity in larger molecules with more than one atom of a given element has also been investigated, but due to the complexity of the structure of accessible electronic states in the two-hole states, fully *ab initio* treatments are not feasible, and the majority of such studies are purely observational. A recent theoretical treatment assumes relaxation to the ground electronic state of the two-valence hole configuration and statistical equilibration of the internal energy prior to fragmentation and reproduces experimental findings, but does not examine initial site-localization effects [55].

We studied these phenomena in the textbook ESCA molecule, ethyl-trifluoroacetate ($\text{CF}_3\text{-CO-O-CH}_2\text{-CH}_3$), where the four different carbon sites differ in binding energy by approximately 10 eV and are easily distinguishable with the notion that a predictive understanding of the dynamics could be obtained. Using the PLEIADES beamline at SOLEIL (10-1000 eV, 20000-100000 resolving power, complete polarization control) equipped with an electron-ion coincidence spectrometer (EPICEA) we measured photoelectron-photoion-photoion coincidences (PEPIPICO) at a photon energy of 411 eV to isolate the ion fragmentation pattern resulting from an initially localized core excitation. Our experiments reveal a subtle carbon-site selectivity, and also an interesting dominant dissociation mechanism, i.e. Coulomb explosion of cations from the ends, CF_3^+ and C_2H_5^+ leaving a relatively momentum-free neutral CO_2 . The mechanism was uncovered through Dalitz plots of the ion momenta, obtained through position-sensitive ion detection with pulsed extraction grids.

We also developed a simple model for non-statistical behavior that can predict both the unusual fragmentation channels as well as the subtle site selectivity. The model is based on a bond-order analysis including all double-valence-hole states, (which number over 700 including both singlets and triplets). The analysis shows that Auger decay populates valence holes broadly distributed over the entire molecule and qualitatively explains the small site-specific trends. This theoretical approach may present a route to efficient modeling of x-ray photofragmentation.

Future Plans: Armed with the knowledge of the dominant dissociation mechanism in this interesting system, it may be possible to use the time-resolved photoelectron emission approach to investigate charge migration, transfer, and separation processes with the requisite time and spatial (site-specific) resolution.

3.3 New approaches for non-linear x-ray spectroscopy

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Project Scope: New operational modes of free electron lasers, ranging from fully coherent pulses in the vacuum ultraviolet spectral regime to sub-Auger lifetime pulses in the soft x-ray regime, will allow transferring non-linear spectroscopy techniques from the optical to the short wavelength regime. We pursue novel spectroscopy approaches involving inner-shell electrons.

Recent Progress: We explored coherent control techniques involving inner-shell levels theoretically. We proposed a scheme to transfer some of the coherent control techniques to the x-ray regime and performed stimulated Raman adiabatic passage (STIRAP) predictions involving inner-hole excited states [18]. Considering the recent developments at the fully seeded FERMI FEL, significantly increasing the quality of the pulse temporal coherence, we expanded our theoretical approach for STIRAP to the vacuum ultraviolet regime. Using the 4d core-hole state in Xe, we

used a three-level system in which $|i\rangle$ is the ground state of Xe atom, $|e\rangle$ is the core-hole state $4d^{-1}6p$, and $|f\rangle$ is the excited final state $5p^56p$. Preliminary calculations show that a maximum transfer of 6% is possible to reach with the experimental conditions at FERMI, which is a significant and experimentally measurable effect.

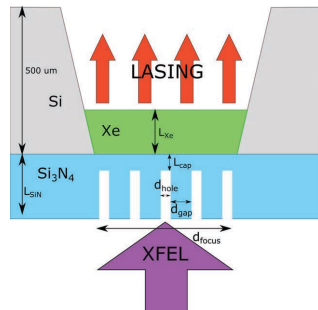


Figure 5: Schematic of sample substrate for stimulated emission experiments developed in collaboration with the Center for Nanomaterials at Argonne. The substrate allows controlled deposition of Xenon films and simultaneously acts as a photon mask.

For novel non-linear x-ray spectroscopy approaches, understanding stimulated emission processes is essential [22]. Early experiments demonstrated stimulated emission for atoms in the gas-phase but in order to develop the approach into a spectroscopic technique the influence of neighboring atoms to the process must be understood. Motivated by that question we investigated stimulated emission from atoms in the gas phase, clusters, and thin solid films with the same optical density. However, going from the gas to any type of condensed phase also implies that the pump geometry is changing from a long excited channel defined by the x-ray beam in the thin medium towards a disc defined by the focal size and absorption length. In collaboration with the Center for Nanomaterials at Argonne, we developed a nanostructured sample support shown in Fig. 5 that allows us to retain the necessary excited channel geometry for forward emission even for condensed samples.

Any non-linear process is highly dependent on the temporal and spectral properties of the x-ray pulses. Ever improving accelerator modes allow manipulation of such characteristics of x-ray pulses at free-electron lasers. However, while accelerator parameters are adjusted to tune the electron bunch phase-space and advanced electron bunch diagnostics exist and electron bunch analysis is rapidly improving [28], the final impact of the electron bunch structure on the x-ray pulse cannot be predicted with sufficient precision. Furthermore, shot-to-shot instabilities cannot be fully suppressed. Therefore, advanced our capabilities for single shot x-ray pulse characterization. We were able to resolve x-ray pulse pairs and characterized them on a single-shot basis with femtosecond resolution through time-resolved photoelectron streaking spectroscopy.

Future Plans: We will use the new attosecond soft X-ray pulses made possible by XLEAP to perform site-specific excitation and observation of electronic rearrangement and relaxation in molecular systems. We will further continue to explore stimulated emission processes and extend this work to stimulated x-ray Raman investigations.

4 X-ray Probes of Photo-excited Dynamics in Solution

4.1 Towards efficient time-resolved x-ray emission spectroscopy using pink beam at the APS

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Scope: Our aim is to extend our high-repetition-rate laser pump/ x-ray probe techniques by taking advantage of the large flux available in the polychromatic output of a synchrotron undulator for time-resolved, non-resonant x-ray emission spectroscopy. By increasing the experimental output by two orders of magnitude, much better sensitivity for core-to-core emission can be achieved, and the chemically sensitive valence-to-core region becomes practical.

Recent Progress: X-ray emission spectroscopy (XES) probes occupied orbitals (core or valence) through radiative decay to inner-shell holes. In non-resonant XES, the incident energy of the x-ray photon responsible for hole creation is not critical, provided it is above the ionization energy (above the absorption edge). Therefore, using the full polychromatic beam from an undulator source (so-called pink beam) instead of monochromatic beam is a potential route to dramatically increase the XES signal. In practice, several additional parameters come into play, especially when desiring to perform time-resolved measurements following light excitation. First, there is a lot of average power in the pink beam, which means that the target must be refreshed often. Second, while the x-ray photon energy only need be above the edge, high harmonics of the fundamental radiation of an undulator present far smaller absorption cross section, and thus participate mostly as a source of elastic scattering background. Finally, in order to use MHz repetition rate lasers for efficient excitation, it is necessary to focus the laser spot, and thus the x-ray spot, down to $\approx 15\mu\text{m}$.

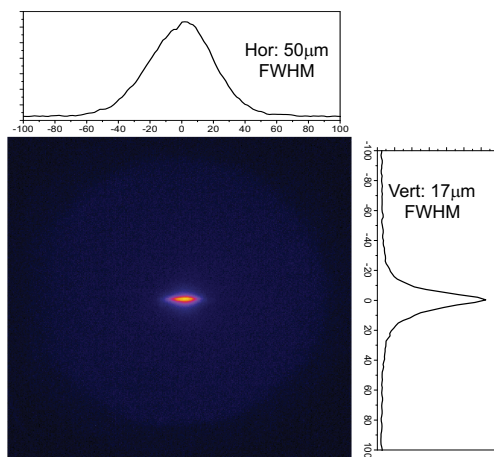


Figure 6: Focused x-ray spot using CRLs at 7ID-B. The elliptical shape is reflective of the source size in current third generation synchrotrons. One can also detect the unfocused higher harmonic remnants in the circular pedestal due to the entrance pinhole in front of the CRLs.

We have developed at Sector 7 of the APS the capability to sort the fundamental harmonic using a harmonic rejection mirror, and to focus the resulting beam using beryllium Compound Refractive Lenses (CRLs). Harmonic selection is performed using a high quality 150 mm rhodium-coated silicon mirror developed in collaboration with the APS Optics group. Because of the significant heat

load from the full undulator beam, this mirror is actively water cooled and housed in a compact vacuum. Careful testing indicated that there is no observable bending of the mirror surface under high load. In a similar way, because the transmissive Be CRLs absorb some radiation, it is necessary to cool the lens stack and a fully motorized and water-cooled Be CRLs mount was adapted. For optical characterization of the microfocus spot size we implemented a scintillator/camera assembly capable of imaging the focus under full beam load. Fig. 6 presents results obtained at optimum focus for the design distance. In parallel to the experimental efforts we used ray tracing techniques (McXtrace) including the properties of the undulator radiation at the APS (XOP software). Comparison between simulations and experimental data showed very good agreement, albeit at a slightly different photon energy which can be attributed to an offset in the undulator calibration. The obtained focal spot sizes in horizontal and vertical directions are perfectly compatible with high-repetition-rate laser excitation, and fast refreshment of the sample between laser or even x-ray pulses by using a fast, microliquid jet that we have previously implemented.

Using the focused pink beam and a reference solution of $[\text{Fe}(\text{CN})_6]^{4-}$ flowed through the liquid jet, we measured $K\alpha$ and $K\beta$ spectra using a dispersive XES spectrometer in the von Hamos geometry in order to verify the final efficiency of the setup regarding XES detection. The expected two orders of magnitude improvement in data collection was obtained.

Future Plans: Following our very successful first steps in handling the high power pink beam, microfocusing it down to spot sizes compatible with MHz laser excitation with full sample refreshment between shots and using it to collect high quality static XES spectra from our liquid jet target, we are ready to fully implement our system into a time-resolved measurement. Using reference samples such as $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, a beamtime this fall will allow us to fully establish the setup and evaluate its sensitivity (i.e. smallest useable concentration, smallest transient strength measurable).

4.2 Pump-probe x-ray spectroscopy utilizing multiple optical laser pulses

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Scope: Hard x-ray spectroscopies are powerful tools for tracking photophysical and photochemical reactions in solution environments. Challenges for these techniques include the isolation and identification of signal from transient photoproducts, particularly when multiple photoproducts, and or sample degradation due to x-ray exposure or laser exposure over the course of the measurement are present. The vast majority of laser-pump, x-ray-probe experiments have used one transform limited laser pulse to pump a sample and initiate a reaction. We are exploring the use of more complex laser pulse schemes to tackle the aforementioned challenges. These include a laser-pump, laser-repump, x-ray probe scheme to tweak the outcome of the reaction and facilitate signal separation and a laser-pump, x-ray-probe, laser-probe scheme to simultaneously collect x-ray and optical transient spectra, enabling one to monitor sample damage but also to obtain complementary information.

Recent Progress: To explore these schemes we studied $[\text{Fe}(\text{CN})_6]^{4-}$ in a water solution. When excited with 355 nm light, $[\text{Fe}(\text{CN})_6]^{4-}$ is known to undergo a ligand substitution reaction with the solvent [56]. A CN^- is detached and subsequently replaced by a water molecule resulting in the photoaquated product $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$. Our single pump measurements of this complex revealed that at moderate laser intensities ($\sim 10^{10}$ W/cm²), signatures of an additional photoproduct appear, most prominently as the appearance of a new pre-edge resonance. The intensity of the new pre-

edge peak has a nonlinear dependence on the pump laser fluence so we therefore speculate that the photoproduct is produced through a multiphoton absorption process that takes place during the course of the 10 ps long pump laser pulse, either through a simultaneously-absorbed-two-photon process from the ground state $[\text{Fe}(\text{CN})_6]^{4-}$ molecule or through a sequential absorption process where one photon yields the photoaquated product that then absorbs another photon. We implemented a laser-pump, laser-repump, x-ray-probe scheme where the two laser pulses, both at 355 nm, had a combined intensity sufficient to produce the multiphoton product but insufficient intensity when alone. By scanning the delay of the pulses relative to each other and monitoring the pre-edge peak we investigated whether the product was formed through a simultaneous or sequential process.

We used aqueous $[\text{Fe}(\text{CN})_6]^{4-}$ to study the laser-pump, x-ray-probe, laser-probe scheme as well. Simultaneous measurement of transient x-ray and optical spectra is of high importance for many interesting photoinduced solution phase reactions. These include those involving samples that are difficult to synthesize in large quantities and that also undergo x-ray/laser damage or produce irreversible photoproducts during the course of the measurement. It is also important for samples that vary considerably from one synthesis batch to another, such as is common for samples involving nanoparticles. For our first test of this scheme we used a (low intensity) 355 nm pump pulse to excite $[\text{Fe}(\text{CN})_6]^{4-}$ and initiate the photoaquation reaction, a time-delayed x-ray pulse to capture the photoaquated product, and a laser-pulse, concurrent with the x-ray pulse, that was tuned to the absorption peak of the photoaquated product (450nm [56]). We established that our optical probe tracked the population of photoaquated product as measured by the x-rays. Since the optical absorption spectrum of $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ is known, we anticipate being able to use the optical probe measurement to quantify the excited state fraction, which will aid our interpretation of the pump, repump, probe results.

Future Plans: We will continue analysis of the $[\text{Fe}(\text{CN})_6]^{4-}$ measurements. Additionally, we will expand our optical transient absorption measurement capabilities to accommodate a high-repetition-rate white-light optical probe. During the course of our measurements on $[\text{Fe}(\text{CN})_6]^{4-}$ we discovered sensitivity to dynamics occurring on timescales shorter than the x-ray pulse duration. This is achieved by temporally scanning the shorter-duration laser pulse inside the envelope of the x-ray pulse. This “time-slicing” technique has been introduced in x-ray scattering measurements [57]. We plan to develop this technique for x-ray spectroscopy.

4.3 Probing transient molecular dynamics in solution

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Scope: Using our constantly improving setup at Sector 7 of the APS, our group has been exploring molecular dynamics following light excitation with ≈ 100 ps resolution using multiple x-ray spectroscopy techniques. The combination of x-ray microprobe with MHz repetition rate lasers, alongside efficient signal collection allows for detecting very small signals, and for quick data acquisition. This is essential to be able to capture several excitation conditions or to compare several systems together. Collaborating with several external groups, problems like identifying the electronic and geometric structure of a transient, excited product[30, 43], and following ligand exchange, a ubiquitous phenomenon in photochemistry, have been successfully studied.

Recent Progress: During this last year, in collaboration with groups from the European XFEL and the Hungarian Academy of Sciences, we have concluded our first demonstration of a complete study using absorption and emission spectroscopy [42], including the transient Valence-to-Core signal, of the high-spin excited state of a spin crossover sample, $[\text{Fe}(\text{terpy})_2]^{2+}$, represented in Fig. 7. The vtc-XES of the transient HS state is found to be reduced in intensity and shifted slightly to higher energy. DFT calculations capture the experimental spectral changes well. The intensity reduction is understood to be a result of the expansion of the Feligand bonds; photoexcitation leads to population of antibonding orbitals which causes elongation of the Feligand bonds, loss of Fe-ligand orbital overlap, and therefore reduction of the Fe p MO character that contributes to the vtc emission lines. The energy shift is also expected from the bond elongation; the blue shift indicates a destabilization of the probed MOs, a result of the diminished orbital overlap. Additionally, calculations reveal that newly populated MOs in the HS state contribute to the high energy side of the $\text{K}_{2,5}$ vtc peak. Fine features of the transient spectrum were difficult to resolve in that measurement, which justifies the current effort described above to greatly increase the feasibility of such spectroscopic studies by using pink beam radiation.

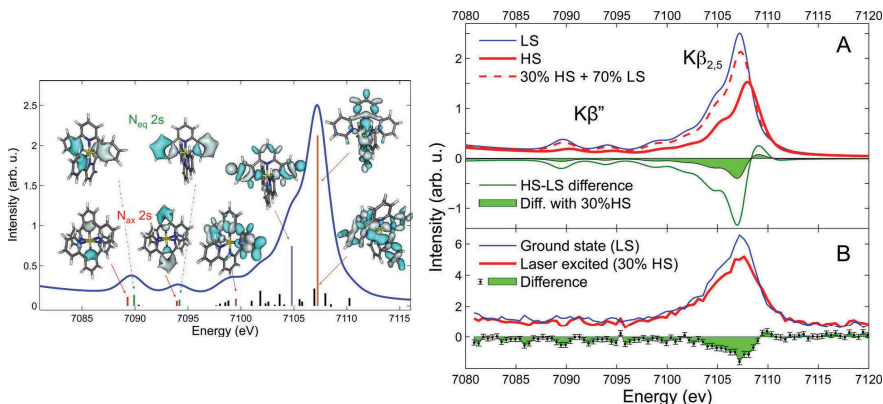


Figure 7: Left: Calculated ground state VTC-XES spectrum, with major orbitals involved represented. Right: Comparison between the calculated and experimental difference signal after laser excitation to the High Spin state. Figure adapted from Ref [42]

In collaboration with a group from SLAC, we have started the study of a class of nickel-based photocatalysts for hydrogen evolution. Those catalysts are hypothesized to vary significantly in how the ligands are involved, or not, in the catalytic process, enabling multiple reduction events to lead to H_2 production. The situation could vary from a ligand that is basically only spectator, to a ligand where both electrons and protons involved during the catalytic process become localized. While these systems have been shown to produce hydrogen upon reduction by a photosensitizer, neither the first nor the second purported intermediate states have been isolated/measured experimentally, such that their oxidation/protonation state is unknown. The Ni-based catalysts absorb light in the UV, which allows for the study of direct excitation. Alternatively, a chromophore can be mixed in, in order to absorb visible light and perform electron transfer to reduce the catalyst. A first attempt was performed at 7ID-D, but only succeeded in detecting the direct excitation, as there appeared to be problems with the photosensitizer in the visible.

Future Plans: We will continue to work with our collaborations about transient molecular dynamics in solution. In addition, our group is initiating a new study to understand the fundamental mechanisms at play in model systems of the di-iron hydrogenase. Those model systems, while

providing opportunities for controlled studies of the biological enzyme, are also very interesting because some have been shown to exhibit catalytic activity on their own. Understanding the mechanisms at play following light excitation would then allow for a more directed route for synthesis of improved systems.

4.4 Charge transfer dynamics in semiconductor nanoparticles for photoconversion processes

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Scope: Our group has developed several collaborations to use the power of time-resolved x-ray spectroscopies to resolve questions regarding the mechanisms for charge separation and trapping in semiconductor nanoparticles following light absorption. These nanoparticles are seen as candidates to improve the efficiency and lifetime of future solar cells. Our studies take advantage of the element specificity of x-ray techniques in order to elucidate the properties of those composite materials. Using the nanoparticles in colloidal suspension allows for using our high-repetition-rate setup at the APS, yielding high quality data.

Recent Progress: Semiconductor nanoparticles (NP) are widely used as promising chromophores, capable of harnessing light to produce charge separated states, and thus eventually produce electricity in solar cells or trigger chemical reactions to produce so-called solar fuels. Numerous attempts are underway to try and improve the efficiency of the different steps in which the NPs are involved, from light absorption, to charge separation, charge trapping and back energy transfer to name a few. Our group has been involved in three such projects this past year.

First, with a group from the Paul Scherrer Institute, we have studied the properties of ZnO NPs following UV excitation. The objective was to identify the nature of the electron/hole traps in the lattice, in order to explain the lower efficiency relative to TiO₂ NPs, hypothesized to be due to much faster charge carrier recombination times. Using a combination of TR-XAS (EXAFS) and TR-XES, and supported by simulations, we were able to identify that photo-excited holes are trapped at singly charged oxygen vacancies, turning them into doubly charged vacancies. Subsequent radiative recombination with the delocalized electrons in the conduction band yields the commonly observed green luminescence. The identification of the hole traps and their evolution will provide new insights for the future design of transition metal oxide NPs.

Second, with a group from the University of Illinois (Urbana-Champaign), we have started to study quantum dot heterostructures, specifically ZnTe/CdSe NPs. Quantum dots in general are seen as very promising chromophores due to the ability to control the absorption properties by the size of the structure. Heterostructures are seen as a way to extend the lifetime of the charge separated state, a crucial property for real world use in solar cells. In the case of CdSe NPs, the heterostructure can extend the lifetime from 10-20 ns to hundreds of nanoseconds. One of the main hypothesis relies on the fact that while the electrons are delocalized over the entire QD, the holes are confined to one of the shells. Using time-resolved XAS, and probing the different elements forming the QD, one can first probe the oxidation state changes, as well as eventually extract the geometry around the hole traps, similarly to the ZnO study. The ability to probe both shells of the heterostructure selectively is crucial. First results were obtained probing at the Se K-edge and the Zn K-edge, suggesting strongly hole localization at Zn sites.

Finally, with a group from the Ecole Polytechnique Federale de Lausanne, we have studied

charge carrier dynamics in inorganic lead halide perovskites (specifically CsPbBr₃). Perovskites have been used to produced record high conversion efficiency for solar conversion (20%), but there are many open questions regarding the mechanisms at play, in particular to explain the long lifetime of the charge separated state. Identifying the sites, as well as localization/delocalization of the charge carriers is crucial, and x-ray spectroscopies are ideal tools. At the APS, we were able to photoexcite a colloidal suspension of perovskite NPs with UV light, and follow the evolution of the system at the Pb L-edge and the Br K-edge. In perovskites, the conduction band is dominated by Pb 6p orbitals, while the valence band is dominated by the Br 4p orbitals, indicating that we are able to separately follow the kinetics of the hole and electron recombination. This will be a crucial indicator to the hypothesis of charge delocalization in the conduction band.

Future Plans: We will continue to explore those collaborative studies since they are a natural fit for our time resolved setup at 7ID-D. Follow up on the perovskite sample will likely require a visit at a free electron laser in order to capture the formation of the charge separated state. The study of the quantum dot heterostructures will continue with an upcoming beamtime this fall where a more complete measurement will be performed.

5 Affiliations of collaborators

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References

Peer-Reviewed Publications Resulting from Subtask 1 (2015-2017)

- [1] P. J. Ho, E. P. Kanter, and L. Young, “Resonance-mediated atomic ionization dynamics induced by ultraintense x-ray pulses,” *Phys. Rev. A* **92**, 063430 (2015).
- [2] R.M.P. Tanyag, C. Bernando, C.F. Jones, C. Bacellar, K.R. Ferguson, D. Anielski, R. Boll, S. Carron, J.P. Cryan, L. Englert, S.W. Epp, B. Erk, L. Foucar, L.F. Gomez, R. Hartmann, D.M. Neumark, D. Rolles, B. Rudek, A. Rudenko, K. R. Siefertmann, J. Ullrich, F. Weise, C. Bostedt, O. Gessner, and A. Vilesov, “X-ray coherent diffractive imaging by immersion in nanodroplets,” *Struc. Dyn.* **2**, 051102 (2015).
- [3] Y. Li, Z. Jiang, X.-M. Lin, H. Wen, D. A. Walko, S. A. Deshmukh, R. Subbaraman, S. K. R. S. Sankaranarayanan, S. K. Gray, and P. J. Ho, “Femtosecond laser pulse driven melting in gold nanorod aqueous colloidal suspension: identification of a transition from stretched to exponential kinetics,” *Scientific Reports* **5**, 8146 (2015).
- [4] L. Young, “A stable narrow-band X-ray laser,” (Invited News & Views article for Nature), *Nature* **524**, 424 (2015).
- [5] R. Santra and L. Young, “Interaction of intense X-ray beams with atoms,” in “Synchrotron Light Sources and Free-Electron Lasers: Accelerator Physics, Instrumentation and Science Applications,” Editors: E. Jaeschke, S. Khan, J. R. Schneider, and J. B. Hastings (Springer, Heidelberg), p 1-24 (2015).
- [6] T. Gorkhover, S. Schorb, R. Coffee, M. Adolph, L. Foucar, D. Rupp, A. Aquila, J. D. Bozek, S. W. Epp, B. Erk, L. Gumprecht, L. Holmegaard, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hömke, N. Kimmel, K.-U. Kühnel, P. Johnsson, M. Messerschmidt, C. Reich, A. Rouzée, B. Rudek, C. Schmidt, J. Schulz, H. Soltau, S. Stern, G. Weidenspointner, B. White, J. Küpper, L. Strüder, I. Schlichting, J. Ullrich, D. Rolles, A. Rudenko, T. Möller, and C. Bostedt, “Femtosecond and nanometer visualisation of structural dynamics in superheated nanoparticles,” *Nature Photonics* **10**, 93 (2016).
- [7] K. R. Ferguson, M. Bucher, T. Gorkhover, S. Boutet, H. Fukuzawa, J. E. Koglin, Y. Kumagai, A. Lutman, A. Marinelli, M. Messerschmidt, K. Nagaya, J. Turner, K. Ueda, G. J. Williams, P. H. Bucksbaum, and C. Bostedt, “Transient lattice compression in the solid-to-plasma transition,” *Science Advances* **2**, 1500837 (2016).
- [8] C. Bostedt, S. Boutet, D. M. Fritz, Z. Huang, H. J. Lee, H. T. Lemke, A. Robert, W. F. Schlotter, J. J. Turner, and G. J. Williams, “The Linac Coherent Light Source: The First Five Years,” *Rev. Mod. Phys.* **88**, 015007 (2016).
- [9] L. Flückiger, D. Rupp, M. Adolph, T. Gorkhover, M. Krikunova, M. Müller, T. Oelze, Y. Ovcharenko, M. Sauppe, S. Schorb, C. Bostedt, S. Düsterer, M. Harmand, H. Redlin, R. Treusch, T. Möller, “Time-resolved x-ray imaging of a laser-induced nanoplasma and its neutral residuals,” *New J. Phys.* **18**, 043017 (2016).
- [10] C.F. Jones, C. Bernando, R.M.P. Tanyag, C. Bacellar, K.R. Ferguson, L.F. Gomez, D. Anielski, A. Belkacem, R. Boll, J.D. Bozek, S. Carron, J. Cryan, L. Englert, S.W. Epp, B. Erk, L. Foucar, R. Hartmann, D. Neumark, D. Rolles, A. Rudenko, K.R. Siefertmann, F. Weise, B. Rudek, F.P. Sturm, J. Ullrich, C. Bostedt, O. Gessner, A.F. Vilesov, “Coupled motion of Xe clusters and quantum vortices in He nanodroplets,” *Phys. Rev. B* **93**, 180510 (2016).
- [11] R. Boll, B. Erk, R. Coffee, S. Trippel, T. Kierspel, C. Bomme, J.D. Bozek, M. Burkett, S. Carron, K.R. Ferguson, L. Foucar, J. Kpper, T. Marchenko, C. Miron, M. Patanen, T. Osipov, S. Schorb, M. Simon, M. Swiggers, S. Techert, K. Ueda, C. Bostedt, D. Rolles, A. Rudenko, “Charge transfer in dissociating iodomethane and fluoromethane molecules ionized by intense femtosecond X-ray pulses,” *Struc. Dyn.* **3**, 043207 (2016).
- [12] D. Rupp, L. Flückiger, M. Adolph, T. Gorkhover, M. Krikunova, J.P. Müller, M. Müller, T. Oelze, Y. Ovcharenko, B. Röben, M. Sauppe, S. Schorb, D. Wolter, R. Mitzner, M. Wöstmann, S. Røling, M. Harmand, R. Treusch, M. Arbeiter, T. Fennel, C. Bostedt, and T. Möller, “Observation of recombination-enhanced surface expansion of clusters in intense soft x-ray laser pulses”, *Phys. Rev. Lett.*, **117**, 153401 (2016).
- [13] Phay J. Ho, Chris Knight, Miklos Tegze, Gyula Faigel, C. Bostedt, and L. Young, “Atomistic 3D coherent X-ray imaging of non-biological systems,” *Phys. Rev. A* **94**, 063823 (2016).
- [14] Phay J. Ho, and Chris Knight, “Large-scale atomistic calculations of cluster in intense x-ray pulses,” *J. Phys. B: At. Mol. Opt. Phys.* **50**, 104003 (2017).
- [15] A. Rudenko, L. Inhester, K. Hanasaki, X. Li, S. J. Robatjazi, B. Erk, R. Boll, K. Toyota, Y. Hao, O. Vendrell, C. Bomme, E. Savelyev, B. Rudek, L. Foucar, S. H. Southworth, C.S. Lehmann, B. Kraessig, T. Marchenko, M. Simon, K. Ueda, K. R. Ferguson, M. Bucher, T. Gorkhover, S. Carron, R. Alonso-Mori, J. E. Koglin, J. Correa, G. J. Williams, S. Boutet, L. Young, C. Bostedt, S.-K. Son, R. Santra, D. Rolles, “Femtosecond response of polyatomic molecules to ultra-intense hard X-rays,” *Nature* **546**, 129 (2017).
- [16] E. C. Bernando, R.M.P. Tanyag, C. Jones, C. Bacellar, M. Bucher, K.R. Ferguson, D. Rupp, M.P. Ziemkiewicz, L.F. Gomez, A.S. Chatterley, T. Gorkhover, M. Mller, J. Bozek, S. Carron, J. Kwok, S.L. Butler, T. Möller, C. Bostedt, O. Gessner, and A.F. Vilesov, “Shapes of rotating superfluid helium nanodroplets,” *Phys. Rev. B* **95**, 064510 (2017).

Peer-Reviewed Publications Resulting from Subtask 2 (2015-2017)

- [17] S. H. Southworth, R. Wehlitz, A. Picón, C. S. Lehmann, L. Cheng, and J. F. Stanton, “Inner-shell photoionization and core-hole decay of Xe and XeF₂,” *J. Chem. Phys.* **142**, 224302 (2015).
- [18] A. Picón, J. Mompert, and S. H. Southworth, “Stimulated Raman adiabatic passage with two-color x-ray pulses,” *New J. Phys.* **17**, 083038 (2015).
- [19] C. Hernández-García, L. Plaja, J. San Román, and A. Picón, “Quantum-path signatures in attosecond helical beams driven by optical vortices”, *New J. Phys.* **17**, 093029 (2015).
- [20] A. Picón, C. S. Lehmann, C. Bostedt, A. Rudenko, A. Marinelli, T. Osipov, D. Rolles, N. Berrah, C. Bomme, M. Bucher, G. Doumy, B. Erk, K. Ferguson, T. Gorkhover, P. J. Ho, E. P. Kanter, B. Krässig, J. Krzywinski, A. A. Lutman, A. M. March, D. Moonshiram, D. Ray, L. Young, S. T. Pratt, and S. H. Southworth, “Hetero-site-specific ultrafast intramolecular dynamics,” *Nature Comm.* **7**, 11652 (2016).
- [21] C. S. Lehmann, A. Picón, C. Bostedt, A. Rudenko, A. Marinelli, D. Moonshiram, T. Osipov, D. Rolles, N. Berrah, C. Bomme, M. Bucher, G. Doumy, B. Erk, K. Ferguson, T. Gorkhover, P. J. Ho, E. P. Kanter, B. Krässig, J. Krzywinski, A. A. Lutman, A. M. March, D. Ray, L. Young, S. T. Pratt, and S. H. Southworth, “Ultrafast measurements of molecular nuclear dynamics using two x-ray pulses,” *Phys. Rev. A* **94**, 013426 (2016).
- [22] V. Kimberg, A. Sanchez-Gonzalez, L. Mercadier, C. Weninger, A. Lutman, D. Ratner, R. Coffee, M. Bucher, M. Mucke, M. Agaker, C. Sathe, C. Bostedt, J. Nordgren, J.-E. Rubensson and N. Rohringer, “Stimulated X-ray Raman scattering a critical assessment of the building block of nonlinear X-ray spectroscopy”, *Faraday Disc.*, DOI: 10.1039/c6fd00103c (2016).
- [23] R. Sullivan, J. Jia, A. Vázquez-Mayagoitia, and A. Picón, “Normal Auger processes with ultrashort x-ray pulses in Neon,” under review, *Phys. Rev. A* (2016).
- [24] L. Rego, J. San Roman, A. Picón, L. Plaja, C. Hernandez-Garcia, “Nonperturbative Twist in the Generation of Extreme-Ultraviolet Vortex Beams,” *Phys. Rev. Lett.* **117**, 163202 (2016).
- [25] T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch, M. Gühr, “Probing ultrafast $\pi\pi^*/n\pi^*$ internal conversion in organic chromophores via K-edge resonant absorption,” *Nature Communications* **8**, 29 (2017).
- [26] T. J. A. Wolf, F. Holzmeier, I. Wagner, N. Berrah, C. Bostedt, J. Bozek, P. Bucksbaum, R. Coffee, J. Cryan, J. Farrell, R. Feifel, T.J. Martinez, B. McFarland, M. Mucke, S. Nandi, F. Tarantellio, I. Fischer, M. Gühr, “Observing Femtosecond Fragmentation Using Ultrafast X-ray-Induced Auger Spectra,” *Appl. Sci.* **7**, 681 (2017).
- [27] A. Picón, “Time-dependent Schrodinger equation for molecular core-hole dynamics,” *Phys. Rev. A* **95**, 0233401 (2017).
- [28] A. Sanchez-Gonzalez, P. Micaelli, C. Olivier, T. R. Barillot, M. Ilchen, A.A. Lutman, A. Marinelli, T. Maxwell, A. Achner, M. Agaker, N. Berrah, C. Bostedt, J. D. Bozek, J. Buck, P. H. Bucksbaum, S. Carron Montero, B. Cooper, J. P. Cryan, M. Dong, R. Feifel, L. J. Frasinski, H. Fukuzawa, A. Galler, G. Hartmann, N. Hartmann, W. Helml, A. S. Johnson, A. Knie, A. O. Lindahl, J. Liu, K. Motomura, M. Mucke, C. O’Grady, J-E Rubensson, E. R. Simpson, R. J. Squibb, C. Sathe, K. Ueda, M. Vacher, D. J. Walke, V. Zhaunerchyk, R. N. Coffee, J. P. Marangos, “Accurate prediction of X-ray pulse properties from a free-electron laser using machine learning”, *Nature Communications* **8**, 15461 (2017).
- [29] L. Young, K. Ueda, M Gühr, P.H. Bucksbaum, M. Simon, S. Mukamel, N. Rohringer, K. Prince, C. Masciovecchio, M. Meyer, A. Rudenko, D. Rolles, C. Bostedt, M. Fuchs, D. Reis, R. Santra, H. Kapteyn, M. Murnane, H. Ibrahim, Francois Légaré, M. Vrakking, M. Isinger, D. Kroon, M. Gisselbrecht, A. L’Huillier, H. J. Wörner and S. R. Leone, “Roadmap on Ultrafast X-ray Atomic and Molecular Physics”, *J. Phys. B.*, in press (2017).

Peer-Reviewed Publications Resulting from Subtask 3 (2015-2017)

- [30] G. Vankó, A. Bordage, M. Pápai, K. Haldrup, P. Glatzel, A. M. March, G. Doumy, A. Britz, A. Galler, T. Assefa, D. Cabaret, A. Juhin, T. B. van Driel, K. S. Kjær, A. Dohn, K. B. Møller, H. T. Lemke, E. Gallo, M. Rovezzi, Z. Németh, E. Rozsályi, T. Rozgonyi, J. Uhlig, V. Sundström, M. M. Nielsen, L. Young, S. H. Southworth, C. Bressler, and W. Gawelda, “Detailed characterization of a nanosecond-lived excited state: x-ray and theoretical investigation of the quintet state in photoexcited [Fe(terpy)₂]²⁺,” *J. Phys. Chem C* **119**, 5888 (2015).
- [31] A. M. March, T. A. Assefa, C. Bressler, G. Doumy, A. Galler, W. Gawelda, E. P. Kanter, Z. Németh, M. Pápai, S. H. Southworth, L. Young, and G. Vankó, Feasibility of valence-to-core x-ray emission spectroscopy for tracking transient species,” *J. Phys. Chem. C* **119**, 14571 (2015).
- [32] R. Reininger, Z. Liu, G. Doumy, and L. Young, “A simple optical system delivering a tunable micrometer pink beam that can compensate for heat-induced deformations,” *J. Synchrotron Rad.* **22**, 930 (2015).
- [33] B. Zimmermann, V. McKoy, S. H. Southworth, E. P. Kanter, B. Krässig, and R. Wehlitz, “Dipole and nondipole photoionization of molecular hydrogen,” *Phys. Rev. A* **91**, 053410 (2015).
- [34] E. M. Dufresne, R. W. Dunford, E. P. Kanter, Y. Gao, S. Moon, D. A. Walko, and X. Zhang, “Pink-beam focusing with a one-dimensional compound refractive lens,” *J. Synchrotron Rad.* **23**, 1082 (2016).

- [35] D.A. Walko, B.W. Adams, G. Doumy, E.M. Dufresne, Y. Li, A.M. March, A.R. Sandy, J. Wang, H. Wen, and Y. Zhu, “Developments in Time-Resolved X-ray Research at APS Beamline 7ID,” 12th International Conference on Synchrotron Radiation Instrumentation, AIP Conf. Proc., **1741**, 030048 (2016).
- [36] Y. Gao, R. Harder, S. Southworth, J. Guest, N. Scherer, Z. Yan, L. Ocola, M. Pelton, and L. Young, “Bragg diffraction from sub-micron particles isolated by optical tweezers,” AIP Conf. Proc. **1741**, 050010 (2016).
- [37] D. Moonshiram, C. Gimbert-Suriñach, A. Guda, A. Picon, C.S. Lehmann, X. Zhang, G. Doumy, A.M. March, J. Benet-Buchholz, A. Soldatov, A. Llobet, and S.H. Southworth “Tracking the Structural and Electronic Configurations of a Cobalt Proton Reduction Catalyst in Water,” J. Am. Chem. Soc. **138**, 10586 (2016).
- [38] D. Moonshiram, A. Guda, L. Kohler, A. Picon, S. Guda, C.S. Lehmann, X. Zhang, S.H. Southworth, and K.L. Mulfort, “Mechanistic Evaluation of a Nickel Proton Reduction Catalyst Using Time-Resolved X-ray Absorption Spectroscopy,” J. Phys. Chem. C, DOI: 10.1021/acs.jpcc.6b06883 (2016).
- [39] C. Suriñach, D. Moonshiram, L. Francas, N. Planas, F. Bozoglian, A. Guda, L. Mognon, I. Lopez, C.J. Cramer, L. Gagliardi, and A. Llobet, “Structural and Spectroscopic Characterization of Reaction Intermediates involved in a Dinuclear Co-Hbpp Water Oxidation Catalyst”, J. Am. Chem. Soc. **138**, 15291 (2016).
- [40] D. Moonshiram, Y. Pineda-Galvan, D. Erdman, M. Palenik. R. Thummel, and Y. Pushkar, “Uncovering the role of oxygen atom transfer in Ru-based catalytic water oxidation,” J. Am. Chem. Soc. **138**, 15605 (2016).
- [41] J. Creus, R. Matheu, I. Penafiel, D. Moonshiram, J. Benet-Buchholtz, J. Garcia-Anton, X. Sala, C. Godard, and A. Llobet, “A Million Turnover Molecular Anode for Catalytic Water Oxidation”, Angew. Chem. Int. Ed. **55**, 15382 (2016).
- [42] A. M. March, T. A. Assefa, C. Boemer, C. Bressler, A. Britz, M. Diez, G. Doumy, A. Galler, M. Harder, D. Khakhulin, Z. Németh, M. Pápai, S. Schulz, S. H. Southworth, H. Yavas, L. Young, W. Gawelda, G. Vankó, “Probing transient valence orbital changes with picosecond valence-to-core X-ray emission spectroscopy,” J. Phys. Chem. C, **121**, 2620 (2017).
- [43] D. Moonshiram, A. Picón, A. Vazquez-Mayagoitia, X. Zhang, M.-F. Tu, P. Garrido-Barros, J.-P. Mahy, F. Avenier, and A. Aukauloo, “Elucidating light-induced charge accumulation in an artificial analogue of methane monooxygenase enzymes using time-resolved X-ray absorption spectroscopy,” Chem. Commun. **53**, 2725 (2017).

Other cited references

- [44] L. Young, E. P. Kanter, B. Krässig, Y. Li, A. M. March, S. T. Pratt, R. Santra, S. H. Southworth, N. Rohringer, L. F. DiMauro, G. Doumy, C. A. Roedig, N. Berrah, L. Fang, M. Hoener, P. H. Bucksbaum, J. P. Cryan, S. Ghimire, J. M. Glowina, D. A. Reis, J. D. Bozek, C. Bostedt, and M. Messerschmidt, “Femtosecond electronic response of atoms to ultra-intense x-rays,” Nature **466**, 56 (2010).
- [45] E. P. Kanter, B. Krässig, Y. Li, A. M. March, P. Ho, N. Rohringer, R. Santra, S. H. Southworth, L. F. DiMauro, G. Doumy, C. A. Roedig, N. Berrah, L. Fang, M. Hoener, P. H. Bucksbaum, S. Ghimire, D. A. Reis, J. D. Bozek, C. Bostedt, M. Messerschmidt, and L. Young, “Unveiling and driving hidden resonances with high-fluence, high-intensity x-ray pulses,” Phys. Rev. Lett. **107**, 233001 (2011).
- [46] S. Schorb, D. Rupp, M. L. Swiggers, R. N. Coffee, M. Messerschmidt, G. Williams, J. D. Bozek, S.-I. Wada, O. Kornilov, T. Möller, and C. Bostedt, “Size-dependent ultrafast ionization dynamics of nanoscale samples in intense femtosecond x-ray free-electron-laser pulses,” Phys. Rev. Lett. **108**, 233401 (2012).
- [47] L. F. Gomez, K. R. Ferguson, J. P. Cryan, C. Bacellar, R. M. P. Tanyag, C. Jones, S. Schorb, D. Anielski, A. Belkacem, C. Bernando, R. Boll, J. Bozek, S. Carron, G. Chen, T. Delmas, L. Englert, S. W. Epp, B. Erk, L. Foucar, R. Hartmann, A. Hexemer, M. Huth, J. Kwok, S. R. Leone, J. H. S. Ma, F. R. N. C. Maia, E. Malmerberg, S. Marchesini, D. M. Neumark, B. Poon, J. Prell, D. Rolles, B. Rudek, A. Rudenko, M. Seifrid, K. R. Siefertmann, F. P. Sturm, M. Swiggers, J. Ullrich, F. Weise, P. Zwart, C. Bostedt, O. Gessner and A. F. Vilesov, “Shapes and vorticities of superfluid helium nanodroplets,” Science **345**, 907 (2014).
- [48] P. J. Ho, C. Bostedt, S. Schorb, and L. Young, “Theoretical tracking of resonance-enhanced multiple ionization pathways in x-ray free-electron laser pulses,” Phys. Rev. Lett. **113**, 253001 (2014).
- [49] T. Gorkhover, M. Adolph, D. Rupp, S. Schorb, S. W. Epp, B. Erk, L. Foucar, R. Hartmann, N. Kimmel, K.-U. Kühnel, D. Rolles, B. Rudek, A. Rudenko, R. Andritschke, A. Aquila, J.D. Bozek, N. Coppola, T. Erke, F. Filsinger, H. Gorke, H. Graafsma, L. Gumprecht, G. Hauser, S. Herrmann, H. Hirsemann, A. Ho mke, P. Holl, C. Kaiser, F. Krasniqi, J.-H. Meyer, M. Matysek, M. Messerschmidt, D. Miessner, B. Nilsson, D. Pietschner, G. Potdevin, C. Reich, G. Schaller, C. Schmidt, F. Schopper, C.D. Schröter, J. Schulz, H. Soltau, G. Weidenspointner, I. Schlichting, L. Strüder, J. Ullrich, T. Möller, and C. Bostedt, “Nanoplasma dynamics of single large xenon clusters irradiated with superintense x-ray pulses from the Linac Coherent Light Source free-electron laser,” Phys. Rev Lett. **108**, 245005 (2012).
- [50] C. Bostedt, E. Eremina, D. Rupp, M. Adolph, H. Thomas, M. Hoener, A. R. B. de Castro, J. Tiggesbunker, K.-H. Meiwes-Broer, T. Laarmann, H. Wabnitz, E. Plönjes, R. Treusch, J. R. Schneider, and T. Möller, “Ultrafast X-Ray Scattering of Xenon Nanoparticles: Imaging Transient States of Matter,” Phys. Rev. Lett. **108**, 093401

- (2012).
- [51] Max Bucher, “Ultrafast Dynamics of Nanoparticles in Highly Intense X-Ray Pulses”, Dissertation, Technische Universität Berlin (2017).
 - [52] Z. Li, O. Vendrell, and R. Santra, “Ultrafast Charge Transfer of a Valence Double Hole in Glycine Driven Exclusively by Nuclear Motion,” *Phys. Rev. Lett.* **115** 143002 (2015).
 - [53] W. Eberhardt, T.K. Sham, R. Carr, S. Krümmacher, M. Strongin, S. L. Weng, and D. Wesner, “Site-Specific Fragmentation of Small Molecules Following Soft-X-Ray Excitation,” *Phys. Rev. Lett.* **50**, 1038 (1983).
 - [54] C. Miron, M. Simon, L. Leclercq, D. L. Hansen, and P. Morin, “Site-selective photochemistry of core excited molecules: Role of the internal energy,” *Phys. Rev. Lett.* **81**, 4104 (1998).
 - [55] E. Kukk, D. T. Ha, Y. Wang, D. G. Piekarski, S. Diaz-Tendero, K. Kooser, E. Itälä, H. Levola, M. Alcamí, E. Rachlew, and F. Martin, “Internal energy dependence in x-ray-induced molecular fragmentation: An experimental and theoretical study of thiophene,” *Phys. Rev. A* **91** 043417 (2015). R. W. Dunford, S. H. Southworth, D. Ray, E. P. Kanter, B. Krässig, L. Young, D. A. Arms, E. M. Dufresne, D. A. Walko, O. Vendrell, S.-K. Son, and R. Santra, “Evidence for interatomic Coulombic decay in Xe *K*-shell-vacancy decay of XeF₂,” *Phys. Rev. A* **86**, 033401 (2012).
 - [56] M. Shirom, G. Stein, “Excited state chemistry of the ferrocyanide ion in aqueous solution. II. Photoaquation,” *J. Chem. Phys.*, **55**, 3379 (1971).
 - [57] J. H. Lee, M. Wulff, S. Bratos, J. Petersen, L. Guerin, J.-C. Leicknam, M. Cammarata, Q. Kong, J. Kim, K. B. Møller, H. Ihee, “Filming the Birth of Molecules and Accompanying Solvent Rearrangement,” *J. Am. Chem. Soc.*, **135**, 3255 (2013).

J.R. Macdonald Laboratory Overview

The J.R. Macdonald Laboratory (JRML) focuses on the interaction of intense laser pulses with matter for the purpose of understanding and even controlling the resulting ultrafast dynamics. The timescales involved range from attoseconds, necessary for studying electronic motion in matter, to femtoseconds and picoseconds for molecular vibration and rotation, respectively. We continue to harness the expertise within the Lab to further our progress in both understanding and control. The synergy afforded by the close interaction of theory and experiment within the Lab serves as a significant multiplier for this effort. To achieve our goals, we are advancing theoretical modeling and computational approaches as well as experimental techniques, such as particle imaging (COLTRIMS, VMI, etc.), molecular alignment, and high-harmonic generation.

Most of our research projects are associated with one of four themes: “Attosecond physics”, “Extending and enhancing harmonic generation”, “Imaging dynamics in large molecules” and “Strong field control of small molecules”. These themes serve as broad outlines only, as the boundary between them is not always well defined. Similarly, in many cases it is hard to distinguish between improving theoretical and experimental “tools” and the resulting science discovery. A few examples are briefly mentioned below, while further details are provided in the individual abstracts of the PIs: I. Ben-Itzhak, B.D. Esry, V. Kumarappan, C.D. Lin, D. Rolles, A. Rudenko, U. Thumm, and C.A. Trallero.

Attosecond physics: Attosecond science is motivated by the idea of observing electronic motion in atoms and molecules on its natural timescale. The retrieval of information, such as laser-pulse or atomic-dipole phase, from attosecond streaking experiments is one of the challenges addressed by theorists. On the experimental side, we have developed a self-referencing attosecond interferometer for high harmonic spectroscopy (HHG). We have also continued our studies of carrier envelope phase effects, as they play a key role in attosecond pulse generation and strong-field phenomena driven by few-cycle pulses.

Extending and enhancing harmonic generation: HHG is usually used to produce attosecond pulses. Our recent theoretical and experimental work focuses on increasing the HHG efficiency and extending its cutoff energy. The harmonics are also a source of high-energy photons, enabling population of specific molecular states which are studied employing pump-probe measurements coupled with 3D momentum imaging techniques. Related work on nonlinear X-ray – matter interaction has been conducted at the LCLS. We have explored theoretically the double ionization of He in an ultrashort intense XUV pulse. We have also continued our HHG spectroscopy studies aimed at retrieving structure information.

Imaging dynamics in large molecules: Our work on this topic ranges from theoretical treatment enabling structure retrieval from laser-induced electron diffraction (LIED) experiments to pump-probe measurements of molecular dynamics. The latter technique has been employed to study the ultrafast UV-induced dissociation dynamics in halogenated hydrocarbons visualized by 3D momentum imaging. In some of these studies we have implemented our recently developed analysis method for three-body breakup. Momentum imaging methods have also been used to study the angular dependence of strong-field ionization of laser-aligned polyatomic molecules.

Strong field control of small molecules: Methods for controlling the motion of heavy particles in small molecules continue to be developed. Work in the Lab has been extended to anion molecular beams. Ionization calculations of the benchmark H_2^+ molecule have been extended to very large internuclear distances revealing unexpected rate oscillations, which explain our experimental observation of enhanced ionization of highly stretched H_2^+ . We have been studying, in collaboration with M. Dantus and E. Wells, the formation of H_3^+ and hydrogen elimination, respectively, in polyatomic molecules exposed to ultrashort intense laser pulses.

A significant fraction of JRML research is done in collaboration with others, either at JRML or elsewhere. For example, M. Dantus from Michigan State University, E. Wells from Augustana University and R.R. Lucchese from Texas A&M University benefit from data measured at JRML. Similarly, some of us conduct experiments at free electron lasers, such as LCLS and FLASH, and at other facilities. Our group is well connected through such collaborations with many AMO groups across the world (ALS, ANL, Århus, FLASH, Univ. of Frankfurt, ICFO Barcelona, Univ. of Jena, LBNL, LCLS, Max-Planck Institutes for Quantum Optics and Kernphysik, the Ohio State Univ., Texas A&M Univ., Tokyo Univ., Weizmann Institute, and others).

Finally, it is worth mentioning the laser facilities available to researchers at JRML. Our high-repetition rate laser, PULSAR, and the high-power, tunable long wavelength laser, HITS, are the main laser systems, while the old workhorse laser, KLS, is still yielding high-quality results. On the personnel side, Carlos Trallero has recently taken a position at the University of Connecticut, and therefore we are searching for a new experimental ultrafast AMO physicist to join our group. Last year Kansas State University approved the hire of an AMO theorist as an expansion of our physics department. We are happy to have Loren Greenman, who is an expert on structure and dynamics in complex molecules, as a new member of our larger AMO group. Even though he is not DOE supported, we anticipate fruitful, close collaborations to develop. Combining the theoretical and experimental expertise within the Lab with our large spectrum of laser and imaging capabilities continues to produce exciting physics.

Structure and Dynamics of Atoms, Ions, Molecules, and Surfaces: Molecular Dynamics with Ion and Laser Beams

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Project Scope: *The goal of this part of the JRML program is to study and control molecular dynamics under the influence of ultrashort intense laser pulses. To this end, we typically study molecular ion beams and have a close collaboration between theory and experiment.¹*

Recent Progress: *A sample of research projects*

Strong field fragmentation of LiO^-

*Ben Berry, Bethany Jochim, T. Severt, Peyman Feizollah, Kanaka Raju P.,
K.D. Carnes, B.D. Esry, and I. Ben-Itzhak*

Studies of the fragmentation of fast molecular ion beams enable coincidence measurements of all fragments including neutral ones. We extended our studies from cation beams, including the benchmark H_2^+ , H_3^+ molecules, to anion beams starting from F_2^- and LiO^- . We have employed coincidence three-dimensional momentum imaging which is similar to the technique used in our previous studies.

We have recently studied multiphoton dissociation of LiO^- [1]. The potentials of this molecular anion are shown in Fig. 1(a). The potential depth can be determined experimentally by measuring the kinetic energy release (KER) following photodissociation into the lowest, $\text{Li} + \text{O}^-$, dissociation limit, as indicated in the figure. However, the rate of this process, using 395 nm photons, is too low.

The photodissociation rate of LiO^- can be significantly enhanced by using resonance-enhanced multiphoton dissociation (REMPD) [4] driven by a 790 nm laser beam. This REMPI-like process involves, for example, exciting the $X^3\Pi(v=0)$ ground state to the $3^3\Sigma^+(v=17,18)$ state, then a second photoabsorption leads to dissociation, as depicted by the red arrows in Fig. 1. The measured KER distribution, shown in Fig. 2, extends down to 0.05 eV, i.e. less than the expected minimum of 0.45 eV, therefore suggesting that the dissociation energy of LiO^-

is close to 3.1 eV and not 2.7 eV as suggested by theory, that is the potential well is deeper than theoretically predicted by at least 0.4 eV.

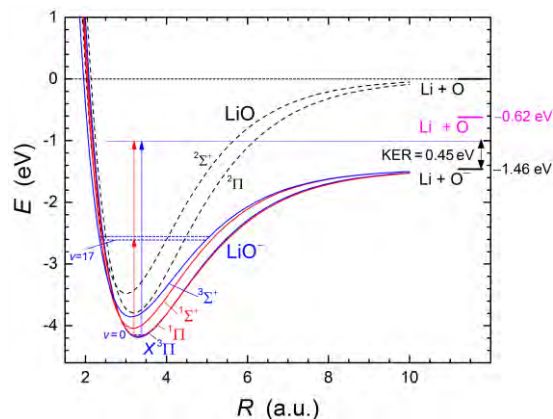


Figure 1. Potential energy curves of LiO^- based on calculations by Bauschlicher *et al.* for $R = 2.8 - 4.4$ a.u. [2]. The potential depth of LiO was taken from Ref. [3]. The blue and red arrows depict photodissociation by 395 and 790 nm, respectively.

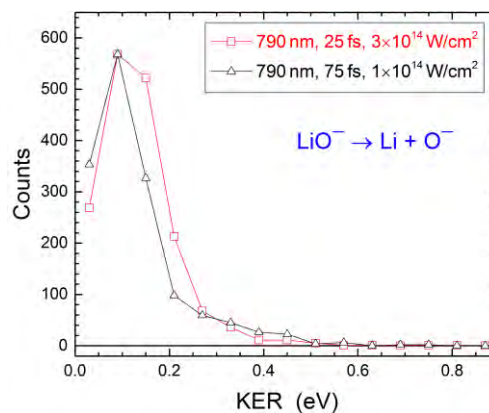


Figure 2. Measured KER distribution of LiO^- dissociation.

Native frames: Separating sequential and concerted three-body fragmentation

T. Severt, Jyoti Rajput, Ben Berry, Bethany Jochim, Peyman Feizollah, Balram Kaderiya, M. Zohrabi, U. Ablikim, Farzaneh Ziaee, Kanaka Raju P., D. Rolles, A. Rudenko, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak

Advances in imaging techniques have led to better understanding of induced molecular fragmentation. Experimentally distinguishing between concerted and sequential (sometimes called “stepwise”) fragmentation mechanisms in polyatomic molecules is a long-standing goal of these efforts. Key to its achievement is the coincidence detection of all fragments, although alternatives without coincidence detection have been suggested [5].

The sequential breakup of triply-charged triatomic molecules may involve an intermediate dication, for example OCS^{3+} fragmentation into $\text{S}^+ + \text{CO}^{2+}$ followed by unimolecular dissociation of $\text{CO}^{2+} \rightarrow \text{C}^+ + \text{O}^+$. In particular we focus on metastable dication states which survive much longer than their rotational period, i.e. $\tau \gg T_R$. This rotation has been invoked to explain a circular feature in a Newton diagram [6-9]. Alternatively, this fragmentation mechanism can be identified as a linear distribution across a Dalitz plot [6-8].

Recently, we developed a more complete way to analyze three-body breakup data that allows us to systematically distinguish sequential fragmentation events as long as the intermediate molecule rotates long enough. This is accomplished by analyzing the data in the native frames associated with each fragmentation step and taking advantage of the flat $N(\theta_{\text{CO,S}})$ distribution [see Fig. 3], where $\theta_{\text{CO,S}}$ is the angle between the relative momenta associated with the first and second breakup steps.

The beauty of this “native frames” method is that it also allows us to “recover” sequential fragmentation events that are masked by competing processes, like concerted breakup, [see $\theta_{\text{CO,S}} < 90^\circ$ in Fig 3(a)], and therefore

enables generation of spectra for concerted breakup events through subtraction of the sequential fragmentation events [see Fig. 4].

To illustrate our ability to separate sequential and concerted breakup we plot the Newton diagrams used to identify sequential breakup via $\text{S}^+ + \text{CO}^{2+}$ in Fig. 4. Panel (a) shows all the $\text{O}^+ + \text{C}^+ + \text{S}^+$ events, while panels (b-d) show the separated contributions of each process.

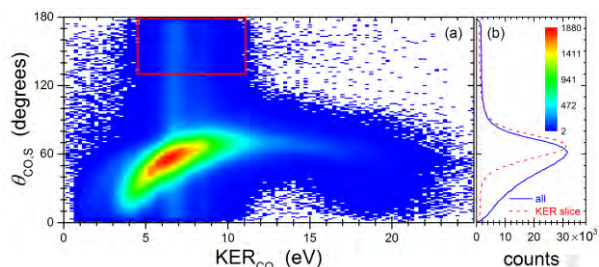


Figure 3. (a) All $\text{O}^+ + \text{C}^+ + \text{S}^+$ events as a function of KER_{CO} and $\theta_{\text{CO,S}}$. The red “box” is used to select sequential breakup events via $\text{CO}^{2+} + \text{S}^+$. (b) The $N(\theta_{\text{CO,S}})$ distributions: (blue) all events and (red) events within $8 \text{ eV} < \text{KER}_{\text{CO}} < 11 \text{ eV}$. The KER slice indicates that the flat distribution extends to small angles.

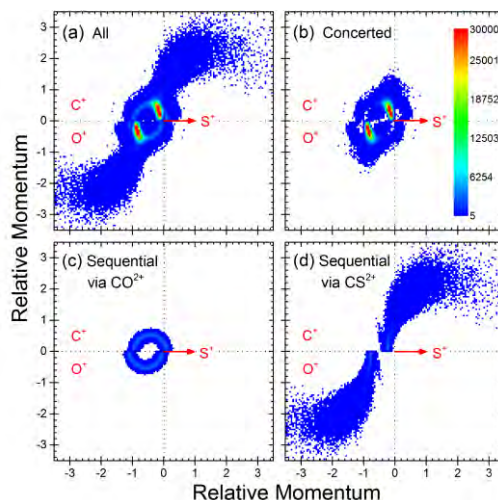


Figure 4. Newton diagrams showing relative momenta with respect to the S^+ momentum, which is set along the x -axis. (a) The whole data set, i.e., all breakup channels, which are presented separately in the other panels, specifically (b) Concerted, (c) Sequential via CO^{2+} , and (d) Sequential via CS^{2+} .

References

1. Ben Berry, PhD thesis, Kansas State University (2017)
2. C. W. Bauschlicher *et al.*, J. Chem. Phys. **99**, 3654 (1993)
3. S. R. Langhoff *et al.*, J. Chem. Phys. **84**, 4474 (1986)
4. D. Ursrey *et al.*, Phys. Rev. A **85**, 023429 (2012)
5. C. E. M. Strauss and P. L. Houston, J. Chem. Phys. **94**, 8751 (1990)
6. N. Neumann *et al.*, Phys. Rev. Lett. **104**, 103201 (2010)
7. B. Wales *et al.*, J. Elec. Spec. Rel. Phenom. **195**, 332 (2014)
8. R. Guillemin *et al.*, Nat. Comm. **6**, 6166 (2015)
9. C. Wu *et al.*, Phys. Rev. Lett. **110**, 103601 (2013)

Future plans: We will continue to probe molecular-ion beams in a strong laser field, specifically exploring challenging two-color, pump-probe and CEP-dependence experiments. We will carry on our studies of more complex systems, including simple polyatomic molecules focusing on three-body breakup, as well as isomerization processes.

This work will also include studies of molecular anion beams using our recently upgraded setup. For example, we plan to explore the isomerization of acetylene–vinylidene using both C₂H₂ cation and anion beam targets for which we have preliminary results.

Further down the line we intend to photo-detach the anion beam and study the response of neutral molecular beams to similar laser pulses.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

21. “[Three-dimensional momentum imaging of dissociation in flight of metastable molecules](#)”, Bethany Jochim, Reid Erdwien, Y. Malakar, T. Severt, Ben Berry, Peyman Feizollah, Jyoti Rajput, B. Kaderiya, W.L. Pearson, K.D. Carnes, A. Rudenko, and I. Ben-Itzhak – New J. Phys. – **accepted**.
20. “[Phase- and intensity-dependence of ultrafast dynamics in hydrocarbon molecules in few-cycle laser fields](#)”, M. Kübel, C. Burger, R. Siemering, Nora G. Kling, B. Bergues, A.S. Alnaser, I. Ben-Itzhak, R. Moshhammer, R. de Vivie-Riedle, and M.F. Kling, **115**, 1835 (2017) – Bandrauk special issue.
19. “[Mechanisms and time-resolved dynamics for trihydrogen cation \(H₃⁺\) formation from organic molecules in strong laser fields](#)”, Nagitha Ekanayake, Muath Nairat, Balram Kaderiya, Peyman Feizollah, Bethany Jochim, Travis Severt, Ben Berry, Kanaka Raju P., Kevin D. Carnes, Shashank Pathak, Daniel Rolles, Artem Rudenko, Itzik Ben-Itzhak, Christopher A. Mancuso, B. Scott Fales, James E. Jackson, Benjamin G. Levine, and Marcos Dantus, Scientific Reports **7**, 4703 (2017).
18. “[The importance of Rydberg orbitals in dissociative ionization of small hydrocarbon molecules in intense few-cycle laser pulses](#)”, Bethany Jochim, R. Siemering, M. Zohrabi, A. Voznyuk, J.B. Mahowald, D.G. Schmitz, K.J. Betsch, Ben Berry, T. Severt, Nora G. Kling, T.G. Burwitz, U. Ablikim, K.D. Carnes, M.F. Kling, I. Ben-Itzhak, E. Wells, and R. de Vivie-Riedle, Scientific Reports **7**, 4441 (2017).
17. “[Unambiguous observation of F-atom core-hole localization in CF₄ through body-frame photoelectron angular distributions](#)”, C.W. McCurdy, T.N. Rescigno, C.S. Trevisan, R.R. Lucchese, B. Gaire, A. Menssen, M.S. Schöffler, A. Gattton, J. Neff, P.M. Stammer, J. Rist, S. Eckart, B. Berry, T. Severt, J. Sartor, A. Moradmand, T. Jahnke, A.L. Landers, J.B. Williams, I. Ben-Itzhak, R. Dörner, A. Belkacem, and Th. Weber, Phys. Rev. A **95**, 011401(R) (2017) – Rapid Communication.
Selected for PRA Kaleidoscope: <http://journals.aps.org/prakaleidoscope/prakaleidoscope/pra/95/1/011401> January 2017.
16. “[A comprehensive study of Interatomic Coulombic Decay in argon dimers: Extracting R-dependent absolute decay rates from the experiment](#)”, J. Rist, T. Miteva, B. Gaire, H. Sann, F. Trinter, M. Keiling, N. Gehrken, A. Moradmand, B. Berry, M. Zohrabi, M. Kunitski, I. Ben-Itzhak, A. Belkacem, T. Weber, A.L. Landers, M. Schöffler, J.B. Williams, P. Kolorenč, K. Gokhberg, T. Jahnke, and R. Dörner, Chem. Phys. **482**, 185 (2017) – Special issue on ICD
15. “[Transition from SAMO to Rydberg state ionization in C₆₀ in femtosecond laser fields](#)”, H. Li, B. Mignolet, Z. Wang, K.J. Betsch, K.D. Carnes, I. Ben-Itzhak, C.L. Cocke, F. Remacle, and M.F. Kling, J. Phys. Chem. Lett. **7**, 4677 (2016).

14. [“Bond-rearrangement and ionization mechanisms in the photo-double-ionization of simple hydrocarbons \(\$C_2H_4\$, \$C_2H_3F\$, and \$1,1-C_2H_2F_2\$ \) near and above threshold”](#), B. Gaire, A. Gatton, F. Wiegandt, J. Neff, C. Janke, S. Zeller, D. Reedy, J. Rajput, I. Ben-Itzhak, A.L. Landers, A. Belkacem, and Th. Weber, *Phys. Rev. A* **94**, 033412 (2016).
13. [“Complete characterization of single-cycle double-ionization of argon from the non-sequential to the sequential ionization regime”](#), M. Kübel, C. Burger, Nora G. Kling, T. Pischke, Lucas Beaufore, I. Ben-Itzhak, G.G. Paulus, J. Ullrich, T. Pfeifer, R. Moshhammer, M. F. Kling, and B. Bergues, *Phys. Rev. A* **93**, 053422 (2016).
12. [“Steering proton migration in hydrocarbons using intense few-cycle laser fields”](#), M. Kübel, R. Siemering, C. Burger, Nora G. Kling, H. Li, A.S. Alnaser, B. Bergues, S. Zharebtsov, A.M. Azzeer, I. Ben-Itzhak, R. Moshhammer, R. de Vivie-Riedle, and M.F. Kling, *Phys. Rev. Lett.* **116**, 193001 (2016).
11. [“Molecular frame photoelectron angular distributions for core ionization of ethane, carbon tetrafluoride and 1,1-difluoroethylene”](#), A. Menssen, C.S. Trevisan, M.S. Schöffler., T. Jahnke, I. Bocharova, F. Sturm, N. Gehrken, B. Gaire, H. Gassert, S. Zeller, J. Voigtsberger, A. Kuhlins, F. Trinter, A. Gatton, J. Sartor, D. Reedy, C. Nook, B. Berry, M. Zohrabi, A. Kalinin, I. Ben-Itzhak, A. Belkacem, R. Dörner, T. Weber, A.L. Landers, T.N. Rescigno, C.W. McCurdy, and J.B. Williams, *J. Phys. B* **49**, 055203 (2016).
10. [“Long term carrier-envelope-phase stabilization of a terawatt-class Ti:Sapphire laser”](#), A. M. Summers, B. Langdon, J. Garlick, X. Ren, D. Wilson, S. Zigo, M. Kling, S. Lei, C. Elles, E. Wells, E. Poliakoff, K. Carnes, V. Kumarappan, I. Ben-Itzhak, and C. Trallero-Herrero, in *Frontiers in Optics 2015*, OSA Technical Digest (online) (Optical Society of America, 2015), paper FTu3F.2.
9. [“Quantum control of photodissociation using intense, femtosecond pulses shaped with third order dispersion”](#), Uri Lev, L. Graham, C.B. Madsen, I. Ben-Itzhak, B.D. Bruner, B.D. Esry, H. Frostig, O. Heber, A. Natan, V.S. Prabhudesai, D. Schwalm, Y. Silberberg, D. Strasser, I.D. Williams, and D. Zajfman, *J. Phys. B* **48**, 201001 (2015) – Fast Track Communication – IOP Select.
8. [“Auger decay and subsequent fragmentation pathways of ethylene following K-shell ionization”](#) B. Gaire, D.J. Haxton, F.P. Sturm, J. Williams, A. Gatton, I. Bocharova, N. Gehrken, M. Schöffler, H. Gassert, S. Zeller, J. Voigtsberger, T. Jahnke, M. Zohrabi, D. Reedy, C. Nook, A.L. Landers, A. Belkacem, C.L. Cocke, I. Ben-Itzhak, R. Dörner, and Th. Weber, *Phys. Rev. A* **92**, 013408 (2015).
7. [“Note: Determining the detection efficiency of excited neutral atoms by a microchannel plate detector”](#), Ben Berry, M. Zohrabi, D. Hayes, U. Ablikim, Bethany Jochim, T. Severt, K.D. Carnes, and I. Ben-Itzhak, *Rev. Sci. Instrum.* **86**, 046103 (2015).
6. [“Coherent electronic wave packet motion in \$C_{60}\$ controlled by the waveform and polarization of few-cycle laser fields”](#), H. Li, B. Migolet, G. Wachter, S. Skruszewicz, S. Zharebtsov, F. Süßmann, A. Kessel, S.A. Trushin, Nora G. Kling, M. Kübel, B. Ahn, D. Kim, I. Ben-Itzhak, C.L. Cocke, T. Fennel, J. Tiggesbäumker, K.-H. Meiwes-Broer, C. Lemell, J. Burgdörfer, R.D. Levine, F. Remacle, and M.F. Kling, *Phys. Rev. Lett.* **114**, 123004 (2015).
5. [“Identification of a previously unobserved dissociative ionization pathway in time-resolved photospectroscopy of the deuterium molecule”](#), Wei Cao, Guillaume Laurent, Itzik Ben-Itzhak and C. Lewis Cocke, *Phys. Rev. Lett.*, **114**, 113001 (2015) – *Editors’ Suggestion*.
4. [“A carrier-envelope-phase stabilized terawatt class laser at 1 kHz with a wavelength tunable option”](#), Benjamin Langdon, Jonathan Garlick, Xiaoming Ren, Derrek J. Wilson, Adam M. Summers, Stefan Zigo, Matthias F. Kling, Shuting Lei, Christopher G. Elles, Eric Wells, Erwin D. Poliakoff, Kevin D. Carnes, Vinod Kumarappan, Itzik Ben-Itzhak, and Carlos A. Trallero-Herrero, *Opt. Exp.* **23**, 4563 (2015). *Featured in Nature Photonics* <http://www.nature.com/nphoton/journal/v9/n4/pdf/nphoton.2015.47.pdf>.
3. [“Fragmentation of \$CD^+\$ induced by intense ultrashort laser pulses”](#), L. Graham, M. Zohrabi, B. Gaire, U. Ablikim, B. Jochim, B. Berry, T. Severt, A.M. Summers, U. Lev, O. Heber, D. Zajfman, I.D. Williams, K.D. Carnes, B.D. Esry, and I. Ben-Itzhak, *Phys. Rev. A* **91**, 023414 (2015).
2. [“Attosecond control of electron emission in two-color ionization of atoms”](#), G. Laurent, W. Cao, I. Ben-Itzhak, and C.L. Cocke, *Ultrafast Phenomena XIX* – Proceedings of the 19th International Conference, Okinawa, Japan, July 2014, edited by Kaoru Yamanouchi, Steven Cundiff, Regina de Vivie-Riedle, Makoto Kuwata-Gonokami, and Louis DiMauro, Springer Proceedings in Physics, Vol. **162** (2015) p. 3.
1. [“Note: Position dependence of time signals picked of a microchannel plate detector”](#), U. Ablikim, M. Zohrabi, Bethany Jochim, B. Berry, T. Severt, K.D. Carnes, and I. Ben-Itzhak, *Rev. Sci. Instrum.* **86**, 016111 (2015).

ⁱ In addition to the close collaboration with the theory group of *Brett Esry*, some of our studies are done in collaboration with others at JRML and elsewhere.

Strong-field dynamics of few-body atomic and molecular systems

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Project Scope

My group’s efforts are focused on developing novel analytical and numerical tools to more efficiently and more generally treat atoms and molecules in strong laser fields. Our goal is to advance the state-of-the-art to enable increasingly complicated processes and systems to be treated in an *ab initio* manner. We specialize in treating few-body systems with minimal approximations, using the results to validate general analytic approaches. Moreover, with more effective tools for such systems, we are able to explore a broader range of physical phenomena and can more realistically contemplate quantitative comparisons with experiment for these highly non-perturbative processes.

Comparing the performance of time-dependent-Schrödinger-equation solvers for the strong-field, one-electron, atomic ionization problem

Recent progress

My group is leading a collaboration to compare the performance of a wide selection of the codes used in our community to solve the time-dependent Schrödinger equation (TDSE) for the strong-field ionization problem. Specifically, we want to benchmark the codes for ionization of a three-dimensional, one-electron atom in a linearly polarized, 800-nm laser pulse. In doing so, we aim to provide the community with concrete information on the most efficient way to solve this ubiquitous problem.

Numerical solutions of the TDSE have been pursued for most of the nearly 40 years since the observation of ATI [R1], leading many in the field to consider it a “solved” problem. While it is “solved” in the sense that many methods do exist for its solution, to this day it is not clear which method is best—or by how much their performance differs. One key reason for this lack of clarity is that, unlike related fields [R2–R5], no direct comparison of a range of methods has been published. Compounding the problem are the facts that neither a code’s runtime performance nor its accuracy are typically discussed in the literature.

We began this project to rectify this situation and thereby provide an informed starting point for future efforts to develop TDSE solvers. In the process, we want to identify the best practices for this problem and make them available to the whole community. We have chosen this specific problem because of its continued central importance to the community and because its efficient solution can form a building block for treating more complex systems. Moreover, there is a large audience of experimentalists that would benefit from having more efficient codes to solve the

linearly polarized, one-electron-atom, 800-nm problem.

Since we believe the most honest comparison will be achieved by having each method’s experts optimize and run their own codes, we invited 39 theory groups from around the world to participate. Of those 39 groups, 14 agreed to participate and 6 said “maybe”. The rest either declined or did not respond.

The only fair way to compare the different methods is to find the minimum time each takes to achieve a given accuracy on a given observable for a given pulse. We completely specified each of these to the collaboration (see Table 1 for the laser pulse parameters), including an explicit equation to define convergence. We did not, however, provide the collaboration with an “exact” solution. It also stands to reason that a direct comparison of runtimes requires that all of the codes run on the same computer. We thus provided the computer and specified how to measure the time.

For simplicity, we identified a single observable for comparison. We chose it such that its correctness implied that all other observables are also correct. To this end, we chose the photoelectron momentum distribution (PMD). It is the most differential ionization observable and generally the hardest to calculate. Getting this correct requires not only representing the energies involved correctly (*e.g.*, via the radial grid), but also getting the angular part correct (*e.g.*, via the phases of the different partial waves).

Although the PMD reduces to two dimensions for linearly polarized light, checking its convergence is still cumbersome. We thus picked a high and low momenta—corresponding to $10U_p$ and $0.1U_p$, respectively, where U_p is the ponderomotive energy—and

looked at the angular distribution. The vast majority of the ionized electron wavepacket should lie between these energies, so their having accurate angular distributions implies the rest of the wavepacket is almost certainly accurate, too. Our accuracy goal was defined such that the angular distributions should be accurate to two digits on average for the largest four orders of magnitude.

We conducted the first round of the comparison as a blind test. That is, everyone carried out their convergence testing completely independently. We collected these results and compared them to a result we obtained accurate to at least four digits to determine an absolute relative error. Ten groups submitted 14 methods at this stage, only 5 of which were actually converged within the agreed-upon tolerance.

This aspect of our comparison is, we believe, a significant contribution in its own right since it represents the submitters good-faith attempt to satisfy our agreed-upon convergence goal. These results therefore also serve as a proxy for the accuracy of results in the literature. Those groups whose results were not converged after the blind test were given the opportunity to redo their calculations since the final comparison of runtimes requires that the contributions have similar errors.

We have so far received 12 accuracy-qualified submissions for our single-threaded benchmark. The runtimes range from 16s to 2:55:04. The slowest contribution is thus $650\times$ slower than the fastest.

We have received 8 accuracy-qualified submissions for our multi-threaded benchmark run on 20 cores across 2 CPUs of a single node. The wall-clock times range from 3s to 67:30—a factor of $1350\times$. The best speedup—*i.e.*, $T_{\text{seq}}/T_{\text{par}}$ —was about 17 and the worst was 2. While the former was nearly ideal, its wall-clock time was still nearly 5 minutes. The best-wall-clock-time code had a speedup of about 6.

While the orders-of-magnitude differences in runtimes is remarkable and is a clear argument for the need of such a study, it is still a snapshot of the performances of the codes. For different laser parameters or different observables, the relative performance could be different. Since it is impractical to do comparisons like this for all possible scenarios, we will do the next best thing and provide the scaling properties of the methods with all the relevant parameters. With this information, the reader should be able to extrapolate from our snapshot to their case of interest and determine which method is preferable.

Future plans

Although we expect this work to have significant impact on many levels, it is not a continuing project. Once the paper is published, we do not expect there to be a need to repeat such a benchmark for at least a few years. In the meantime, our results can likely prevent the waste of substantial computing resources. They can also serve as the yardstick for any new TDSE solver proposed in the future.

Table 1: Laser pulse parameters. The second row shows the numbers in atomic units. The second row provided the definitive values of the parameters for our test to avoid units-conversion issues.

ω	τ	τ_{FWHM}	Intensity	\mathcal{E}_0	U_p
800 nm	8.0 fs	2.9 fs	10^{14} W/cm ²		6.0 eV
0.05695 a.u.	331.0 a.u.			0.05338 a.u.	0.2196 a.u.

Strong-field two-center effect in molecular ionization at large internuclear distances

Recent Progress

Building on our efficient existing TDSE methods, my student, Youliang Yu, recently developed a code to solve for the fixed- R , two-center electronic dynamics in a strong field. He can thus treat fixed- R ionization for H_2^+ essentially exactly. Moreover, the code is efficient enough that he can calculate the dynamics at internuclear distances R well beyond 100 a.u. We know of no other codes with this capability.

Part of our motivation for constructing this code was to help understand a recent experiment performed by I. Ben-Itzhak’s group. That experiment, a pump-probe study on HD^+ , revealed ionization enhancements at very long internuclear delays. Specifically, they pumped HD^+ with a relatively weak 780-nm pulse to initiate dissociation on the lowest potentials—*i.e.*, to $p+\text{D}(1s)$ and $\text{H}(1s)+d$. The enhancement delays were so long, though, that they

corresponded to internuclear distances where the system should, by all expectations, behave as individual atoms and thus show no dependence on R .

This experimental work was itself undertaken to try to validate a model and mechanism we had postulated to explain an even earlier experiment. The mechanism in question is above-threshold Coulomb explosion (ATCE) [R6], invoked to explain roughly equispaced peaks in the proton energy spectrum following strong-field ionization of H_2^+ . The model used in Ref. [R6] to explain ATCE was an extension of the usual Floquet-Born-Oppenheimer potentials to include the continuum. More specifically, the ionization threshold ($1/R$ in this case) was shifted by n photons and the resulting crossings with the dressed bound-state potentials indicated the opening of the n -photon ionization channel. In the spirit of coupled-potential pictures, the bound-continuum crossings were expected to correspond to an increased probability of ionization. Since there are crossings at distances well beyond $R=10$ a.u., the extended Floquet-Born-Oppenheimer picture predicts ionization enhancements at large R .

Initially, the experiments appeared to confirm this prediction since I. Ben-Itzhak's group did indeed see enhancement at large delays. Upon closer inspection, though, the delays were not reasonably correlated to the R of the crossing. We thus sought a less-approximate theoretical treatment to understand the physics. Solving the ionization problem at fixed R was feasible, would address the experimental findings, and would also directly check the ATCE picture.

We solve the TDSE in spheroidal coordinates using a b-spline spatial representation and propagate in time via a Neumann expansion of the Padé[1/1] approximant to the short-time propagator. We evaluate the total yield through a combination of a complex absorbing potential and eigenstate projection at the final time. We believe the yields are accurate to two digits, but further testing is required to fully convince ourselves. While feasible, the calculations are still not trivial, with runtimes on the order of hours to a day.

Figure 1 shows the ionization probability for R out to 150 a.u. for $1s\sigma_g$ and $2p\sigma_u$ initial states. Since the potentials are degenerate to a high degree already by $R \sim 15$ a.u., one would expect simple atomic-like behavior for all larger R . Given that the yields show considerable structure for these R , their behavior is clearly not atomic, although they do approach the atomic yield on average for the largest R .

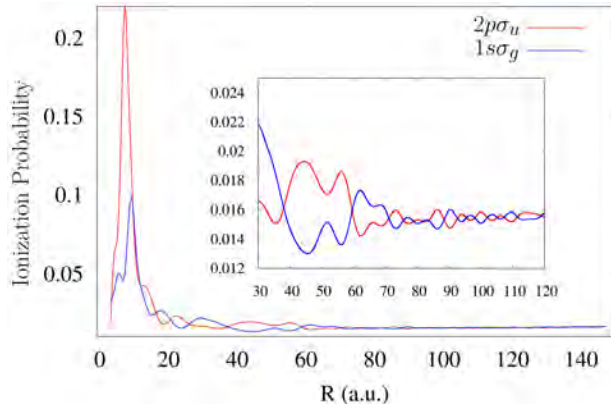


Figure 1: Fixed- R ionization probability for H_2^+ for molecular initial states to very large R . The laser pulse is a 10-fs, 780-nm, 1×10^{14} -W/cm² Gaussian.

The R dependence in Fig. 1 also does not obviously support the ATCE picture. In that picture, there is one crossing for this wavelength at around $R=38$ a.u. and none for larger R . From the figure, nothing particularly special is happening at $R=38$ a.u.—in fact, it just appears to be part of a larger pattern extending over all R . So, even though the channel opening represented by the crossing in the Floquet-Born-Oppenheimer curves is physical and must play a role, that role is much more complicated than the simple ATCE picture assumes.

All of this begs the question: what is the explanation for the behavior in the figure? One feature does look familiar—the double-peaked structure at small R for the $1s\sigma_g$ state. This is the structure labeled charge-resonance-enhanced ionization (CREI) by Zuo and Bandrauk [R7]. Note that ionization from $2p\sigma_u$ is another $2.5 \times$ bigger, which is not necessarily explained by the CREI model. Plotted together like this, however, the behavior of the two states' yields looks complementary, and the CREI structure takes on a different palor.

The behavior in the figure actually suggests that the structure is the result of a two-center effect. To explore this possibility, one can take the usual approach of writing the molecular $1s\sigma_g$ and $2p\sigma_u$ states in terms of atomic states $1s_A$ and $1s_B$ and use the linearity of the time-evolution operator U to find

$$\begin{aligned}
 P_{g,u} &= \int dE |\langle E | U \Psi_{g,u} \rangle|^2 \\
 &= \int dE \left[\frac{1}{2} |\langle E | U \Psi_A \rangle|^2 + \frac{1}{2} |\langle E | U \Psi_B \rangle|^2 \right. \\
 &\quad \left. \pm \text{Re} \langle E | U \Psi_A \rangle^* \langle E | U \Psi_B \rangle \right]. \quad (1)
 \end{aligned}$$

In this form, the molecular-state ionization probabilities are explicitly written in terms of the atomic-state ionization amplitudes. The next-to-last line gives the incoherent contribution, while the last line gives the interference. These terms can be isolated by taking the sum and difference of P_g and P_u and are plotted in Fig. 2.

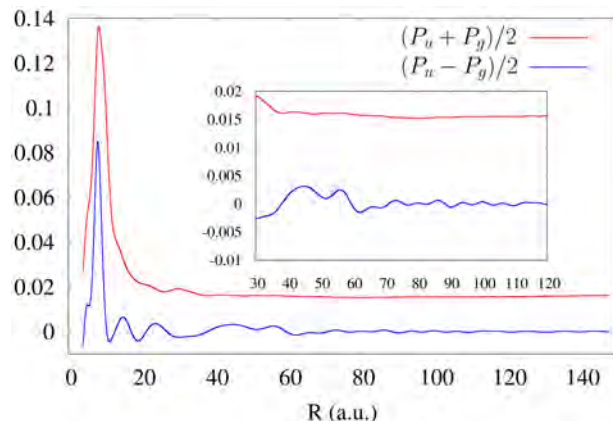


Figure 2: Fixed- R ionization probability for H_2^+ for atomic initial states to very large R , obtained using Eq. (1) and $P_{g,u}$ from Fig. 1.

Figure 2 shows that the incoherent contribution does indeed become essentially structureless at large R . Since all the large- R structure from Fig. 1 can be accounted for by the interference term alone, this strongly suggests that a multiphoton two-center ef-

References

- [R1] P. Agostini, F. Fabre, G. Mainfray, G. Petite, and N. K. Rahman, *Phys. Rev. Lett.* **42**, 1127 (1979).
- [R2] C. Leforestier, R. Bisseling, C. Cerjan, M. Feit, R. Friesner, A. Guldberg, A. Hammerich, G. Jolicard, W. Karrlein, H.-D. Meyer, N. Lipkin, O. Roncero, and R. Kosloff, *J. Comp. Phys.* **94**, 59 (1991).
- [R3] R. Kosloff, *Annu. Rev. Phys. Chem.* **45**, 145 (1994).
- [R4] A. Castro, M. A. L. Marques, and A. Rubio, *J. Chem. Phys.* **121**, 3425 (2004).
- [R5] K. Kormann, S. Holmgren, and H. O. Karlsson, *J. Chem. Phys.* **128**, 184101 (2008).
- [R6] B. D. Esry, A. M. Sayler, P. Q. Wang, K. D. Carnes, and I. Ben-Itzhak, *Phys. Rev. Lett.* **97**, 013003 (2006).
- [R7] T. Zuo and A. D. Bandrauk, *Phys. Rev. A* **52**, R2511 (1995).

Peer-reviewed publications resulting from this project (2015–2017)

- [P1] L. Graham, M. Zohrabi, B. Gaire, U. Ablikim, B. Jochim, B. Berry, T. Severt, K. J. Betsch, A. M. Summers, U. Lev, O. Heber, D. Zajfman, I. D. Williams, K. D. Carnes, B. D. Esry, and I. Ben-Itzhak, “Fragmentation of CD^+ induced by intense ultrashort laser pulses,” *Phys. Rev. A* **91**, 023414 (2015).
- [P2] U. Lev, L. Graham, C. B. Madsen, I. Ben-Itzhak, B. D. Bruner, B. D. Esry, H. Frostig, O. Heber, A. Natan, V. S. Prabhudesai, D. Schwalm, Y. Silberberg, D. Strasser, I. D. Williams, and D. Zajfman, “Quantum control of photodissociation using intense, femtosecond pulses shaped with third order dispersion,” *J. Phys. B* **48**, 201001(FTC) (2015).
- [P3] Y. Yu, S. Zeng, J. V. Hernández, Y. Wang, and B. D. Esry, “Influence of the initial angular distribution on strong-field molecular dissociation,” *Phys. Rev. A* **94**, 023423 (2016).

fect is responsible.

This explanation by itself is still not entirely satisfactory, however. One point to note in trying to gain a deeper understanding is that the final-time atomic amplitudes in Eq. (1) were obtained with both centers present during the pulse. That is, only the initial state was atomic—the Hamiltonian was otherwise the same. The next question is thus whether two-center *interference* or two-center *dynamics*—or both—are responsible. To try to answer this question, we calculated the purely atomic response and superposed them in the usual way. The resulting yield did indeed oscillate with R , but with a very different period. Since this exercise involved only two-center interference and no two-center dynamics, it shows that two-center dynamics is a critical aspect of the behavior shown in the figures.

Future Plans

Seeing any R -dependent structure in the H_2^+ ionization yield at such large R is surprising. Most people’s expectation would be that the system is atomic by $R=20$ a.u.—but that seems to be not entirely correct. We are testing the generality of this phenomenon by, for instance, repeating the calculations for a heteronuclear system to see if the oscillation at large R is entirely a consequence of two-center dynamics. We will continue our efforts to understand these effects and connect them to the experimental observations.

Controlling rotations of asymmetric top molecules: methods and applications

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Project Scope:

The goal of this program is to improve molecular alignment methods, especially for asymmetric top molecules, and then use well-aligned molecules for further experiments in ultrafast molecular physics. We use multi-pulse sequences for 1D alignment and orientation, and for 3D alignment of molecules. Our main focus now is to further develop our method for extracting orientation-resolved information from rotational wavepacket dynamics, particularly for asymmetric top molecules. We are particularly interested in applying this method to obtain molecular frame photoelectron angular distributions.

Recent Progress:

In the past few years we have shown that the rotational wave packet dynamics induced by impulsive alignment of a molecule can be exploited to obtain the orientation dependence of probe-driven processes as well as the time evolution of the molecular axis distribution. Briefly, the angle-dependence of the measured signal is expressed as an expansion in a Wigner function basis, and the delay-dependent signal as a convolution of the time-dependent molecular axis distribution and the angle dependence of the probe process. The algorithm uses TDSE calculations of the rotational wavepacket and linear regression to deconvolve the two functions. In the case of asymmetric top molecules, this method (which we call Orientation Resolution from Rotational Coherence Spectroscopy, or ORRCS) can extract the dependence of probe-driven processes as a function of the two Euler angles that are necessary to specify the orientation of the molecule relative to a linearly polarized field. In many cases— non-dissociative ionization by an ultrashort laser pulse, for instance—this method is unique in this capability. ORRCS is also the only method available for determining the full 2D rotational wavepacket dynamics in asymmetric tops. We are currently using this method to study angle-resolved strong field ionization in asymmetric tops and developing new measurement techniques based on ORRCS.

Strong field ionization of carbon dioxide:

We returned to a linear molecule (CO_2) to clarify both the angle dependence of its strong-field ionization—which has been the subject of some experimental controversy and some disagreement between various theoretical approaches—and to test the limits of our approach to molecular frame measurements using rotational wavepackets. Some technical improvements in our gas source have made it possible to routinely reach rotational temperatures 1-2 K range, which also prompted us to make high-resolution measurements of the ionization of CO_2 . To reach a very high degree of alignment, we used a two-pump approach (which we have previously been used to reach $\langle \cos^2 \theta \rangle \sim 0.82$ for nitrogen [1]), in which we apply a second alignment pulse just before the 3/4th revival of alignment. Such a high degree of alignment requires at rotational wavepacket that is much broader than the initial thermal distribution of rotational states. A probe pulse singly ionizes the molecules

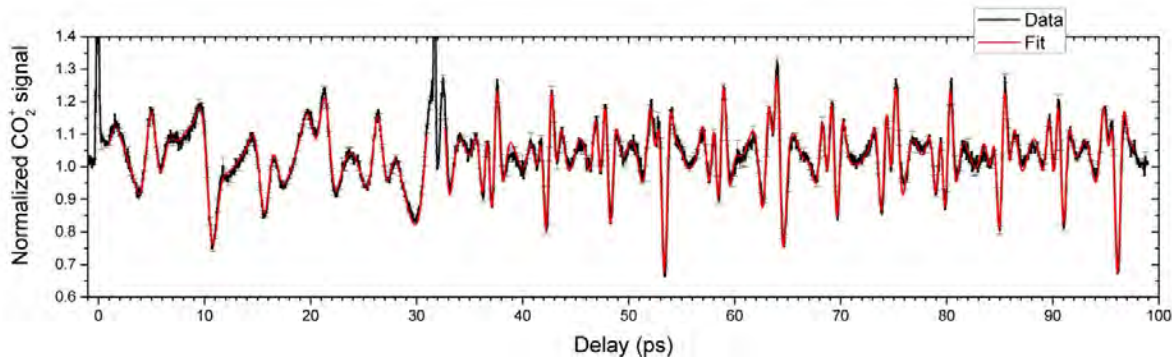


Figure 1: Measured angle-integrated yield of CO_2^+ as a function of delay after an impulsive alignment pulse at zero delay. A second alignment pulse was applied just before the three-quarter revival at ~ 32 ps. The solid red line is the best fit obtained using the ORRCS algorithm. The best alignment achieved after the second pulse is $\cos^2 \theta = 0.89$.

and the ionization yield measured as a function delay. We then fit the measured delay dependence using a Legendre polynomial expansion for the angle dependence of ionization. The data and the fit are shown in Fig. 1. The fitting procedure also extracts gas temperature and pump fluences from data.

The peak alignment we were able reach after the second pump in CO_2 was $\langle \cos^2 \theta \rangle = 0.89$ —the highest degree of alignment achieved in impulsive alignment experiments to the best of our knowledge. The rotational wavepacket that results in this high degree of alignment contains high-order coherences of sufficient magnitude to allow us to use a Legendre polynomial expansion up to $L = 16$ for the angle dependence of the strong-field ionization of CO_2 . The angular dependence was found to vary little as the size of the model was increased from $L = 4$ to $L = 16$ (Fig. 2). It was also found to vary very little when only the data before the second pump pulse was used for the fit, although the number of coefficients that could be extracted reliably was smaller.

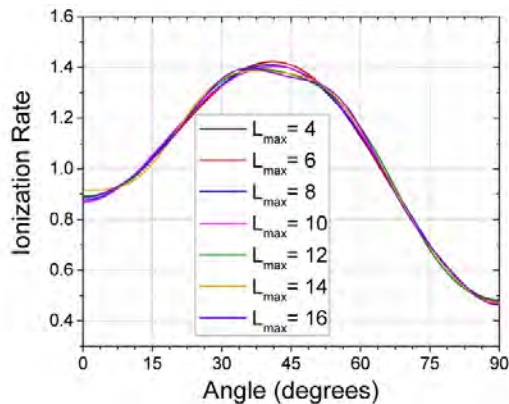


Figure 2: Angle dependence of ionization of CO_2 by a 35 fs, 800 nm pulse at $2 \times 10^{14} \text{ W/cm}^2$. L_{max} the largest order of Legendre polynomials used for the fit to the delay dependent data.

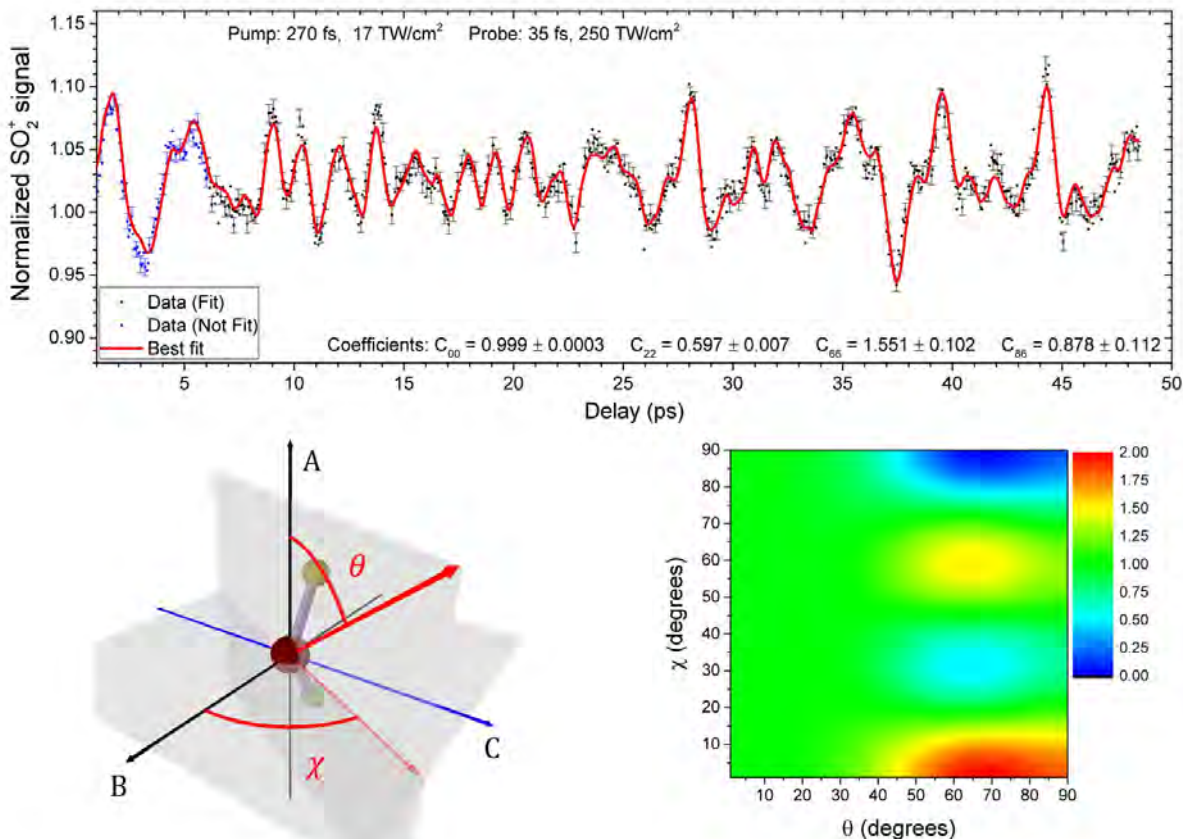


Figure 3: Top: Measured angle-integrated yield of SO_2^+ as a function of delay after an impulsive alignment pulse at zero delay. The solid red line is the best fit obtained using the ORRCS algorithm. Values of significant fit coefficients are shown. Bottom left: the Euler angles in terms of the laser polarization in the molecular frame. Bottom right: Angle dependence of ionization, normalized to the isotropic value.

Strong field ionization and fragmentation of sulphur dioxide:

In the case of asymmetric top molecules, we can extract the dependence of the probe process on two Euler angles (the polar angle θ and the azimuthal angle χ of the laser polarization in the molecular frame) from experiments in which cylindrical symmetry is maintained by using collinearly polarized pump and probe pulses. We repeated our measurement of the angle-dependence of the strong-field ionization of SO_2 at ~ 1.7 K (from ~ 15 K before). The modulation in the ion yield signal was enhanced by about a factor of five at the reduced temperature, resulting in much better signal-to-noise ratio and higher angular resolution. In particular, we were able to reliably determine several coefficients of the Wigner function expansion up to $J = 8, K = 6$ (most were near zero), whereas at 15 K we were only about to obtain the $J = 2$ coefficients. This revealed additional structure (the maximum and minimum at $\chi \approx 60^\circ$ and $\chi \approx 30^\circ$, respectively) in the angle dependence that were hidden in the lower resolution measurement. The fit and the extracted angle dependence are shown in Fig. 3.

We improved our statistical analysis by using cross-validation, in which a random subset of the data is used for fitting and the remaining data is used to validate the model. Cross validation helps picking an appropriate model size and in avoiding over-fitting.

Future plans:

The breakdown of the axial recoil approximation limits the utility of momentum imaging methods in determining molecular frame distributions. By comparing the molecular axis distribution obtained using ORRCS and directly measured using velocity map imaging of molecular fragments, we will quantify the extent to which this breaks down in various fragmentation pathways. These experiments will first be attempted in linear molecules (CO_2 and CS_2), and then in asymmetric top molecules (SO_2 and C_2H_4). VMI measurements of photoelectrons will also be made and analyzed using ORRCS to extract molecular frame photoelectron angular distributions. With $\langle \cos^2 \theta \rangle \sim 0.9$, the degree of alignment is comparable to that obtained for state-selected linear molecules in an adiabatic laser field, the state-of-the-art technique for producing tightly aligned molecules, without the complications caused by the presence of the strong adiabatic field.

In experiments of CO_2 reported in Ref. [P2], we showed the coupling of electronic and vibration excitation on the one hand, and electronic and rotational excitation on the other by using pump and probe pulses of different durations. The short pulses used for exciting vibrational wavepackets precluded significant rotational excitation. With a three-pulse experiment, we will investigate the role of molecular orientation in vibrational and spin-orbit wavepackets in this molecule.

Peer-Reviewed Publications Resulting from this Project (2015-2017):

- [P1] Benjamin Langdon, Jonathan Garlick, Xiaoming Ren, Derrek J. Wilson, Adam M. Summers, Stefan Zigo, Matthias F. Kling, Shuting Lei, Christopher G. Elles, Eric Wells, Erwin D. Poliakoff, Kevin D. Carnes, Vinod Kumarappan, Itzik Ben-Itzhak, and Carlos A. Trallero-Herrero, “Carrier-envelope-phase stabilized terawatt class laser at 1 kHz with a wavelength tunable option,” *Opt. Express* 23, 4563-4572 (2015).
- [P2] Artem Rudenko, Varun Makhija, Aram Vajdi, Thorsten Ergler, Markus Schuerholz, Rajesh K Kushawaha, Robert Moshhammer, Joachim Ullrich, and Vinod Kumapparann, “Strong-field-induced wave packet dynamics in carbon dioxide molecule”, *Faraday Discuss.*, 194, 463-478, (2016).
- [P3] Utuq Ablikim, Cédric Bomme, Hui Xiong, Evgeny Savelyev, Razib Obaid, Balram Kaderiya, Sven Augustin, Kirsten Schnorr, Ileana Dumitriu, Timur Osipov, René Bilodeau, David Kilkoyne, Vinod Kumarappan, Artem Rudenko, Nora Berrah, Daniel Rolles “Identification of absolute geometries of *cis* and *trans* molecular isomers by Coulomb Explosion Imaging”, *Scientific Reports* 6, 38202 (2016).
- [P4] Jan Troß, Xiaoming Ren, Varun Makhija, Sudipta Mondal, Vinod Kumarappan, and Carlos A. Trallero-Herrero, “ N_2 HOMO-1 orbital cross section revealed through high-order-harmonic generation”, *Phys. Rev. A* 95, 033419 (2017).

References:

- [1] X. Ren, *et al.*, *Physical Review A* 88, 043421 (2013).

Strong field rescattering physics and attosecond physics

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Project Scope:

We investigated the interaction of ultrafast intense laser pulses, and of attosecond pulses, with atoms and molecules. The most notable accomplishment in the past year is the development of a new method to retrieve the phase of isolated attosecond pulses. The new method removes the inherent error in the widely used FROG-CRAB method and it has significant implications in all streaking experiments that have been carried out so far. Various other accomplished projects and other ongoing projects are also summarized.

1. Retrieval of XUV, IR or atomic dipole phase in attosecond streaking experiments

Recent progress

Since 2016 we began to examine the theory of metrology of isolated attosecond pulses (IAP). Although IAPs have been around since 2001, its characterization continues to be a topic of discussion in the attosecond physics community. The standard FROG-CRAB retrieval method is known to have a number of limitations that may affect the accuracy of the extracted phase of the XUV pulse duration, but the accuracy has never been quantified. The “world” record of a shortest attosecond pulse clearly is limited by the uncertainty of the retrieval method.

In 2016 we performed simulations to investigate the accuracy of the FROG-CRAB method. Using known theoretical input parameters to generate the photoelectron streaking spectra, we followed the FROG-CRAB method to test if we can recover the input data. We found that the FROG-CRAB becomes less accurate as the chirp of the XUV pulse increases. The errors are of a few attoseconds if the chirp is such that the chirped pulse does not double the pulse duration. For shorter pulses, the FROG-CRAB begins to fail. In particular, the method would not converge in attosecond pulses in the water window region where the spectral width is 50 eV or higher.

It turns out that the phase of the XUV pulses is the easiest to retrieve so long as the chirp of the XUV is not too large. The FROG-CRAB method also returns the IR pulse used in the streaking experiment. It is harder to retrieve the IR accurately since the vector potential of the IR enters in the exponential oscillating function. The error in the IR also affects how accurately the phase of the atomic transition dipole can be retrieved in the so-called “photoionization time delay” experiments. This has the consequence that it affects severely the retrieval of the so-called “photoionization time delay” with the implications that most of the retrieved “time delays” in the literature are of questionable quality.

We have since developed a new phase retrieval method with the aim of replacing the FROG-CRAB. The method is called Phase Retrieval of Broadband PULSES (PROBP). This method removes the so-called central momentum approximation and other approximations used in FROG-CRAB. As reported in Pub. [A5], the PROBP method allows us to retrieve XUV pulses accurately, much better than the FROG-CRAB. For narrow attosecond pulses, the PROBP improves the accuracy of the retrieved phase of the XUV pulse. For broadband pulses, the FROG-CRAB does not converge, but the PROBP can accurately retrieve broadband pulses in

the water window region, even when the streaking field is the mid-infrared lasers with wavelength of 2000-nm. The PROBP simultaneously can retrieve the streaking IR or Mid-IR pulses accurately. In Pub. [A5] the method was applied to retrieve the amplitude and phase of multi-color synthesized broadband IR-UV waveforms that are used to generate isolated attosecond pulses.

It is desirable that the PROBP method be applied to characterize real streaking data from experiments. Even though streaking spectra involving water-window continuum harmonics have been “reported”, the signal is quite weak and the noises are quite large.

Ongoing projects and future plan

In our previous publication, Pub. [A13], we examined the accuracy of the atomic dipole phase retrieval using the FROG-CRAB method. It was concluded that the errors in terms of the group delay can be quite large if the XUV pulse has chirp. We concluded that the so-called time delay difference of 20 as between photoionization from 3s and 3p shell of Ne as reported in Schultze et al Science 328, 1658 (2010) was likely arising from the limitation of the retrieval method.

Since the PROBP is a more accurate retrieval algorithm, in the last few months we moved on to retrieve the atomic dipole phase (or equivalently the photoionization group delay). We found that with the PROBP the retrieved group delay (over the bandwidth of the XUV pulse) indeed improves significantly over the one retrieved from FROG-CRAB. We did a further check theoretically the group delay difference over a photon energy range of 30 eV on the group delay between Ar and Ne targets, at the center photon energy of 60 eV. The results from FROG-CRAB and PROBP methods are compared. The FROG-CRAB can easily get an error of group delay difference of up to 50 to 100 as for the chirped XUV pulses. Using PROBP the errors are consistently within a few attoseconds.

The above results are obtained using streaking spectrogram generated using the SFA model. Two newer developments are underway. One is to use PROBP to retrieve group delay difference using spectrograms generated from solving the TDSE. We will be checking how much error the retrieved group delay difference is. The TDSE results are taken as experimental data in this exercise.

So far practically all the phase retrieval analysis consider photoelectrons along the co-linear polarization direction only. For XUV photoionization, the photoelectron wave packets along different directions are not independent. At a given photoelectron energy for photoionization from rare gas atoms (excluding He), the unknowns are the amplitude of the s-wave and d-wave, and their phase difference. It would be desirable to retrieve these parameters over the whole spectral bandwidth together using XUV alone data and XUV+IR streaking spectrograms. Our second new direction is to use PROBP to obtain such information. This would then derive all the fundamental photoionization dipole amplitude and phase over the whole bandwidth based on the streaking measurements to accomplish a “complete” experiment for photoionization.

Lastly, we are also working with the streaking data in the water-window region using the data from Biegert’s group. The data are not as good as one would like to have because of the low signal to noise ratio. While experiments will be continued again, we are checking if we can obtain a reasonable pulse duration out of the present set of data.

2. Other miscellaneous topics ***Recent progress and future plans***

- (i) **Extending harmonic cutoff energy and increasing harmonic yields with synthesized waves.** We are continuing the study of phase matching optimization by doing simulations of high harmonics generated by a two-color waveform in a waveguide or in a gas cell. In this period we studied the extension of harmonic cutoff using the “defocusing-assisted phase matching” method in the highly ionized short gas cell. Simulations were used to explain the experimentally observed cutoff energy extension. The result of this combined theoretical and experimental investigation was reported in a paper in *Optica*, see Pub. [A1]. Extending this work to longer wavelength driving lasers in experiment and simulations will be continued. Work along Pub. [A3] will also continue to test the scaling properties of HHG propagation in the gas medium.
- (ii) **Structure retrieval from LIED experiments.** We are continuing collaboration with Biegert’s group on LIED data. This collaboration was halted by the replacement of the person who was performing this investigation on the experimental side, but it is expected to renew in the next few months. Anh Thu Le will be doing the simulations.
- (iii) **The QRS theory for retrieving target structure information from few-cycle bicircular laser fields.** This project was initiated, and carried out by Anh Thu Le; with the help of a short-term visitor from Vietnam. Unlike the QRS for linearly polarized lasers developed by us in the past, for the bicircular field the returning electron comes back at a different angle from the initial ionization direction. In Pub. [A7], it shows how to extract the structure information using photoelectron momentum spectrum calculated from solving the TDSE.
- (iv) **Terahertz generation and carrier-envelope phase (CEP) characterization of phase-stabilized few-cycle pulses.** With the help of a visiting scholar Dr. Zhou, the mechanism of terahertz generation by two-color pulses was investigated by associating it to the left-right asymmetry of photoelectrons. The emission was attributed to the free-free transition between the even-parity with odd-parity continuum electrons within the same ATI peak, see Pub. [A6]. In another paper, Pub. [A8], a method was developed to retrieve the absolute value of the CEP from the high-energy photoelectron spectrum. The absolute CEP is not known to the experimentalist even if the CEP is stabilized. This suggested method also can determine the pulse duration and the laser intensity used in the experiment.
- (v) **Two longer-range research projects were initiated in the last few months.** The first one is to begin to implement commercial molecular software packages and integrate them to new programs that are being developed to calculate the dissociation dynamics of small polyatomic molecules. Currently two visitors are working with Anh Thu Le to develop codes for this purpose. The other project is to begin the investigation of HHG in solids. With the help from a visitor some progress has already been made. In fact, a manuscript reporting the condition for observing only odd harmonics or both even and odd harmonics was established. Current theory for explaining this simple question was incorrect.
- (vi) **Notable events.** In the last year, two papers were published in *Science* from our group. In addition, a book entitled “Attosecond and strong field physics” was completed. It is to be published by Cambridge University Press in 2018.

Peer-Reviewed Publications Resulting from this Project (2016- 2017)

A1. Hung-Wei Sun, Pei-Chi Huang, Yi-Hsuan Tzeng, Jen-Ting Huang, C. D. Lin, Cheng Jin, and Ming-Chang Chen, “Extended phase matching of high harmonic generation by plasma-induced defocusing”, *Optica*, 8, 976 (2017).

A2. Xu Wang, Anh-Thu Le, Zhaoyan Zhou, Hui Wei and C D Lin, “Theory of retrieving orientation-resolved molecular information using time-domain rotational coherence spectroscopy”, *Phys. Rev. A* 96, 023424 (2017).

- A3. Cheng Jin, Kyung-Han and C D Lin, “Macroscopic scaling of high-order harmonics generated by two-color” optimized waveforms in a hollow waveguide”, *Phys. Rev. A* **96**, 013422 (2017).
- A4. Zhaoyan Zhou, Xu Wang, Zhangjin Chen and C. D. Lin, “Retrieval of parameters of few-cycle laser pulses from high-energy photoelectron spectra of atoms by a genetic algorithm”, *Phys. Rev. A* **95**, 063411 (2017).
- A5. Xi Zhao, Hui Wei, Yan Wu, and C.D. Lin, “A new phase retrieval algorithm for characterization of broadband single attosecond pulses,” *Phys. Rev. A* **95** , 043407 (2017).
- A6. Zhaoyan Zhou, Xu Wang, and C. D. Lin, “Analysis of THz generation through the asymmetry of photoelectron angular distribution”, *Phys. Rev. A* **95**, 033418 (2017).
- A7. Van-Hung Hoang, Van-Hoang Le, C. D. Lin, and Anh-Thu Le, “Retrieval of target structure from laser-induced photoelectrons by few-cycle bicircular laser fields, *Phys. Rev. A* **95**, 031402(R) (2017).
- A8. Van-Hung Hoang, Song-Feng Zhao, Van-Hoang Le, and Anh-Thu Le, “ Influence of permanent dipole and dynamic core-electron polarization on tunneling ionization of polar molecules”, *Phys. Rev. A* **95**, 023407 (2017).
- A9. Stefan Zigo, Anh-Thu Le, PratapTimilsina, Carlos A.Trallero-Herrero, "Ionization Study of Isomeric Molecules in Strong-field Laser Pulses" *Scientific Reports* **7**, 42149 (2017)
- A10. Cheng Jin , Kyung-Han Hong , C. D. Lin, “Optimal generation of spatially coherent soft X-ray isolated attosecond pulses in a gas-filled waveguide using two-color synthesized laser pulses, *Scientific reports*, **6**, 38165 (2016).
- A11. A. Kaldun, A. Blättermann ,V. Stooß , S. Donsa , H. Wei , R. Pazourek , S. Nagele , C. Ott , C. D. Lin, J. Burgdörfer and T. Pfeifer, “ Observing the ultrafast build-up of a Fano resonance in the time domain”, **Science** **354**, **738** (2016)
- A12. B. Wolte, M. G. Pullen, A.-T. Le, M. Baudisch, K. Doblhoff-Dier, A. Senfleben, M. Hemmer, C. D. Schröter, J. Ullrich, T. Pfeifer, R. Moshhammer, S. Gräfe, O. Vendrell, C. D. Lin, J. Biegert, “Ultrafast electron diffraction imaging of bond breaking in acetylene dication”, **Science** **354**, **308** (2016).
- A13. Hui Wei and C. D. Lin, “Critical evaluation of attosecond time delays retrieved from photoelectron streaking measurements”, *Phys. Rev. A* **93**, 053412 (2016)

[Ten additional publications from 2016 were not listed here.]

Imaging Ultrafast Electron and Nuclear Dynamics in Polyatomic Molecules

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Project Scope: *This program focuses on imaging nuclear and electronic dynamics during photochemical reactions by means of femtosecond pump-probe experiments with laboratory-based laser sources complemented by experiments with free-electron lasers and 3rd generation synchrotrons. The aim of these experiments is to study exemplary reactions in gas-phase molecules with the goal of clarifying their reaction mechanisms and pathways.*

Recent Progress: Several major instrumental development projects performed in close collaboration with other experimental groups at J.R. Macdonald Laboratory that were started when I joined the program two and a half years ago have come to fruition this year: (i) We have performed first XUV-NIR pump-probe experiments on Xe, CO₂, and CH₃I using a velocity map electron and ion imaging spectrometer in conjunction with a high harmonic generation source, demonstrating the capability to study electronic and nuclear dynamics in atoms and molecules induced by both valence and inner-shell ionization with ~30 fs temporal resolution. (ii) We have added a third-harmonic generation setup including a double-prism compressor to our “workhorse” COLTRIMS experiment, which allows UV-IR pump-probe experiments to investigate UV-induced dissociation and isomerization processes with sub-70 fs resolution. (iii) A new instrument that enables coincident detection of fragment ions with high-energy electrons produced by our XUV HHG source was assembled and recently commissioned and can now also be used for the pump-probe experiments described in (i). In addition, I have continued to simultaneously pursue an active research program using external user facilities such as the LCLS, the ALS, and FLASH, where I have performed several experiments within various international collaboration.

(i) XUV-NIR pump-probe experiments using a 10-kHz HHG source at JRML, S.J. Robotjazi, S. Pathak, W.L. Pearson, Kanaka Raju P., A. Rudenko, and D. Rolles

Over the last two years, we have developed a setup for femtosecond pump-probe experiments on atoms, molecules, and nanoparticles using a 10 kHz high-harmonic generation (HHG) source in combination with an optical femtosecond laser. The HHG source delivers extreme ultraviolet (XUV) radiation of ~30 fs pulse duration in the photon energy range of ~17 eV to 100 eV. It can be coupled to a conventional velocity map imaging (VMI) setup or to a double-sided VMI spectrometer equipped with two delay-line detectors for coincidence studies, which is described in more detail below. Figure 1 shows the results of an inner-shell ionization experiment on xenon, which we have conducted in order to characterize the performance of the pump-probe setup. For this experiment, a zirconium filter was used to suppress photon energies below 60 eV such that the dominant XUV ionization pathway was through Xe(4*d*) inner-shell ionization. In that case, single or cascade Auger decay leads to the production of Xe²⁺ and Xe³⁺ ions, respectively. Some of the Xe²⁺ ions are created in metastable, highly excited states and can be further ionized to Xe³⁺ by a subsequent, weak NIR pulse. The ratio of the Xe³⁺ to Xe²⁺ ion yield measured in an XUV-pump NIR-probe experiment therefore exhibits a step function around zero delay with a rise time corresponding to the cross correlation between the two pulses. From the data shown in Fig. 1, we obtain a pulse duration of the XUV pulse of ~30 fs (FWHM), when assuming an NIR pulse duration of 25 fs (FWHM). In addition to the ion yields, we have also recorded the corresponding photoelectron spectra for Xe(4*d*) inner-shell ionization and have performed a similar pump-probe experiments on molecular targets that are currently under analysis.

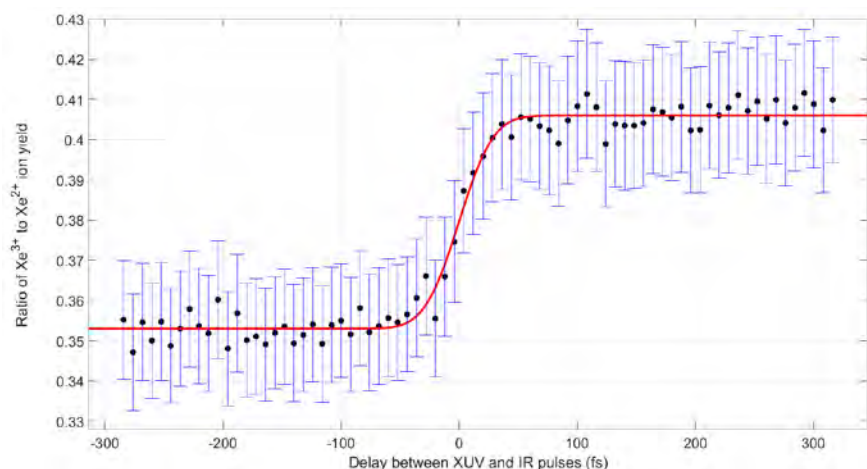


Figure 1: Ratio of Xe^{3+} to Xe^{2+} ion yield as a function of delay between the $>60\text{-eV}$ XUV-pump and the 800-nm NIR-probe pulse. The solid line is a fit of a Gaussian cumulative distribution function (CDF) to the experimental data, which yields a Gaussian width of $\sigma = 23.1 \pm 4.8$ fs. Negative delays correspond to the IR pulse arriving before the XUV pulse.

(ii) Probing the ultrafast UV-induced dissociation dynamics in halogenated hydrocarbons, *F. Ziaee, U. Ablikim B. Kaderiya, S. Pathak, Y. Malakar, W.L. Pearson, K.R. Pandiri, I. Ben-Itzhak, A. Rudenko, D. Rolles, E. Savelyev¹, R. Boll¹, B. Erk¹, S. Techert¹, J. Küpper¹, K. Amini², M. Brouard², A. Rouzee³, T. Marchenko⁴, M. Simon⁴, H. Stapelfeldt⁵, N. Berrah⁵*; ¹DESY, Hamburg, Germany; ²Oxford University, UK; ³Max-Born-Institut, Berlin, Germany; ⁴UPMC/CNRS, Paris, France; ⁵Arhus University, Denmark; ⁵University of Connecticut.

Extending our prior work on halomethanes to larger systems including dihalomethanes, dihaloethanes/ethenes, and halobenzenes, we have studied the UV-induced dissociation dynamics in halogenated hydrocarbons using time-resolved Coulomb explosion imaging and time-resolved photoelectron spectroscopy. In particular, we have focused on exploring the influence of different probe wavelengths and the effect of the molecular environment on the dissociation and Coulomb explosion processes. These systematic studies were only possible by closely linking our experiments performed at JRML, at the Advanced Light Source (ALS) synchrotron radiation source, and at the LCLS and FLASH free-electron lasers. For the laser experiments at JRML, we set up a double-prism UV compressor in collaboration with the Rudenko and the Ben-Itzhak groups, which now allows UV-pump NIR-probe experiments with sub-70 fs temporal resolution using our COLTRIMS setup.

At FLASH, we performed UV-pump XUV-probe experiments on the same molecules within a large international collaboration led by K-State (*Savelyev2017, Amini2017*). Figure 2 shows exemplary results of time-resolved Coulomb explosion imaging experiments on iodomethane (CH_3I) and 2,6-difluoroiodobenzene (DFIB). The kinetic energy release spectra, measured as a function of the delay between the UV and the XUV pulse, show similar features for both molecules, namely a low-energy contribution (“channel III”) corresponding to the site-selective inner-shell ionization of atomic iodine created by neutral dissociation, and a channel exhibiting a delay-dependent kinetic energy (“channel II”), which is due to absorption of two XUV photons, one on each of the two dissociation products. The relative yield of channel II is much enhanced in DFIB due to the larger photoionization cross section of the difluorobenzene radical as compared to the methyl radical in the case of CH_3I .

The FEL experiment were also complemented by studies with synchrotron radiation at the ALS, done in collaboration with the Berrah group at UConn, in order to characterize the XUV photoionization and fragmentation dynamics of CH_3I , DFIB, and other molecules that we studied during our FEL experiments (*Ablikim2016, Ablikim2017*).

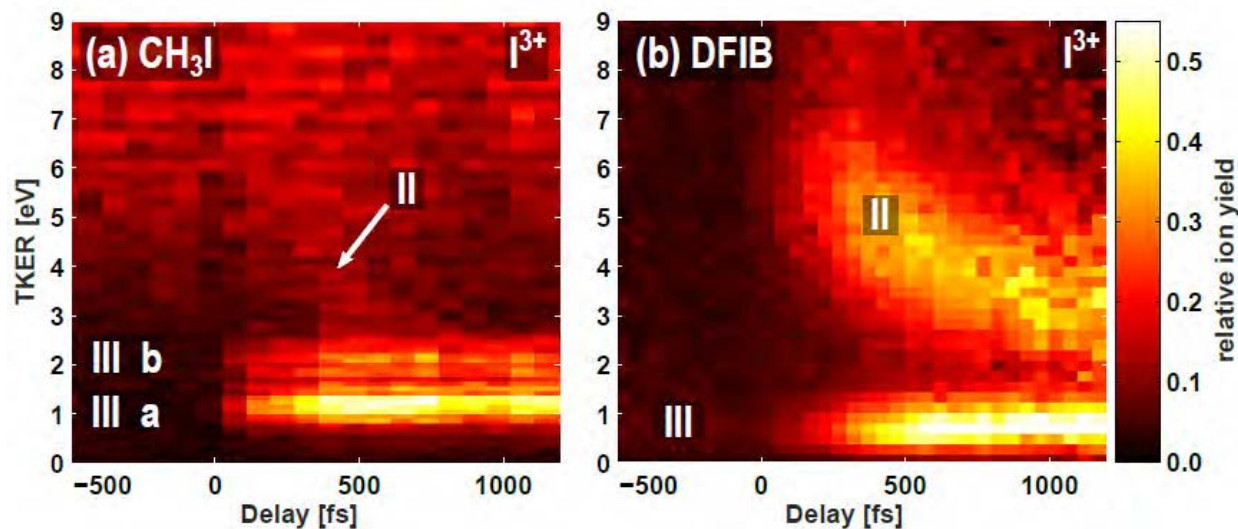


Figure 2: Total kinetic energy release spectrum of the Coulomb explosion of (a) iodomethane and (b) 2,6-diiodobenzene molecules into triply charged iodine ions as a function of the delay between the 266-nm UV-pump and 108-eV XUV-probe pulses. Negative delays correspond to the XUV pulse arriving before the UV pulse. Different fragmentation channels are labeled II and III and are discussed in the text. The figure is taken from E. Savelyev et al., *Struct. Dyn.*, submitted (2017).

(iii) A new electron-ion coincidence momentum imaging setup for XUV-NIR pump-probe experiments, S. Pathak, S.J. Robotjazi, J. Tross, A. Rudenko, and D. Rolles

Up to now, the pump-probe experiments with our 10-kHz XUV sources at JRML, described above in section (i), were performed using a conventional velocity map imaging (VMI) spectrometer that can detect either electrons or ions, depending on the extraction voltages applied to the spectrometer. However, because of the high repetition rate of the drive laser and the HHG source, the system is, in principle, ideally suited for electron-ion coincidence momentum imaging experiments, which would allow highly differential measurements that can yield much deeper insights into the dynamical processes under study. We have therefore constructed a new instrument designed around a double-sided VMI spectrometer equipped with two delay-line anodes, which enables the momentum-resolved, coincident detection of both electrons and ions simultaneously. In order to facilitate the close connection between our in-house experiments and the studies performed at free-electron lasers, our new instrument at JRML was designed to be fully compatible with the electron and ion momentum imaging end-stations at FLASH and LCLS, such that new components developed at JRML can easily be used for FEL experiments and vice versa.

Future Plans:

Using the newly developed experimental capabilities for pump-probe and coincidence experiments with our laboratory light sources at JRML, we plan to continue and extend our studies of dissociation and isomerization reactions in halogenated hydrocarbons with a special focus on disentangling the interplay between electronic and nuclear dynamics in small model systems. To this end, we plan a number of experiments with different combinations of pump and probe wavelengths that will focus on time-resolved photoelectron spectroscopy in coincidence with ion momentum imaging, starting on simple polyatomics such as CH_3I . The interpretation of our experimental results will be aided by a close collaboration with our theory colleagues at JRML, in particular our new faculty member Loren Greenman, who has significant experience in computational approaches for dealing with polyatomic molecules.

We will also continue our FLASH, LCLS, and ALS experiments and have approved beamtimes scheduled at all three facilities in the coming months. While some of these experiments also aim at studying ultrafast reaction dynamics, a new project will investigate the prospects of XUV-assisted high harmonic generation using both free-electron lasers as well as our in-house light sources.

Peer-Reviewed Publications Resulting from this Project (2015-2017):

1. A. Rudenko, ..., D. Rolles, *Femtosecond response of polyatomic molecules to ultra-intense hard X-rays*, [Nature](#) **546**, 129-132 (2017).
2. N. Ekanayake, ..., D. Rolles, A. Rudenko, I. Ben-Itzhak, ..., M. Dantus, *Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields*, [Scientific Reports](#) **7**, 4703 (2017).
3. U. Ablikim, ..., A. Rudenko, N. Berrah, D. Rolles, *Isomer-Dependent Fragmentation Dynamics of Inner-Shell Photoionized Difluoriodobenzene*, [Phys. Chem. Chem. Phys.](#) **19**, 13419 (2017).
4. K. Amini, ..., A. Rudenko, ..., D. Rolles, *Alignment, Orientation, and Coulomb Explosion of Difluoriodobenzene Studied with the Pixel Imaging Mass Spectrometry (PImMS) Camera*, [J. Chem. Phys.](#) **147**, 013933 (2017).
5. E. Savelyev, ..., N. Berrah, ..., A. Rudenko, D. Rolles, *Jitter-Correction for IR/UV-XUV Pump-Probe Experiments at the FLASH Free-Electron Laser*, [New J. Phys.](#) **19**, 043009 (2017).
6. I. Dumitriu, ..., D. Rolles, ..., N. Berrah, *Inner-Shell Photodetachment from Ni^- : A giant Feshbach resonance*, [Phys. Rev. A](#) **96**, 023405 (2017).
7. H. Xiong, ..., D. Rolles, N. Berrah, *Soft X-ray induced ionization and fragmentation dynamics of $Sc_3N@C_{80}$ investigated using an ion-ion coincidence momentum imaging technique*, [Phys. Phys. A](#) **96**, 033408 (2017).
8. U. Ablikim, ..., V. Kumarapan, A. Rudenko, N. Berrah, D. Rolles, *Separation of cis and trans geometric isomers by Coulomb Explosion Imaging*, [Scientific Reports](#) **6**, 38202 (2016).
9. J. Rothhardt, ..., D. Rolles, *High-repetition-rate and high-photon-flux 70 eV high-harmonic source for coincidence ion imaging of gas-phase molecules*, [Optics Express](#) **24**, 18133-18147 (2016).
10. A. Picon, ..., A. Rudenko, ..., D. Rolles, ..., S. H. Southworth, *Hetero-site-specific ultrafast intramolecular dynamics*, [Nat. Commun.](#) **7**, 11652 (2016).
11. T. Gorkhover, ..., D. Rolles, A. Rudenko, T. Möller, C. Bostedt, *Femtosecond and nanometer visualization of structural dynamics in superheated nanoparticles*, [Nature Photon.](#) **10**, 93-97 (2016).
12. R. Boll, ..., D. Rolles, A. Rudenko, *Charge transfer in dissociating iodomethane and fluoromethane molecules ionized by intense femtosecond X-ray pulses*, [Struct. Dyn.](#) **3**, 043207 (2016).
13. C. S. Lehmann, ..., A. Rudenko, ..., D. Rolles, ..., S. H. Southworth, *Ultrafast x-ray-induced nuclear dynamics in diatomic molecules using femtosecond x-ray-pump – x-ray-probe spectroscopy*, [Phys. Rev. A](#) **94**, 013426 (2016).
14. C. F. Jones, ..., D. Rolles, A. Rudenko, ..., C. Bostedt, O. Gessner, A.F. Vilesov, *Coupled motion of Xe clusters and quantum vortices in He nanodroplets*, [Phys. Rev. B](#) **93**, 180510(R) (2016).
15. C. E. Liekhus-Schmaltz, ..., D. Rolles, A. Rudenko, ..., P.H. Bucksbaum, V.S. Petrovic, *Ultrafast Isomerization Initiated by X-Ray Core Ionization*, [Nature Commun.](#) **6**, 8199 (2015).
16. R.M.P. Tanyag, ..., D. Rolles, ..., A. Rudenko, ..., C. Bostedt, O. Gessner, A.F. Vilesov, *X-ray coherent diffractive imaging by immersion in nanodroplets*, [Struct. Dyn.](#) **2**, 051102 (2015).
17. T. Kierspel, ..., D. Rolles, A. Rudenko, ..., J. Küpper, *Strongly aligned gas-phase molecules at Free-Electron Lasers*, [J. Phys. B: At. Mol. Opt. Phys.](#) **48**, 204002 (2015).
18. A. Rudenko and D. Rolles, *Time-resolved studies with FELs*, [J. Electron Spectrosc. Relat. Phenom.](#) **204**, 228-236 (2015).
19. K. Schnorr, ... A. Rudenko, ..., D. Rolles, ..., R. Moshhammer, *Time-Resolved Study of ICD in Ne Dimers Using FEL Radiation*, [J. Electron Spectrosc. Relat. Phenom.](#) **204**, 245-256 (2015).
20. T. Ekeberg, ..., D. Rolles, A. Rudenko, ..., J. Hajdu, *Three-dimensional reconstruction of the giant mimivirus particle with an X-ray free-electron laser*, [Phys. Rev. Lett.](#) **114**, 098102 (2015).

Imaging Light-Induced Dynamics of Small Quantum Systems: From Infrared to Hard X-ray Domain

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Project Scope: The main goals of this research are (i) to understand basic physics of (non-linear) light-matter interactions in a broad span of wavelengths, from terahertz and infrared to XUV and x-ray domains, and (ii) to apply the knowledge gained for real-time imaging of ultrafast photo-induced reactions. These goals are being pursued using both, lab-based laser and high-harmonic sources, and external free-electron laser (FEL) facilities. The program aims at studying light-induced phenomena in systems of increasing complexity, from isolated atoms to small and mid-size molecules, extending to gas-phase nanoscale particles. In particular, it focuses at understanding multiple ionization processes in atoms and molecules, multidimensional imaging of light-induced molecular wave packets, structural rearrangement reactions and charge dynamics, and developing new strong-field and X-ray imaging tools.

Recent Progress:

1. Nonlinear X-ray – matter interaction in hard x-ray domain

(in collaboration with D. Rolles, Argonne National Lab group and theory division at CFEL, Hamburg)

The advent of high-intensity, short-pulsed XUV and x-ray radiation sources promises revolutionary new imaging techniques in diverse scientific fields, approaching angstrom spatial and femtosecond (or even sub-femtosecond) temporal resolution [1-12]. The basic prerequisite for designing these experiments is understanding the response of individual atoms, and subsequent electronic and nuclear dynamics in the vicinity of the atom that absorbed X-ray photon(s), which was one of the central research themes of this program over the last few years [2,8-12,16,21]. Main developments within the last year focused on extending these experiments to the regime of hard x-rays and ultrahigh intensities.

Since XFEL imaging experiments mentioned above ideally require angstrom wavelengths and extreme intensities ($> 10^{20}$ W/cm²) to reach atomic resolution, there is a strong need to extend basic experiments on individual atom / small molecule response into this parameter regime. Recently we have accomplished first steps in this direction by studying ionization of rare gas atoms and small polyatomic molecules by ultra-intense X-ray radiation in 5-8 keV photon energy range. The experiments were performed using the nanofocus of the coherent imaging beamline (CXI) at LCLS. Focusing few mJ, 40 fs hard X-ray LCLS pulses to a spot size less than 250 nm in diameter, we were able to reach the intensities approaching 10^{20} W/cm², unprecedented for this photon energy range. Under these conditions we were able to strip all electrons from argon atoms, all but two 1s electrons from krypton, and reached the record 48+ charge state for xenon ionization at 8.3 keV. Even though the highest charge states is reached at the highest photon energy (8.3 keV), the wavelength dependence of the spectra shows significant overall enhancement in the production of charge states from Xe³⁰⁺ to Xe⁴⁰⁺ at the intermediate photon energies (~ 6.5 keV). Comparing the data with the calculations of R. Santra's group (based on the extended XATOM model), we conclude that the simple sequential ionization picture needs to be modified to include relativistic effects as well as resonant excitations to explain the obtained results.

Following the approach we developed earlier for the XUV and the soft x-ray domains, we compared the ionization of isolated xenon atoms and iodine atoms embedded into molecular systems, and obtained first experimental results on ultrafast charge rearrangement in CH₃I and C₆H₅I molecules [16]. As illustrated in Fig. 1a, we observed I⁴⁷⁺ ions from CH₃I at 8.3 keV compared to Xe⁴⁸⁺, and even for larger systems like C₆H₅I, the maximum charge state observed is ~ I⁴⁵⁺. Taking into account charges carried by carbon and hydrogen atoms (estimated from the coincident measurements), this indicates that in contrast to our results in the soft x-ray regime, under ultraintense hard x-ray light the molecules containing a single high-Z element are ionized considerably higher than an isolated atom with similar absorption cross section. Combined experimental and theoretical analysis [16] shows that the reason for this is an efficient charge rearrangement filling the created vacancies on the heavy atom site with the electrons from the neighbouring atoms along with a very large photon density allowing for further ionization of partially neutralized iodine. To verify this, we collaborated on similar experiments on Xe / CH₃I at the Japanese XFEL facility SACLA, which were also performed at hard X-ray photon energies, but at much lower intensities [2,11,12,21]. There, the outcome was rather similar to earlier results in the soft-X-ray domain, confirming that this is the high photon densities on target which results in higher ionization of molecules.

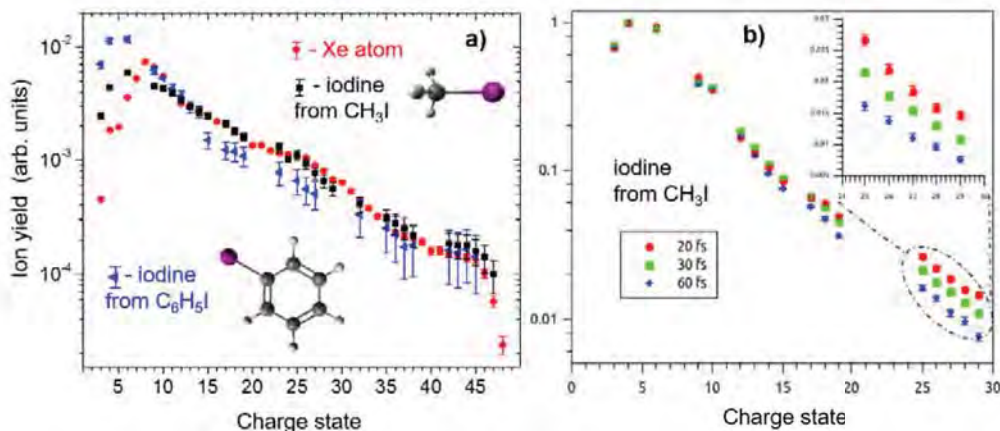


Fig. 1. a) Charge-state distributions of iodine ions emitted from CH_3I (black squares) and $\text{C}_6\text{H}_5\text{I}$ (blue triangles) molecules upon irradiation by 1.1 mJ, 30 fs 8.3 keV pulses. Red circles show the charge-state distribution obtained from atomic xenon under the same conditions. b) Same for CH_3I molecule irradiated by 0.3 mJ, 8.3 keV pulses of different durations.

To further elucidate mechanisms of charge-rearrangement enhanced ionization, we study how extreme multiphoton hard x-ray ionization of CH_3I molecule depends on a pulse duration. As illustrated in Fig. 1b, for fixed pulse energy we observe enhanced production of the highest iodine charge states for shorter pulses. This can be explained by higher photoabsorption rate during the shorter pulse, which results in creating vacancies at the iodine site at shorter internuclear distances and, thus, enhancing the efficiency of charge transfer from the neighbouring atoms.

2. 3D imaging of strong-field induced molecular dynamics in polyatomic molecules (in collaboration with D. Rolles, V. Kumarappan and I. Ben-Itzhak)

This part of the program aims at visualizing, understanding and controlling strong-field driven nuclear dynamics in small polyatomic molecules. These studies rely on coincident momentum imaging of ionic fragments combined with channel-selective Fourier spectroscopy and pump-probe scheme with two near-infrared (NIR) pulses. Starting with one of the simplest polyatomic systems, CO_2 [13], we have recently focused on the dynamics of bound and dissociating nuclear wave packets triggered by intense 800 nm pulses in halomethane molecules, in particular, in CH_3I , CH_2I_2 and CH_2ICl . Halomethanes represents rather simple yet important polyatomic molecules, which often serve as model systems for studying laser controlled chemistry and x-ray induced dynamics [2,8,16,21]. We visualize vibrational wave packet motion in the ground and low-lying excited ionic states as well as in the ground state of the neutral molecules. We traced signatures of both, stretching and bending vibrations, and found direct correlation between the latter and molecular fragmentation pathways, in particular $\text{I}_2 / \text{I}_2^+$ elimination. Our latest efforts focused on three-body coincident measurements, which can yield direct access to the evolving molecular geometry. As an illustrative example, Fig. 2 shows four different Coulomb explosion (CE) patterns depicting time-evolution of bound and continuum dissociation wave packets in CH_2I_2 . In Fig. 2a the pump and the probe pulses arrive at the same time, and the pattern is dominated by the CE of the bound molecule / parent molecular ion (region 1). Events in region 2, which are also observed in Fig. 2a, were attributed to the sequential breakup of the intermediate metastable states of either CH_2I^{++} or I_2^{++} . This was confirmed applying a novel “native frame” analysis technique described in I. Ben-Itzhak’s contribution. Events in regions (1) and (2) are also observed at larger delays (Fig. 2b-d). Even though no clear delay dependence can be observed for these regions in Fig. 2 with rather large delay steps, both, the yield and the KER measured for region 1 exhibit oscillatory behavior reflecting

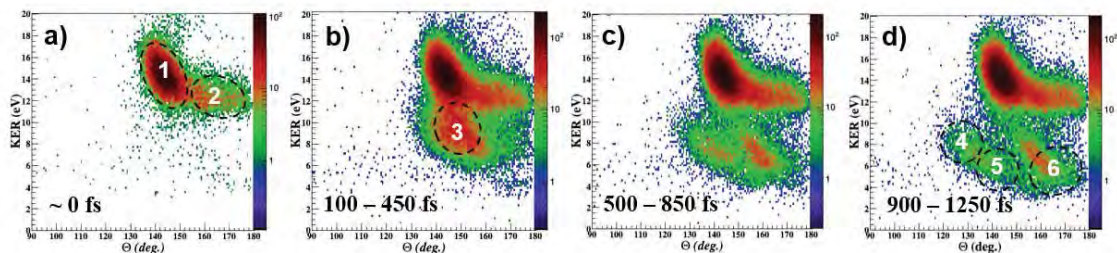


Fig. 2. Delay-dependent Coulomb explosion imaging of CH_2I_2 fragmentation. Here, the yield of the three-body triply charged final state for different delays between the two 800 nm, 25 fs pulses are shown as a function of the measured total kinetic energy release and the angle between the momentum vectors of the two iodine ions. Different fragmentation pathways are indicated in the figure. Pump and probe intensities are $\sim 2 \cdot 10^{14}$ and $6 \cdot 10^{14}$ W/cm^2 , respectively

bending vibrations (the “scissors mode”) of the molecule. More pronounced feature observed in Fig. 2b-d is the evolution of the low-energy part of the spectrum, manifesting signatures of different dissociation pathways induced by the pump. While region 3 highlighted in Fig. 2b shows the onset of all dissociation channels, which are still mixed, they can be clearly disentangled at larger delays in Fig. 2c,d. Using the asymptotic dissociation energies retrieved from single-pulse data, we can identify contributions reflecting the $\text{CH}_2\text{I}^+\text{I}$ (region 3) and $\text{CH}_2\text{I}+\text{I}^+$ (region 4) pathways, as well as the channels involving $\text{I}_2 / \text{I}_2^+$ formation resulting in almost back to back emission of the two I^+ ions in the three-body CE final state (region 6).

3. Dissociation dynamics of molecular ions studied in HHG pump – NIR probe experiments (in collaboration with D. Rolles and I. Ben-Itzhak)

To complement our efforts aimed at characterizing nuclear wave packet dynamics induced by strong field ionization or excitation described in the previous section, we performed a series of measurements employing an XUV source based on high-harmonics generation (HHG) as a single-photon pump. To elucidate the role of different ionic states and their mutual couplings, we used two complementary HHG sources: one delivering a narrowband, single harmonic pulses of ~ 100 fs duration capable of state-selective excitation [R1], and another one generating broadband multi-harmonic ~ 25 fs pulses. After the first experiments on simple diatomic molecules such as D_2 [R1] and O_2 [R2], we applied both of these sources to study the NIR-induced dissociation of the photoionized CO_2 molecule. While some of our results for broadband XUV pulses are consistent with the outcome of an earlier experiment described in [R3], by varying the spectrum of the XUV pump pulse and, thus, selecting the range of ionic states populated, we can manipulate the time-dependent yield of CO^+ and O^+ dissociation products. We also observe a picosecond-scale oscillation of the CO^+ yield with the time constant consistent with the strength of the LS coupling between the ionic ground state and the lowest repulsive state.

Future Plans

We plan to continue research activities in all three areas outlined above. The efforts in the experiments using intense, ultrafast X-rays will focus on understanding the response of larger polyatomic systems (like iodobenzene), on the effect of self-seeded pulses, and on developing schemes for time-resolved studies of ultrafast charge migration. For studies of molecular wave-packets created by NIR and XUV excitation the experiments using the NIR probe will be complemented by similar measurements employing a single-photon XUV probe. We will employ a new electron-ion coincidence momentum imaging setup recently developed at the JRML for studies of dynamics triggered by valence- or inner-shell XUV absorption. Finally, we will continue working on the data analyses and interpretation for the experiments on laser-driven nanoparticles imaged with ultrafast x-ray scattering, which have been performed at LCLS and at FLASH in 2015 and 2017, respectively.

References

- [R1] “Identification of a previously unobserved dissociative ionization pathway in time-resolved photospectroscopy of the deuterium molecule”, W. Cao, G. Laurent, I. Ben-Itzhak and C.L. Cocke, Phys. Rev. Lett., 114, 113001 (2015).
 [R2] “State-selective dissociation dynamics of oxygen molecule studied with single harmonic pump and infrared probe pulses”, Y. Malakar, F. Wilhelm, D. Trabert, Kanaka Raju P., X. Li, W.L. Pearson, W. Cao, B. Kaderyia, C.L. Cocke, I. Ben-Itzhak and A. Rudenko, to be submitted.
 [R3] “Coherent electron hole dynamics near a conical intersection”, H. Timmers, Z. Li, N. Shivaram, R. Santra, O. Vendrell and A. Sandhu, Phys. Rev. Lett. 113, 113003 (2014).

Peer-Reviewed Publications Resulting from this Project (2015-2017):

- [1] “Time-resolved studies with FELs”, A. Rudenko and D. Rolles, J. Electr. Spectr. Rel. Phen. 204, 228 (2015).
 [2] “Charge transfer and nuclear dynamics following deep inner-shell multiphoton ionization of CH_3I molecules by X-ray free-electron laser pulses”, K. Motomura, E. Kukuk, H. Fukuzawa, S. Wada, K. Nagaya, S. Ohmura, S. Mondal, T. Tachibana, Y. Ito, R. Koga, T. Sakai, K. Matsunami, A. Rudenko, C. Nicolas, X.-J. Liu, C. Miron, Y. Zhang, Y. Jiang, J. Chen, M. Anand, D. Kim, K. Tono, M. Yabashi, M. Yao, and K. Ueda, J. Phys. Chem. Lett. 6, 2944 (2015).
 [3] “Ultrafast Isomerization Initiated by X-Ray Core Ionization”, C. Liekhus-Schmaltz, I. Tenney, T. Osipov, A. Sanchez-Gonzalez, N. Berrah, R. Boll, C. Bomme, C. Bostedt, J. Bozek, S. Carron, R. Coffee, J. Devin, B. Erk, K. Ferguson, R. Field, L. Foucar, L. Frasiniski, J. Glowina, M. Gühr, J. Krzywinski, H. Li, J. Marangos, T. Martinez, B. McFarland, S. Miyabe, B. Murphy, A. Natan, D. Rolles, A. Rudenko, M. Siano, E. Simpson, L. Spector, M. Swiggers, D. Walke, S. Wang, T. Weber, P. Bucksbaum, and V. Petrovic, Nature Commun. 6, 8199 (2015).
 [4] “Time-resolved study of ICD in Ne dimers using FEL radiation”, K. Schnorr, A. Senftleben, G. Schmid, S. Augustin, M. Kurka, A. Rudenko, L. Foucar, K. Meyer, D. Anielski, R. Boll, D. Rolles, M. Kubel, M. F. Kling, Y. Jiang, K. Ueda, T. Marchenko, M. Simon, G. Brenner, R. Treusch, V. Averbukh, J. Ullrich, T. Pfeifer, C. Schroter, and R. Moshhammer, J. Electr. Spectr. Rel. Phen. 204, 245 (2015). (2015).
 [5] “Strongly aligned gas-phase molecules at Free-Electron Lasers”, T. Kierspel, J. Wiese, T. Mullins, J. Robinson, A. Aquila, A. Barty, R. Bean, R. Boll, S. Boutet, P. Bucksbaum, H.N. Chapman, L. Christensen, A. Fry, M. Hunter, J.E. Koglin, M. Liang, V. Mariani, A. Morgan, A. Natan, V. Petrovic, D. Rolles, A. Rudenko, K. Schnorr, H. Stapelfeldt, S. Stern, J. Thøgersen, C. H. Yoon, F. Wang, S. Trippel, J. Küpper, J. Phys. B: At. Mol. Opt. Phys. 48, 204002 (2015).
 [6] “X-ray coherent diffractive imaging by immersion in nanodroplets”, R.M.P. Tanyag, C. Bernardo, C.F. Jones, C. Bacellar, K.R. Ferguson, D. Anielski, R. Boll, S. Carron, J.P. Cryan, L. Englert, S.W. Epp, B. Erk, L. Foucar, L.F. Gomez, R. Hartmann, D.M.

- Neumark, D. Rolles, B. Rudek, A. Rudenko, K.R. Siefertmann, J. Ullrich, F. Weise, C. Bostedt, O. Gessner, A.F. Vilesov, *Struct. Dyn.* **2**, 051102 (2015).
- [7] “*Femtosecond and nanometre visualization of structural dynamics in superheated nanoparticles*”, T. Gorkhover, S. Schorb, R. Coffee, M. Adolph, L. Foucar, D. Rupp, A. Aquila, J.D. Bozek, S.W. Epp, B. Erk, L. Gumprecht, L. Holmegaard, A. Hartmann, R. Hartmann, G. Hauser, P. Holl, A. Hömke, P. Johnsson, N. Kimmel, K.-U. Kühnel, M. Messerschmidt, C. Reich, A. Rouzée, B. Rudek, C. Schmidt, J. Schulz, H. Soltau, S. Stern, G. Weidenspointner, B. White, J. Küpper, L. Strüder, I. Schlichting, J. Ullrich, D. Rolles, A. Rudenko, T. Möller, C. Bostedt, *Nature Photonics* **10**, 93 (2016).
- [8] “*Charge transfer in dissociating iodomethane and fluoromethane molecules ionized by intense femtosecond X-ray pulses*”, R. Boll, B. Erk, R. Coffee, S. Trippel, T. Kierspel, C. Bomme, J.D. Bozek, M. Burkett, S. Carron, K.R. Ferguson, L. Foucar, J. Küpper, T. Marchenko, C. Miron, M. Patanen, T. Osipov, S. Schorb, M. Simon, M. Swiggers, S. Techert, K. Ueda, C. Bostedt, D. Rolles, A. Rudenko, *Structural Dynamics* **3**, 043207 (2016).
- [9] “*Hetero-site-specific X-ray pump-probe spectroscopy for femtosecond intramolecular dynamics*”, A. Picón, C.S. Lehmann, C. Bostedt, A. Rudenko, A. Marinelli, T. Osipov, D. Rolles, N. Berrah, C. Bomme, M. Bucher, G. Doumy, B. Erk, K.R. Ferguson, T. Gorkhover, P.J. Ho, E.P. Kanter, B. Krässig, J. Krzywinski, A.A. Lutman, A.M. March, D. Moonshiram, D. Ray, L. Young, S.T. Pratt, S.H. Southworth, *Nature Communications* **7**, 11652 (2016).
- [10] “*Ultrafast x-ray-induced nuclear dynamics in diatomic molecules using femtosecond x-ray-pump-x-ray-probe spectroscopy*”, C.S. Lehmann, A. Picón, C. Bostedt, A. Rudenko, A. Marinelli, D. Moonshiram, T. Osipov, D. Rolles, N. Berrah, C. Bomme, M. Bucher, G. Doumy, B. Erk, K.R. Ferguson, T. Gorkhover, P.J. Ho, E.P. Kanter, B. Krässig, J. Krzywinski, A.A. Lutman, A.M. March, D. Ray, L. Young, S.T. Pratt, S.H. Southworth, *Phys. Rev. A* **94**, 013426 (2016).
- [11] “*Ultrafast Dynamics of a Nucleobase Analogue Illuminated by a Short Intense X-ray Free Electron Laser Pulse*”, K. Nagaya, K. Motomura, E. Kukuk, H. Fukuzawa, S. Wada, T. Tachibana, Y. Ito, S. Mondal, T. Sakai, K. Matsunami, R. Koga, S. Ohmura, Y. Takahashi, M. Kanno, A. Rudenko, C. Nicolas, X.-J. Liu, Y. Zhang, J. Chen, M. Anand, Y.H. Jiang, D.-E. Kim, K. Tono, M. Yabashi, H. Kono, C. Miron, M. Yao, K. Ueda, *Phys. Rev. X* **6**, 021035 (2016).
- [12] “*Femtosecond charge and molecular dynamics of I-containing organic molecules induced by intense X-ray free-electron laser pulses*”, K. Nagaya, K. Motomura, E. Kukuk, Y. Takahashi, K. Yamazaki, S. Ohmura, H. Fukuzawa, S. Wada, S. Mondal, T. Tachibana, Y. Ito, R. Koga, T. Sakai, K. Matsunami, K. Nakamura, M. Kanno, A. Rudenko, C. Nicolas, X.-J. Liu, C. Miron, Y. Zhang, Y. Jiang, J. Chen, M. Anand, D. E. Kim, K. Tono, M. Yabashi, M. Yao, H. Kono and K. Ueda, *Faraday Discussions*, **194**, 537 (2016).
- [13] “*Strong-field-induced wave packet dynamics in carbon dioxide molecule*”, A. Rudenko, V. Makhija, A. Vajdi, Th. Ergler, M. Schuerholz, R. Moshhammer, J. Ullrich, V. Kumapparan, *Faraday Discussions*, **194**, 493 (2016).
- [14] “*Coupled motion of Xe clusters and quantum vortices in He nanodroplets*”, C. F. Jones, C. Bernardo, R.M. Tanyag, C. Bacellar, K.R. Ferguson, L.F. Gomez, D. Anielski, A. Belkacem, R. Boll, J. Bozek, S. Carron, J. Cryan, L. Englert, S.W. Epp, B. Erk, L. Foucar, R. Hartmann, D.M. Neumark, D. Rolles, A. Rudenko, K.R. Siefertmann, F. Weise, B. Rudek, F. Sturm, J. Ullrich, C. Bostedt, O. Gessner, A.F. Vilesov, *Phys. Rev. B* **93**, 180510(R) (2016).
- [15] “*Separation of cis and trans geometric isomers by Coulomb Explosion Imaging*”, U. Ablikim, C. Bomme, H. Xiong, E. Savelyev, R. Obaid, B. Kaderiya, S. Augustin, K. Schnorr, I. Dumitriu, T. Osipov, R. Bilodeau, D. Kilcoyne, V. Kumarappan, A. Rudenko, N. Berrah, D. Rolles, *Scientific Reports* **6**, 38202 (2016).
- [16] “*Femtosecond response of polyatomic molecules to ultra-intense hard X-rays*”, A. Rudenko, L. Inhester, K. Hanasaki, X. Li, S. Robotjazi, B. Erk, R. Boll, K. Toyota, Y. Hao, O. Vendrell, C. Bomme, E. Savelyev, B. Rudek, L. Foucar, S. Southworth, C. Lehmann, B. Kraessig, T. Marchenko, M. Simon, K. Ueda, K. Ferguson, M. Bucher, T. Gorkhover, S. Carron, R. Alonso-Mori, J. Koglin, J. Correa, G. Williams, S. Boutet, L. Young, C. Bostedt, S.-K. Son, R. Santra, and D. Rolles, *Nature* **546**, 129-132 (2017).
- [17] “*Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields*”, N. Ekanayake, M. Nairat, B. Kaderiya, P. Feizollah, B. Jochim, T. Severt, B. Berry, Kanaka Raju P., K. D. Carnes, S. Pathak, D. Rolles, A. Rudenko, I. Ben-Itzhak, C. A. Mancuso, B. S. Fales, J. E. Jackson, B. G. Levine and M. Dantus, *Scientific Reports* **7**, 4703 (2017).
- [18] “*Isomer-Dependent Fragmentation Dynamics of Inner-Shell Photoionized Difluoroiodobenzene*”, U. Ablikim, C. Bomme, E. Savelyev, H. Xiong, R. Kushawaha, R. Boll, K. Amini, T. Osipov, D. Kilcoyne, A. Rudenko, N. Berrah and D. Rolles, *Phys. Chem. Chem. Phys.* **19**, 13419 (2017).
- [19] “*Alignment, Orientation, and Coulomb Explosion of Difluoroiodobenzene Studied with the Pixel Imaging Mass Spectrometry (PImMS) Camera*”, K. Amini, R. Boll, A. Lauer, M. Burt, J. Lee, L. Christensen, F. Brauße, T. Mullins, E. Savelyev, U. Ablikim, N. Berrah, C. Bomme, S. Düsterer, B. Erk, H. Höppner, P. Johnsson, T. Kierspel, F. Krecinic, J. Küpper, E. Müller, M. Müller, H. Redlin, A. Rouzee, N. Schirmel, J. Thørgersen, S. Techert, S. Toleikis, R. Treusch, S. Trippel, A. Ulmer, J. Wiese, C. Vallance, A. Rudenko, H. Stapelfeldt, M. Brouard and D. Rolles, *J. Chem. Phys.* **147**, 013933 (2017).
- [20] “*Jitter-Correction for IR/UV-XUV Pump-Probe Experiments at the FLASH Free-Electron Laser*”, E. Savelyev, R. Boll, C. Bomme, N. Schirmel, H. Redlin, B. Erk, S. Düsterer, E. Müller, H. Höppner, S. Toleikis, J. Müller, M. K. Czwalińska, R. Treusch, T. Kierspel, T. Mullins, S. Trippel, J. Wiese, J. Küpper, F. Brauße, F. Krecinic, A. Rouzee, P. Rudawski, P. Johnsson, K. Amini, A. Lauer, M. Burt, M. Brouard, L. Christensen, J. Thørgersen, H. Stapelfeldt, N. Berrah, M. Müller, A. Ulmer, S. Techert, A. Rudenko, D. Rolles, *New J. Phys.* **19**, 043009 (2017).
- [21] “*Ultrafast coulomb explosion dynamics of the diiodomethane molecule induced by an X-ray free-electron laser pulse*”, T. Takanashi, K. Nakamura, E. Kukuk, K. Motomura, H. Fukuzawa, K. Nagaya, S.-I. Wada, Y. Kumagai, D. Iablonskyi, Y. Ito, Y. Sakakibara, D. You, T. Nishiyama, K. Asa, Y. Sato, T. Umemoto, K. Kariyazono, K. Ochiai, M. Kanno, K. Yamazaki, K. Kooser, C. Nicolas, C. Miron, T. Asavei, L. Neagu, M. Schöffler, G. Kastirke, X.-J. Liu, A. Rudenko, S. Owada, T. Katayama, T. Togashi, K. Tono, M. Yabashi, H. Kono, and K. Ueda, *Phys. Chem. Chem. Phys.* **19**, 19707 (2017).
- [22] “*Three-dimensional momentum imaging of dissociation in flight of metastable molecular ions*”, B. Jochim, R. Erdwien, T. Severt, B. Berry, P. Feizollah, J. Rajput, Y. Malakar, B. Kaderiya, W.L. Pearson, K. Carnes, A. Rudenko and I. Ben-Itzhak, *New J. Phys.*, accepted, DOI:10.1088/1367-2630/aa81ab (2017).

Structure and Dynamics of Atoms, Ions, Molecules and Surfaces

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A. Generalized Volkov states for inhomogenous fields

Project scope: To provide numerically convenient final electronic states of controllable accuracy for the modeling of time-resolved photoemission triggered or assisted by spatially varying external laser electric fields.

Recent progress: Available as simple analytical expressions, exact solutions of the time-dependent Schrödinger (TDSE) and Dirac equations for the motion of an electron in homogeneous continuum-wave external electromagnetic fields, so-called Volkov states, are routinely employed to represent the electronic final state in photoemission processes [1]. Their convenient numerical implementation, however, is often not justified physically due to (i) the competition of Coulomb and laser forces on the emitted photoelectron [R1], (ii) the spatial extent of the target implying the breakdown of the dipole approximation [2,3], and (iii) the rapid spatial variation of external fields due to the incident pulse's screening, reflection, and plasmonic enhancement [4,5]. To remedy this situation, we are developing a versatile semi-classical approach that systematically includes corrective terms beyond the strong-field approximation [S1]. By expanding the photoelectron's wavefunction according to $\psi(\mathbf{r}, t) = \exp\left\{\frac{i}{\hbar} \sum_{n=0}^{\infty} \hbar^n S_n(\mathbf{r}, t)\right\}$, we rewrite the TDSE for the photoelectron's dynamics in *any* net electromagnetic field ($A(r, t)$ $\Phi(r, t)$) in terms of coupled partial differential equations for the complex phases $\{S_n(\mathbf{r}, t)\}$. Subject to appropriate initial conditions, we solve these equation iteratively for successive orders n , starting with the classical action $S_0(\mathbf{r}, t)$ and propagating along the classical trajectories defined by the Hamilton–Jacobi equation for $S_0(\mathbf{r}, t)$. In simple tests, we verified that starting with plane waves for electrons incident with 50 eV, the addition of a Coulomb potential or laser field reproduces excellent approximations to known Coulomb and Volkov waves, respectively (Fig. 1).

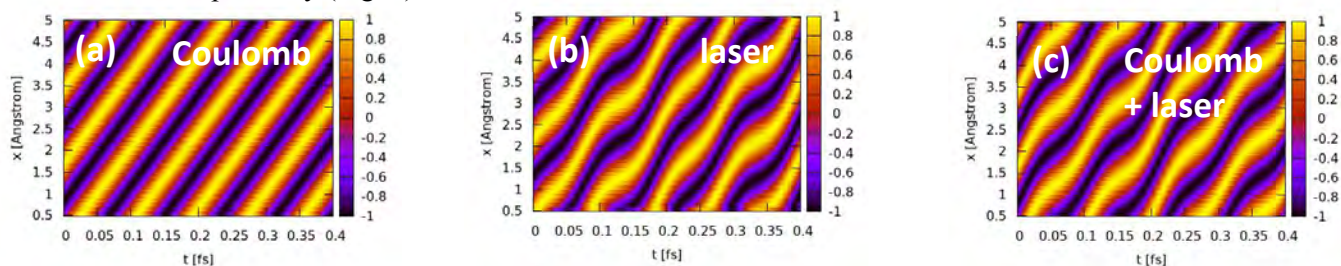


Fig. 1: Semi-classical approximations, obtained by starting the iterative solution of the TDSE with 50 eV plane electron waves propagating in $+x$ direction. Shown is $\psi(x, 0, 0, t)$ for (a) the Coulomb potential of a proton, (b) a 62 nm 10^{14} W/cm² alternating electric field linearly polarized along the x -axis, and (c) the superposition of Coulomb and 62 nm fields.

Future plans: We are implementing semi-classical approximations for the final photoelectron state in calculations of streaked [6,S2] and two-photon-interference (RABBITT, cf. section C below) photoemission spectra [S3,S4] from metal surfaces [6,S3,S4] and nanoparticles [2,S2], where Volkov final states are inappropriate.

B. XUV double ionization (DI) of He

Project scope: To examine, with atomic resolution in time, correlation effects, photoexcitation, and photoemission mechanisms during the ionization of atoms and diatomic molecules in intense short XUV pulses.

Recent progress: Solving the TDSE *ab initio* with our recently developed implementation of a fully dimensional finite-element discrete-variable representation scheme [7,8] for few-photon DI of helium atoms, we quantified sequential and non-sequential contributions in one- and two-photon DI of ground-state and excited He atoms by intense ultrashort XUV pulses. We are currently investigating XUV DI of the excited states He(1s2s¹S) and He(1s2s¹P). Our investigation of electronic correlation, as observable in joint photoelectron energy distributions [7] and joint angular distributions for one-photon DI [R2], reveals two different pathways to DI: (i)

photoabsorption by the inner K-shell electron followed by L-shell emission (favoring a 136 degree angular difference between the emitted photoelectrons) and (ii) photoabsorption by the outer L-shell electron followed by K-shell emission (occurring predominantly at an angular difference of 65 degrees) (Fig. 2). If the spectrum of the incident XUV pulse overlaps with both, the sequential and non-sequential DI regimes, sequential and non-sequential DI mechanisms are difficult to distinguish. By tracking the DI asymmetry in joint photoelectron angular distributions, we find the two-electron forward-backward-emission asymmetry [6] to be an appropriate measure for quantifying sequential and non-sequential contributions.

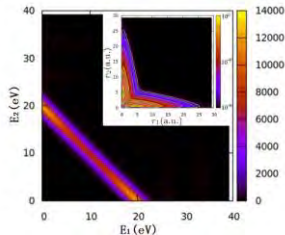


Fig. 2: Normalized joint photoelectron energies distributions for double ionization of He(1s2s1S) by a single 78 eV photon. The XUV pulse has a peak intensity of 5×10^{14} W/cm² and pulse length of 2.12 fs (40 o.c.). The inset shows the undistorted excited initial state. The linear color bar is in arbitrary units.

Future plans: We intend (i) to extend these studies to laser-assisted DI with variable delay between ultrashort XUV and IR pulses. Such delay scans will allow us to resolve in time the correlated two-electron dynamics during and after sequential and non-sequential DI in ultrashort XUV pulses [6,7]. We further envision to (iii) compute laser-dressed autoionization of He, (iv) compare our *ab initio* results with our previous heuristic model for the decay of laser-coupled autoionizing states [R3,R4], and (v) extend this line of work to the DI of H₂.

C. Time-resolved photoelectron photoelectron spectroscopy of flat solid surfaces

Project scope: To numerically model and understand IR-streaked and IR side-banded XUV photoelectron emission and Auger decay in XUV pump – IR probe experiments with atoms and molecules, and to quantitatively assess the fidelity at which material properties and the collective electronic dynamics in solids can be imaged in streaking and RABBITT spectra.

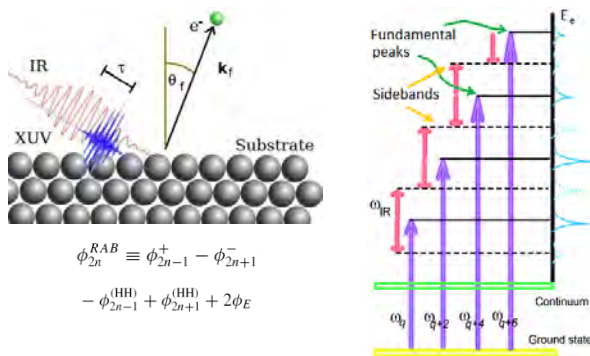


Fig. 3: RABBITT chronoscopy of surfaces. Delay-dependent photoelectron energy distributions and photoemission time delays (phase shifts) from solid or gaseous targets are used to eliminate the unknown spectral (higher harmonics) phases $\{\phi_{2n\pm 1}^{HH}\}$ of the attosecond XUV pulse train. Side-band photoelectron yields oscillate with twice the IR-laser frequency. Adjacent sideband yields are phase-shifted by ϕ_{2n}^{RAB} , including a shift $2\phi_E$ due to Fresnel reflection of the assisting IR pulse and the shifts $\phi_{2n\pm 1}^{\pm}$ characterizing the two interfering two ionization pathways [4,9].

Recent progress: Continued progress in ultrafast laser technology enabled the generation of attosecond pulse trains [4,9] and isolated attosecond pulses [1] that are perfectly synchronized with the driving IR laser and allow for investigations of the electronic dynamics in atoms, molecules, and condensed matter systems. These time-resolved investigations complement traditional energy-domain spectroscopies. They are performed in two types of experimental setups: streaked photoelectron emission [1] and reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) [4]. We have continued to develop and improve quantum-mechanical simulations for streaked and side-banded [R5] photoemission from the valence-bands of Pt, Ag, Au, Cu, and Ni atomically flat surfaces with (100) and (111) crystalline orientations [4,S3,S4] by single attosecond XUV pulses and XUV attosecond pulse trains into the electric field of assisting delayed fs IR pulses. Our current simulations were motivated by recent and emerging experiments [9,R6,R7]. In order to reproduce recently measured RABBITT spectra, we found it necessary to improve our existing simulations by refining our modeling of the target electronic structure within a tight-binding approach [S2] and to include the Fresnel-reflected IR pulse [4].

Example 1: Time-resolved photoemission from Ag(111) and Au(111). Motivated by very recent time-resolved photoemission experiments [R6], we calculated RABBITT spectra from Ag(111) and Au(111) surfaces, focusing on the modeling of the unperturbed valence electronic structure. We compared numerical results obtained by representing the d -valence band of the target by either eigenstates of a parameterized effective potential (“Chulkov potential”) [4,6] or tight-binding states [S3,S4]. We found RABBITT spectra based on tight-binding initial states to be in better agreement with the experimental spectra in Refs. [9,R6,R7] (Fig. 4). We further found it necessary to include - through an appropriate modification of field-dressed free-electron (Volkov) states (cf. section A above) - the Fresnel transmission and reflection of the streaking IR-laser pulse at the vacuum-solid interface [4,S3,S4]. Fresnel reflection of the incident IR pulse enhances the side-band yield and induces a harmonic-order-independent phase shift of 1.24 rad [S4]. The Chulkov and tight-binding initial-state models predict similar phases [Fig. 4(d)]. The agreement between experimental and theoretical spectra is best for kinetic energies < 20 eV [Figs. 4 (a-c)].

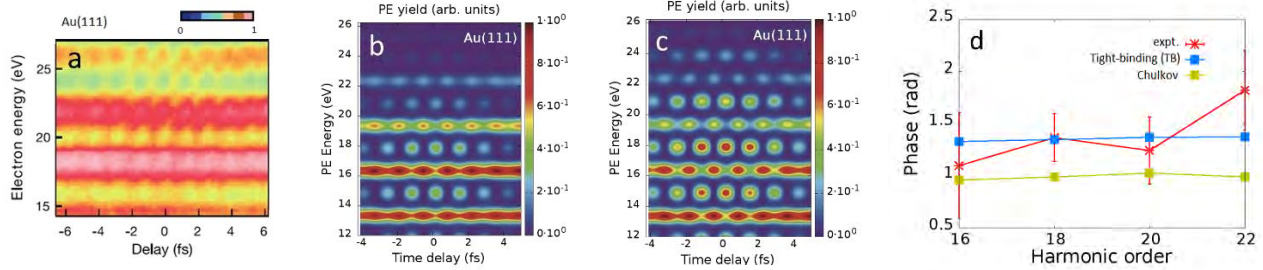


Fig. 4: (a) Experimental (not background-corrected) RABBITT spectrum for Au(111) [R6]. Simulated spectra [S4] for initial d -valence-band states represented within (b) a density-functional model (“Chulkov states” [4]) and (c) our implementation of a tight-binding model. (d) RABBITT phases for the spectra in (a-c) relative to Ar gas reference phases (cf. [S4,R6]). The experimental phases include an overall unknown phase offset and are shifted by 1.8 rad relative to their values given in [R6].

Example 2: Comparative time-resolved photoemission from Cu(111) and Cu(100). Our numerical simulations of RABBITT photoemission spectra from Cu(100) and Cu(111) surfaces predict distinct differences in delay-dependent photoelectron energy distributions and photoemission time delays. These can be distinguished experimentally with existing technology in a suggested *in situ* comparative RABBITT configuration [4] by placing the two surfaces on a sliding platform while keeping all optical components and path lengths fixed (Fig. 5a). As Fresnel reflection reduces the IR skin depth, our calculations show that the inclusion of the Fresnel-reflected incident IR pulse at the metal-vacuum interface modifies photoelectron spectra and photoemission time delays from bulk and surface states differently, revealing their different degrees of spatial location [R8,S3]. Our simulation further indicate that the initial-state kinetic-energy distribution largely determines the photoelectron yield as a function of its final energy and that the valence-density-of-state structure is noticeable in RABBITT spectra and RABBITT phases [i.e., in relative spectral time delays, Figs. 5 (b-d)].

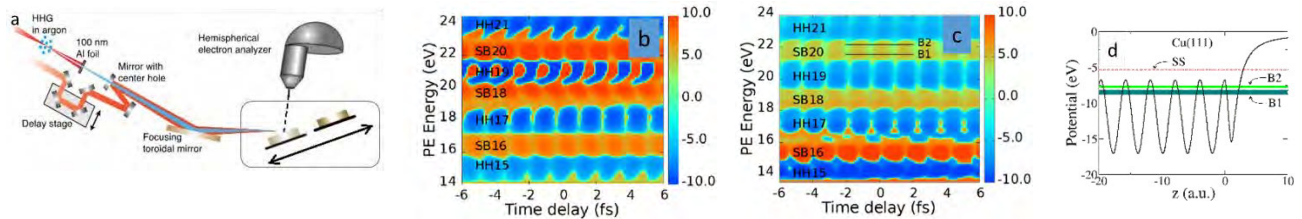


Fig. 5: (a) Suggested comparative RABBITT experimental setup. RABBITT spectra after subtraction of the single-XUV-photon yield for (b) Cu (100) and (c) Cu(111). (d) Sub-bands “B1” and “B2” of the Cu (111) valence band from recent angle-resolved photoelectron spectra [R9]. This sub-band structure is imaged in (c).

Future plans: We intend to refine our modeling of (i) streaked and side-banded photoemission from solid surfaces and nanoparticles [2,3,4,6,9] and (ii) the transport of photo-released electrons inside complex targets [1,5]. We plan to extend our models to time- and angle-resolved photoemission in order to scrutinize in more detail the substrate band-structure [4,9]. We keep collaborating with experimental groups to explore the feasibility of and ideal parameters for the observation of dielectric response (plasmonic) effects during and after the XUV-pulse-triggered release of photoelectrons from metal surfaces [R10] and nanoparticles [2,S2,S5].

Peer-reviewed publications resulting from this project (2015-2017) ([1-9] addressed in this abstract)

- [1] *Attosecond Physics: attosecond streaking spectroscopy of atoms and solids*, U. Thumm, Q. Liao, E. M. Bothschafter, F. Süßmann, M. F. Kling, R. Kienberger, Handbook of Photonics, Vol. 1, Chap. XIII (Wiley, 2015).
- [2] *Attosecond time-resolved streaked photoelectron spectroscopy of transition-metal nanospheres*, J. Li, E. Saydanzad, and U. Thumm, Phys. Rev. A **95**, 043423 (2017).
- [3] *Retrieving plasmonic near-field information: a quantum-mechanical model for streaking photoelectron spectroscopy of gold nanospheres*, J. Li, E. Saydanzad, U. Thumm, Phys. Rev. A **94**, 051401(R) (2016).
- [4] *Comparative time-resolved photoemission from Cu(100) and Cu(111) surfaces*, M. Ambrosio, U. Thumm, Phys. Rev. A **94**, 063424 (2016).
- [5] *Characterization of nanoplasmonic fields in time-resolved photoemission: a classical trajectory approach applied to gold nanospheres*, E. Saydanzad, J. Li, U. Thumm, Phys. Rev. A **95**, 053406 (2017).
- [6] *Attosecond time-resolved streaked photoemission from Mg-covered W(110) surfaces*, Q. Liao, U. Thumm, Phys. Phys. Rev. A **92**, 031401(R) (2015).
- [7] *A criterion for distinguishing sequential from non-sequential contributions to two-photon double ionization of helium in ultrashort XUV pulses*, A. Liu, U. Thumm, Phys. Rev. Lett. **115**, 183002 (2015).
- [8] *Laser-assisted XUV double ionization of helium: energy-sharing dependence of joint angular distributions*, A. Liu, U. Thumm, Phys. Rev. A **91**, 043416 (2015).
- [9] *Distinguishing attosecond electron-electron scattering and screening in transition metal*, C. Chen, Z. Tao, A. Carr, P. Matyba, T. Szilvási, S. Emmerich, M. Piecuch, M. Keller, D. Zusin, S. Eich, M. Rollinger, W. You, S. Mathias, U. Thumm, M. Mavrikakis, M. Aeschlimann, P. M. Oppeneer, H. Kapteyn, M. Murnane, Proc. Natl. Acad. Sci. **114**, E5300 (2017).
- [10] *Probing O^{2+} potential-energy curves with an XUV – IR pump – probe experiment*, P. Cörlin, A. Fischer, M. Schönwald, A. Sperl, T. Mizuno, U. Thumm, T. Pfeifer, R. Moshhammer, Phys. Rev. A **91**, 043415 (2015).

Submitted manuscripts resulting from this project

- [S1] *A semi-classical approach to solving the time-dependent Schrödinger equation in inhomogeneous pulses of electromagnetic radiation*, J. Li, U. Thumm, Phys. Rev. A.
- [S2] *Imaging the plasmonically enhanced electric field near Au nanospheres with spatiotemporal resolution using attosecond streaking spectroscopy*, J. Li, E. Saydanzad, U. Thumm, Phys. Rev. Lett.
- [S3] *Electronic localization effects in Cu(111) RABBITT spectra*, M. Ambrosio, U. Thumm, Phys. Rev. Lett.
- [S4] *Time-resolved photoemission spectra of Au and Ar surfaces*, M. Ambrosio, U. Thumm, Phys. Rev. A.
- [S5] *A classical trajectory model for imaging the plasmonic near fields on metal nanospheres*, E. Saydanzad, J. Li, U. Thumm, Phys. Rev. A.

References ([R1-R5,R8] acknowledge our previous DOE support)

- [R1] *Electron-ion interaction effects in attosecond time-resolved photoelectron spectra*, C.-H. Zhang, U. Thumm, Phys. Rev. A **82**, 043405 (2010).
- [R2] *Laser-assisted XUV few-photon double ionization of helium: joint angular distributions*, A. Liu, U. Thumm, Phys. Rev. A **89**, 063423 (2014).
- [R3] *Attosecond time-resolved autoionization of argon*, H. Wang, M. Chini, S. Chen, C.-H. Zhang, F. He, Y. Cheng, Y. Wu, U. Thumm, Z. Chang, Phys. Rev. Lett. **105**, 143002 (2010).
- [R4] *Attosecond probing of instantaneous AC Stark shifts in helium atoms*, F. He, C. Ruiz, A. Becker, U. Thumm, J. Phys. B **44**, 211001 (fast track comm., 2011).
- [R5] *Laser-assisted photoemission from adsorbate-covered metal surfaces: time-resolved core-hole relaxation dynamics from side-band profiles*, C.-H. Zhang, U. Thumm, Phys. Rev. A **80**, 032902 (2009).
- [R6] *Energy-dependent photoemission from noble metal surfaces by attosecond interferometry*, R. Locher, L. Castiglioni, M. Lucchini, M. Greif, L. Gallmann, J. Osterwalder, M. Hengsberger, U. Keller, Optica **2**, 405 (2015).
- [R7] *Direct time-domain observation of attosecond final-state lifetimes in photoemission from solids*, Z. Tao, C. Chen, T. Szilvási, M. Keller, M. Mavrikakis, H. Kapteyn, M. Murnane, Science **353**, 62 (2016).
- [R8] *Effects of wave-function localization on the time delay in photoemission from surfaces*, C.-H. Zhang, U. Thumm, Phys. Rev. A **84**, 065403 (2011).
- [R9] *Angle-resolved photoemission from Cu single crystals; known facts and a few surprises about the photoemission process*, F. Roth, C. Lupulescu, E. Darlatt, A. Gottwald, W. Eberhardt, J. Electron Spectrosc. Relat. Phenom. **208**, 2 (2016).
- [R10] *Probing dielectric response effects with attosecond time-resolved streaked photoelectron spectroscopy of metal surfaces*, C.-H. Zhang, U. Thumm, Phys. Rev. A **84**, 063403 (2011).

Strong-Field Time-Dependent Spectroscopy

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1 Project Scope

The main scope of my research is to perform coherent measurements of the time dependent molecular structure with ultrafast time resolution. As a complement of this goal I also develop new optical sources.

2 Recent progres

2.1 A self referencing attosecond interferometer with zeptosecond precision

High harmonic generation (HHG) can be used as a coherent, time dependent measurement of the molecular structure. In particular, it can be used to extract amplitude and phases of transition dipoles as they evolve in time. In this work we generate harmonics from two optical foci (f_1 and f_2) produced by a system of a two-dimensional spatial light modulator (SLM) and a lens (Fig. 1 a). The two foci are generated using two intertwined phase masks (Fig. 1 b) with opposite wavefront tilt. We start with an intense 30 fs pulse incident on the SLM to produce peak intensities at the foci of $\approx 10^{14}\text{W}/\text{cm}^2$ where harmonics are generated. As the harmonics propagate towards the detector they interfere in the far field. An example of the measured interference pattern of harmonics 11th (71.4 nm, 17.4 eV) and 19th (41.3 nm, 30 eV) is shown in Fig. 1 c). By applying an offset to one mask relative to the other we can control the delay or phase (within one cycle) of one pulse relative to the other. Because the mask is a phase change across the entire beam profile, there is only one beam with two diverging wavefronts. In other words, we are able to generate two beams that share almost exactly the same beam path. They only become distinguishable at approximately one Rayleigh range before the focus.

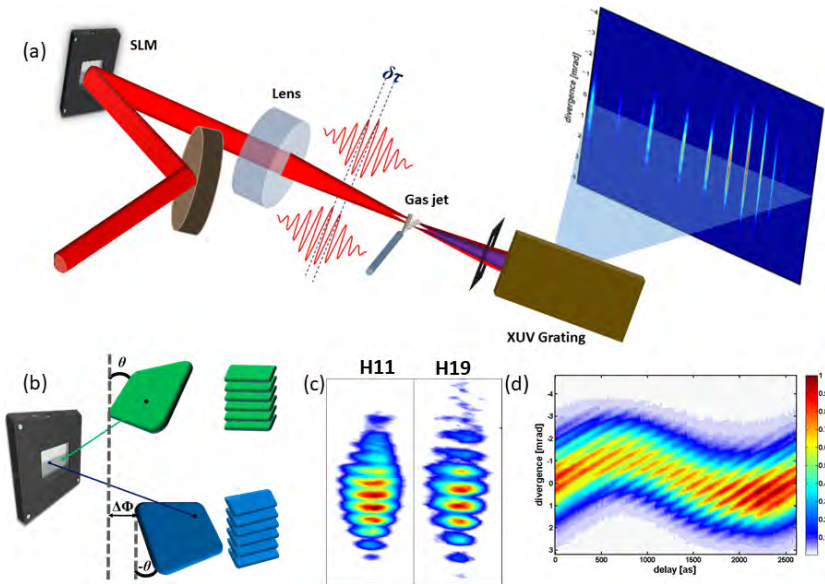


Figure 1: (a) Experimental setup scheme. Light is reflected from an SLM and is focused into a gas jet using a lens ($f=50$ cm) to produce harmonics from two foci. The harmonics propagate and interfere in the far field (spectrometer detector). (b) Working schematics of the applied phase masks. The two masks are applied to the entire beam in a check pattern. The phases are wrapped in multiples of 2π . (c) Profiles of the 11th and 19th harmonic showing the interference pattern. The number of peaks changes with the wavelength (harmonic order) and with the distance between foci. (d) Evolution of the interference pattern of harmonic 11 as a function of the relative offset phase between the two masks $\Delta\Phi_{SLM}$.

To preserve phase matching the Rayleigh range is chosen to be much larger than the interacting region ($500 \mu\text{m}$ in our case). Also, the distance between the two foci ($100 \mu\text{m}$) is smaller than the inner diameter of the glass capillary used to generate the gas jet. Practically, this means that differences in the optical path will be dictated by changes in pressures of 10^{-4} to 10^{-5} Torr over one Rayleigh range. Therefore, we are certain that all measured changes in the carrier phase of the electric field come from the phases imparted to the SLM.

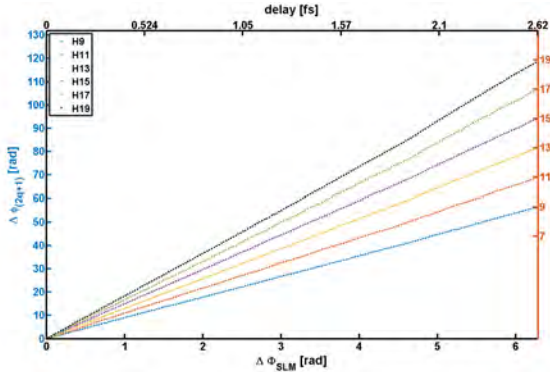


Figure 2: Phase of harmonics 9 to 19 (left axis) measured from the interferograms as shown in Fig. 1 c) as a function of the relative SLM phase $\Delta\Phi_{SLM}$ (bottom axis). The right axis is the phase in units of 2π showing that the phase evolution of each harmonic $2q + 1$ is $\Delta\phi_{(2q+1)} = (2q + 1) \times \Delta\Phi_{SLM}$. Top axis is the corresponding delay time for a 785 nm wavelength pulse. The SLM has access to 205 phase values thus capable of a resolution of 12.8 attoseconds.

ative phase values thus capable of a resolution of 12.8 attoseconds. This resolution was confirmed by measuring the amount the fringes moved for each harmonic. To further demonstrate the power of our method, we calculate the jitter for harmonics 9 to 19 using 17 independent experiments at each delay. The jitter is calculated from the standard error of the phase using the 17 measurements comprised of 600 lasers shots each.

The results are summarized in Table 1. The SE column reports the standard error of the jitter and the deviation column is the standard deviation from the same distribution. From both, we can clearly observe that we have a precision better than one attosecond. Harmonic 13 has the best precision of 680 zeptoseconds followed by harmonic 15 with a precision of 710 zeptoseconds.

In conclusion we have demonstrated a new kind of attosecond interferometer that is self-referencing in the sense that all phases are almost perfectly balanced. We were able to measure a phase unbalance or equivalent time jitter of 0.7 attoseconds. The scheme was used to demonstrate that when all propagation phases are neglected the harmonics phase scale relative to the fundamental as in perturbative optics $\Delta\phi_{(2q+1)} = (2q + 1) \times \Delta\Phi_{fund}$

2.2 Characterization of Bessel beams for strong field science

We examine the profiles of Bessel-like beams generated with the combination of a lens and an axicon by controlling the focal length of the lens (f) and the distance between the lens and the axicon (L). We use two laser sources, a continuous-wave (CW) HeNe laser and a femtosecond laser (Kansas Light Source) delivering 35 fs FWHM pulses. Figure 3 shows the beam shape on the transverse plane (Figs. 3(a) and 3(b)) and the longitudinal sections (Figs. 3(c) and 3(d)), for the two laser types. These measurements were taken using a lens with a focal length of 200 mm and a distance L of 10 mm.

We observe similarities between the two cases. Bright cores start to form at around $Z=85$ mm, where Z is the distance between the axicon and the observation plane. Concentric rings appear at a further distance ($Z=90-100$ mm), resembling those of Bessel and Bessel-Gauss beams. The most striking and important feature observed in these measurements is the incredibly long distance over which the peak intensity is maintained. This is most apparent for the pulsed laser. The central core intensity stays at or above 50% of the peak intensity for over 40 mm, more than 20 times longer than a Gaussian beam with a similar spot diameter. In addition, the peak intensity occurs at approximately 105 mm, much longer than if just a sharp angle axicon was used individually. The combination of both optics allow for both long depth of field and long working distance simultaneously.

With this approach we are able to extract the relative phase between the two harmonic sources $\Delta\phi_q$, as a function of the relative CEP of the two foci. $\Delta\phi_q$ is measured as the phase of the fringe frequency in the Fourier spectrum. Phases for harmonics 9 to 19 (left axis) using the frequency Fourier analysis is shown in Fig. 2. The right axis shows the phase in units of 2π for each harmonic. From this plot the scaling of phase $\Delta\phi_{(2q+1)}$, for each order $2q + 1$, as a function of $\Delta\Phi_{SLM}$ is clear, $\Delta\phi_{(2q+1)} = (2q + 1) \times \Delta\Phi_{SLM}$. From a time-domain point of view, the interpretation of Fig. 2 is also clear. For each oscillation period of the fundamental there are exactly $(2q + 1)$ oscillations in the electromagnetic field for harmonic order $(2q + 1)$. To be able to observe oscillations in the harmonics we of course need attosecond resolution in our time steps. The top axis in Fig. 2 shows the corresponding delay time for a 785 nm center wavelength pulse. Our SLM has access to 205 effective

HO	SE [as]	deviation [as]
9	3.10	2.8
11	0.80	0.72
13	0.68	0.60
15	0.71	0.63
17	0.80	0.71
19	1.10	0.94

Table 1: Experimentally measured jitter for different harmonic orders (HO). Column “SE” are the standard error estimates calculated from 17 images taken for each harmonic with each image consisting of 600 laser shots. Since we can assume uncorrelated errors for the temporal jitter, we can also use the 205 delay “experiments” as measurements for the error.

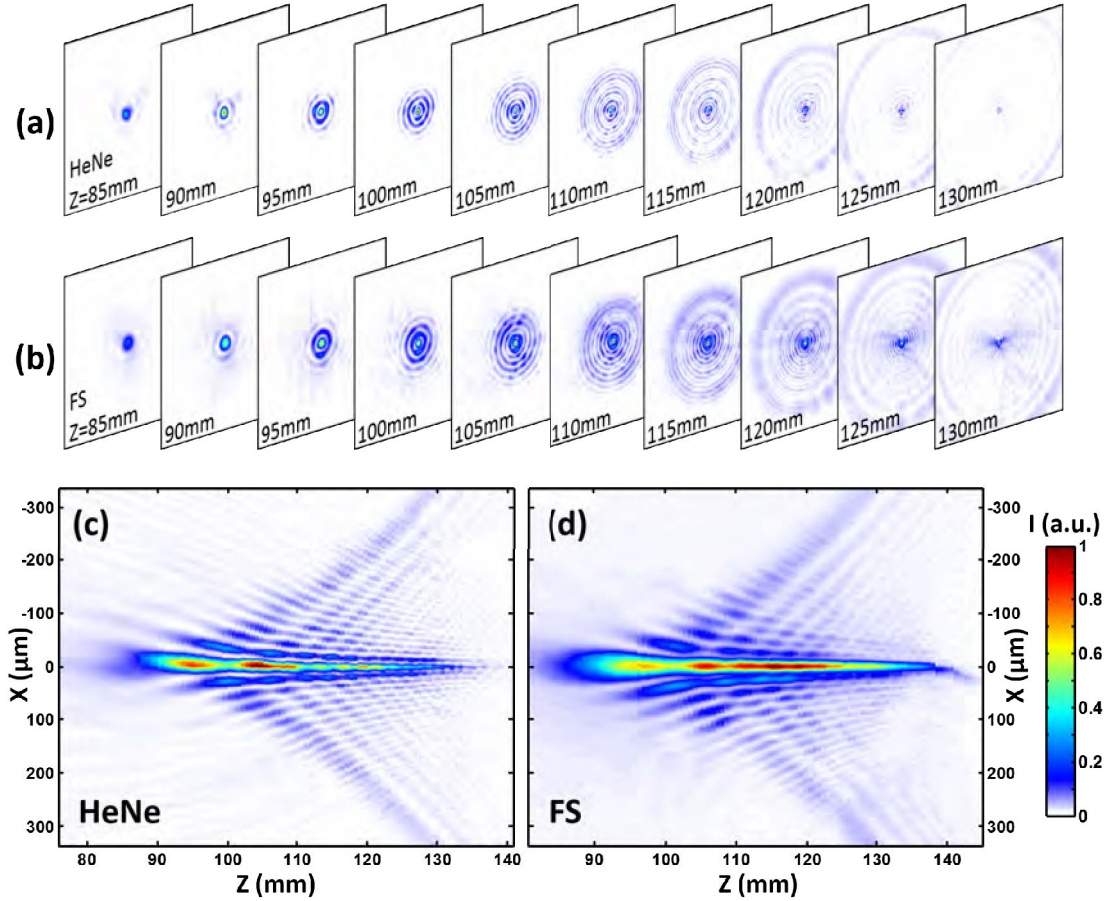


Figure 3: (a, b) Bessel-like beams observed at various distances (Z) from the axicon for (a) HeNe and (b) femtosecond (FS) lasers. (c, d) Longitudinal profiles of laser beams for (c) HeNe and (d) femtosecond lasers. Intensities are normalized to the peak values in the two cases

The pulse duration of the Bessel-like beam was not measured in this study. However, it is not expected to significantly differ from pulse durations achievable using a standard transmissive lens. We believe this is particularly so for the case of a shallow axicon like the one used in this study.

Next, we investigate the beam profiles for various lens-to-axicon distances L . Figure 4 demonstrates the flexibility of tuning the axial length of the generated Bessel-like beams by changing the lens-axicon distance L and the focal length of the lens. To this end, we choose three focal lengths, $f=100$, 200 and 300 mm, and record beam profiles for various L distances. The figure shows the 80% energy radii $R_{0.8}$ calculated for each data set.

To summarize this section, we have shown that Bessel-like beams present many desirable features. In particular, the range of both spot sizes and working distances achievable with our geometry are much better than with a lens system. For certain combinations of lens and axicon, the central core remains at or above 50% of the peak intensity over distances that are more than 20 times longer than a Gaussian beam with a similar spot diameter. Therefore, proper manipulation of Bessel-like beams can produce tight focuses while maintaining long work distances, a very important property for many optics experiments.

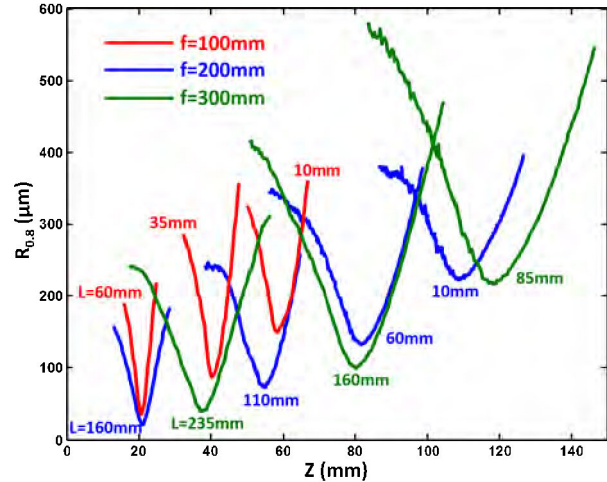


Figure 4: The 80%-energy beam size measured for three focal lengths (f) and various distances from the axicon (L). Axicon is at $Z=0$

3 Peer-Reviewed Publications Resulting from this Project (2015-2017)

- “The N₂ HOMO-1 orbital cross-section revealed through high harmonic generation”, Jan Troß, Xiaoming Ren, Varun Makhija, Sudipta Mondal, Vinod Kumarappan, Carlos A. Trallero-Herrero, *Physical Review A*, **95**, 033419, (2017)
- “Spatial characterization of Bessel-like beams for strong-field physics”, Adam M. Summers, Xiaoming Yu, Xinya Wang, Maxime Raoul, Josh Nelson, Daniel Todd, Stefan Zigo, Shuting Lei, And Carlos A. Trallero-Herrero, *Optics Express*, **25**, 1646, (2017)
- “Ionization Study of Isomeric Molecules in Strong-field Laser Pulses”, Stefan Zigo, Anh-Thu Le, Pratap Timilsina, Carlos A. Trallero-Herrero, *Scientific Reports*, **7**, 42149, (2017)
- “Internal modification of intrinsic and doped silicon using infrared nanosecond laser”, Xiaoming Yu, Xinya Wang, Margaux Chanal, Carlos A. Trallero-Herrero, David Grojo, and Shuting Lei, *Applied Physics A*, **122**, 1001, (2016)
- “High order harmonic generation from SF₆: Deconvolution of macroscopic effects”, B.P. Wilson, K.D. Fulfer, S. Mondal, X. Ren, J. Tross, E.D. Poliakoff, J. Jose, Anh-Thu Le, R. R. Lucchese, C. Trallero-Herrero, *Journal of Chemical Physics*, **145**, 224305 (2016)
- “An Atomic Photoionization Experiment by Harmonic Generation Spectroscopy”, M. V. Frolov, T. S. Sarantseva, N. L. Manakov, K. D. Fulfer, B. D. Wilson, J. Troß, X. Ren, E. D. Poliakoff, A. A. Silaev, N. V. Vvedenskii, A. F. Starace and C. A. Trallero-Herrero, *Physical Review A: Rapid Communications*, **93**, 031403(R), (2016)
- “Materials processing with superposed Bessel beams”, Xiaoming Yu, Carlos A. Trallero-Herrero and Shuting Lei, *Applied Surface Science*, **360**, 833, (2015)
- “A carrier-envelope-phase stabilized terawatt class laser at 1 kHz with a wavelength tunable option”, Benjamin Langdon, Jonathan Garlick, Xiaoming Ren, Derrek J. Wilson, Adam M. Summers, Stefan Zigo, Matthias F. Kling, Shuting Lei, Christopher G. Elles, Eric Wells, Erwin D. Poliakoff, Kevin D. Carnes, Vinod Kumarappan, Itzik Ben-Itzhak and Carlos A. Trallero-Herrero, *Optics Express*, **23** 4563 (2015)

Atomic, Molecular and Optical Sciences at the Lawrence Berkeley National Laboratory

C. William McCurdy (PI), Co-Investigators: Ali Belkacem, Oliver Gessner, Robert R. Lucchese, Martin Head-Gordon, Stephen R. Leone, Daniel M. Neumark, Thomas N. Rescigno, Daniel S. Slaughter, Thorsten Weber

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Project Scope: The AMOS Program at LBNL seeks to answer fundamental questions in atomic, molecular and chemical sciences that are central to the mission of the Department of Energy's Office of Science. The essential strategy is to apply a broad span of existing and currently emerging tools such as synchrotron radiation, lasers, laboratory-based extreme ultraviolet sources, and low-energy electron beams together with state-of-the-art experimental techniques including momentum imaging, coincidence techniques, electron and x-ray absorption spectroscopy, scattering, and transient absorption, in combination with the development of advanced theoretical methodologies, to studies across a broad range of time scales and systems. This approach provides deep insight into the chemistry and physics of the fundamental interactions that drive key chemical processes in simple molecules, complex molecular systems and molecules in complex environments. The current emphasis of the program is in three major areas with important connections and overlap: inner-shell photo-ionization and multiple-ionization and dissociation dynamics of small molecules; time-resolved studies of charge dynamics involving molecules in the gas phase, in the condensed phase and at interfaces using a combination of attosecond to picosecond x-rays and laser pulses; and low-energy electron impact and dissociative electron attachment of molecules. The theory component of the program focuses on the development of new methods for solving, from first-principles, complex multi-atom and multi-electron processes that play a key role in these systems. The theory and experimental parts of the program are closely coupled. They are designed to work together to tackle problems of scale that are inaccessible without a strong and continuous collaboration and interaction.

The Atomic, Molecular and Optical Sciences Program at LBNL consists of three subtasks:

- 1. Photon and electron driven processes in atoms and small molecules.**
- 2. Photon and electron driven processes in complex molecular systems and molecules in complex environments.**
- 3. First-principles theory of dynamics and electronic structure.**

The co-investigators participate in multiple subtasks, collaborating and using common techniques in an effort in which experiment and theory are tightly integrated.

Subtask 1: Photon and Electron Driven Processes in Atoms and Small Molecules.

(A. Belkacem, S. R. Leone, R. R. Lucchese, C. W. McCurdy, D. M. Neumark, T. Rescigno, D. S. Slaughter, Th. Weber)

Attosecond Dynamics (S. R. Leone, D. M. Neumark)

The goal of the attosecond dynamics subgroup is to probe ultrafast dynamics stemming from electron correlations with exceptional time and energy resolution. Spectrally broad, sub-femtosecond extreme ultraviolet (XUV) pulses created by high harmonic generation are utilized in conjunction with delayed few-cycle near infrared (NIR) pulses to perform time-resolved spectroscopic investigations in gas-phase atomic and molecular systems. In a collinear beam geometry, this technique produces rich, yet highly complex spectra that often require significant theoretical input to interpret due to overlapping spectral effects from multiple NIR-induced processes. To investigate these effects more selectively, pioneering experiments are extending the principles of four wave mixing (FWM) into the XUV regime. FWM is a nonlinear technique commonly employed in visible and infrared spectroscopies to produce background-free measurements. A noncollinear beam geometry exploits the inherent phase matching conditions

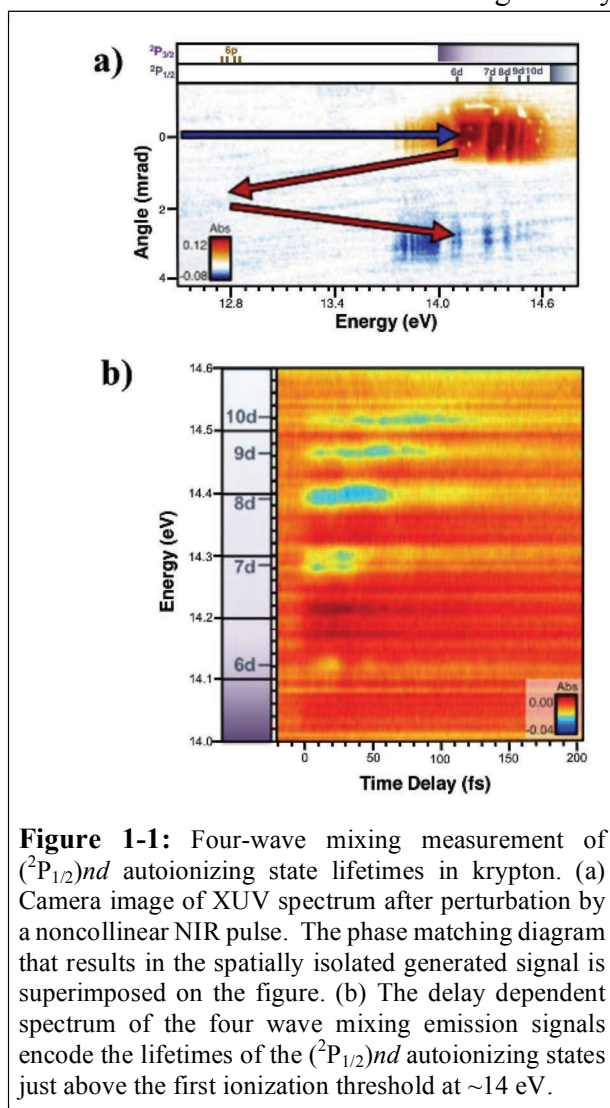


Figure 1-1: Four-wave mixing measurement of $(^2P_{1/2})nd$ autoionizing state lifetimes in krypton. (a) Camera image of XUV spectrum after perturbation by a noncollinear NIR pulse. The phase matching diagram that results in the spatially isolated generated signal is superimposed on the figure. (b) The delay dependent spectrum of the four wave mixing emission signals encode the lifetimes of the $(^2P_{1/2})nd$ autoionizing states just above the first ionization threshold at ~ 14 eV.

characteristic of nonlinear wave mixing processes to spatially isolate individual FWM pathways. Examination of these isolated emission signals results in highly specific measurements of electronic wavepacket dynamics in long-lived Rydberg states with sub-femtosecond resolution (Cao, et al., *Phys. Rev. A*, **94**, 053846 (2016)). Continued development of this technique will provide the foundation for multidimensional XUV spectroscopy with the power to observe electronic correlations explicitly.

Recent Progress: Initial FWM mixing experiments utilized two NIR photons derived from a single beam, which allowed only for the angular isolation of signals from ladder-type coupling pathways and a single time delay. The recent addition of a second, independently delayed NIR beam permits more sensitive control and selective detection of specific dynamics through the manipulation of pulse angles, sequence, wavelength, and polarization. The enhanced capabilities provided by this second arm are illustrated by recent lifetime measurements of autoionizing states in krypton and the characterization of a poorly understood dark state in molecular nitrogen.

Previous time domain measurements of autoionizing state lifetimes in a collinear beam geometry effectively retrieved lifetimes

comparable to linewidth measurements, but the results were complicated by multiple competing processes and finite spectrometer resolution (Li, et al., *J. Phys. B* **48**, 125601 (2015)). Background-free FWM measurements promise to circumvent some of these limitations. To demonstrate that this novel technique can accurately probe ultrafast time dynamics, NIR pulses noncollinear with both the XUV pulse and each other couple the XUV-induced ($^2P_{1/2}$)nd autoionizing states to themselves through the one photon dipole forbidden ($^2P_{3/2}$)6p states via a V-type coupling pathway (Fig. 1-1 (a)). Examination of the spatially isolated emission features as a function of XUV-NIR time delay reveals that the lifetimes of the ($^2P_{1/2}$)nd autoionizing states scale as expected with principal quantum number (Fig. 1-1(b)). Furthermore, fits of the time dependent features retrieve lifetimes of 37.3 fs and 50.6 fs for the ($^2P_{1/2}$)7d and ($^2P_{1/2}$)8d states, respectively, in agreement with those extracted from frequency domain measurements (Maeda, et al., *J. Phys. B* **26** (1993)). These results not only represent the first observation of a FWM XUV emission signal from rapidly decaying states, but also suggest that this newly developed technique retains the high temporal resolution that characterizes attosecond spectroscopies.

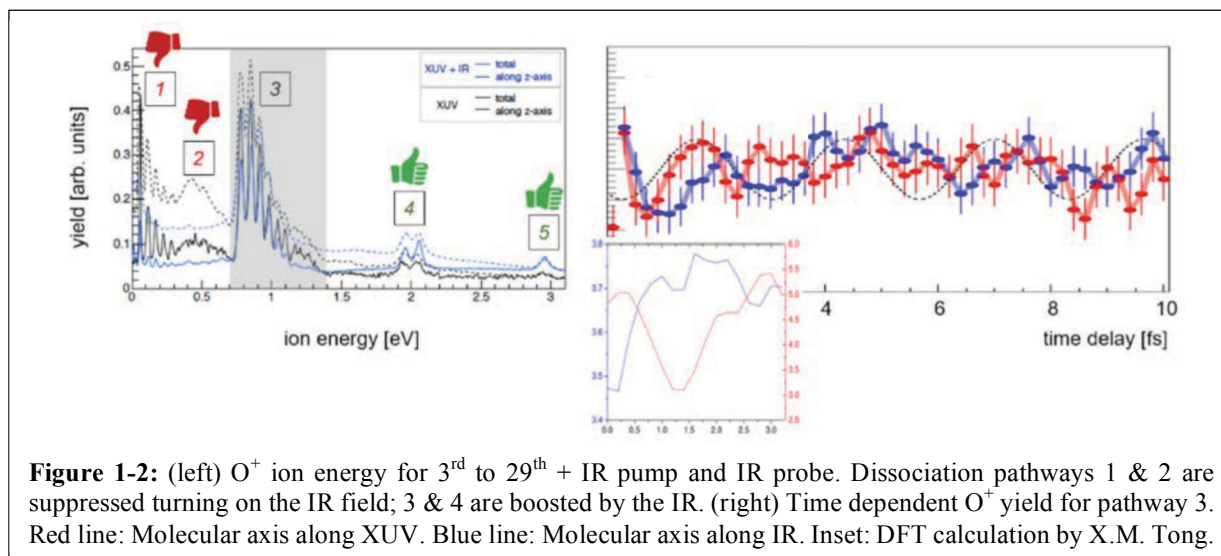
Manipulation of the pulse sequence in addition to beam geometry has allowed for the retrieval of electronic structure from states inaccessible by other techniques. Previous work in molecular nitrogen measured the anharmonicity of the b' Σ_u^+ state potential via the quantum beats that arise due to NIR induced coupling through the double well a" Σ_g^+ dark state (Warrick, et al., *Chem. Phys. Lett.* **683** (2017)). While the electronic structure of the inner well of this dark state is well known, the outer well remains poorly characterized by current techniques. By fixing the delay of one of the NIR pulses relative to the XUV pulse, a wavepacket is formed in the dark state that can subsequently be probed by the remaining NIR pulse. Modification of this fixed XUV-NIR delay results in distinct, spatially isolated emission signals in the b' Σ_u^+ state from either the inner or the outer well of the a" Σ_g^+ dark state. When the XUV and fixed NIR pulse are time coincident, the quantum beat period of the FWM emission signal is 15.25 fs, corresponding to an energy level spacing of 0.271 eV that matches the known vibrational spacing of the a" Σ_g^+ inner well (Salumbides, et al., *JPCA* **113** (2009)). The implementation of a 25 fs fixed delay results in a distinct quantum beat period of 43 fs, indicating a vibrational energy level spacing of 0.096 eV in the outer well. Further analysis of these results will provide insights into the structure of a poorly understood state and demonstrate the versatility and sensitivity of the FWM technique for the control and measurement of dynamics.

Future Plans: Future work will focus on the development of a fully multidimensional XUV spectroscopy that will permit the examination of ultrafast dynamics with unprecedented precision. The next step toward this goal involves the implementation of a pulse shaping apparatus that can be employed to both isolate particular states of interest and create two-dimensional spectra that explicitly show electronic correlations. Preliminary studies utilizing a spatial light modulator-based pulse shaping apparatus to sequentially eliminate frequencies from the NIR pulse before interaction with an argon target indicate that a two-dimensional map of the FWM signal as a function of NIR and XUV wavelengths can be created without significantly compromising the temporal resolution of the experiment. The increased selectivity afforded by this newly developed pulse shaping capability will allow for the examination of ultrafast dynamics in more complex systems. In these more complicated systems, wavepackets created in states that decay on few-femtosecond timescales through processes such as autoionization, Auger decay, predissociation, and radiationless transitions at conical intersections can be probed selectively despite high spectral congestion via a multidimensional, FWM based technique. Initial targets for these experiments include core level states of HBr and valence excited states of water vapor. In HBr, Auger decay

and predissociation are believed to occur on similar timescales and thus the system will exhibit a breakdown of the Born-Oppenheimer approximations. An accurate determination of the timescales of these processes can only be studied in the time domain because of spectral broadening due to the repulsive state. Water vapor provides an opportunity to examine ultrafast decay through a conical intersection that has yet to be observed experimentally in the neutral species. Together, these experiments represent a significant advance toward a versatile and highly specific method for characterizing ultrafast processes in complex chemical systems.

Investigation and Coherent Attosecond Control of Oxygen Dissociation in XUV-IR-Fields using 3D Momentum Imaging (*A. Belkacem, Th. Weber*)

Recent Progress: In this COLTRIMS project at the 50 Hz high harmonics generation (HHG) laser source (F.P. Sturm et al., *Rev. Sci. Instrum.*, **2016**, *87*, 063110), we used the inherent sub-optical-cycle time resolution (~ 170 as) of our pump-probe delay stage to coherently control dissociative ionization processes of O_2 by means of the attosecond XUV frequency comb and the femtosecond infrared field. High resolution 3D ion momentum spectroscopy allowed a close examination of the delay dependent yield of O^+ ions for a vibrationally resolved region of the ion kinetic energy (0.72 - 1.4 eV). This was identified as the excitation of the $B^2\Sigma_g^-$ state of O_2^+ , by single ionization of O_2 with the 15th harmonic, followed by non-adiabatic coupling to the $1^2\Sigma_g^+$, $f^4\Pi_g$, $d^4\Sigma_g^+$ states and subsequent dissociation to the L1 dissociation limit. The data is further split up into ions emitted along the polarization axis of the XUV beam (red) and along the IR polarization axis (blue) in Fig. 1-2. The time-dependent ion yields clearly exhibit statistically



significant oscillations with a varying phase relationship. A phase shift in the oscillations was revealed for parallel and perpendicular orientations of the molecular axis with respect to the XUV polarization. The results also show contributions from optical interference from the IR field in both the pump and probe arm, and quantum interference from mixing different dissociative pathways.

Due to the rapid dissociation processes enabled via non-adiabatic couplings, we speculate that the electron wave-packet interferences are strongly coupled with nuclear wave-packet dynamics, rendering theoretical calculations to disentangle such non-Born-Oppenheimer dynamics particularly challenging, even in a simple linear molecule such as O_2 . We are in close collaboration with X.M. Tong from the Center for Computational Sciences at the University of Tsukuba. His

time-dependent DFT calculation only extends to 3 fs but shows a similar $\pi/2$ phase shift as that seen in the experiment (note that our experimental time zero is not well known).

Time-Resolved Molecular Reaction Pathways of Electronically Excited OCS and NH₃ (A. Belkacem, R. R. Lucchese, C. W. McCurdy, T. Rescigno, D. S. Slaughter, Th. Weber)

Recent Progress: With L. Greenman (now at Kansas State University), non-adiabatic dynamics of electronic excited states were recently investigated on sub-10 fs timescales by combining time-resolved photoelectron spectroscopy with detailed electronic structure calculations of electronic excited states in methanol (Champenois et al., manuscript in preparation). The experimental pump-probe scheme consists of single photon excitation at 156 nm and delayed ionization by a 260 nm probe. Photoion and photoelectron velocity map imaging were performed with the same apparatus under almost identical conditions. Photoelectron spectral features were correlated, by appearance and decay times, with either of two final states: CH₃OH⁺ or CH₂O⁺ + H. The dissociative channel was confirmed to be C-H break by repeating the experiment on deuterated methanol. Energy-resolved signal onset (Fig. 1-3a) and decay times were extracted from the measured photoelectron spectra to describe the coupled electronic and nuclear dynamics with precision better than 10 fs, far shorter than the 25 fs pump and probe pulse durations. With *ab initio* calculations of the excited state potential energy surfaces (PES), the excited wavepacket is tracked along both the nuclear and electronic degrees of freedom (Fig. 1-3b). Within 15 fs of photoexcitation, we observe nuclear motion involving C-O-H bending and C-O stretch, through a conical intersection, resulting in methyl hydrogen-loss.

Future Plans: We strive to increase both the complexity and detail in the investigation of molecular dynamics and kinematics of excited states and their control. Previous time-resolved photoelectron and photoion imaging studies (e.g. E. G. Champenois et al., *J. Chem. Phys.*, **2016**, *144* and T.W. Wright et al., *Phys. Rev. A*, **2017**, *95*) and COLTRIMS results (F.P. Sturm et al., *Phys. Rev. A*, **2016**, *95*, 012501) involving HHG, show that there is a clear advantage in ultrafast pump-probe experiments to measure electrons and ions in coincidence. This capability is necessary to follow the molecular dynamics of excited states on the PESs and reveal non-Born Oppenheimer behavior. It is especially important because HHG laser sources do not deliver monochromized light pulses, even after sending the beam through filter systems, which can lead to ambiguity in the interpretation of the complicated dynamics, unless the electron energy can be determined

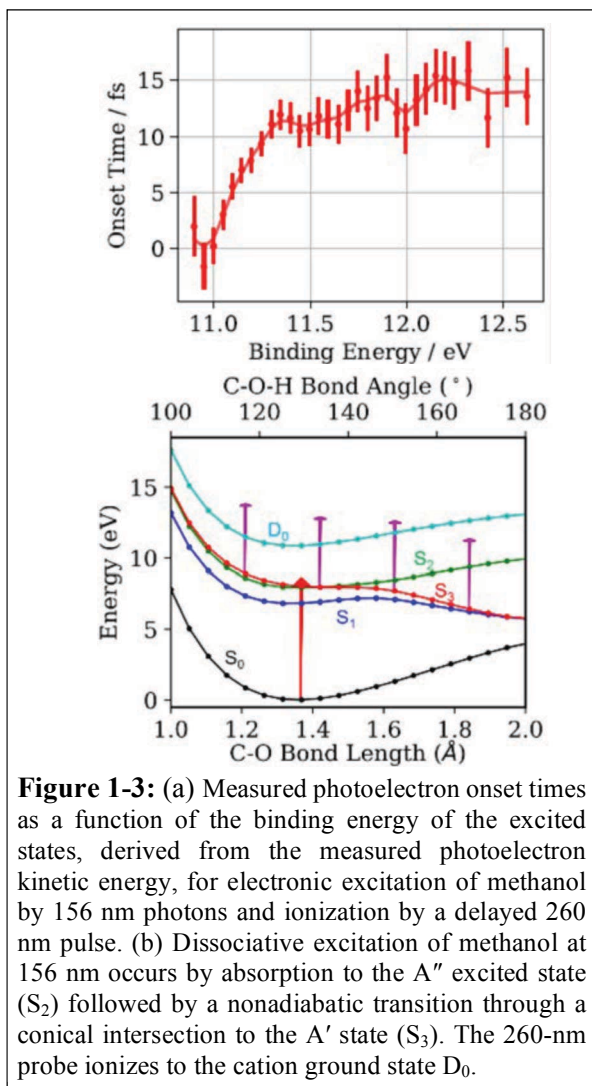


Figure 1-3: (a) Measured photoelectron onset times as a function of the binding energy of the excited states, derived from the measured photoelectron kinetic energy, for electronic excitation of methanol by 156 nm photons and ionization by a delayed 260 nm pulse. (b) Dissociative excitation of methanol at 156 nm occurs by absorption to the A'' excited state (S₂) followed by a nonadiabatic transition through a conical intersection to the A' state (S₃). The 260-nm probe ionizes to the cation ground state D₀.

simultaneously. Besides the pump-probe delay, photon energies, and pulse intensities, control over the relative orientation of the polarization directions between the excitation and subsequent ionization step is a helpful tool to follow the evolution on the PESs. By controlling the relative orientation between the IR and VUV/XUV we may access and identify dark states, mix states and control their relative population. We hence strive to image electrons, realize electron-ion coincidences, and control the polarization directions for our time resolved studies.

The proposed investigations will target triatomic molecules (OCS and NH₃). These benchmark systems serve as fundamental models for studies on larger and more complicated polyatomic systems in the future. Both molecular targets have valence electronic state excitations near the 5th harmonic (7.75eV) of the laser system. Following photoexcitation by 5th harmonic photons, the molecule momentarily evolves before it is subsequently probed by either a 3rd (4.66eV) or 5th harmonic photon. In this scheme, a single photon from the pump or probe pulse cannot ionize by single photon absorption, hence background ionization is predominantly eliminated. Given the flux in the 3rd and 5th harmonics ($\sim 10^{10}$ photons/shot) the event rate for these experiments will be approximately one photoionization event per shot at an acquisition rate of 50 Hz. When the 5th harmonic is used as a probe, additional dissociation pathways are allowed that do not appear through absorption of a 5th plus a 3rd harmonic photon. By studying these additional fragmentation paths, more insight can be gained in characterization of the states and energy transfer and sharing processes between the electrons and ions inside these molecules. Studies on these systems will involve a high level of collaboration between the experimental (Weber and Slaughter) and theory teams (McCurdy and Lucchese).

Establishing a Two-Color Excitation-Ionization COLTRIMS Scheme at the Advanced Light Source (*D. S. Slaughter, Th. Weber*)

Recent Progress: Recent results of ultrafast particle spectroscopy pump-probe experiments using HHG laser systems (e.g. E. G. Champenois et al., *J. Chem. Phys.*, **2016**, *144* and T.W. Wright et al., *Phys. Rev. A*, **2017**, *95*, and F.P. Sturm et al., *Phys. Rev. A*, **2016**, *95*, 012501) illustrate the complexity of excited molecular states dynamics and the challenge to interpret it, even in such small diatomic systems as H₂ and O₂. Two-color experiments employing monochromatic XUV beams to precisely excite the target, ion-electron coincidences to clearly trace the non-Born Oppenheimer dynamics, and controllable light polarizations to distinguish the influence of each photon on the transitions, can contribute a complementary level of detail on the excited states, even when the pulses are too long to perform time resolved pump-probe schemes. This prompted us to

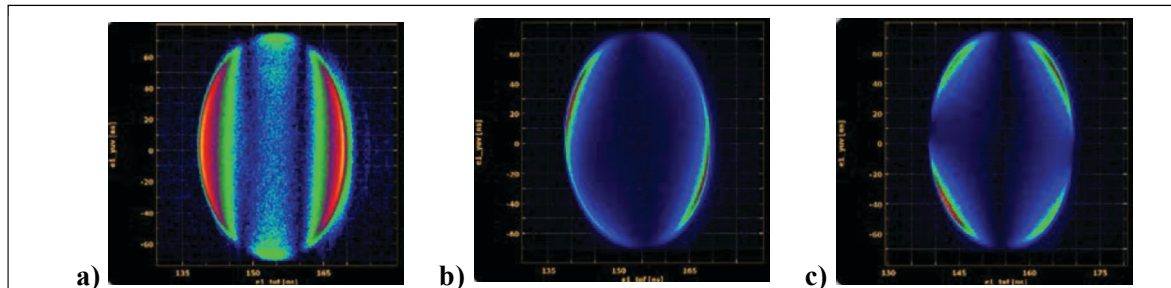


Figure 1-4: Measured photoelectron momentum images from highly excited He atoms (XUV-excitation + IR-ionization). Position of impact on the electron detector (y -direction) as a function of the Time Of Flight (TOF) of the electrons for a pump energy of the ALS of 23.75 eV (linear, horizontally polarized) and the ionization of such target via the 1030nm probe laser for (a) horizontal, (b) 45 deg. and (c) *almost* vertical linear polarization of the IR light (it appears that relative angle between IR and XUV is off by ~ 4 deg.). These background free two color events were recorded at a rate of 1 kHz while the overall He ionization rate from both the laser and the ALS was 6 kHz.

set up a roll-up two-color scheme at the ALS with a powerful 100 W laser prototype. In this setup the IR laser (1030 nm, 10 ps, 1.5 MHz) is synchronized with the ALS and co-propagated via a back-focusing mirror with the XUV beam at BL10.0.1 at the ALS. This is an extraordinary challenging enterprise, leveraging space at the ALS and the unique laser system from Accelerator Physics Division at LBNL. Besides the beam overlap in four dimensions, nine dimensions were accessed: Three ion and three electron momentum coordinates were measured while the XUV energy, the IR intensity, and polarization direction were controlled. In a proof of principle experiment, we excited an atomic Helium target to high lying Rydberg states with tunable, high energy resolution XUV photons and monitored the photoelectron momentum following ionization with the IR laser for three relative polarization angles (see Fig. 1-4).

Control of Bound and (Quasi)Free Electrons in Molecular Dissociation Processes (R. R. Lucchese, C. W. McCurdy, D. S. Slaughter, Th. Weber)

Future Plans: We will apply our new XUV-IR excitation-ionization method at the ALS to study Conical Intersections (CIs) which usually appear in the PESs of molecules consisting of more than two atoms. A diatomic molecule in a laser field, however, has a second degree of freedom defined by the laser polarization. When viewed in a Floquet basis of laser-dressed electronic states, a molecule coupled by this field can exhibit a so called light-induced conical intersection (LICI). Combining high resolution XUV photons with a moderate IR laser field at the ALS, we are in the unique position to identify LICIs by electron-ion energy correlation maps and investigate the Molecular Frame Photoelectron Angular Distributions (MFPADs) relative to the polarization direction of each beam with respect to the molecular axis. We will excite high vibrational states of an H_2^+ ion with a linear polarized XUV photon and hence move it out of equilibrium. The IR probe (1.2 eV, $< 7 \cdot 10^{11} \text{ W/cm}^2$) will produce a LICI and drive the cation to dissociation introducing non-adiabatic couplings between two nuclear degrees of freedom (vibration and rotation), which will be interrogated using the COLTRIMS technique. We expect to measure detailed signatures of the dynamics of the H_2^+ nuclear wavepacket as it avoids or passes through the LICI for various conditions of XUV and IR intensity and polarization with respect to the molecular frame.

In the next step, we will extend the approach to investigate the control of electrons in the (quasi)continuum during dissociative photoionization. Recently we established an experimental fragmentation scheme which exploits the retroaction of an escaping low-energy photoelectron onto its source, i.e. the dissociating molecule, to localize the bound electron without an external field (M. Waitz et al., Phys. Rev. Lett., **2016**, *116*, 043001). We showed that the transient field of the photoelectron, which was ejected by single photon ionization leaving an H_2^+ ion, is sufficient to preferentially localize the bound electron at one side of the molecule, polarizing it (see Fig. 1-5).

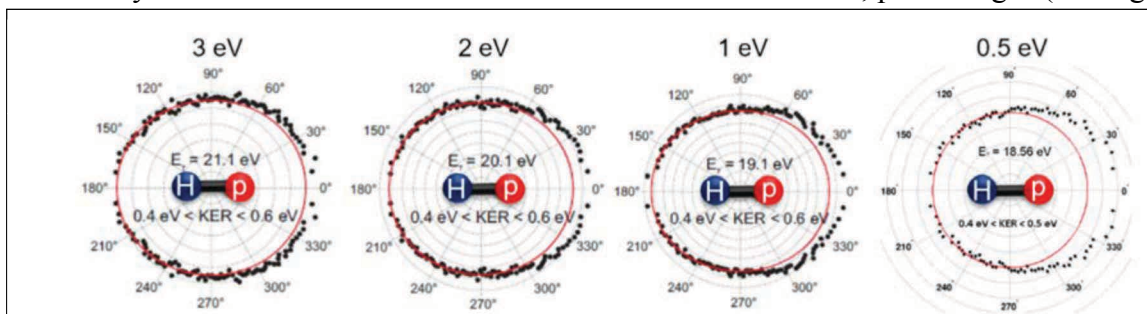


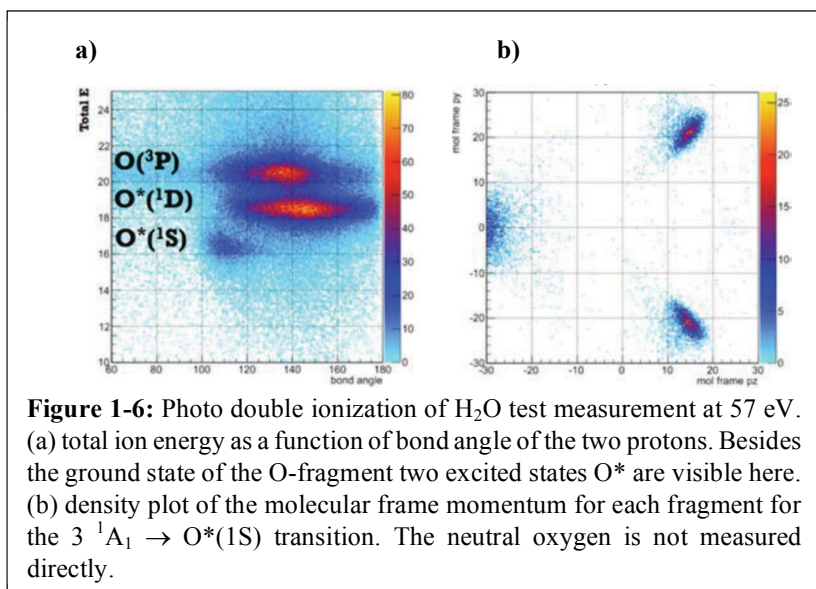
Figure 1-5: MFPADs for photo electrons with 3, 2, 1 and 0.5 eV after single photo ionization of H_2 . The proton always goes to the right. The asymmetry increases with decreasing electron energy.

The charge becomes unequally distributed on the fragments, even for homonuclear diatomic molecules, and results in a break in symmetry in the MFPAD. Such a retroacting low-energy photoelectron can thus be thought of as a sensitive probe to selectively trigger molecular dynamics in dissociation processes. We intend to apply our new capability of superimposing an IR laser field during the XUV-driven dissociation processes performed at the ALS. This could address whether an additional moderate external field will modify the polarizing effect of the retroacting electron on the molecular dissociation or if the presence of the retroacting electron can modify a LICl.

Kinematically Complete Investigation of Photo Double Ionization (Pdi) of a Tri-Atomic Molecule (*R. R. Lucchese, C. W. McCurdy, T. N. Rescigno, D. S. Slaughter, Th. Weber*)

Future Plans: A detailed description of dissociative photo double ionization (PDI) of a polyatomic molecule is highly challenging due to the coupling of electronic states within ionization continua, and because the potential energies and lifetimes of those states depend on more than one internuclear coordinate. To date, the only kinematically complete PDI experiments have been performed on atoms and diatomic systems. A kinematically complete investigation of PDI in a triatomic molecule would be indispensable to understand correlated double photo ejection dynamics of complex systems relevant to fundamental photochemistry. We will hence investigate the energetics and correlated angular distributions of the two emitted electrons with respect to the molecular frame of H₂O. Specifically, we aim to understand the difference in probability and dynamics of the inter- and intra-shell ionization processes, and to address the question of whether a two-active electron picture is applicable to understand the PDI of a polyatomic molecule.

In a recent test measurement at the ALS, the dissociation dynamics of H₂O showed a marked dependence on both bond angle and KER distribution for the three body breakup channel $\gamma + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{H}^+ + \text{O} + 2e^-$ (see Fig. 1-6a). The analysis is very challenging, because the concerted bending and a/symmetric stretching of the bonds play a key role in the dissociation dynamics. These first data, in which we can distinguish up to eight dication states with the help of the theory team (McCurdy, Rescigno and Lucchese), suggest a unique opportunity to perform a kinematically complete investigation on molecular frame electronic correlation effects in H₂O. Of particular interest is the transition of the 3^1A_1 dication state leaving behind an excited state $\text{O}^*(^1S)$ fragment. In comparison with theory, the triatomic nuclear momentum frame (see Fig. 1-6b) reveals a fast fragmentation within the axial recoil approximation. This channel hence represents an ideal candidate to benchmark highly differential cross sections in the body fixed frame for both experiment and theory.



Subtask 2: Photon and Electron Driven Processes in Complex Molecular Systems and Molecules in Complex Environments.

(A. Belkacem, O. Gessner, M. Head-Gordon, S. R. Leone, R. R. Lucchese, C. W. McCurdy, D. M. Neumark, T. N. Rescigno, D. S. Slaughter, Th. Weber)

Ultrafast Dynamics in Ortho-Nitrophenol (A. Belkacem, R. R. Lucchese, C. W. McCurdy, D. S. Slaughter)

Ortho-nitrophenol (ONP) consists of an electron withdrawing NO_2 group and electron donating OH group on neighboring carbon atoms of a benzene ring. Upon electronic excitation, complex isomerization processes can occur resulting in the elimination of an NO molecule and the formation and elimination of the HNO_3 molecule. There is some evidence to believe these processes occur on the S4 state at an energy of around 4.6 eV.

Recent Progress: Ion fragment mass spectra of ONP following photodissociation were measured by multi-photon ionization using 260 nm pulses (20 fs, 10^{13} W/cm²), to determine possible fragmentation pathways leading to HNO_3^+ , NO_2^+ , NO^+ , among other photoion fragments. In a time-resolved investigation, weaker 260 nm pulses were employed to excite o-nitrophenol to the S4 state and probe the evolving excited state by IR multiphoton ionization, to measure the kinetic energies of photofragments as a function of pump-probe time delay. We initially used a strong IR pulse as a multiphoton probe after a variable time delay to determine the different timescales involved. The measurements show that the timescale for elimination of NO is much shorter than for HNO_3 and both channels exhibit a delayed onset compared to the parent ion signal, suggesting isomerization processes involving the nitro and hydroxyl functional groups in the neutral excited state or the dissociating cation.

Preliminary photo-ion pump-probe measurements, using a 7th harmonic (11.1 eV) probe pulse, were performed to observe timescales similar to those measured with the strong IR probe (Fig. 2-1a). The NO^+ fragment has two kinetic energy peaks with different decay shapes and timescales. This indicates the involvement of multiple pathways for the elimination of NO upon excitation to the S4 state. While these results are encouraging, time-resolved photoion yield measurements alone will most likely not be sufficient to understand such complex processes with multiple competing channels.

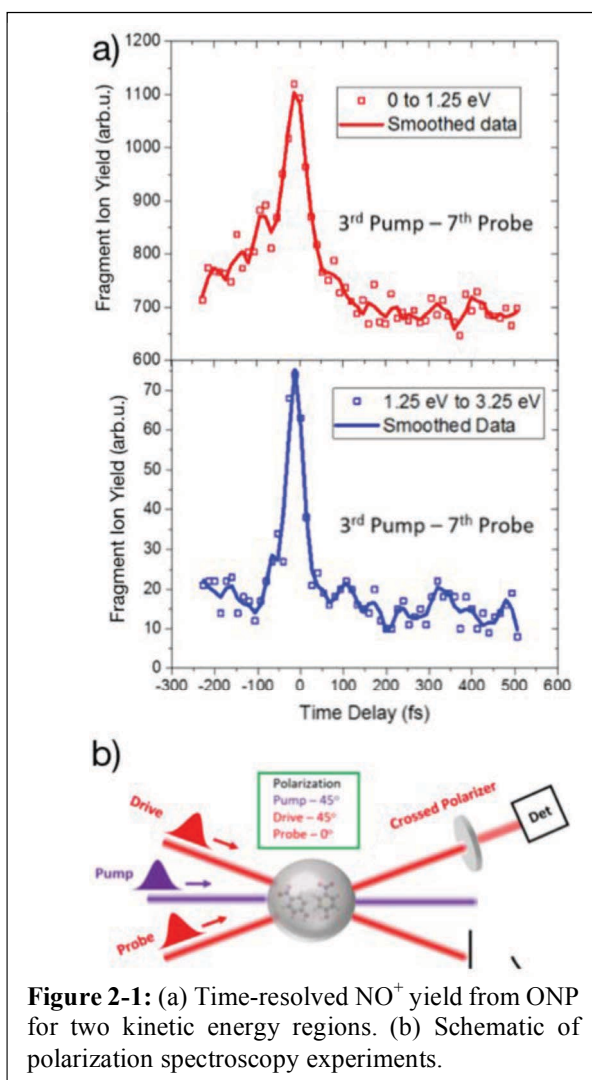


Figure 2-1: (a) Time-resolved NO^+ yield from ONP for two kinetic energy regions. (b) Schematic of polarization spectroscopy experiments.

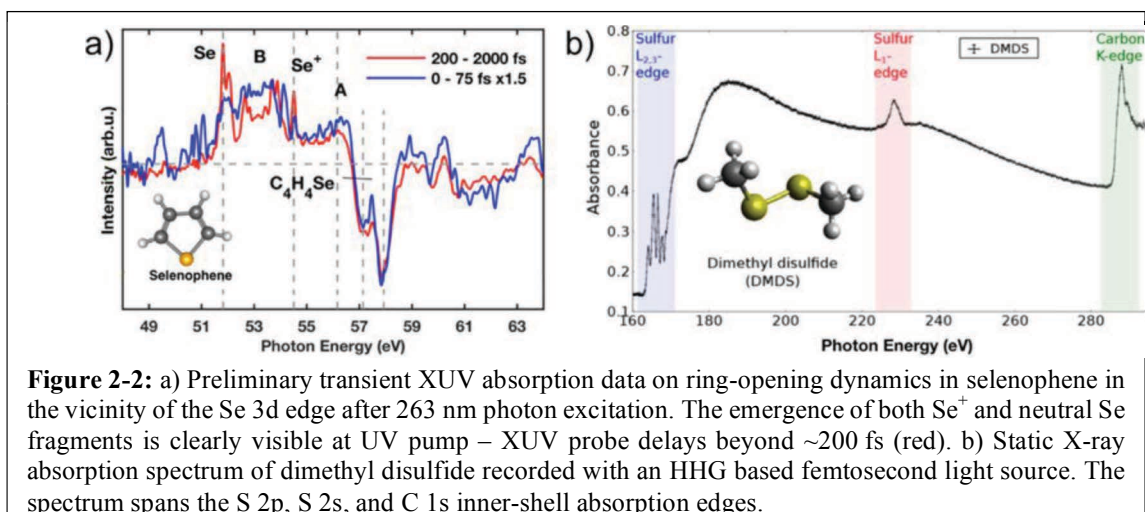
Future Plans: To complement transient photoexcitation-ionization pump-probe experiments on relatively complex molecules, a new probe of ultrafast molecular dynamics, based on concepts of optical Kerr spectroscopy, applied to electronically excited states in the XUV regime is under development. Our initial implementation of this technique uses three laser beams (Fig. 2-1b) providing a UV pump pulse to access the excited state manifold, as well as a moderately strong drive pulse and a weaker probe pulse to monitor the excited state dynamics by homodyne and heterodyne detection. The drive- and probe-beams cross at a small angle inside the sample and their polarization axes are tilted by 45° with respect to each other. After passing through the sample, the spatially separated probe beam encounters a polarizer that is aligned perpendicular to the original probe polarization axis. For the heterodyne detection scheme, a quarter wave plate may be placed in the probe beam path. One major advantage of this approach is that it is virtually background-free enabling up to 3 orders of magnitude higher sensitivity than signal intensity changes in conventional transient absorption experiments. Since the optically induced birefringence depends on the third-order susceptibility of the sample (and therefore its electronic configuration), the probe signal modulations can be associated with the instantaneous electronic structure of the sample. We expect that this scheme will be extremely sensitive to, for example, changes in electronic character near conical intersections and other coupled electronic-nuclear dynamics in complex molecules.

Ultrafast Molecular Dynamics Monitored by Femtosecond Time-Resolved Inner-Shell Transient Absorption Spectroscopy (*O. Gessner, S. R. Leone, D. M. Neumark*)

In this effort, unimolecular dynamics in isolated molecules are studied by HHG-enabled ultrafast inner-shell transient absorption spectroscopy. The method provides an element-specific perspective of the coupled motion of electrons and nuclei during photoinduced isomerization and dissociation processes.

Recent Progress: Two concerted experimental-theoretical efforts provided new insight into ring-opening dynamics in strong-field ionized selenophene (Lackner, et al., *J. Chem. Phys.* **145**, 234313 (2016)) and dissociation dynamics in strong-field ionized ferrocene (Chatterley, et al., *J. Phys. Chem. A* **120**, 9509 (2016)). More recently, studies using strong-field NIR ionization to reach electronically excited manifolds have been complemented by single- and multi-photon excitation/ionization schemes using moderately intense UV (263 nm) light. This opens the possibility to study a different class of ring-opening and dissociation channels that lead to the production of neutral selenium fragments in addition to Se^+ ions. Preliminary data indeed show the appearance of both fragment channels with a predominant contribution from neutral Se (Fig. 2-2a), in stark contrast to the product distribution from NIR ionization, where these were entirely absent. The analysis of the data is ongoing.

Future Plans: The current focus is to push the technique toward the study of a larger variety of chemically relevant systems, with much better selectivity of the excited state potential energy landscape. The latter will be accomplished by a continued move away from strong-field ionization induced dynamics toward few- and single-photon excitation schemes. Taking advantage of recent developments in HHG techniques using long (≥ 1200 nm) wavelength driving pulses, the reach of the technique will be expanded to probe dynamics in the vicinity of the sulfur 2p (~ 160 eV), sulfur 2s (~ 230 eV) and carbon 1s (~ 290 eV) inner-shell absorption edges. First experiments to probe UV-induced dissociation dynamics in dimethyl disulfide are ongoing, using an existing long wavelength HHG setup at UC Berkeley (Fig. 2-2b). The experiments will be complemented by *ab initio* calculations of inner-shell transition energies in the Head-Gordon group (see Subtask 3).



Ultrafast X-ray Studies of Interfacial Electron Dynamics (*O. Gessner*)

This new effort builds on capabilities developed during the DOE Early Career Research Program Award period of Oliver Gessner. The key driver for this project is to gain a fundamental, predictive understanding of photoinduced electronic and chemical dynamics in heterogeneous, condensed phase assemblies from a molecular perspective. A particular focus of the effort is to connect single-molecule dynamics with domain-wide processes, ultimately up to application-scale systems.

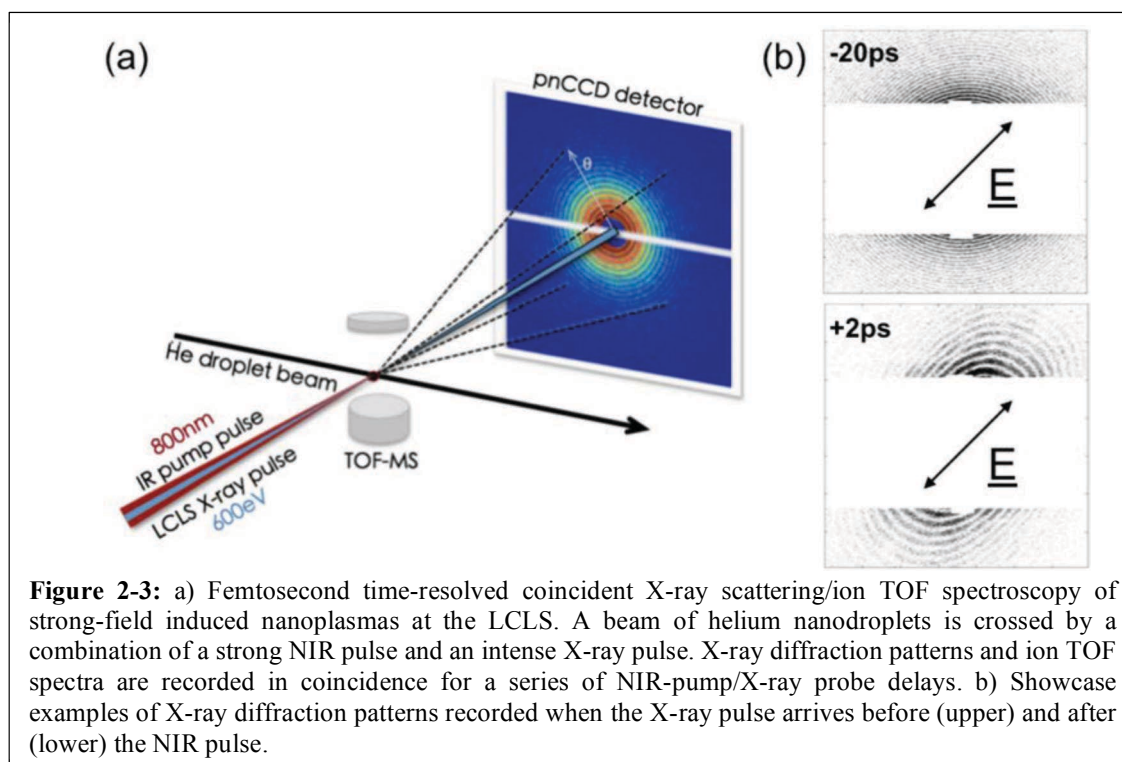
Recent Progress: Previous work related to this activity has been funded through Gessner's DOE Early Career Award and is reported in a separate abstract.

Future Plans: The Early Career efforts enabled the implementation of two new experimental capabilities at the Advanced Light Source (ALS): a picosecond time-resolved X-ray photoelectron spectroscopy setup and a picosecond time-resolved X-ray absorption spectroscopy setup. Both techniques are based on a combination of a mobile, high-repetition rate picosecond laser system with experimental setups employing time-stamping techniques to efficiently use the available X-ray flux and pulse structure of the ALS. Compared to conventional laser-synchrotron pump-probe techniques, single-laser-pump – multiple-X-ray-probe experiments have significantly higher data acquisition rates and lower target damage rates, both of which are critical enablers for time-domain X-ray studies on non-replenishing condensed phase samples that are the focus of this activity. In the future, these new capabilities will be exploited in order to advance our understanding of the fundamental electronic and chemical dynamics underlying novel light harvesting and molecular electronics concepts based on hybrid molecule-semiconductor, molecule-molecule, and molecule-semiconductor-metal designs. In particular, systems based on nanoscale designs of light absorbers, charge-separating interfaces, and chemically active sites offer great potential for new applications, but the fundamental dynamics that enable and limit their performance are often poorly understood. The elemental site-specificity of the newly developed X-ray spectroscopy techniques and their capability to simultaneously monitor dynamics across timescales spanning 6+ orders of magnitude will provide a unique perspective of the coupled electronic – chemical dynamics from within each molecular/nanoscale building block and across entire assemblies.

Ultrafast XUV Spectroscopy and X-ray Scattering Studies of Coupled Electronic-Nuclear Dynamics and Quantum Hydrodynamics in Superfluid Nanodroplets (*O. Gessner, S. R. Leone, D. M. Neumark*)

This effort employs superfluid helium nanodroplets with up to $\sim 10^{10}$ atoms to study collective phenomena in large scale ensembles and the interaction of atoms and molecules with complex matrix environments. Studies are performed within a wide range of excitations, including vorticity in the rotational motion of micron-scale droplets in electronic ground states to coupled electronic-nuclear dynamics in single-photon excited and strong-field ionized droplets. Laboratory high-order harmonic generation (HHG) light sources and X-ray free electron lasers are used for both ultrafast spectroscopy and imaging studies of electronic and atomic motion.

Recent Progress I: The creation and long-term evolution of a strong-field induced nanoplasma has been studied by femtosecond time-resolved coincident X-ray scattering/ion time-of-flight (TOF) spectroscopy at the Linac Coherent Light Source (LCLS, Fig. 2-3). Interaction of ~ 600 nm



large droplets containing $\sim 10^9$ helium atoms with a very intense ($>10^{15}$ W/cm²) near-infrared (NIR) pump pulse induces the formation of a nanoplasma. The evolution of the plasma is monitored with femtosecond temporal resolution by recording single-shot X-ray diffraction patterns with NIR/X-ray time delays up to 100 ps. For each diffraction pattern, an ion TOF spectrum is recorded in coincidence. The combination of single-shot imaging and spectroscopy data gives access to transient plasma shapes, densities, and ion kinetic energies. The experiment connects initial femtosecond-scale surface expansion dynamics with long-term plasma shape changes, ultimately leading up to its complete disintegration. The evolution of anisotropies on several spatial and temporal scales is observed (Fig. 2-3a). The plasma evolution is analyzed within a numerical plasma expansion model that contains previously observed dynamics as a limiting

case for smaller systems, while extending the description to include the transition between \sim nm/fs and \sim μ m/ps scale dynamics.

Future Plans I: The results of the LCLS experiment indicate extremely efficient coupling between the (sub-)fs electronic dynamics during exposure to the NIR pulse and the long-term evolution of the plasma long after the light pulse has passed through the system (Fig. 2-3b). The focus of future studies will be to better understand the underlying coupling mechanisms, which proceed on timescales of electron motion. Recent developments at LCLS and, in particular, projected performance parameters of LCLS II will give access to the entire range of dynamic timescales and spatial scales such that a single experiment will be able to probe the entire evolution of intense light – matter interaction from the initial ionization cascade to the asymptotic product distribution.

Recent Progress II: Complementing studies in the strong-field regime at the LCLS, laboratory-based studies using high-order harmonic generation (HHG) light sources are performed to explore the character and dynamics of single-photon induced cluster excitations. A particular theme of thrust is the extension of the experimental capabilities to probe energy- and charge-transfer between electronically excited helium nanodroplets and dopant atoms and molecules. First static photoelectron signals associated with host-dopant interactions have been recorded (Fig. 2-4) and are in qualitative agreement with previous synchrotron based measurements. Most recently, a new HHG technique has been implemented that uses exclusively the 2nd harmonic of the NIR fundamental to drive the HHG process. This method leads to both substantially more intensity in the 14th NIR harmonic (i.e. the 7th harmonic of the 400 nm driver) and a 4-fold increase in harmonic energy spacing compared to the previous method. These achievements represent major progress toward pump-probe studies involving the droplet 2p absorption band, as they will enable more manageable data acquisition times and virtually eliminate the overlap of photoelectron signals from neighboring harmonics in a photon energy range where multilayer mirrors have very limited wavelength selectivity. The experimental efforts within this thrust are supported by *ab initio* calculations in the Head-Gordon group as described in Subtask 3.

Future Plans II: The new experimental capabilities will be applied to gain a deeper understanding of heterogeneous energy- and charge-transfer phenomena in doped helium nanodroplets. Our previous synchrotron based experiments on Kr and Xe doped helium droplets strongly indicated the existence of an efficient indirect ionization mechanism, whereby the host droplet absorbs XUV light at \sim 21.5 eV and the dopant is subsequently ionized by host-guest energy transfer. In a more recent synchrotron experiment on Ar doped helium droplets, however, Mudrich and co-workers did not find any indication for this process, but instead identified hole transfer from ionized droplets as the only significant ionization channel for noble gas dopants. We will use HHG based ultrafast photoelectron and ion imaging to probe the relative importance of the two processes and, in particular, to elucidate the underlying dynamics of energy and/or charge transfer by probing their evolution in real time. The measurements will also help clarify whether the host-

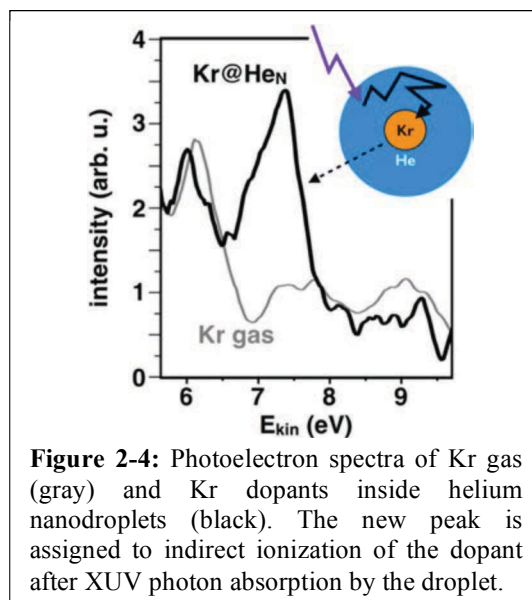


Figure 2-4: Photoelectron spectra of Kr gas (gray) and Kr dopants inside helium nanodroplets (black). The new peak is assigned to indirect ionization of the dopant after XUV photon absorption by the droplet.

dopant energy transfer mechanism might be better characterized by a short-range Penning-like or a long-range ICD-like process.

Dynamics of Dissociative Electron Attachment to Molecular Dimers (*R. R. Lucchese, C. W. McCurdy, T. N. Rescigno, D. S. Slaughter, Th. Weber*)

Several urgent questions persist regarding the dynamics of dissociative electron attachment (DEA) to molecular clusters. Does an electron attach to one unit of a dimer to form a transient anion resonance, analogous to the resonances in the isolated constituent molecules? Does the attached electron become considerably delocalized to form a larger electron-dimer complex? What dynamical processes proceed in the complex transient anion resonance and how are the electronic and nuclear motions coupled?

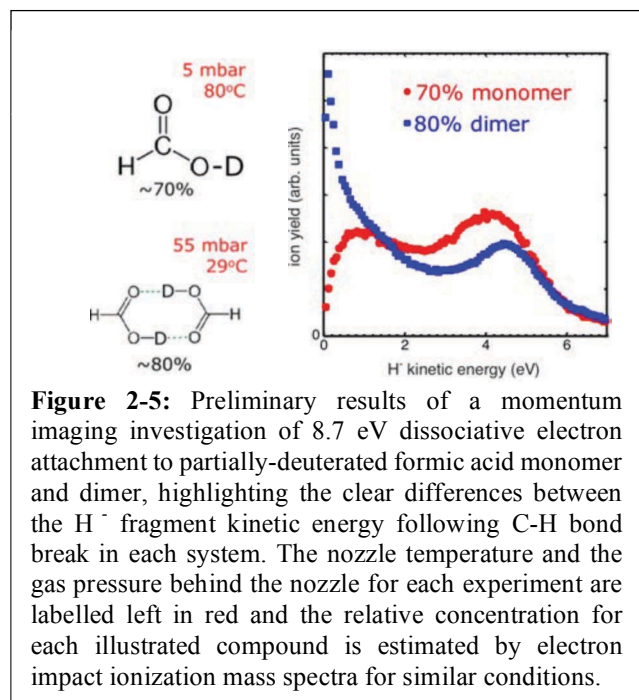


Figure 2-5: Preliminary results of a momentum imaging investigation of 8.7 eV dissociative electron attachment to partially-deuterated formic acid monomer and dimer, highlighting the clear differences between the H^+ fragment kinetic energy following C-H bond break in each system. The nozzle temperature and the gas pressure behind the nozzle for each experiment are labelled left in red and the relative concentration for each illustrated compound is estimated by electron impact ionization mass spectra for similar conditions.

Recent Progress: Results of a preliminary DEA fragment imaging experiment on partially deuterated formic acid (HCOOD) and its dimer are displayed in Fig. 2-5. H^+ fragment kinetic energies were measured using an anion momentum imaging apparatus based on the COLTRIMS ion momentum imaging technique (Slaughter, et al., *J. Phys. B* **49** 222001 (2016)). Electron impact ionization mass spectra were recorded using the same apparatus, which verified that the different source conditions produce either a high relative abundance of monomers or dimers. Under the nominal monomer conditions, C-H dissociation occurs with a high kinetic energy release of 3 to 5 eV (blue). When the formic acid source conditions favor dimers, C-H break also occurs, but with a significantly different fragment kinetic energy spectrum, favoring low kinetic energies.

Future Plans: New instrumentation will be developed to extend this experimental approach to other dimer systems, such as $(\text{NO})_2$. Electron attachment and transient anion dynamics in this class of dimers can be investigated in much greater detail by a close collaboration between the momentum imaging efforts in Subtask 2 and *ab initio* calculations of the molecular frame electron attachment probabilities in Subtask 3 (Slaughter et al., *J. Phys. B* **49** 222001 (2016)). Individual electron-initiated reaction channels will be selected and interrogated by new experimental approaches exploiting recent advances in cold molecular beam technology, high resolution mass spectrometry and highly-differential 3D ion momentum imaging spectroscopy. In the future, these studies will be extended to understand effects of microhydration on transient anion dynamics by performing electron attachment experiments on small heteromolecular clusters containing one or two water molecules. We will then begin to address the dynamics responsible for the different dissociation products observed for gas phase and condensed phase systems under similar electron attachment conditions.

Subtask 3: First-Principles Theory of Dynamics and Electronic Structure.

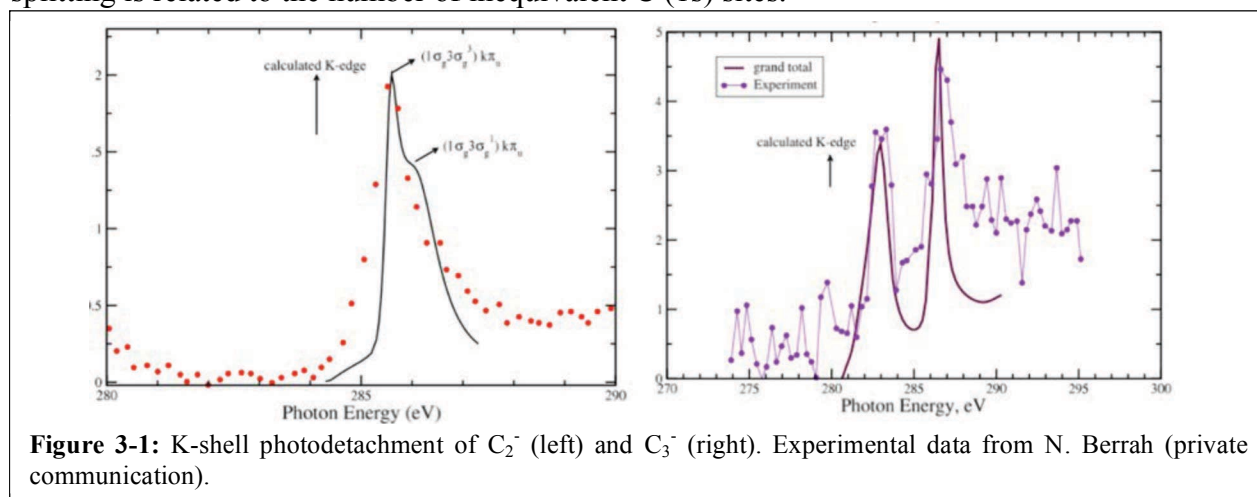
(*M. Head-Gordon, C. W. McCurdy, R. R. Lucchese, T. N. Rescigno*)

Core-Hole Ionization and Photodetachment of Polyatomic Molecules (*R. R. Lucchese, C. W. McCurdy, T. N. Rescigno*)

Recent Progress: Our recent and future work in the broad area of continuum electron dynamics makes use of (1) Electron-molecule scattering and electron-ion scattering calculations using the Complex Kohn Variational method and the Schwinger Variational approach developed by us and representing the leading state-of-the-art, (2) Extensive correlated electronic structure calculations on the neutral and anionic states of molecules and (3) Grid-based methods for treating two electrons in the continuum. In 2016 our studies of core hole localization fluorine in core ionization of CF_4 and of dissociative electron attachment to NH_3 appeared together with experimental results from the AMOS program at LBNL making use of the ALS for photoionization and the LBNL COLTRIMS apparatus for dissociative attachment.

K-shell Photodetachment of C_n^- Ions (*T. N. Rescigno*)

Recent Progress: The linear chains of carbon have bound negative ions. K-shell photodetachment of the simplest anion, C^- , is characterized by a prominent shape resonance ($1s \rightarrow 2p$) close to threshold. Recent K-shell photodetachment experiments at the ALS by N. Berrah and coworkers have shown that this shape resonance persists in the carbon anion chains, but that the resonance splits into multiple peaks in the heavier chains. To explain this observation, we have carried out, in collaboration with Nicolas Douguet (U. Central Florida) and Samantha Fonseca (Rollins College), a theoretical study of K-shell photodetachment of C_2^- and C_3^- . In contrast to neutral photoionization, the final states (electron + neutral radical) are highly correlated and are not dominated by a Coulomb interaction. The target states were described using natural orbitals extracted from configuration-interaction calculations on the carbon $1s^{-1}$ hole states and the cross sections were obtained from coupled-channel complex Kohn scattering calculations. Our results for C_2^- and C_3^- in Fig. 3-1 are found to be in good agreement with experiment. The calculations show that the resonance structure comes from $\text{C}(1s) \sigma_g \rightarrow k \pi_u$ shape resonances and that the splitting is related to the number of inequivalent C (1s) sites.



Dissociative Attachment to CF_4 (C. W. McCurdy, T. N. Rescigno)

Future Plans: We are undertaking a new theoretical study of dissociative electron attachment to CF_4 , which has been the object of several recent experimental studies, but for which no previous theoretical work has been carried out. DEA to CF_4 produces both F^- and CF_3^- through a broad resonance peak centered about 6.5 eV electron energy. Preliminary calculations show this feature to result from two overlapping shape resonances of T_2 and A_1 symmetry. The tetrahedral symmetry of neutral CF_4 is lowered to C_{3v} following electron capture and the triply degenerate T_2 resonance splits into an a_1 and doubly degenerate e components. We find the a_1 component of the T_2 resonance to dissociate directly to $\text{CF}_3 + \text{F}^-$; the anion fragment angular distribution we obtain for this channel from *ab initio* calculations of the entrance amplitude are in good agreement with experiment (Fig. 3-2). The dynamics leading to CF_3^- production are considerably more complicated and will be the subject of our future studies on this system.

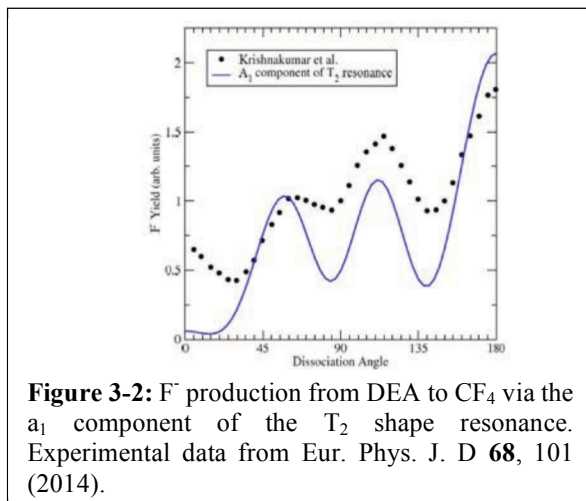


Figure 3-2: F^- production from DEA to CF_4 via the a_1 component of the T_2 shape resonance. Experimental data from Eur. Phys. J. D **68**, 101 (2014).

Molecular Frame and Recoil Frame Ionization of Polyatomic Molecules (R. R. Lucchese, C. W. McCurdy, T. N. Rescigno)

Recent Progress: Recent COLTRIMS experiments at the ALS on valence photoionization of CF_4 have shown that several of the lowest states of the CF_4^+ cation dissociate to $\text{CF}_3^+ + \text{F}$ thereby allowing the measurement of recoil frame photoelectron angular distributions (RFPADs) for valence ionization. In the channel corresponding to ionization from the $4t_2$ orbital the experiment shows a striking reversal in the angular distribution of the photoejected electron over a narrow range energies less than 2 eV. In collaboration with Prof. Cynthia Trevisan (California State University, Maritime) we have performed coupled channel photoionization calculations using the complex Kohn method to verify that this remarkable shift, shown in Fig. 3-3, originates from the interference of a pair of overlapping shape resonances lying close in energy. This is not an alternation between angular dependences associated with the two resonances separately and is exclusively a result of their combined contribution to the photoionization amplitude. Further comparisons of theory and experiment are underway.

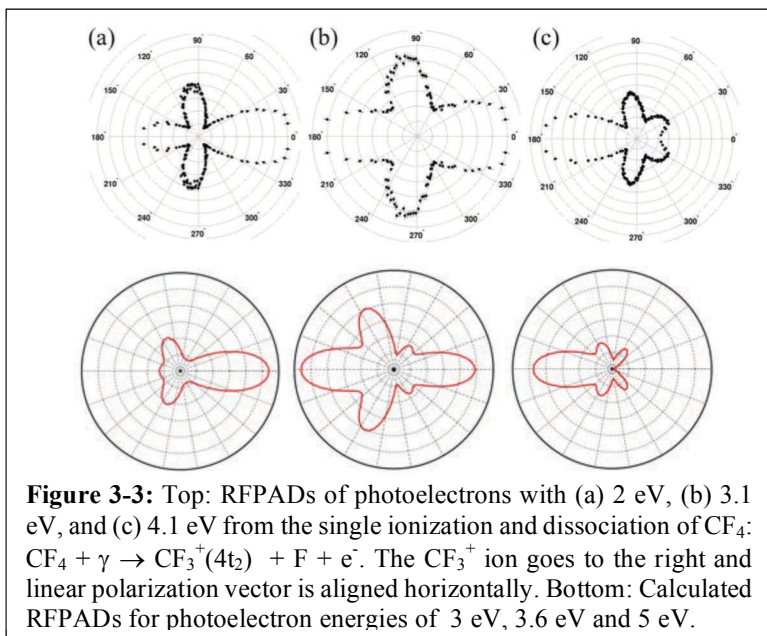


Figure 3-3: Top: RFPADs of photoelectrons with (a) 2 eV, (b) 3.1 eV, and (c) 4.1 eV from the single ionization and dissociation of CF_4 : $\text{CF}_4 + \gamma \rightarrow \text{CF}_3^+(4t_2) + \text{F} + \text{e}^-$. The CF_3^+ ion goes to the right and linear polarization vector is aligned horizontally. Bottom: Calculated RFPADs for photoelectron energies of 3 eV, 3.6 eV and 5 eV.

Future Plans: If our recently published interpretation of the striking evidence we found for F-atom core-hole localization in CF_4 is correct (McCurdy et al., Phys. Rev. A **95**, 011401(R) (2017)), similar effects should also be found in other molecules with symmetry-equivalent F atoms. To this end, in collaboration with Cynthia Trevisan (California State University, Maritime) we will carry out Complex Kohn calculations on three isomers of *difluoroethylene* ($\text{C}_2\text{H}_2\text{F}_2$) – 1,1 difluoroethylene, as well as cis- and trans-1,2 difluoroethylene using both localized and delocalized F-1s orbitals. We expect all three molecules to show strong effects of core-hole localization in their MFPADs, but when the latter are averaged about the F - $\text{C}_2\text{H}_2\text{F}$ recoil axis to produce an experimentally observable RFPAD, significant detail is lost and the evidence for localization may be more evident in some isomers than others.

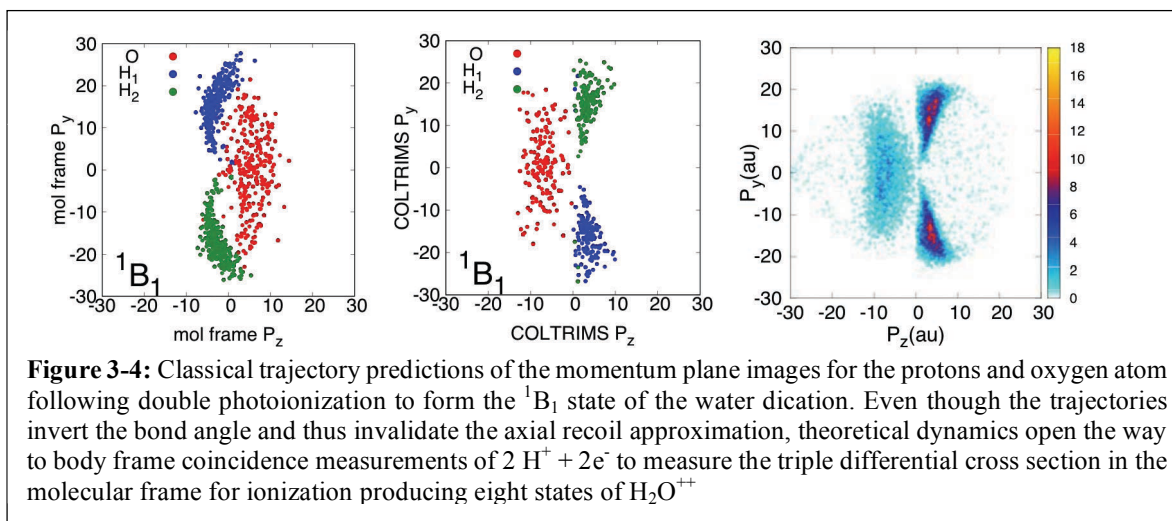
DEA to Molecular Dimers (*R. R. Lucchese, C. W. McCurdy, T. N. Rescigno*)

Future Plans: Experiments on dissociative attachment to *molecular dimers* are proposed at LBNL in subtask II with the goal of developing for the first time a vocabulary of the fundamental processes whereby charge and energy are transferred between molecules in the metastable anion of the dimer. The $(\text{NO})_2$ dimer and the $\text{CO}_2 \bullet \text{H}_2\text{O}$ dimer are practical experimental targets, and we propose to perform complex Kohn electron-molecule scattering and electronic structure calculations to help interpret and guide those experiments. Our first target will be DEA to the NO dimer. We have studied the low lying resonances of the monomer in vibrational excitation and DEA, and a good deal is known about the electronic states of the neutral dimer. The dimer electronic states are understood as excimer combinations of excitations of the same state of each monomer and charge transfer states. The shape resonances of NO^- appear stabilized as bound charge transfer excited states like $\text{NO}^+ \bullet \text{NO}^-$, suggesting that the dimer anions could appear either as Feshbach resonances below those thresholds or as symmetric and antisymmetric combinations of shape resonances of the form $\text{NO} \bullet \text{NO}^-$.

Double Photoionization of Water: Nuclear Dynamics of the Dissociation for Double Ionization Producing Nine States of H_2O^{++} (*R. R. Lucchese, C. W. McCurdy, T. N. Rescigno*)

Future Plans: We are undertaking a major new effort to calculate the body frame triple angular dependence of the one-photon double ionization of the water molecule. Preliminary experiments at the ALS showed that several electronic states of the water dication are produced in the process $\text{H}_2\text{O} + h\nu \rightarrow \text{H}_2\text{O}^{++} + 2e^- \rightarrow \text{O} + 2\text{H}^+ + 2e^-$, and that the two protons and two electrons can be observed in coincidence, opening the possibility that for the first time the angular dependence of the two ejected electrons could be measured in the body frame for a polyatomic molecule. But an understanding of the dissociation dynamics is a prerequisite for interpreting such an experiment. We have performed a complete classical trajectory study on potential surfaces of the lowest nine states of the water dication computed at the multireference CI singles and doubles level. Those theoretical studies have allowed (1) identification of the eight states of H_2O^{++} that are observed in the experiment, (2) the prediction of which states dissociate directly (axial recoil) and which do not, and (3) the verification of that dynamics by predicting, as shown in Fig. 3-4, the momentum plane images as they would be observed in an analysis of COLTRIMS data under the necessary assumption of axial recoil. This study opens the way to extract the body frame cross sections even when the axial recoil approximation breaks down for the first time in a COLTRIMS experiment. In collaboration with Prof. Frank Yip (California State University, Maritime) we are extending our former work on one-photon double ionization on atoms and the H_2 molecule to compute the triple differential cross sections (TDCS) for a water in the molecular frame, which

will be a massive computational project based on our atomic work in the two-active-electron approximation.



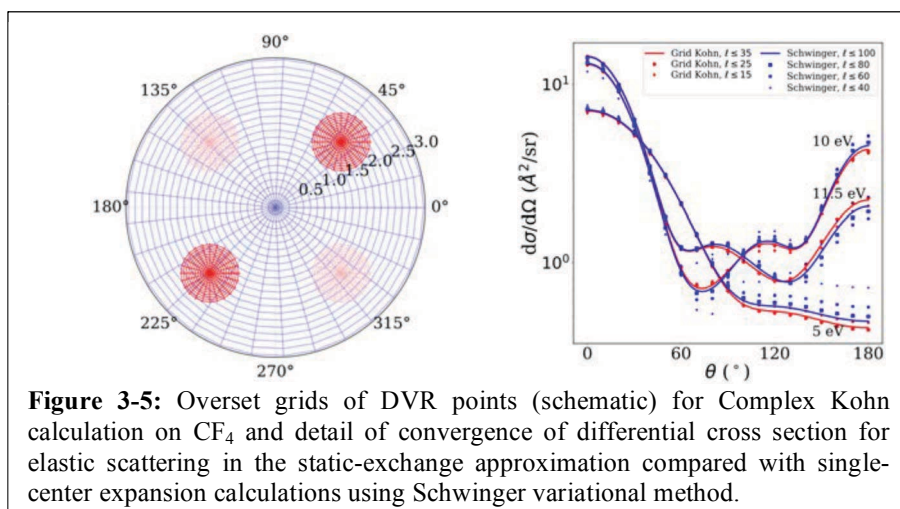
Overset Grid Based Complex Kohn Method for Electron-Polyatomic Molecule and Ion Scattering (R. R. Lucchese, C. W. McCurdy)

Recent Progress:

We are developing a new computational implementation of the complex Kohn variational method that describes the scattered or ionized electron in each electronic channel using only numerical grid representations. The new method uses overlapping grids in a method, called “overset grids” in the applied mathematics

literature, that is shown schematically in Fig. 3-5 together with some results we have obtained for e -CF₄ scattering.

At this point the essential features of the new method have been implemented and tested for small molecules in single-channel static-exchange calculations: (1) A Krylov-Arnoldi-type solution method for evaluating the complex Kohn variational expression with Krylov vectors, $[G_0^+ V]^n \Phi_k^0$, based on repeatedly operating with the free-particle Green’s function, thereby applying outgoing wave boundary conditions. (2) Efficient quadrature algorithms for acting with G_0^+ and all Coulomb and exchange operators. (3) Construction of the central quantity of the complex Kohn method, the matrix element involving the scattering solution and unscattered wave function $\langle \Phi_k^0 | (E - H) | \Psi^{sc} \rangle$, without calculating *any* derivatives numerically on the overset grid by exploiting the fact that $(E - T) G_0^+ = \mathbf{1}$. (4) This basis of vectors automatically provides a rapidly convergent series of Padé approximants to the full solution of the scattering problem.



Future Plans: Having demonstrated all the necessary components of the new method in full calculations for electron-molecule scattering, we will first extend it to Coulomb boundary conditions for photoionization calculations. Then we will then develop multichannel close-coupling capability, initially using single-configuration representations of the target states, and then using correlated target states. The planned theoretical and computational developments will ultimately produce a modern, easy-to-use, and general electron-molecule collision code, parallelized with OpenMPI that will be made available to other users and will support experiments planned at LBNL in dissociative electron attachment and molecular photoionization.

New Theory of Conversion of Resonances to Bound States in Coulomb Potentials and the Computation of Autoionization Lifetimes from Quantum Defects (*R. R. Lucchese, T. N. Rescigno, C. W. McCurdy*)

Recent Progress: A central concept of collision theory is the idea that bound states can become metastable states with finite lifetimes (scattering resonances) and vice versa as the strength of the interaction potential is varied. This phenomenon is well known in electron-molecule scattering, where it provides the mechanism for dissociative attachment of electrons to molecules and dissociative recombination (DR) of electrons to molecular cation.

In the case of scattering potentials which behave asymptotically as attractive Coulomb potentials, a pole of the S matrix in the fourth quadrant of the complex k plane that is associated with a scattering resonance, *does not become a pole corresponding to a bound state* which is created as the short range part of the potential is made more attractive. However, we have shown that it is paired exactly with a zero in the first quadrant that modifies the Rydberg series at negative energy.

In single-channel scattering, the S -matrix is related to the phase shift, δ , through $S(k) = \exp[i2\delta(k)]$. Defining a corresponding M -matrix which is related to the quantum defect, μ , through $M(k) = \exp[i2\pi\mu(k)]$, we have shown that for a potential which is asymptotically attractive with a charge of one we have

$$\frac{1}{M(k)} = \frac{1}{S(k)} [1 - e^{-2\pi/k}] + e^{-2\pi/k}$$

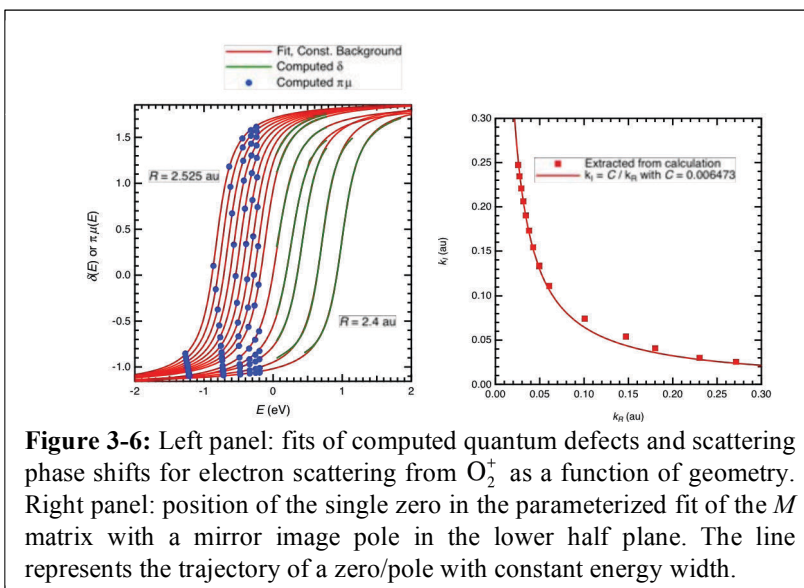
We can then see that when $\text{Re}(2\pi/k) \gg 1$, that is when k is close to the real axis and not too large, then M and S will be the same. Along the imaginary k axis, where S has a series of zeros and poles, M is quite smooth. Additionally, away from the imaginary k axis the zeros of S and M will occur at the same locations. With its simple analytic structure, M can be parameterized using a form such as

$$M(k) = \frac{(k - k_{res}^*)(k + k_{res}^*)}{(k - k_{res})(k + k_{res})}$$

when there is a single pole/zero pair in S . This form satisfies the condition that the S matrix is unitary, i.e. δ is real, when k is real, and the quantum defect μ is real when k pure imaginary.

We have applied this parameterization to electron scattering from O_2^+ which has a resonance of $^1\Sigma_u^+$ symmetry with the electronic configuration $3\sigma_g^2 1\pi_u^3 1\pi_g^3$. In the left panel of Fig. 3-6, we have plotted, for a range of bond lengths, the quantum defects for the bound states of this symmetry as well as scattering phase shifts from scattering calculations at positive energies. We see that at shorter bond lengths there is a resonance at positive scattering energies, whereas for longer bond lengths, the scattering resonance is gone but the Rydberg levels are strongly perturbed. This

behavior can be fit using a single k_{res} , which depends on bond length, as shown in the right panel in Fig. 3-6. This study provides the correct connection between low-energy scattering resonances and energy dependent quantum defects, with changing geometry. This connection can be applied in the study of dissociative recombination.



Complex (c) and General (G) Hartree-Fock (HF) Wavefunctions (*M. Head-Gordon*)

Recent Progress: The description of electronic structure begins with identifying the essential configurations at the molecular orbital (MO) level. In standard electronic structure codes, only spin-paired restricted HF (RHF) and spin-polarized unrestricted HF (UHF) are employed. However more general HF configurations exist, using either complex orbitals (cRHF, cUHF), or non-collinear general spin orbitals (GHF, cGHF). We have developed an object-oriented HF program that can evaluate all possible MO variants, and characterize their stability. This was employed to explore the largely ignored cRHF method, and we showed that cRHF solutions describe a class of strongly correlated ground states (e.g. transition states for D_{4h} cyclobutadiene, Be insertion into H_2 , Woodward-Hoffman forbidden ring-opening in *cis*-bicyclo[2.1.0]pent-2-ene to form *cis,cis*-cyclopenta-1,3-diene), and even certain classes of conical intersections! These results are possible because cRHF is rigorously a limited multi-configurational wavefunction. Turning to GHF, which can describe spin-frustration, we have developed the first method that can fully characterize whether or not spin non-collinearity exists in a GHF solution. This diagnostic should be routinely evaluated whenever GHF solutions are discovered. The effort necessary to develop this software has already enabled other related projects, such as using these determinants for nonorthogonal CI (NOCI) calculations, the cRHF code (in the c-norm) was used to describe resonances via complex absorbing potentials, as well as for a modern implementation of the non-Hermitian HF method (a collaboration between Head-Gordon and McCurdy that yielded the first unrestricted results – see below).

Electronic Structure Methods for Excited States of Clusters (*M. Head-Gordon*)

Recent Progress: To permit electronic structure calculations of the excited state bands associated with large homogeneous clusters (e.g. the $n=2$ or $n=3$ bands of clusters of helium atoms), we have formulated a configuration interaction with singles (CIS) excited state method that retains a number of amplitudes that scales only linearly with the size of the cluster. Physically, this model corresponds to superposing excitations that are localized on individual monomers, and discarding charge-transfer (CT) excitations. This was rigorously accomplished using absolutely localized molecular orbitals (ALMOs) that are non-orthogonal between different molecules. In contrast to NOCI above, ALMO-CIS uses the same orbitals for all configurations to enable the

Hamiltonian to be explicitly constructed and directly diagonalized to yield the large numbers of states necessary to describe absorption and dynamics in large clusters.

A production version of the implementation has been completed and applied to clusters as large as 485 atoms, to yield 4850 excited states, which is about 10 times larger than we could previously simulate. This is possible because the method scales as the cube of the number of atoms in the cluster, whilst still giving a representation of a cluster band of states whose number increases linearly with the cluster size. Neglect of CT was numerically demonstrated to yield errors relative to full CIS that gradually increase from the red edge of the $n=2$ band to the blue edge. While the ALMO-CIS results are qualitatively reasonable, it is desirable to remove this error, and for molecular clusters (where CT is more important than for rare gas clusters), this is probably essential.

Therefore, we have completed a new theory to correct the ALMO-CIS model for neglected CT excitations, which we term ALMO-CIS+CT. To retain the scaling advantages of ALMO-CIS, ALMO-CIS+CT uses a distance criterion to define a neighbor list for each monomer of the cluster, and using the same tensor theory, CT configurations are included to the neighbors. For a large cluster this yields the same scaling. We have had to overcome substantial technical challenges in order to achieve an efficient implementation, but this is now completed and just published. Numerical tests show that the ALMO-CIS+CT model differs negligibly from full CIS for He_{25} clusters where direct comparison is possible. The computational challenge in efficient implementation comes from increasing the overall Hilbert space dimension by over a factor of 6 relative to ALMO-CIS, which would lead to a factor of 6^3 increase in computational effort for diagonalization. Improved algorithms, which include a special adaptive diagonalizer, cause the overall computational cost for computing entire bands of states to increase by only a factor of 4 relative to ALMO-CIS.

Simulations of Helium Clusters in Excited States (*M. Head-Gordon*)

Recent Progress: The newly developed ALMO-CIS+CT method has been applied to model the size-dependence of helium cluster spectra, up to systems of 300 helium atoms. To correctly simulate the clusters, path integrals were applied to the nuclear motion, at a temperature of 3K (above the superfluid transition), and spherical boundary conditions were employed to establish a droplet-vapor equilibrium. The results, some of which are shown in Fig. 3-7, illustrate several interesting features. First, the size-dependence of the width of the 2p band (21.2 to 22.0 eV) emerges nicely from the simulations, in qualitative agreement with experiments. Second, signatures of the droplet versus dense gas can be established by removing the attractive part of the potential, and comparing the spectra simulated using different cutoff radii (giving different gas densities in the gas case, and different fractions of gas versus droplet atoms in the droplet-vapor equilibrium case). The dense gas simulation shows narrower bandwidth, and that bandwidth depends strongly on the gas density, while the droplet spectrum is as shown in the figure.

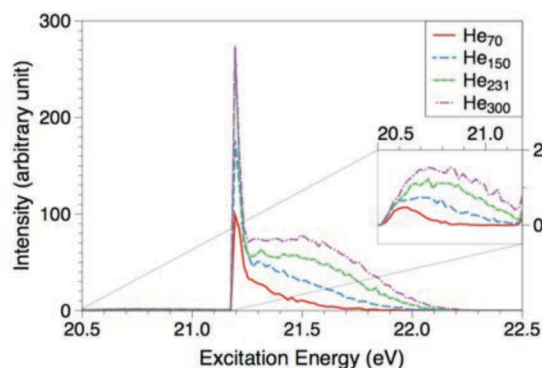


Figure 3-7: *Ab initio* calculations of the size-dependence of helium cluster excitation spectra, calculated using the newly developed ALMO-CIS+CT treatment of the electrons, together with path-integral treatment of nuclear motion.

Resonances Using Quantum Chemistry Methods: (M. Head-Gordon, C. W. McCurdy)

Recent Progress: In contrast to scattering methods, the goal is to harness appropriately generalized versions of the powerful tools of bound state quantum chemistry. Examples include techniques such as complex absorbing potentials (CAPs), complex basis functions (CBFs), or stabilizing potentials. Under a one-off DOE SciDAC grant that recently ended, we (Head-Gordon and McCurdy) have implemented the CBF method in a modern quantum chemistry program exploiting object-oriented tools including the new SCF package developed under the support of this program. Efficient algorithms for the complex two-electron matrix elements were developed, and applied to the simple static exchange (SE) model, non-Hermitian Hartree-Fock (NH-HF), MP2 and we have recently completed equation-of-motion coupled cluster theory with single and double substitutions (EOM-EA-CCSD). EOM-EA-CCSD with CBFs is quite accurate (within 0.2 eV) for a range of shape resonances and the $1s2s^2$ Feshbach resonance in He^- . Additionally, an accurate and efficient analytic continuation (AC) method was very recently developed that uses a series of Hermitian bound state quantum chemistry calculations performed with stabilizing potentials to determine (the lowest) shape resonance. New appropriate continued fraction (CF) forms were determined for the Pade approximant, and a new formally justifiable stabilizing potential was introduced for the analytic continuation, defining what we term the CFAC method. This approach was used with HF and CCSD(T) methods.

Calculations and Analysis of Excited States of Clusters and Aggregates (M. Head-Gordon)

Future Plans: Experimental studies of excited states of clusters, such as the helium clusters, and related systems studied experimentally by Gessner motivate further developments in electronic structure theory. Whilst computational methodology has made tremendous advances in providing calculations of excited states in molecules, there is a corresponding challenge in analyzing those computational results that is as yet incompletely addressed. We would like to unravel the origin of red or blue shifts relative to the monomer or the origin of changes in the character in the state. The answers to these questions require quantifying the contributions from resonance, charge-transfer, etc., to excimer and/or exciplex binding. The methods we have recently developed provide a major hint about how one might attack this problem. Fig. 3-8 compares ALMO-CIS with ALMO-CIS+CT (and CIS itself); a comparison that quantifies the effect of charge transfer. Specifically CT is near zero at the red edge of the 2p band, and approaches 0.5 eV at the blue edge of the 2p band. We are working on a new variational energy decomposition analysis (EDA) method to analyze exciplex, excimer and excited states of clusters. Variational EDAs impose a sequence of physically motivated constraints to quantify the energy lowering associated with physical effects such as Pauli repulsions, induced electrostatics, donor-acceptor charge-transfer, etc. EDA methods are well developed for ground state binding in non-bonded complexes, and even single chemical bonds, but there has been virtually no work on excited state variational EDAs. We are in the process of formulating expressions for a “frozen energy” which excludes

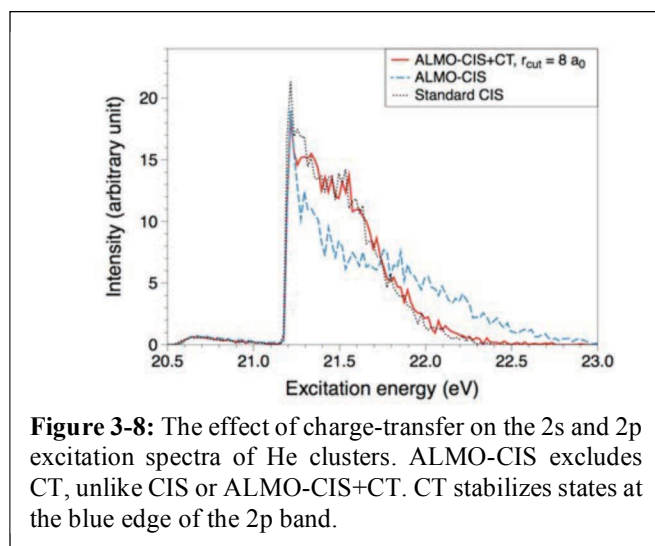


Figure 3-8: The effect of charge-transfer on the 2s and 2p excitation spectra of He clusters. ALMO-CIS excludes CT, unlike CIS or ALMO-CIS+CT. CT stabilizes states at the blue edge of the 2p band.

orbital and amplitude relaxation from monomer to cluster, within-monomer polarization effects, and inter-monomer charge transfer within the framework of one-electron excited state theories such as CIS and TDDFT. Our first step is to treat environment effects on a solute-localized excitation followed by appropriate modifications to properly treat the excimer problem. Gaining direct insight into these questions, which control interesting phenomena such as energy flow in aggregates, charge injection, aspects of organic electronics, etc., is the long-run purpose of developing these new computational tools.

Development and Application of NOCI Methods (*M. Head-Gordon*)

Future Plans: We are working on extensions of the non-orthogonal CI (NOCI) method, which offers probably the most compact description possible for states where there is significant charge resonance, such as mixed valence states that mix ionic and covalent character. Another example is core-excited states, where we are currently collaborating with Gessner and Leone an application project to calculation core excitations of dimethyl disulfide. The core hole in a core-excited state leads to significant valence orbital relaxation that is natural to capture within a NOCI treatment, using cation orbitals, appropriate to core-ionizing each atom of the target type. For example, in butadiene, 4 different sets of cation orbitals (one for each C atom) are appropriate for the NEXAFS states associated with a C 1s hole. As the simplest systematic theory that builds on this idea, we are developing a non-orthogonal CIS (NOCIS) model for NEXAFS. This NOCIS model includes all particle states associated with each localized atomic hole, thus giving configurations that are non-orthogonal in any molecule with more than one atom of a given type. We believe that NOCIS model must dramatically improve the performance of standard CIS whose orthogonal orbitals cannot describe the valence relaxation effects associated with core holes (it is of course well-known that CIS core excitations are very strongly blue shifted with respect to experiment). If this can be established, the resulting theory will potentially be applicable to quite large molecules, and may also form a suitable starting point for further dynamic correlation corrections.

Peer-Reviewed Publications Resulting from this Program (2015–2017)

1. A. R. Beck, D. M. Neumark, and S. R. Leone, “Probing Ultrafast Dynamics with Attosecond Transient Absorption” *Chem. Phys. Lett.* **624**, 119 (2015).
2. X. Li, B. Bernhardt, A. R. Beck, E. Warrick, A. Pfeiffer, M. J. Bell, D. Haxton, C. McCurdy, D. M. Neumark, and S. R. Leone, “Investigation of Coupling Mechanisms in Attosecond Transient Absorption of Autoionizing States: Comparison of Theory and Experiment in Xenon” *J. Phys. B: At. Mol. Opt. Phys.* **48**, 125601 (2015).
3. Douguet, N., Slaughter, D. S., Adaniya, H., Belkacem, A., Orel, A. E., Rescigno, T. N., “Signatures of Bond Formation and Bond Scission Dynamics in Dissociative Electron Attachment to Methane” *Phys Chem Chem Phys* **17**, 25621 (2015).
4. Kosugi, S., Iizawa, M., Kawarai, Y., Kuriyama, Y., David Kilcoyne, A.L., Koike, F., Kuze, N., Slaughter, D. S., Azuma, Y., “PCI Effects and the Gradual Formation of Rydberg Series due to Photoelectron Recapture, in the Auger Satellite Lines upon Xe 4d⁻¹_{5/2} Photoionization” *J. Phys. B At. Mol. Opt. Phys.* **48**, 115003. (2015).
5. B. Gaire, I. Bocharova, F.P. Sturm, N. Gehrken, J. Rist, H. Sann, M. Kunitski, J. Williams, M.S. Schoeffler, T. Jahnke, B. Berry, M. Zohrabi, M. Keiling, A. Moradmand, A.L. Landers, A. Belkacem, I. Ben-Itzhak, R. Doerner, and Th. Weber, “Auger Decay and Subsequent Fragmentation Pathways of Ethylene Following K-Shell Ionization” *Phys. Rev. A* **92**, 013408 (2015).
6. C.E. Liekhus-Schmaltz, I. Tenney, T. Osipov, A. Sanchez-Gonzalez, N. Berrah, R. Boll, C. Bomme, C. Bostedt, J.D. Bozek, S. Carron, R. Coffee, J. Devin, B. Erk, K.R. Ferguson, R.W. Field, L. Foucar, L.J. Frasinski, J.M. Glowia, M. Guehr, A. Kamalov, J. Krzywinski, H. Li, J.P. Marangos, T.J. Martinez, B.K. McFarland, S. Miyabe, B. Murphy, A. Natan, D. Rolles, A. Rudenko, M. Siano, E.R. Simpson, L. Spector, M. Swiggers, D. Walke, S.

- Wang, Th. Weber, P.H. Bucksbaum, V. S. Petrovic, "Ultrafast Isomerization Initiated by X-Ray Core Ionization" *Nature Communications*, 6:8199, June 2015.
7. W. Cao, E. Warrick, D. M. Neumark, and S. R. Leone, "Attosecond Transient Absorption of Argon Atoms in the Vacuum Ultraviolet Region: Line Energy Shifts Versus Coherent Population Transfer" *New J. Phys.* **18**, 013041 (2016).
 8. K. Ramasesha, S. R. Leone, D. M. Neumark, "Real-Time Probing of Electron Dynamics Using Attosecond Time-Resolved Spectroscopy" *Annu. Rev. Phys. Chem.* **67**, 41-63 (2016).
 9. L. J. Borja, M. Zürich, C. D. Pemmaraju, M. Schultze, K. Ramasesha, A. Gandman, J. S. Prell, D. Prendergast, D. M. Neumark, and S. R. Leone, "Extreme Ultraviolet Transient Absorption of Solids from Femtosecond to Attosecond Timescales" *J. Opt. Soc. Am. B* **33**, 000C57 (2016).
 10. Z. Chang, P. B. Corkum, and S. R. Leone, "Attosecond Optics and Technology: Progress Today and Future Prospects" *J. Opt. Soc. Am. B*, **33**, 1081 (2016).
 11. M. Waitz, D. Aslituerk, N. Wechselberger, H.K. Gill, J. Rist, F. Wiegandt, C. Goihl, G. Kastirke, M. Weller, T. Bauer, D. Metz, F. P. Sturm, J. Voigtsberger, S. Zeller, F. Trinter, G. Schiwietz, T. Weber, J.B. Williams, M.S. Schoeffler, L. Ph. H. Schmidt, T. Jahnke, and R. Doerner, "Electron Localization in Dissociating H_2^+ by Retroaction of a Photoelectron onto its Source" *Phys. Rev. Lett.* **116**, 043001 (2016).
 12. A.J. Menssen, C. S. Trevisan, M.S. Schoeffler, A. Gatton, J. Sartor, M. Zohrabi, B. Berry, B. Gaire, F. Trinter, A. Belkacem, T. Jahnke, R. Doerner, A.L. Landers, C. W. McCurdy, T. N. Rescigno, Th. Weber, J. B. Williams, "Molecular Frame Photoelectron Angular Distributions for Core Ionization of Ethane, Carbon Tetrafluoride and 1,1-Difluoroethylene" *J. Phys. B: At. Mol. Opt. Phys.* **49**, 055203 (2016).
 13. F. P. Sturm, T.W. Wright, D. Ray, I. Zalyubovskaya, N. Shivaram, D. S. Slaughter, P. Ranitovic, A. Belkacem, and Th. Weber, "Time Resolved 3D Momentum Imaging of Ultrafast Dynamics by Coherent VUV-XUV Radiation" *Rev. Sci. Instrum.*, **87**, 063110 (2016)
 14. M. Waitz, D. Metz, J. Lower, C. Schober, M. Keiling, M. Pitzer, K. Mertens, M. Martins, J. Viefhaus, S. Klumpp, T. Weber, H. Schmidt-Böcking, L. Ph. H. Schmidt, F. Morales, S. Miyabe, T. N. Rescigno, C.W. McCurdy, F. Martín, J.B. Williams, M. S. Schöffler, T. Jahnke, and R. Dörner, "Two-Particle Interference of Electron Pairs on a Molecular Level" *Phys. Rev. Lett.* **117**, 083002 (2016).
 15. Wright, T.W., Champenois, E. G., Cryan, J.P., Shivaram, N., Yang, C-S., Belkacem, A., "Ultrafast Dynamics of the Lowest Lying Neutral States in Carbon Dioxide" *Phys. Rev. A* **95**, 023412 (2017).
 16. Champenois, E. G., Shivaram, N. H., Wright, T.W., Yang, C-S., Belkacem, A., Cryan, J. P., "Involvement of a Low-Lying Rydberg State in the Ultrafast Relaxation Dynamics of Ethylene" *J. Chem. Phys.* **144**, 014303 (2016).
 17. Shivaram, N., Champenois, E. G., Cryan, J. P., Wright, T. W., Wingard, T., Belkacem, A., "Focal Overlap Gating in Velocity Map Imaging to Achieve High Signal-to-Noise Ratio in Photo-Ion Pump-Probe Experiments" *App. Phys. Lett.* **109**, 25, 254101 (2016).
 18. Larsen, K. A., Cryan, J.P., Shivaram, N., Champenois, E. G., Wright, T. W., Ray, D., Kostko, O., Ahmed, M., Belkacem, A., Slaughter, D. S., "VUV and XUV Reflectance of Optically Coated Mirrors For Selection of High Harmonics" *Opt. Express* **24**, 18209. (2016).
 19. Rescigno, T. N., Trevisan, C. S., Orel, A. E., Slaughter, D. S., Adaniya, H., Belkacem, A., Weyland, M., Dorn, A., McCurdy, C. W., "Dynamics of Dissociative Electron Attachment to Ammonia" *Phys. Rev. A* **93**, 52704. (2016).
 20. B. Gaire, A. Gatton, F. Wiegandt, J. Neff, C. Janke, S. Zeller, D. Reedy, J. Rajput, I. Ben-Itzhak, A. L. Landers, A. Belkacem, and Th. Weber, "Bond-Rearrangement and Ionization Mechanisms in the Photo-Double-Ionization of Simple Hydrocarbons (C_2H_4 , C_2H_3F , and 1,1- $C_2H_2F_2$) Near and Above Threshold" *Phys. Rev. A* **94**, 033412 (2016).
 21. F.P. Sturm, X.M. Tong, A. Palacios, T.W. Wright, I. Zalyubovskaya, D. Ray, N. Shivaram, F. Martin, A. Belkacem, P. Ranitovic, and Th. Weber, "Mapping and Controlling Ultrafast Dynamics of Highly Excited H_2 Molecules by Attosecond VUV Radiation", *Phys. Rev. A* **95**, 012501 (2016).

22. J. Rist, T. Miteva, B. Gaire, H. Sann, F. Trinter, M. Keiling, N. Gehrken, A. Moradmand, B. Berry, M. Zohrabi, M. Kunitski, I. Ben-Itzhak, A. Belkacem, T. Weber, A. L. Landers, M. Schoeffler, J. B. Williams, P. Kolorenc, K. Gokhberg, T. Jahnke, and R. Doerner, "A Comprehensive Study of Interatomic Coulombic Decay in Argon Dimers: Extracting R-dependent Absolute Decay Rates from the Experiment" *Chem. Phys.* **482**, 185-191 (2016).
23. E. R. Warrick, W. Cao, D. M. Neumark, and S. R. Leone, "Probing the Dynamics of Rydberg and Valence States of Molecular Nitrogen with Attosecond Transient Absorption Spectroscopy" *J. Phys. Chem. A* **120**, 19 (2016).
24. W. Cao, E. R. Warrick, A. Fidler, S. R. Leone, and D. M. Neumark, "Near-resonant Four-Wave-Mixing of Attosecond Extreme Ultraviolet Pulses with Near-Infrared Pulses in Neon: Detection of Electronic Coherences" *Phys. Rev. A* **94**, 021802 (2016).
25. W. Cao, E. R. Warrick, A. Fidler, D. M. Neumark and S. R. Leone, "Noncollinear Wave Mixing of Attosecond XUV and Few-Cycle Optical Laser Pulses in Gas-Phase Atoms: Toward Multidimensional Spectroscopy Involving XUV Excitations" *Phys. Rev. A* **94**, 053846 (2016).
26. S.R. Leone, D.M. Neumark, "Attosecond Science in Atomic, Molecular, and Condensed Matter Physics" *Faraday Discuss.* **194**, 15-39 (2016).
27. D.S. Slaughter, A. Belkacem, C.W. McCurdy, T.N. Rescigno, D.J. Haxton, "Ion-Momentum Imaging of Dissociative Attachment of Electrons to Molecules" *J. Phys. B: Atomic, Molecular and Optical Physics* **49**, 222001 (2016).
28. C.W. McCurdy, T.N. Rescigno, C. Trevisan, R.R. Lucchese, B. Gaire, A. Menssen, M.S. Schoeffler, A. Gatton, J. Neff, P. Stammer, J. Rist, S. Eckart, B. Berry, T. Severt, J. Sartor, A. Moradmand, A. Landers, J. Williams, I. Ben-Itzhak, R. Doerner, A. Belkacem, and Th. Weber, "Unambiguous Observation of F Atom Core-Hole Localization in CF₄ Through Body-Frame Photoelectron Angular Distribution" *Phys. Rev. A* **95**, 011401(R) (2017).
29. E.R. Warrick, J.E. Bækhoj, W. Cao, A.P. Fidler, F. Jensen, L.B. Madsen, S.R. Leone, D.M. Neumark, "Attosecond Transient Absorption Spectroscopy of Molecular Nitrogen: Vibrational Coherences in the b' ¹Σ_u⁺ State" *Chem. Phys. Lett.* **683**, 408–415 (2017).
30. S.R. Leone et al., "Attosecond Science: from Transient Absorption to Multidimensional Spectroscopies" *J. Phys. B: Roadmap for Ultrafast X-ray Atomic and Molecular Physics* accepted for publication (2017).
31. K. Hong, H. Cho, R.W. Schoenlein, T.-K. Kim, and N. Huse, "Element-Specific Characterization of Transient Electronic Structure of Solvated Fe(II) Complexes with Time-Resolved Soft X-ray Absorption Spectroscopy" *Acc. Chem. Res.* **48**, 2957 (2015).
32. M. P. Ziemkiewicz, D. M. Neumark, and O. Gessner, "Ultrafast Electronic Dynamics in Helium Nanodroplets" *Int. Rev. Phys. Chem.* **34**, 239 (2015).
33. R. M. P. Tanyag, C. Bernardo, C. F. Jones, C. Bacellar, K. R. Ferguson, D. Anielski, R. Boll, S. Carron, J. P. Cryan, L. Englert, S. W. Epp, B. Erk, L. Foucar, L. F. Gomez, R. Hartmann, D. M. Neumark, D. Rolles, B. Rudek, A. Rudenko, K. R. Siefertmann, J. Ullrich, F. Weise, C. Bostedt, O. Gessner, and A. F. Vilesov, "Communication: X-ray Coherent Diffractive Imaging by Immersion in Nanodroplets" *Struct. Dyn.* **2**, 051102 (2015).
34. B.E. van Kuiken, H.Cho, K. Hong, M. Khalil, R.W. Schoenlein, T.K. Kim, and N. Huse, "Time-Resolved X-ray Spectroscopy in the Water Window: Elucidating Transient Valence Charge Distributions in Aqueous Fe(II) Complexes" *J. Phys. Chem. Lett.* **7**, 465 (2016).
35. C. F. Jones, C. Bernardo, R. M. P. Tanyag, C. Bacellar, K. R. Ferguson, L. F. Gomez, D. Anielski, A. Belkacem, R. Boll, J. Bozek, S. Carron, J. Cryan, L. Englert, S. W. Epp, B. Erk, L. Foucar, R. Hartmann, D. M. Neumark, D. Rolles, A. Rudenko, K. R. Siefertmann, F. Weise, B. Rudek, F. P. Sturm, J. Ullrich, C. Bostedt, O. Gessner, and A. F. Vilesov, "Coupled Motion of Xe Clusters and Quantum Vortices in He Nanodroplets" *Phys. Rev. B* **93**, 180510(R) (2016).
36. A. S. Chatterley, F. Lackner, D. M. Neumark, S. R. Leone, and O. Gessner, "Tracking Dissociation Dynamics of Strong-Field Ionized 1,2-dibromoethane with Femtosecond XUV Transient Absorption Spectroscopy" *Phys. Chem. Chem. Phys.* **18**, 14644 (2016).

37. S. Neppel, J. Mahl, A. S. Tremsin, B. Rude, R. Qiao, W. Yang, J. Guo, and O. Gessner, "Towards Efficient Time-Resolved X-Ray Absorption Studies of Electron Dynamics at Photocatalytic Interfaces" *Faraday Discuss.* **194**, 659 (2016).
38. A. S. Chatterley, F. Lackner, C. D. Pemmaraju, D. M. Neumark, S. R. Leone, and O. Gessner, "Dissociation Dynamics and Electronic Structures of Highly Excited Ferrocenium Ions Studied by Femtosecond XUV Absorption Spectroscopy" *J. Phys. Chem. A* **120**, 9509 (2016).
39. F. Lackner, A. S. Chatterley, C. D. Pemmaraju, K. D. Closser, D. Prendergast, D. M. Neumark, S. R. Leone, and O. Gessner, "Direct Observation of Ring-Opening Dynamics in Strong-Field Ionized Selenophene Using Femtosecond Inner-Shell Absorption Spectroscopy" *J. Chem. Phys.* **145**, 234313 (2016).
40. C. Bernardo, R. M. P. Tanyag, C. Jones, C. Bacellar, M. Bucher, K. R. Ferguson, D. Rupp, M. Ziemkiewicz, L. F. Gomez, A. S. Chatterley, T. Gorkhover, M. Mueller, J. Bozek, S. Carron, J. Kwok, S. L. Butler, T. Moeller, C. Bostedt, O. Gessner, and A. F. Vilesov, "Shapes of Rotating Superfluid Helium Nanodroplets" *Phys. Rev. B* **95**, 064510 (2017).
41. S. Fonseca dos Santos, N. Douguet, A. E. Orel and T. N. Rescigno, "Ligand Effects in Carbon K-Shell Photoionization of Small Linear Molecules" *Phys. Rev. A* **91**, 023408 (2015).
42. K. Varela, L. R. Hargreaves, K. Ralphs, M. A. Khakoo, C. Winstead, V. McKoy, T. N. Rescigno and A. E. Orel, "Excitation of the 4 Lowest Electronic Transitions in Methanol by Low-Energy Electrons" *J. Phys. B* **48**, 115208 (2015).
43. T. N. Rescigno, C. S. Trevisan and C. W. McCurdy, "Tracking Hole Localization in K-Shell and Core-Valence-Excited Acetylene Photoionization via Body-Frame Photoelectron Angular Distributions" *Phys. Rev. A* **91**, 023429 (2015).
44. F. L. Yip, A. Palacios, F. Martín, T. N. Rescigno and C. W. McCurdy, "Two-photon Double Ionization of Atomic Beryllium with Ultrashort Laser Pulses" *Phys. Rev. A* **92** 53404 (2015).
45. J. R. Jones, F.-H. Rouet, K. V. Lawler, E. Vecharynski, K. Z. Ibrahim, S. Williams, B. Abeln, C. Yang, W. McCurdy, D. J. Haxton, X. S. Li and T. N. Rescigno, "An Efficient Basis Set Representation for Calculating Electrons in Molecules" *Molecular Physics* **114** 2014 (2016).
46. D. J. Haxton, K. V. Lawler, and C. W. McCurdy, "Qualitative Failure of a Multiconfiguration Method in Prolate Spheroidal Coordinates in Calculating Dissociative Photoionization of H_2^+ " *Phys. Rev. A* **91**, 062502 (2015).
47. D. J. Haxton and C. W. McCurdy, "Two Methods for Restricted Configuration Spaces Within the Multiconfiguration Time-Dependent Hartree-Fock Method" *Phys. Rev. A* **91**, 012509 (2015).
48. X. Li, D. J. Haxton, M. Gaarde, K. J. Schafer, C. W. McCurdy, "Direct Extraction of Intense-Field Induced Polarization in the Continuum on the Attosecond Time Scale From Transient Absorption" *Phys. Rev. A* **93** 023401 (2016).
49. F. L. Yip, T. N. Rescigno and C. W. McCurdy, "Fully Differential Single-Photon Double Photoionization of Atomic Magnesium" *Phys. Rev. A* **94**, 063414 (2016).
50. L. Greenman, B. K. Whaley, D. J. Haxton and C. W. McCurdy, "Optimized Pulses for Raman Excitation Through the Continuum: Verification Using the Multiconfigurational Time-Dependent Hartree-Fock Method" *Phys. Rev. A* **96**, 013411 (2017).
51. L. Greenman, R. R. Lucchese and C. W. McCurdy, "Variational Treatment of Electron-Polyatomic Molecule Scattering Calculations Using Adaptive Overset Grids" *Phys. Rev.* accepted for publication (2017).
52. Y. Shao, Z. Gan, E. Epifanovsky, A.T.B. Gilbert, M. Wormit, J. Kussmann, A.W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey, P.R. Horn, L.D. Jacobson, I. Kaliman, R.Z. Khaliullin, T. Kus, A. Landau, J. Liu, E.I. Proynov, Y.M. Rhee, R.M. Richard, M.A. Rohrdanz, R.P. Steele, E.J. Sundstrom, H.L. Woodcock, P.M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G.J.O. Beran, Y.A. Bernard, E. Berquist, K. Brandhorst, K.B. Bravaya, S.T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S.H. Chien, K.D. Closser, D.L. Crittenden, M. Didenhofen, R.A. DiStasio Jr., H. Do, A.D. Dutoi, R.G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M.W.D. Hanson-Heine, P.H.P. Harbach, A.W. Hauser, E.G. Hohenstein, Z.C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyayev, J. Kim, J. Kim, R.A. King, P. Klunzinger, D. Kosenkov,

- T. Kowalczyk, C.M. Krauter, K.U. Lao, A. Laurent, K.V. Lawler, S.V. Levchenko, C.Y. Lin, F. Liu, E. Livshits, R.C. Lochan, A. Luenser, P. Manohar, S.F. Manzer, S.-P. Mao, N. Mardirossian, A.V. Marenich, S.A. Maurer, N.J. Mayhall, E. Neuscamman, C.M. Oana, R. Olivares-Amaya, D.P. O'Neill, J.A. Parkhill, T.M. Perrine, R. Peverati, A. Prociuk, D.R. Rehn, E. Rosta, N.J. Russ, S.M. Sharada, S. Sharma, D.W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A.J.W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M.A. Watson, J. Wenzel, A. White, C.F. Williams, J. Yang, S. Yeganeh, S.R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B.R. Brooks, G.K.L. Chan, D.M. Chipman, C.J. Cramer, W.A. Goddard III, M.S. Gordon, W.J. Hehre, A. Klamt, H.F. Schaefer III, M.W. Schmidt, C.D. Sherrill, D.G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A.T. Bell, N.A. Besley, J.-D. Chai, A. Dreuw, B.D. Dunietz, T.R. Furlani, S.R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D.S. Lambrecht, W.-Z. Liang, C. Ochsenfeld, V.A. Rassolov, L.V. Slipchenko, J.E. Subotnik, T. Van Voorhis, J.M. Herbert, A.I. Krylov, P.M.W. Gill and M. Head-Gordon, "Advances in Molecular Quantum Chemistry Contained in the Q-Chem 4 Program Package" *Mol. Phys.* **113**, 184–215 (2015).
53. D.W. Small, E.J. Sundstrom, and M. Head-Gordon, "A Simple Way to Test for Collinearity in Spin Symmetry Broken Wave Functions: Theory and Application to Generalized Hartree-Fock" *J. Chem. Phys.* **142**, 094112 (2015).
54. K.D. Closser, Q. Ge, Y. Mao, Y. Shao, and M. Head-Gordon, "A Local Excited State Method using Single Substitutions in the Absolutely Localized Molecular Orbital Basis with Application to Spectra of Large Helium Clusters" *J. Chem. Theory Comput.* **11**, 5791–5803 (2015).
55. D.W. Small, E.J. Sundstrom, and M. Head-Gordon, "Restricted Hartree Fock using Complex-Valued Orbitals: A Long-Known but Neglected Tool in Electronic Structure Theory" *J. Chem. Phys.* **142**, 024104 (18 pages) (2015).
56. A.F. White, C.J. Heide, P. Saalfrank, M. Head-Gordon, and E. Luppi, "Computation of High-Harmonic Generation Spectra of the Hydrogen Molecule Using Time-Dependent Configuration-Interaction" *Mol. Phys.* **114**, 947-956 (2016).
57. S. Lehtola, M. Head-Gordon, and H. Jónsson, "Complex Orbitals, Multiple Local Minima and Symmetry Breaking in Perdew-Zunger Self-Interaction Corrected Density-Functional Theory Calculations" *J. Chem. Theory Comput.* **12**, 3195-3207 (2016).
58. A.F. White, M. Head-Gordon, and C.W. McCurdy, "Stabilizing Potentials in Bound State Analytic Continuation Methods for Electronic Resonances in Polyatomic Molecules" *J. Chem. Phys.* **146**, 044112; (2017).
59. Q. Ge, Y. Mao, A.F. White, E. Epifanovsky, and M. Head-Gordon, "Simulating the Absorption Spectra of Helium Clusters (n=70, 150, 231, 300) using a Charge-Transfer Correction to Superposition of Fragment Single Excitations" *J. Chem. Phys.* **146**, 044111; (2017).
60. A.F. White, E. Epifanovsky, C.W. McCurdy, and M. Head-Gordon, "Second Order Moller-Plesset and Coupled Cluster Singles and Doubles Methods with Complex Basis Functions for Resonances in Electron-Molecule Scattering" *J. Chem. Phys.* **146**, 234107; (2017).

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Early Career: Ultrafast X-ray Studies of Intramolecular and Interfacial Charge Migration

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Project Scope: At the heart of many emerging sunlight-to-fuel and molecular photovoltaic concepts are interfacial processes that require an optimized, concerted flow of charge and energy on a molecular level. This program is focused at developing and applying time-domain X-ray spectroscopy techniques that enable an atomic-scale understanding of the fundamental mechanisms underlying interfacial electronic and chemical dynamics. In particular, ultrafast dynamics at interfaces between molecules, molecular domains, and semiconductors are studied by time-resolved X-ray photoelectron spectroscopy (TRXPS) and time-resolved X-ray absorption spectroscopy (TRXAS) techniques, which are deployed at the Linac Coherent Light Source (LCLS) and the Advanced Light Source (ALS).

Recent Progress: A major achievement of the past cycle has been the successful implementation of a technique to probe the coupling between interfacial electron dynamics and interfacial potential energies with picosecond temporal resolution and molecular-scale sensitivity (Fig. 1). Picosecond TRXPS experiments on films of N3 dye-sensitized ZnO nanocrystals were performed at the ALS using a 532 nm laser pump pulse to excite the dye molecules and multiple X-ray probe pulses to monitor the induced dynamics. Experiments

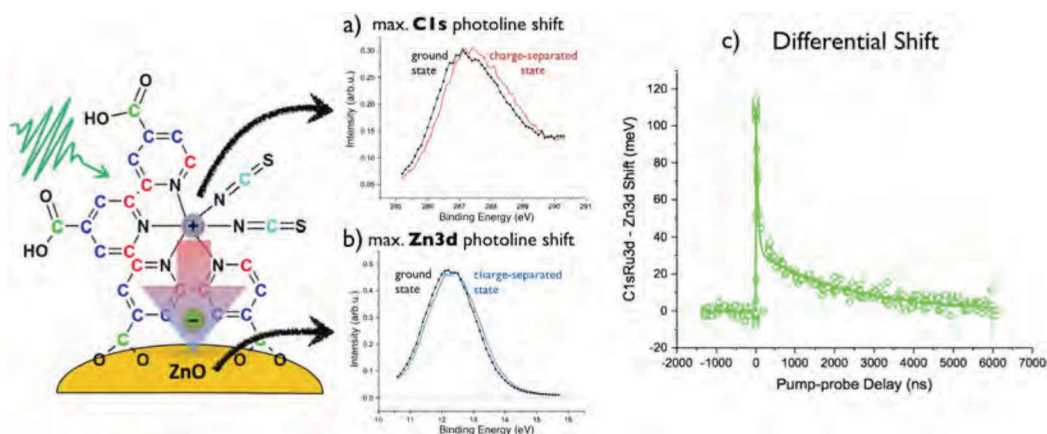


Fig. 1: Photoinduced electronic dynamics at a molecule-semiconductor interface monitored by time-resolved XPS. Charge injection from an N3 molecular chromophore into a ZnO semiconductor substrate is initiated with a visible pump pulse. Significant differences are observed in the dynamic response of the C1s photoline associated with the pyridine groups of the adsorbate (a) and the Zn3d line of the substrate (b). The difference between the photoline shifts as a function of the visible pump – X-ray probe time delay provides a real-time probe of transient interfacial potentials with atomic-scale sensitivity (c).

probing both the C1s photoline associated with the pyridine groups of the dye and the Zn3d photoline associated with the substrate were performed quasi-simultaneously and for the same sample.

Both photolines exhibit a shift to higher binding energies as a result of photoinduced charge transfer between the molecule and the substrate (Fig. 1a,b). The magnitudes of the shifts, however, differ notably. By analyzing the difference as a function of laser pump – X-ray probe delay, a time-dependent, molecular-scale view of the local potential energy difference across the molecule-semiconductor interface emerges (Fig. 1c). The technique provides a new tool to study the mutual dependence of charge dynamics and potential energy landscapes during interfacial photoelectric and photochemical processes. Note that the time-stamping TRXPS technique developed in this program provides simultaneous access to dynamics proceeding on picosecond to microsecond timescales (Fig. 1c), connecting fast charge injection dynamics with much slower relaxation and recombination dynamics. The analysis of the data is ongoing.

A second series of TRXPS experiments focuses on photoinduced charge carrier dynamics in bi-layer systems of Copper-Phthalocyanine (CuPc) and C₆₀ molecules, which have emerged as important model systems for the study of photodynamics in organic electronics. In previous work, we demonstrated that TRXPS of the C1s photolines associated with either CuPc or C₆₀ provides molecule-specific information on transient charge carrier densities.¹ Employing this sensitivity, comparative measurements have been performed for two different sample configurations with alternating layer orderings and layer thicknesses. The TRXPS spectra of the two configurations exhibit both clear similarities as well as distinct differences. Efforts are currently underway to derive a consistent description of the underlying charge dynamics across several time- and length-scales.

The TRXAS activities that enabled the study of photoinduced dynamics in Cu₂O during the previous cycle⁴ have been extended to other transition metal semiconductors such as TiO₂, ZnO, CuO, Fe₂O₃, and Co₃O₄ as well as preliminary tests with N3 dye-sensitized TiO₂ and ZnO. Photoinduced effects are clearly visible for several of these systems and we are currently preparing comparative temperature-dependent static measurements in order to distinguish between electronic and lattice dynamics.

Future Plans: The Early Career Research Program Award period for this program ended in July 2017. We have proposed to include future activities emerging from this work in the AMOS program at LBNL. Future plans are, therefore, presented in the abstract of the AMOS program.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. T. Arion, S. Neopl, F. Roth, A. Shavorskiy, H. Bluhm, Z. Hussain, O. Gessner, and W. Eberhardt, "Site-specific probing of charge transfer dynamics in organic photovoltaics," *Appl. Phys. Lett.* **106**, 121602 (2015).
2. S. Neopl, and O. Gessner, "Time-resolved X-ray Photoelectron Spectroscopy Techniques for the Study of Interfacial Charge Dynamics," *J. Electron. Spectrosc. Relat. Phenom.* **200**, 64 (2015).
3. O. Gessner, and M. Gühr, "Monitoring Ultrafast Chemical Dynamics by Time-Domain X-ray Photo- and Auger-Electron Spectroscopy," *Acc. Chem. Res.* **49**, 138 (2016).

4. S. Neopl, J. Mahl, A. S. Tremsin, B. Rude, R. Qiao, W. Yang, J. Guo, and O. Gessner, "Towards efficient time-resolved X-ray absorption studies of electron dynamics at photocatalytic interfaces," *Faraday Discuss.* **194**, 659 (2016).

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PULSE Ultrafast Chemical Science

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Mission: The PULSE Ultrafast Chemical Science program focuses on ultrafast chemical physics research at SLAC that is enabled by SLAC's x-ray and relativistic electron facilities, including LCLS, SSRL, Ultrafast Electron Diffraction (UED) and in the future, LCLS-II. Our research at SLAC makes optimal use of these unique tools for fundamental discoveries and new insights in ultrafast science. The two distinguishing advantages of this program are the on-site presence of the LCLS; and our connection to Stanford University. These help to keep us competitive on an international level.

Major Themes: The Ultrafast Chemical Science program has connections to many of the themes in the current BESAC Transformation Opportunities. We have particular emphasis on the transformation opportunities of "Imaging Matter across Scales", "Harnessing Coherence in Light and Matter". We also have high relevance to the Grand Challenges in the areas of "Energy and Information on the Nanoscale" and "Control at the Level of Electrons."

Imaging matter across scales: The nanoscale in space and the femtoscale in time. Microscopy at its most essential level in both space and time is paramount to the BES mission to control matter. Non-periodic nano-structures and ultrafast timescales dominate the workings of biology and chemistry. To understand and control function we therefore must first observe structure and motion on these scales.

X-ray lasers are revolutionary sources of short wavelength coherent radiation for investigations on the nanoscale, and ultrafast electrons or High Harmonics complement this new capability. PULSE subtasks are devoted to developing science using time-resolved imaging techniques at x-ray free electron lasers, (NPI and SPC subtask) ultrafast electron diffraction facilities (EIM subtask) and with laboratory sources (ATO and SFA subtasks).

Much of chemistry happens at the femtosecond scale, and it is necessary to develop new methods to simultaneously achieve this level of temporal resolution with simultaneous chemical and structural sensitivity. FEL and laser-based sources of x-ray and extreme ultraviolet radiation afford the opportunity for atomic specificity combined with femtosecond resolution. To realize this opportunity, pump-probe spectroscopy at visible and infrared wavelengths must be extended to the soft and hard x-ray range, and to new sources such as FELs. Much of our efforts are devoted to developing new methods and advancing ultrafast science in this area, including impulsive stimulated Raman and other nonlinear x-ray scattering methods.

Energy and Information: The architecture of light conversion chemistry. Light from the sun is the primary source of energy on earth, and so we are exploring light conversion to electron motion and then to chemical bonds. Some molecules are particularly adept at this conversion and we would like to understand how they work. For example, how does non-adiabatic dynamics affect the process of photocatalysis within coordination complexes and similar materials.

Energy conversion is initiated by charge separation, and we know that the charge distribution of the electron and hole, as well as the presence of low-energy ligand field excited states greatly influence the lifetime of optically generated charge transfer excited states. The detailed mechanism for the excited state quenching remains unclear. New methods of linear and nonlinear spectroscopy, and especially x-ray spectroscopy involving short-pulse FELs, can help provide the answer.

An equally important problem is the protection of some chemical bonds, particularly in biology, from destruction in the presence of ultraviolet sunlight. Photoprotection is also an ultrafast process involving charge transfer, and so these new techniques such as ultrafast x-ray absorption and Auger emission can show how critical bonds are protected.

The incorporation of theory within this FWP is critical for rapid progress in light conversion chemistry, and helps us to focus our efforts in areas of greatest impact.

Harnessing coherence on the eV scale in time, space, and field strength. This is the fundamental scale that determines structure and dynamics of electrons in molecules, and motivates advances in sub-femtosecond time-resolution and Angstrom spatial resolution in theory and experiments. To achieve an adequate view of the molecular realm at this level, we must interrogate atoms with fields comparable to Coulomb binding fields and even beyond this, and on time scales set by the fundamental energy splittings in atoms.

One method to reach this scale is through nonlinear frequency conversion, known as high harmonic generation (HHG). We now have sources of attosecond pulsed vacuum ultraviolet radiation based on HHG, and are beginning to use them to develop new spectroscopies that can detect the motion of electrons within molecules.

We are particularly interested in the response of atoms to ultrastrong fields, from infrared to x-rays. Issues here range from mechanisms for enhanced ionization of infrared light, to new discoveries in nonlinear x-ray Compton scattering, to our most recent first test of nonlinear nuclear photoabsorption using the strongest available focused x-ray fields. New theoretical approaches are also required for this, and we are tackling these as well.

LCLS is also capable of sub-femtosecond or few femtosecond pulses, and these have the unique property of wavelengths short enough to reach the most deeply bound electrons in first through third row atoms. We can use LCLS to image the strong-field electronic response during HHG in solids at the atomic-scale in length and time, and to explore nonlinear x-ray Compton scattering and other coherent multi-x-ray processes as a means to achieve simultaneous chemical and structural sensitivity. Through the use of novel methods such as low bunch charge, double-slotted spoilers, enhanced SASE, strong laser fields, and novel data sorting methods, as well as future methods such as self-seeding, we will incorporate LCLS fully as a tool for sub-femtosecond spectroscopy.

Management Structure: This Ultrafast Chemical Science research program resides within the Chemical Science Division within the SLAC Science Directorate. The current CS Director is Tony Heinz. JoAnne Hewett is the Acting Associate Laboratory Director for the Science Directorate.

Space allocations: Most of our research activities take place in laboratories in SLAC Building 40a. SLAC currently provides office space for our research groups, and also allocates approximately 8000 square feet to research laboratories and a computer room for this FWP. The co-location of most of our program within Building 40 and 40a is a distinct advantage, but is not entirely sufficient for the space requirements of this program, and so we also perform some of this research in PULSE Institute space within the Varian Physics Lab and the Mudd Chemistry Lab on the Stanford campus (approximately 1000 square feet, including offices and labs, in each building). Further details are in the Facilities and Resources Section 11 of this document.

We are currently working with SLAC to plan utilization of a new laboratory building, the Arillaga Science Center, which is nearing completion adjacent to the PULSE laboratories. We would especially like to use this new space to create space for joint activities with scientists at LCLS and LCLS-II.

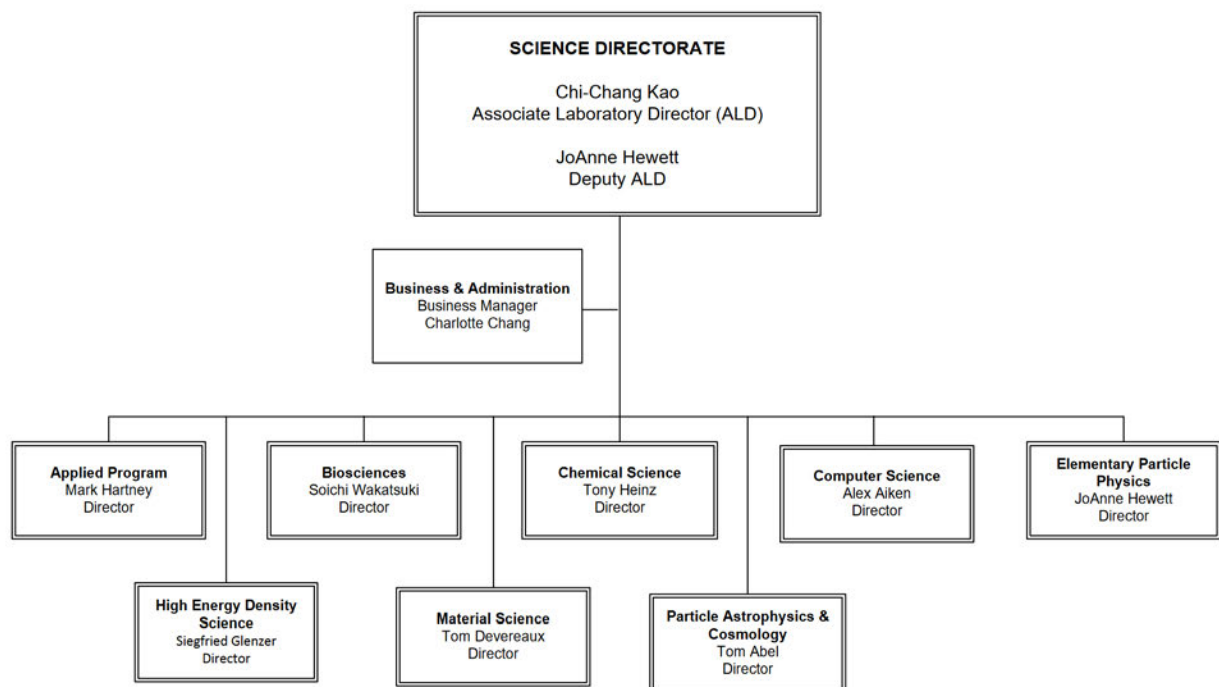


Figure 1. Partial organization chart for SLAC, showing the relation of the Ultrafast Chemical Science FWP to other units with close research ties.

Subtasks and allocations: Seven key personnel are responsible for six subtasks, which represent six different areas of expertise:

1. UTS: Ultrafast Theory and Simulation (Martinez)
2. ATO: Attoscience (Cryan, Bucksbaum)
3. SPC: Solution Phase Chemistry (Cordones-Hahn, Gaffney)
4. NPI: Non-periodic X-ray Imaging (Natan)
5. SFA: Strong Field AMO Physics (Bucksbaum, Natan)
6. NLX: Nonlinear X-ray Science (Reis, Ghimire)
7. EDN: Electron Dynamics on the Nanoscale (Heinz)
8. EIM: Excitations in Molecules (Wolf)

A key change in the past twelve month was the successful search for a new leader of the NPI (x-ray imaging) task. Dr. Adi Natan has accepted this position at the level of Associate Staff Scientist. His task now emphasizes ultrafast hard x-ray diffraction from transiently excited molecular ensembles in the gas or liquid phase, and they are off to a great start with several runs completed or planned at LCLS and SACLA. In addition, Dr. Amy Cordones-Hahn has assumed the role of co-PI with Prof. Kelly Gaffney of the SPC (ultrafast chemistry) task. Our Ultrafast Chemical Science programs are described more fully in the abstracts for those subtasks.

Support operations (finance, HR, safety, purchasing, travel) are directed by the Associate Laboratory Director for Science and the Chemical Sciences Director and their staff. They provide oversight and delegate the work to appropriate offices in the SLAC Operations Directorate or to the staff of the Stanford PULSE Institute.

Connections to other units within the SLAC organizational structure: Close collaborations are maintained with the Science R&D Division within the LCLS Directorate; the Materials Science Division

(SIMES) within the Science Directorate; SSRL; and the SUNCAT Center within our own Chemical Sciences Division, as shown in figure 4.1. Our location near these facilities and research organizations at SLAC greatly aids collaboration.

Other important connections: The PIs have affiliations with other Stanford University research and academic units: All members of this FWP are members of the Stanford PULSE Institute, and several are affiliated with the SIMES Institute, Bio-X, the Ginzton Laboratory, and the Departments of Chemistry, Physics, and Applied Physics.

We also have collaborative connections to other outside research labs, including DESY, the Lawrence Berkeley Laboratory, the Center for Free Electron Lasers (CFEL) in Hamburg, and BES funded groups at the University of Michigan, the Ohio State University, the University of Connecticut, Louisiana State University, Weizmann Institute, and Northwestern University.

Knowledge transfer to LCLS and LCLS-II: Transfer of knowledge to and from LCLS and LCLS-II is extremely fluid and critical to our success. Much of our research creates benefits for the x-ray laser facilities by providing new research methods and research results, and in addition there are several more direct transfers of our research product to help LCLS:

- We continue to help to commission several LCLS-II instruments and setup space. Particularly noteworthy are:
 - We are helping to design, build, and commission attosecond streak capabilities for the XLEAP attosecond pulse initiative, which is scheduled for its first trial this fall.
 - We have secured LDRD funding to build and commission experimental instruments that can use the LCLS-II prototype 100 kHz OPCPA for attosecond x-ray transient absorption.
- Some of our graduate students provide user support through to LCLS users, particularly in cooperation with CXI, AMO, and the Laser Division, and they receive salary supplements for this work. This activity has been endorsed by review panels and is supported by the Associate Laboratory Directors and the SLAC Director.
- Several of our postdocs and students have transferred to permanent staff positions at LCLS.
- Several LCLS Scientists and Staff have become members of the PULSE Institute, and this provides a connection to the larger research community of Stanford.
- Some LCLS Instrument Scientists have a direct connection to the research activities of this FWP. In the previous year this included collaborations with XPP, AMO, and CXI scientists.
- PULSE has helped LCLS to institute a Graduate Fellowship program, and PULSE manages several LCLS graduate student campus appointments.
- PULSE conducts an annual Ultrafast X-ray Summer School to train students and postdocs about LCLS science opportunities.

Advisory committee. The SLAC Science Policy Committee advises SLAC and the Stanford Provost on all science activities at the laboratory. Neither the SLAC Chemical Sciences Division nor the SLAC Science Directorate has their own standing science advisory committee at present. The PULSE External Advisory Board advises us on our DOE activities. This board meets annually and reports to the PULSE Director and to the Stanford Dean of Research. The reports are also forwarded to the SLAC Director, the ALD for Science, and to the SLAC Science Policy Committee.

Educational programs and outreach activities. We have an active outreach and visitors program supported by Stanford through the PULSE Institute. In this past year we have hosted Stefan Pabst from ITAMP at Harvard, and Joe Subotnik from the University of Pennsylvania.

PULSE continues to serve the larger ultrafast community with our annual Ultrafast X-ray Summer School. This school, which was founded by the PIs of this FWP in 2007, continues to be a main mechanism for expanding the research community interested in using x-ray free electron lasers for their research. The twelfth annual UXSS will be at SLAC in Summer, 2018.

Ultrafast Theory and Simulation, Todd J. Martínez PI

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Project Scope: This program is focused on developing and applying new methods for describing molecular dynamics on electronically excited states, as well as the interaction of molecules with radiation fields. We continue to develop and apply the *ab initio* multiple spawning (AIMS) method that solves the electronic and nuclear Schrodinger equations simultaneously from first principles, including the treatment of cases where the Born-Oppenheimer approximation breaks down (e.g. around conical intersections where two or more electronic states are exactly degenerate). We are working to extend this methodology to incorporate the effects of novel pump and probe pulses using high energy photons, including those obtained from modern x-ray sources such as LCLS. We also focus on understanding the behavior of molecular excited states in paradigmatic phenomena such as light-induced isomerization, excited state proton transfer, and excitation energy transfer.

Recent Progress and Future Plans

Extending Ab Initio Multiple Spawning to Attosecond and Strong Field Laser Pulses: Building on our previous method to account for *both* light field and nonadiabatic coupling-induced breakdown of the Born-Oppenheimer approximation (Kim, Tao, Martinez and Bucksbaum 2015), we developed the eXternal Field Ab Initio Multiple Spawning (XFAIMS) method (Mignolet, Curchod and Martinez 2016) which is applicable to arbitrary excitation laser pulses including strong field and attosecond pulses. The new XFAIMS method prescribes spawning of new basis functions during the interaction with the laser pulse. A schematic is shown in Figure 1 for a single cycle attosecond pulse. The new method was shown to be quantitatively accurate for a number of model problems and also directly applicable to large molecules and compatible with “on the fly” calculation of the electronic structure. We are exploring the use of this new method for modeling molecular dynamics in the presence of strong field and attosecond excitation pulses.

GPU-Based Electronic Structure For Nonadiabatic Dynamics: We used our newly developed GPU-based time-dependent density functional theory (TDDFT) method to study excited state dynamics of DMABN, a prototypical twisted intramolecular charge transfer (TICT) system. (Curchod, Sisto and Martinez 2017) Interestingly, we find that the molecule decays from S_2 to S_1 without significant twisting, as shown in Figure 2. This is in contrast to textbook knowledge about TICT molecules and suggests that there may be reason to revisit the excited state dynamics in order to determine the detailed mechanism. Because such studies would require modeling of the nonadiabatic transition to the ground electronic state, they are not possible with TDDFT. However, we plan to use our GPU-accelerated CASSCF nonadiabatic dynamics code (Snyder, Curchod and Martinez 2016) to explore a series of TICT molecules including DMABN. We continue to

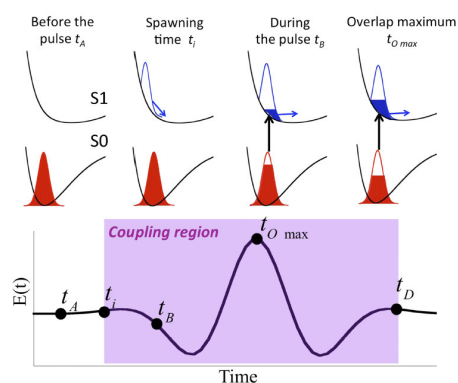


Figure 1. Schematic representation of spawning in XFAIMS.

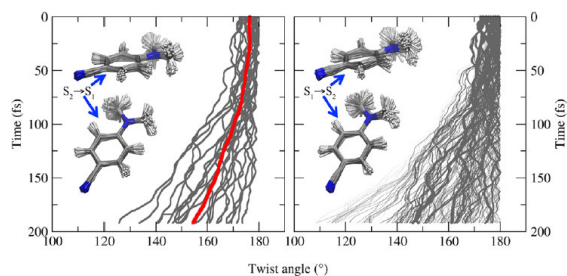


Figure 2. Twist angle of the DMA group during AIMS dynamics of DMABN after photoexcitation to S_2 . Left panel shows twist angle for basis functions on S_2 , demonstrating that twist is unimportant to the S_2/S_1 nonadiabatic transition (which occurs in less than 100fs). Right panel shows the twist angle for basis functions on either S_2 or S_1 , showing that the molecule does eventually twist on S_1 .

explore (Filatov, Liu, Kim and Martinez 2016, Filatov, Martinez and Kim 2016, Filatov, Liu and Martinez 2017) new methods that can incorporate dynamic electron correlation in CASSCF by using DFT-like corrections and the ensemble DFT formalism.

Ab Initio Exciton Models: We applied our ab initio exciton model to the LH2 protein and carried out some preliminary nonadiabatic dynamics (Sisto, Stross, van der Kamp, O'Connor, McIntosh-Smith, Johnson, Hohenstein, Manby, Glowacki and Martinez 2017). This is the first such calculation, with nonadiabatic transitions in a molecule containing more than 3000 atoms. We have extended (Li, Parrish, Liu, Kokkila Schumacher and Martinez 2017) the ab initio exciton model to include excited states that exhibit charge transfer between the chromophores. We are working to incorporate the full ab initio exciton model into our AIMS method for nonadiabatic dynamics.

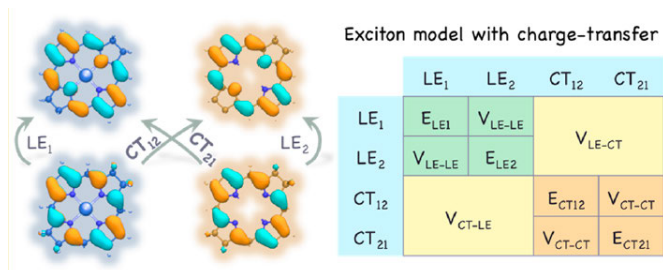


Figure 3. Schematic of the ab initio exciton model for two chromophores showing the form of the Hamiltonian matrix and the types of excitations that are included – local single excitations on each chromophore and single electron charge transfer between chromophores.

Future Plans: We are implementing AIMS dynamics within the context of the ab initio exciton model to describe nonadiabatic effects and explore the role of electronic coherence in photosynthetic systems like LH2 as well as singlet fission in pentacene and related materials. We will explore the possibility of using ab initio exciton ideas for metal-ligand complexes – essentially an ab initio ligand field theory. We are also planning to devote effort to the modeling of excited state dynamics in coordination complexes containing transition metals. This is now feasible with the GPU-accelerated methods, the effective core potentials we have implemented on GPUs, and the GAIMS method for modeling both internal conversion and intersystem crossing. It remains to implement a Breit-Pauli Hamiltonian (and the required integrals) to compute spin-orbit couplings within our GPU-accelerated framework. This will allow us to investigate excited state dynamics of paradigmatic inorganic photochemical systems such as Fe(CO)₅, as well as energy-relevant complexes like Ru(bpy)₃ and Fe-containing analogs.

Publications Supported by the AMOS Program

- Kim, J., H. Tao, T. J. Martinez and P. Bucksbaum (2015). "Ab initio Multiple Spawning on Laser-Dressed States: A Study of 1,3-Cyclohexadiene Photoisomerization via Light-Induced Conical Intersections." *J. Phys. B* **48**: 164003.
- Liekhus-Schmaltz, C. E., I. Yenny, T. Osipov, A. Sanchez-Gonzalez, N. Berrah, R. Boll, C. Bomme, C. Bostedt, J. D. Bozek, S. Carron, R. Coffee, J. Devin, B. Erk, K. R. Ferguson, R. W. Field, L. Foucar, L. J. Frasinski, J. M. Glowacki, M. Guehr, A. Kamalov, J. Krzywinski, H. Li, J. P. Marangoni, T. J. Martinez, B. K. McFarland, S. Miyabe, B. Murphy, A. Natan, D. Rolles, A. Rudenko, M. Siano, E. R. Simpson, L. S. Spector, M. Swiggers, D. Walke, S. Wang, T. Weber, P. H. Bucksbaum and V. S. Petrovic (2015). "Ultrafast Isomerization Initiated by X-ray Core Ionization." *Nature Comm.* **6**: 8199.
- Song, C., L.-P. Wang, T. Sachse, J. Preiss, M. Presselt and T. J. Martinez (2015). "Efficient implementation of effective core potential integrals and gradients on graphical processing units." *J. Chem. Phys.* **143**: 014114.
- Curchod, B. F. E., C. Rauer, P. Marquetand, L. Gonzalez and T. J. Martinez (2016). "Communication: GAIMS-Generalized Ab Initio Multiple Spawning for Both Internal Conversion and Intersystem Crossing Processes." *J. Chem. Phys.* **144**: 101102.
- Filatov, M., F. Liu, K. S. Kim and T. J. Martinez (2016). "Self-consistent implementation of ensemble density functional theory method for multiple strongly correlated electron pairs." *J. Chem. Phys.* **145**: 244104.

- Filatov, M., T. J. Martinez and K. S. Kim (2016). "Using the GVB Ansatz to Develop Ensemble DFT Method for Describing Multiple Strongly Correlated Electron Pairs." *Phys. Chem. Chem. Phys.* **18**: 21040.
- Liu, L., J. Liu and T. Martinez (2016). "Dynamical Correlation Effects on Photoisomerization: Ab Initio Multiple Spawning Dynamics with MS-CASPT2 for a Model trans-Protonated Schiff Base." *J. Phys. Chem. B* **120**: 1940-1949.
- Mignolet, B., B. F. E. Curchod and T. J. Martinez (2016). "Rich Athermal Ground-State Chemistry Triggered by Dynamics through a Conical Intersection." *Ang. Chem.* **55**: 14993-14996.
- Mignolet, B., B. F. E. Curchod and T. J. Martinez (2016). "Communication: XFAIMS - eXternal Field Ab Initio Multiple Spawning for electron-nuclear dynamics triggered by short laser pulses." *J. Chem. Phys.* **145**: 191104.
- Snyder, J. W., B. F. E. Curchod and T. Martinez (2016). "GPU-Accelerated State-Averaged Complete Active Space Self-Consistent Field Interfaced with Ab Initio Multiple Spawning Unravels the Photodynamics of Provitamin D3." *J. Phys. Chem. Lett.* **7**: 2444-2449.
- Curchod, B. F. E., A. Sisto and T. J. Martinez (2017). "Ab Initio Multiple Spawning Photochemical Dynamics of DMABN Using GPUs." *J. Phys. Chem. A* **121**: 265-276.
- Filatov, M., F. Liu and T. J. Martinez (2017). "Analytical derivatives of the individual state energies in ensemble density functional theory method. I. General formalism." *J. Chem. Phys.* **147**: 034113.
- Lefrancois, D., D. Tuna, T. J. Martinez and A. Dreuw (2017). "The Spin-Flip Variant of the Algebraic-Diagrammatic Construction Yields the Correct Topology of S0/S1 Conical Intersections." *J. Chem. Theo. Comp.* **13**: 4436-4441.
- Li, X., R. M. Parrish, F. Liu, S. I. L. Kokkila Schumacher and T. J. Martinez (2017). "An Ab Initio Exciton Model Including Charge-Transfer Excited States." *J. Chem. Theo. Comp.* **13**: 3493-3504.
- Li, Z., L. Inhester, C. E. Liekhus-Schmaltz, B. F. E. Curchod, J. W. Snyder, N. Medvedev, J. Cryan, T. Osipov, S. Pabst, O. Vendrell, P. Bucksbaum and T. J. Martinez (2017). "Ultrafast isomerization in acetylene dication after carbon K-shell ionization." *Nature Comm.* **8**: 453.
- Martinez, T. J. (2017). "Ab Initio Reactive Computer Aided Molecular Design." *Acc. Chem. Res.* **50**: 652-656.
- Sisto, A., C. Stross, M. W. van der Kamp, M. O'Connor, S. Mcintosh-Smith, G. T. Johnson, E. G. Hohenstein, F. R. Manby, D. R. Glowacki and T. J. Martinez (2017). "Atomistic non-adiabatic dynamics of the LH2 complex with a GPU-accelerated ab initio exciton model." *Phys. Chem. Chem. Phys.* **19**: 14924-14936.
- Wolf, T. J. A., R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch and M. Guehr (2017). "Probing ultrafast pi-pi*/n-pi* internal conversion in organic chromophores via K-edge resonant absorption." *Nature Comm.* **8**: 29.

ATO: Attosecond Science

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Project Scope: All photochemical transformations are initially driven by electron motion. Thus in order to more fully understand photon driven chemistry, we would like to track the evolution of electrons on their intrinsic timescale. For isolated molecules in the gas phase, this natural timescale is in the attosecond domain.

Extreme ultraviolet, and x-ray laser pulses with more than a few electron volts of bandwidth can excite superpositions of valence-excited electronic states in isolated molecular systems. These excitations can then be probed by subsequent interactions with either short laser pulses or phase-lock infrared pulses. The ATO task is focused on understanding how coherent superpositions of electronic states evolve in time, and how these superpositions couple to other degrees of freedom in the molecular system. Moreover, the ability to measure real-time information of electron dynamics on attosecond timescales leads to a number of open-ended questions. For example,

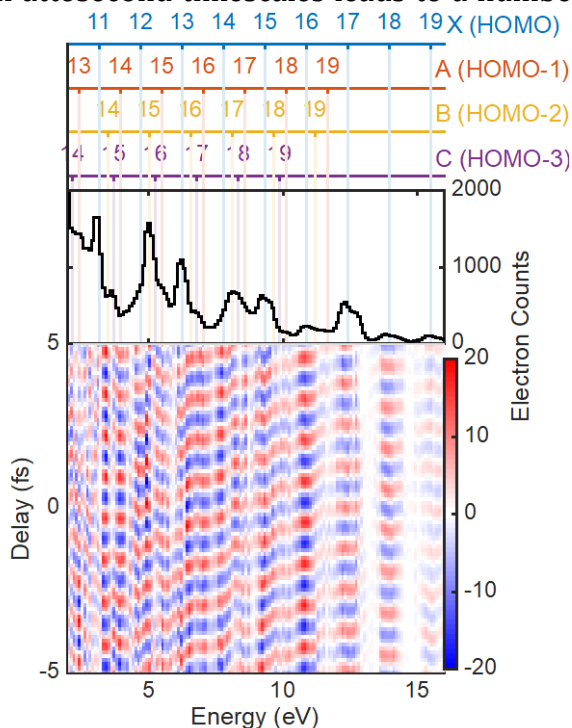


Figure 1 – Measured photoelectron kinetic energy spectrum from CO₂ exposed to an attosecond pulse train (top). The colored axes show the expected energetic position of electrons for the different cationic states of CO₂. The lower panel shows the yield of photoelectrons as the delay between the IR and XUV pulses is changed. The time-averaged spectrum has been subtracted to increase the contrast.

the nature of the information that is encoded in attosecond measurements, and how this information can be retrieved from the measurement, is still an active field of study.

Recent Progress: One of the current research focuses of the ATO task is to understand the effect of the molecular potential on the dynamics of photoionization. To this end, we employ the well-known RABITT technique to measure so-called photoionization delay associated with molecular photoionization [1]. The RABITT technique has been used to resolve ionization dynamics in a number of different atomic systems. However, to date, very little has been done in molecular systems. We have collected RABITT traces for a number of molecular systems (CO, CO₂, SF₆, and H₂). So far our analysis has focused on the CO₂ data, which is shown in Fig.1. This data clearly shows the characteristic 2ω oscillation

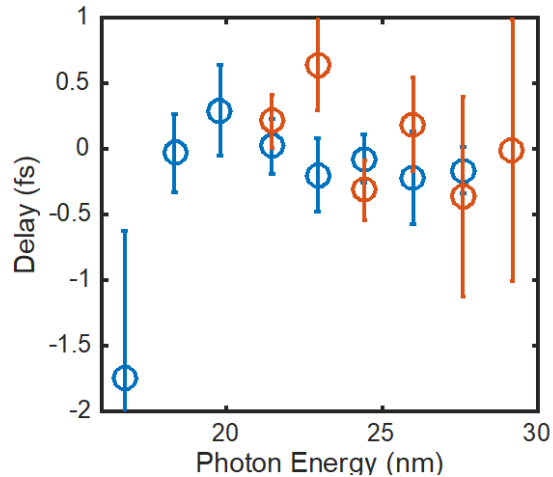


Figure 2 – Differential delay of photoelectrons for different cationic states of CO₂ {X-state (blue) and B-state (red)} and the Ar reference as a function of photon energy. Negative numbers represent an advance of the overall electron phase relative to Ar.

differential phase shift between a specific cationic state of CO₂ and the Argon reference. Figure 2 shows this differential phase shift.

The other focal point of the ATO task is to develop high pulse energy isolated attosecond pulses. We have been pursuing this goal both in the laboratory and at the free electron laser (FEL) facility at LCLS. As a part of this project we have developed an algorithm to reconstruct the temporal profile of an isolated attosecond pulse from angularly streaked photoelectrons. This reconstruction is a variant of the well-known “attosecond streak camera” techniques [2]. We have simulated the photoelectron momentum spectrum resulting from the interaction of a linearly polarized IAP and a circularly polarized infrared streaking pulse with an atomic target. Our technique requires the collection of the “streaked” photoelectron momentum spectrum, as shown in Fig. 3. We employ a joint time-frequency representation for the ionized electron wavepacket and then use a non-linear fitting algorithm to reconstruct the temporal profile of the IAP. A typical result of the fitting procedure is shown in Fig. 3.

Future Plans: In the coming year, we have many projects that should yield interesting results. Firstly, we will continue to analyze the large dataset we have accumulated on molecular photoionization dynamics. In addition to the data we have already collected, we have secured a number of beam times at the LCLS.

of the electron yield with XUV-IR delay. The electron kinetic energy dependent phase variation of this RABITT oscillation is the result of many contributions. The largest contribution comes from the spectral phase of the attosecond pulse train. Additional contributions to the phase variation come from the photoionization delay (which we want to extract), and a measurement induced phase shift, which results from an interaction with the dressing IR-laser field. Comparing our high fidelity data to a known reference system (in this case argon), we can easily remove the phase variation due to the spectral phase of the attosecond pulse train. After subtraction, we are left with the

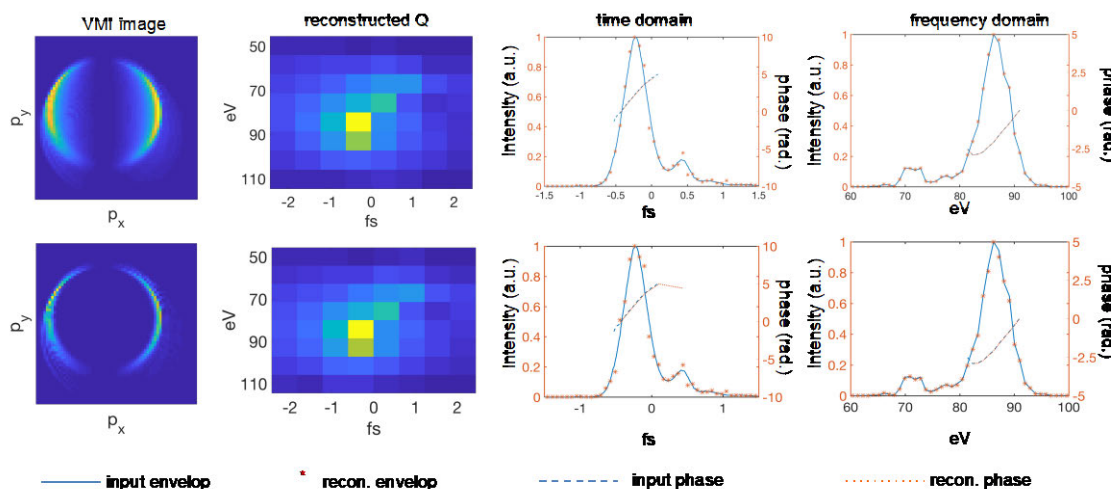


Figure 3 – The left column shows the 2-D projection of the simulated 3-D photoelectron momentum distribution (top) and a slice of the simulated 3-D photoelectron momentum distribution in the plane of the circularly polarized laser pulse. The second column shows the joint time-frequency distribution (von Neumann representation) of the laser pulse reconstructed from the simulated data. The right two columns show the time domain and frequency domain projection of the reconstructed pulses (dots) compared to the initial input pulse (solid line).

In November 2017, we will test our IAP reconstruction technique with the new sub-femtosecond mode of LCLS (part of the XLEAP project). In addition to the pulse diagnostic capabilities of our technique, we will also record dynamical data of molecular x-ray photoionization. This should provide a nice complement to the RABITT data we have already collected. Then in February 2018, we have been granted beamtime to investigate the feasibility of impulsive electronic Raman redistribution. We have a long-standing collaboration with Daniel Haxton, which focuses on calculating impulsive electronic Raman redistribution cross-sections [3,4]. This beamtime will provide us with a benchmark for the calculations. This experiment will also showcase the feasibility for using impulsive electronic Raman redistribution as a method for controlling the time-dependent electronic distribution in a molecule and observe how various deformations affect the persistence of charge motion. Thus allowing us to explore the very important role of electronic coherence, electron-electron correlations, and electron-nuclear coupling in chemical reactions. This will effectively open a new field of electronic wavepacket control to explore electron-electron correlations.

References:

1. P. M. Paul, E. S. Toma, P. Breger, G. Mullot, F. Auge, Ph. Balcou, H. G. Muller, P. Agostini, *Science* 292, 1689 (2001)
2. J. Itatani, F. Quéré, G. L. Yudin, M. Y. Ivanov, F. Krausz, and P. B. Corkum, “Attosecond Streak Camera,” *Phys. Rev. Lett.*, vol. 88, no. 17, p. 173903, Apr. 2002.
3. Matthew R Ware, Philip H Bucksbaum, James P Cryan, Daniel J Haxton, “The attosecond regime of impulsive stimulated electronic Raman excitation.” arXiv preprint arXiv:1610.01190 (2016)

4. James P Cryan, Matthew R Ware, Daniel J Haxton, "Optimizing impulsive X-ray Raman scattering for population transfer in atomic systems." arXiv preprint arXiv:1609.04175 (2016)
5. Matthew R Ware, Philip H Bucksbaum, James P Cryan, Daniel J Haxton, "The attosecond regime of impulsive stimulated electronic Raman excitation." arXiv preprint arXiv:1610.01190 (2016).
6. James P Cryan, Matthew R Ware, Daniel J Haxton, "Optimizing impulsive X-ray Raman scattering for population transfer in atomic systems." arXiv preprint arXiv:1609.04175 (2016).
7. James P. Cryan, Andrei Kamalov, Matthew R. Ware, Shungo Miyabe, Daniel J. Haxton, and Philip H. Bucksbaum, 2016. "Impulsive Stimulated Raman Scattering by Attosecond Pulses." *Ultrafast Phenomena* 2016.

Peer-Reviewed Publications Resulting from this Project (2015-2017):

1. JM Glowacki, A Natan, JP Cryan, R Hartsock, M Kozina, MP Minetti, S Nelson, J Robinson, T Sato, T van Driel, G Welch, C Weninger, D Zhu, PH Bucksbaum, "Self-referenced coherent diffraction X-ray movie of Ångstrom-and femtosecond-scale atomic motion" *Physical Review Letters* **117**, 153003 (2016).
2. Chelsea Liekhus-Schmaltz, Gregory A McCracken, Andreas Kaldun, James P Cryan, and Philip H Bucksbaum 2016. "Coherent control using kinetic energy and the geometric phase of a conical intersection." *The Journal of Chemical Physics* **145** 144304 (2016).
3. S. Miyabe and P. H. Bucksbaum, "Tranient Impulsive Electronic Raman Redistribution," *Phys. Rev. Lett.* **114** 143005 (2015).

SPC: Solution Phase Chemistry (Kelly Gaffney (PI), Amy Cordones-Hahn (co-PI)), SLAC National Accelerator Laboratory, gaffney@slac.stanford.edu, acordon@slac.stanford.edu

Project Scope: Electronic excited state phenomena provide a compelling intersection of fundamental and applied research interests in inorganic chemistry. Harnessing the strong optical absorption and photocatalytic activity of compounds depends on our ability to control fundamental physical and chemical phenomena associated with the non-adiabatic dynamics of electronic excited states. The central events of excited state chemistry can all critically influence the dynamics of electronic excited states, including internal conversion and intersystem crossing events governed by non-adiabatic interactions between electronic states in close proximity to conical intersections, as well as solvation and electron transfer.

The research opportunities enabled by LCLS direct both the scientific and technical focus of the Solution Phase Chemistry (SPC) sub-task. Scientifically, this sub-task focuses on two critical aspects of electronic excited state dynamics emphasizing the fundamental understanding of phenomena relevant to solar energy applications:

- We use ultrafast time resolution measurements, simple ligand exchange reactions, and simulation to understand the molecular properties that control excited state relaxation dynamics in coordination compounds.
- We use photo-excitation to change the electronic structure and reactivity of inorganic complexes and track site specific changes in metal solvation and coordination dynamics with ultrafast time-resolved measurements and molecular simulation.

In order to harness the strong optical absorption and photocatalytic activity of coordination complexes in solar energy applications we must robustly characterize the metal center inner shell electronic and nuclear dynamics. We are achieving this goal by utilizing a wide range of ultrafast non-linear spectroscopic methods and developing two critical ultrafast x-ray methods: (1) simultaneous hard x-ray diffuse scattering (XDS) and x-ray emission spectroscopy (XES) as probes of charge, spin, and metal-ligand bonding dynamics in electronic excited states and (2) soft x-ray Resonant Inelastic X-ray Scattering (RIXS) to probe metal-ligand covalency in electronic excited states.

Recent Progress and Future Plans

Controlling MLCT excited state lifetimes in 3d coordination complexes ((Wernet 2015; Zhang 2015; Kunnus 2016a; Kunnus 2016b; Kunnus 2016c; Kjaer 2017; Lemke 2017; Liang 2017; Mara 2017; Wolf 2017; Zhang 2017)): Cost effective solar energy applications necessitate the use of abundant materials, but the majority of inorganic artificial photosynthetic materials have been based on rare 4d and 5d transition metals. Replacing ruthenium dyes with iso-electronic iron dyes has been a long standing target for solar energy applications, but to date the ultrafast spin crossover dynamics have inhibited the usefulness of iron dyes. A schematic of our strategy for manipulating the relaxation rate and mechanism appears in Figure 1. Suppressing spin crossover requires destabilizing high (5MC) and intermediate (3MC) spin metal-centered excited states relative to the optically allowed charge transfer excited states. For metal to ligand charge transfer (MLCT) excited states, this can be achieved by using a single ligand with a low lying electron acceptor molecular orbital, and choosing the other ligands to maximize the ligand field splitting energy.

Understanding the non-radiative relaxation mechanisms of electronic excited state requires a detailed characterization of multiple electronic excited state potential energy surfaces, the nuclear motions that access degeneracies between surfaces, and how the distinct levels couple with one another. Given the complexity of the phenomena, a coordinated effort including experiment, synthesis, theory, and

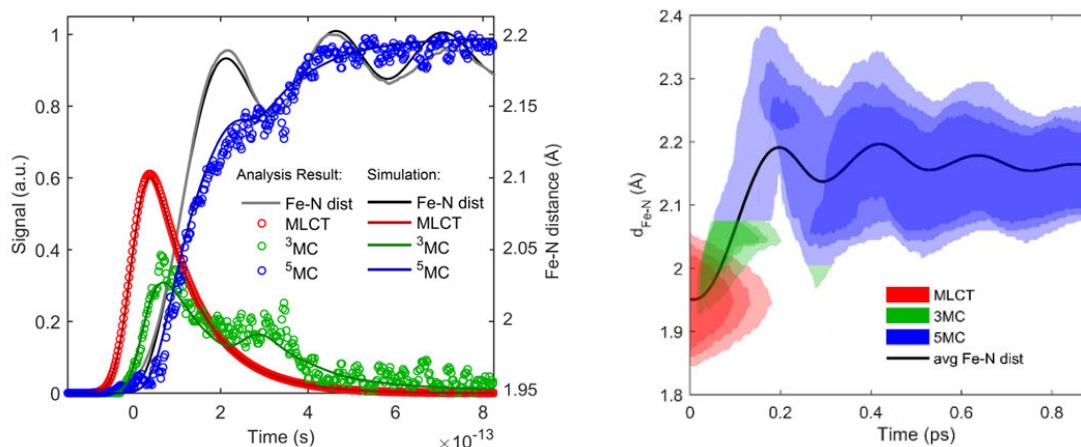


Figure 1: Ultrafast photoinduced spin crossover dynamics in $[\text{Fe}(\text{2,2-bipyridine})_3]^{2+}$ measured with ultrafast x-ray emission and x-ray scattering. (A) Time dependent population of MLCT (red), 3MC (green), and 5MC excited states measured with x-ray emission and time dependent Fe-N bond length (gray line) measured with diffuse x-ray scattering. Note the back transfer of population from 5MC to the 3MC state when the 5MC excited state population hits the inner turning point at roughly 300 fs after photoexcitation. (B) Classical simulation of population distribution as a function of Fe-N bond length. The bond length at which the forward transfer occurs differs from the bond length for back transfer. This indicates an additional vibrational degree of freedom is critically involved in the non-adiabatic transitions between the 3MC and 5MC excited states.

simulation increases the rate of progress. Our development and application of femtosecond resolution x-ray spectroscopic probes of charge and spin dynamics in electronic excited states puts us in an excellent position to investigate the mechanism and rate of charge transfer excited state relaxation in transition metal complexes. Our research has two complementary foci:

- The application of novel ultrafast x-ray methods to the investigation of internal conversion and intersystem crossing mechanisms in molecular systems well characterized by ultrafast optical methods. This has included solution phase studies of $[\text{Fe}(\text{2,2-bipyridine})_3]^{2+}$, $\text{Fe}(\text{CO})_5$, and cytochrome C.
- Joint ultrafast optical and x-ray studies of charge transfer excited state relaxation in a series of mixed ligand complexes $[\text{Fe}(\text{L})_3\text{-N}(\text{CN})_{2\text{N}}]^{2-3\text{N}}$, where L is a series of polypyridyl ligands. The interplay between chemical synthesis and ultrafast measurements has enabled us to investigate the impact of metal-ligand covalency, as well as ligand field strength and symmetry, on the rate and mechanism of internal conversion and intersystem crossing in $3d$ transition metal complexes.

Our most recent investigations of $[\text{Fe}(\text{bpy})_3]^{2+}$ have demonstrated the power of ultrafast x-ray absorption, x-ray emission, and x-ray scattering studies to acquire a mechanistic characterization of non-adiabatic internal conversion and intersystem crossing in $3d$ transition metal complexes (see Fig. 1). We have extended this approach to other Fe based complexes with the intent of transitioning our work from characterization to identifying and manipulating the key electronic and nuclear degrees of freedom that control non-radiative relaxation.

We also are preparing for the commissioning of the LCLS-II where we will use the power of ultrafast soft x-ray spectroscopy to determine the influence of excited state electron and spin density, as well as multi-electron dynamic correlation, on charge transfer excited state relaxation. Critical to this process will be the development and application of soft x-ray RIXS at the Fe L-edge and the N K-edge. At present, these measurements prove very challenging at LCLS, but are ideally suited to the capabilities of LCLS-II.

Site-specific solvation and coordination dynamics in model photo-catalysts studied with X-ray diffuse scattering and spectroscopy (Biasin 2016; van Driel 2016; Yang 2016a; Yang 2016b): The site-specific interaction of solvent and reactants with metal centers in electronically excited molecules controls many photocatalytic reactions. Femtosecond resolution x-ray scattering provides a means of measuring the site-specific solvation and coordination dynamics of photocatalysts. Ultrafast x-ray diffuse scattering (XDS) directly probes the time dependent changes in the distribution of distances between all unique pairs of atoms, a property directly available from molecular dynamics simulations. This makes the comparison between experiment and simulation straight forward by avoiding the often complex conversion of simulation results to spectroscopic observables. These properties of ultrafast XDS make the method an optimal approach to study the dynamics occurring locally around the photocatalytically active $[\text{Ir}_2(\text{dimen})_4]^{2+}$, where $\text{dimen} = \text{para-diisocyanomethane}$. These studies were able to resolve the fast, few picosecond, response of the solvent cage to the changes in structure and electronic configuration upon photoexcitation. This result highlights the ability to resolve the specific solute-solvent interactions critical to photocatalytic reaction steps, such as substrate abstraction from solvent.

Extending these studies beyond model systems to applied photocatalytic reactions directs our future objectives. A combination of X-ray scattering and spectroscopy will resolve both the photocatalyst structure and interaction with the solvent cage, as well as the electronic excited state dynamics during the photoinduced reaction. We plan to apply these methods to investigate a class of Ni-centered hydrogen evolving catalysts with redox-active ligands. The use of such ‘non-innocent’ ligands is a common design strategy for first row transition metal-based catalysts, where the ligand is intended to store charge or bind substrate to prevent uncommon oxidation or bonding states of the metal center. The unique level of mechanistic detail to be gained by the combination of X-ray spectroscopy and scattering will allow us to determine the role of metal- or ligand-based active sites in proton abstraction from the solvent during hydrogen evolution.

Initially, these studies will focus on Ni-centered complexes with a range of dithiolene-inspired ligands (Figure 2a). Although each of these complexes is known to evolve hydrogen, both electrocatalytically and by photoexcitation (direct and photosensitized), their proposed mechanisms vary significantly by ligand

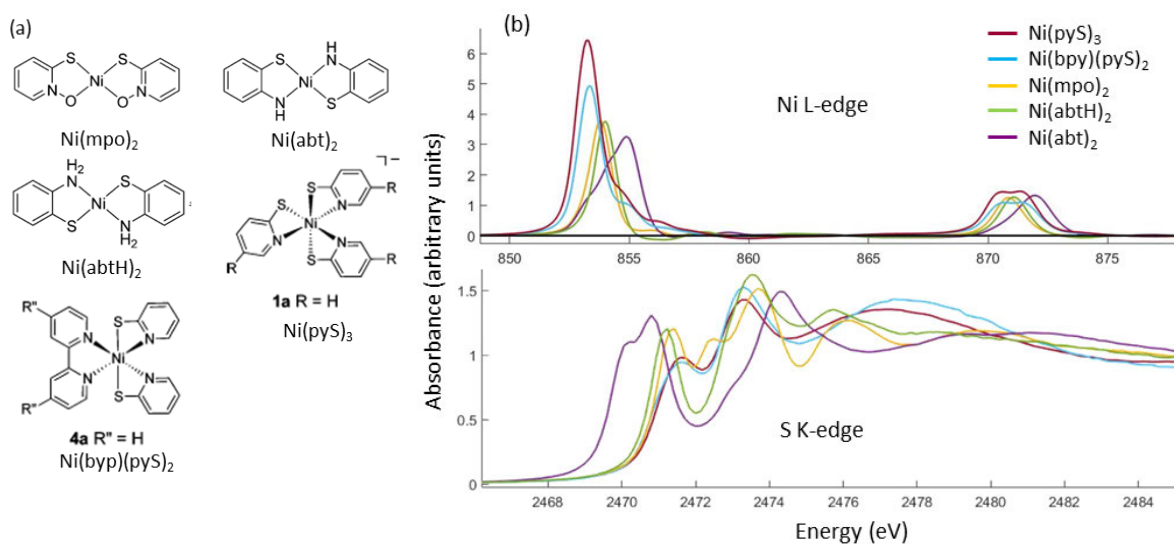


Figure 2: Ni-centered hydrogen evolution catalysts (a). X-ray absorption spectra at the Ni and S edges highlight the sensitivity of these techniques to ligand design and its effect on metal-ligand covalency and charge distribution of the complex.

design and their dynamics are entirely unknown. Future studies will leverage the sensitivity of soft X-ray spectroscopy to the evolving charge density and metal-ligand covalency of the catalyst to systematically probe the effect of ligand design on the excited state dynamics and reaction mechanisms (Figure 2b). X-ray scattering will provide the complimentary view of the required nuclear structural changes that occur as the catalyst interacts with the solvent cage to abstract protons from water and evolve H₂.

Peer-Reviewed Publications Resulting from this Project (2015-2017):

Biasin, E., T. B. van Driel, K. S. Kjaer, et al. (2016). Femtosecond X-Ray Scattering Study of Ultrafast Photoinduced Structural Dynamics in Solvated Co(terpy)₂²⁺. *Phys. Rev. Lett.* **117**: 013002.

Kjaer, K. S., Z. Wenkai, R. Alonso-Mori, et al. (2017). Ligand manipulation of charge transfer excited state relaxation and spin crossover in Fe(2,2'-bipyridine)₂(CN)₂. *Struct. Dyna.* **4**: 044030

Kunnus, K., I. Josefsson, I. Rajkovic, et al. (2016a). Anti-Stokes Resonant X-ray Raman Scattering for atom specific and excited state selective dynamics. *New J. Phys.* **18**: 103011.

Kunnus, K., I. Josefsson, I. Rajkovic, et al. (2016b). Identification of the dominant photochemical pathways and mechanistic insights to the ultrafast ligand exchange of Fe(CO)₅ to Fe(CO)₄EtOH. *Struct. Dyna.* **3**: 043204.

Kunnus, K., W. K. Zhang, M. G. Delcey, et al. (2016c). Viewing the Valence Electronic Structure of Ferric and Ferrous Hexacyanide in Solution from the Fe and Cyanide Perspectives. *J. Phys. Chem. B* **120**: 7182.

Lemke, H., K. S. Kjær, R. W. Hartsock, et al. (2017). Coherent structural trapping through wave packet dispersion during photoinduced spin state switching. *Nature Comm.* **8**: 15342.

Liang, H. W., T. Kroll, D. Nordlund, et al. (2017). Charge and Spin-State Characterization of Cobalt Bis(o-dioxolene) Valence Tautomers Using Co K β X-ray Emission and L-Edge X-ray Absorption Spectroscopies. *Inorg. Chem.* **56**: 737.

Mara, M. W., R. G. Hadt, M. E. Reinhard, et al. (2017). Metalloprotein entatic control of ligand-metal bonds quantified by ultrafast x-ray spectroscopy. *Science* **356**: 1276.

van Driel, T. B., K. S. Kjær, R. W. Hartsock, et al. (2016). Atomistic Characterization of the Active-Site Solvation Dynamics of a Model Photocatalyst. *Nature Comm.* **7**: 13678.

Wernet, P., K. Kunnus, I. Josefsson, et al. (2015). Orbital-specific mapping of the ligand exchange dynamics of Fe(CO)₅ in solution. *Nature* **520**: 78.

Wolf, T. J. A., R. H. Myhre, J. P. Cryan, et al. (2017). Probing ultrafast pi pi*/n pi* internal conversion in organic chromophores via K-edge resonant absorption. *Nature Comm.* **8**: 29.

Yang, J., M. Guehr, T. Vecchione, et al. (2016a). Femtosecond Gas Phase Electron Diffraction with MeV Electrons. *Faraday Discuss.* **194**: 563.

Yang, J., M. Guehr, T. Vecchione, et al. (2016b). Diffractive imaging of a rotational wavepacket in nitrogen molecules with femtosecond megaelectronvolt electron pulses. *Nature Comm.* **7**: 11232.

Zhang, W. K. and K. J. Gaffney (2015). Mechanistic Studies of Photoinduced Spin Crossover and Electron Transfer in Inorganic Complexes. *Acc. Chem. Res.* **48**: 1140.

Zhang, W. K., K. S. Kjaer, R. Alonso-Mori, et al. (2017). Manipulating charge transfer excited state relaxation and spin crossover in iron coordination complexes with ligand substitution. *Chem. Sci.* **8**: 515.

NPI: Non Periodic Imaging

Principal investigator: Adi Natan, Phil Bucksbaum
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Collaborators and Students: Matthew Ware, James Glowonia (LCLS), Claudiu Stan

Project scope:

The NPI program was reorganized in FY17 to phase out biochemistry and injector studies, and emphasize the nature of time-resolved short wavelength scattering on photoexcited molecular systems. We explore ways to image quantum dynamics de-novo using experimental and computational approaches with the aim to produce molecular movies of structural dynamics of systems of increased complexity in the sub-angstrom and femtosecond scales. We have demonstrated how to image electronic population transfer, vibrational motion, dissociation, rotational dephasing and Raman transitions in a diatomic system. We have also observed non-adiabatic population transfer via interference of electronic states and dynamics of a driven diatomic in a solvent environment.

Recent Progress:

Imaging different physical mechanism in photoexcited systems via Legendre decomposition:

We have identified and implemented a simple and robust analysis tool that has a universal role in x-ray scattering from photoexcited systems. The Legendre decomposition is a complete basis set in angle that can be used to expand the scattering operator terms $e^{-i\vec{Q}\cdot\vec{R}} \sim \sum_l i^{2l} P_{2l}(\cos\theta) j_{2l}(QR)$ in spherical Bessel function, that also captures the physical nature of the anisotropy created via dipole allowed absorption of one or more photons. As a result, we show in subsequent sections that it can be used to filter various molecular dynamics processes with high fidelity.

Imaging of non-adiabatic excited dynamics in I₂:

We demonstrate that femtosecond x-ray scattering from molecules prepared in a superposition of electronic states moving through an avoided crossing has new features not found in diffraction from the corresponding classical mixed state. Photo-absorption in molecular iodine at 520 nm produces a coherent superposition of two different dipole-allowed nearly degenerate excited states, namely B and B'. After about 50 fs, these states interact via non-adiabatic coupling in the vicinity of the avoided crossing between them. We show that the mixing of the nuclear wavepackets from the two electronic states at the avoided crossing leads to ultrafast changes in the angular composition of the scattering pattern. This is the result of a cross correlation term that contains the multiplication of the initial symmetries of each of the states. This type of signal is separable using the Legendre decomposition method as it appears solely on higher orders. This observation provides a new way to study transitions in excited molecular systems, and a possible approach to identify dynamics near conical intersections, and level crossings, which are ubiquitous in larger systems. We reconstruct a movie of the nuclear probability density arising from this interference.

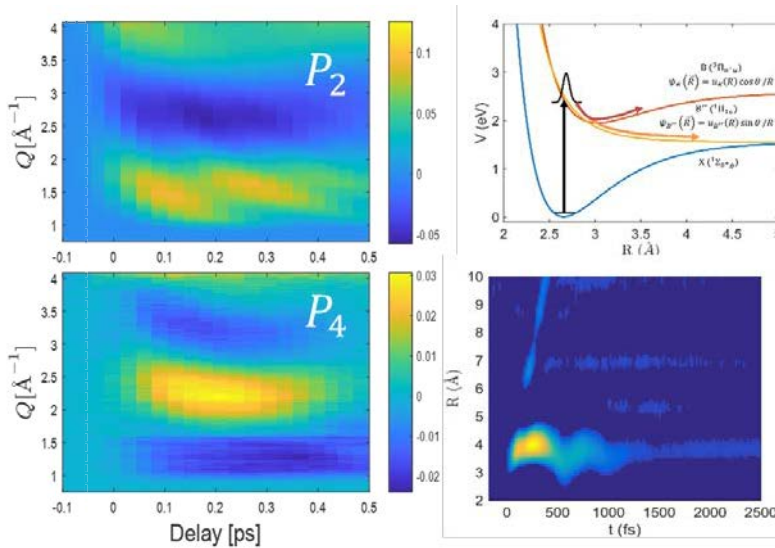


Fig 1: (Left) We observe that the P_4 term is delayed by ~ 55 fs compared to P_2 capturing the time it takes the excited wavepacket to travel to where the B and B' potential curves are closest, as seen at (Right). Following non-adiabatically population transfer the populations are mixed, creating a $\cos \cdot \sin$ term in angular distribution that can appear only on higher Legendre projections (P_4 leading). The real space reconstruction of P_4 captures the dissociation and vibration

mixing terms. Note that signals start at 3 Å in agreement of where the mixing takes place.

Imaging resonant Raman transitions via heterodyne amplification:

We induce a resonant Raman transition in molecular iodine using strong 800nm pulses, and create a superposition of vibrational states on the ground electronic state which after some time delay is probed using x-ray scattering. In this excitation, the ground vibrational state acts as a heterodyne reference for the excited vibrational states, which modulates the scattered x-ray pattern. Using the ground state as a reference amplifies the measured Raman signal by factor of 20 when comparing the excitation fraction to the maximum scattered signal amplitude. We develop use temporal Fourier methods to isolate and understand the details of how vibration and dissociation signals can be obtained without the need to Fourier transform in momentum space.

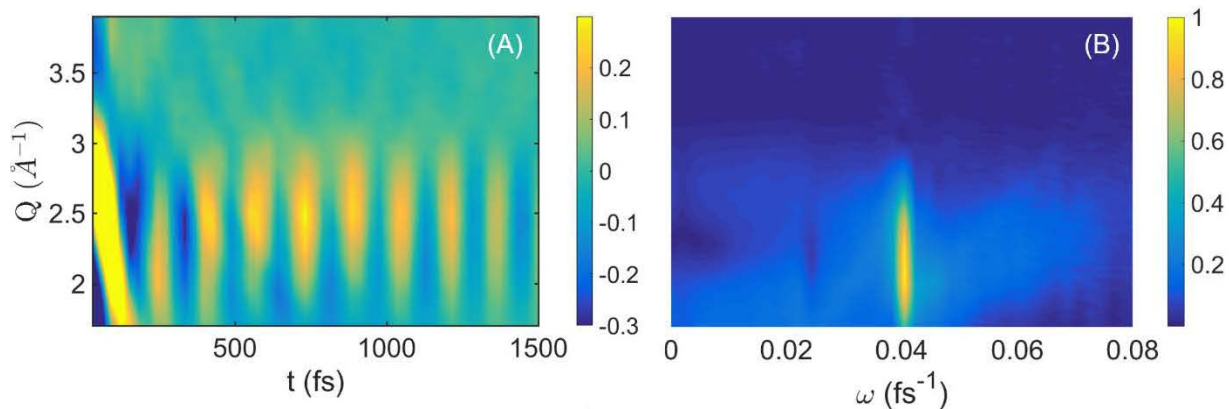


Fig 2: (A) the Legendre polynomial P_2 are function of delay captured the Raman nature with high fidelity. Fourier transform in the time domain (B) recovers the ground state vibration of I_2 .

Imaging ultrafast dynamics of Iodine in a solvent environment: In June 2017, we studied in SACLA how coherent diffraction can be used to image molecular motion in the condensed phase. We used wide angle x-ray scattering of 480 nm optically pumped molecular iodine dissolved in methanol. Preliminary analysis shows how iodine dissociates until it encounters the effective solvent cage at about 6 Å in a 200 fs timescale. There, Iodine atoms relaxes into a new bond distance where vibration motion is completely damped. We are in the process of analyzing the data form the experiment as well as modeling the angle resolved cage dynamics to obtain an effective image of iodine in methanol, and the mechanical propertied of the solvent solute interaction.

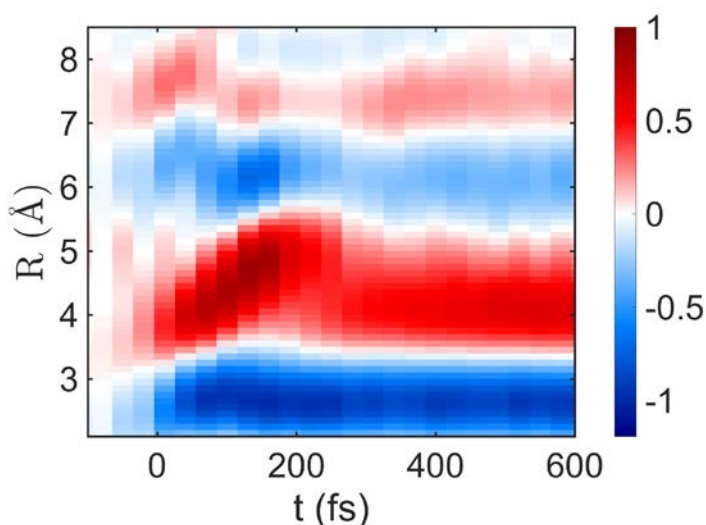


Fig 3: Preliminary analysis of real space pair correlation of iodine in methanol using P_0 of the x-ray diffraction data.

Future Plan:

Imaging molecular dynamics in larger

systems: In October 2017, we will lead a study in LCLS to create a molecular movie of the photo-physics of CO loss from the transition metal carbonyl complex $\text{Fe}(\text{CO})_5$ and the transient structural motion of the intermediate $\text{Fe}(\text{CO})_x$ complex. An understanding at the atomic level of how transition-metal complexes catalyze reactions, and the role of the short-lived and reactive intermediate states involved is of great importance for future control of photocatalytic hydrogen production and selective carbon–hydrogen bond activation.

Complete Mapping of femtosecond dynamics in I_2 : In February 2018, we will revisit I_2 in LCLS where we will systematically map the dynamics pumping with tunable light from 480 to 600 nm, elucidating the relative weight and position of different dipole allowed transitions. We will investigate how field free aligned ensembles alter the signal and analysis.

Double blind holography in Legendre space: We are developing a new type of holographic approach that makes use of the results mentioned above, namely, to measure separately the autocorrelation of excited states via lower order Legendre projection, and the cross-correlation following population mixing via higher order Legendre, to obtain the amplitude and phase of the wavepacket. This a new way of thinking about holography in functional space rather than in position space or time, that allows to apply a protocol similar to double blind Fourier holography in a way that utilizes the fact the cross-correlation appears in a different basis coefficient than the autocorrelation, reducing the problem to a system of linear equations. We are investigating how finite detector size and noise can be overcome to fulfill the compact support requirement that permits retrieval of the phase of the individual object under study. We propose to use CS_2 , where a 200 nm photon will excite to both $S(^1\text{D})$ and $S(^3\text{P})$ quasi-bound channels, creating a coherent beat with time period of 80 fs that decays in about 500 fs, with several vibration periods are also taking place. Because the geometry changes during the excitation, the initial nuclear motion proceeds along the bending and symmetric stretch coordinates. During the bending and stretching

the excited state adiabatically develop from Σ_u^+ into Π_g . We will use field free alignment and probe how CS₂ electronic coherence evolves and affect the x-ray diffraction in the ways mentioned above.

Expand tools for polyatomic systems and aligned ensembles: While the current approach is generic and proved successful for diatomic systems, it is not necessarily optimal for larger systems, aligned ensembles or systems with more than one rovibrational modes, where the angular distributions can have a more complex form, for example, as given by generic 3D spherical harmonics. We suggest studying triatomic systems such as CS₂ as detailed in the previous section, and SO₂, a quantum asymmetric top whose coherent rotational dynamics is aperiodic and display irregular coherent transients that depend on the inertial polarizability tensor. Extending our efforts to polyatomic systems will advance the understanding of the connection between coherence and function in complex systems, a subject that is only just emerging within the scientific community.

References

- Ware, M. R. *et al.* Filming non-adiabatic population transfer with x-ray diffraction. Status: In review, *arXiv:1708.03847 [physics]* (2017).
- Natan, A., Ware, M. R. & Bucksbaum, P. H. Experimental Signature of Light Induced Conical Intersections in Diatomics. in *Ultrafast Phenomena XIX* (eds. Yamanouchi, K., et al.) **162**, 122–125 (Springer International Publishing, 2015).

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- Glownia, J. M. *et al.* Self-Referenced Coherent Diffraction X-Ray Movie of \AA{}- and Femtosecond-Scale Atomic Motion. *Phys. Rev. Lett.* **117**, 153003 (2016).
- Glownia, J. M. *et al.* Glownia et al. Reply: *Phys. Rev. Lett.* **119**, 069302 (2017).
- Natan, A. *et al.* Observation of Quantum Interferences via Light-Induced Conical Intersections in Diatomic Molecules. *Physical Review Letters* **116**, (2016).
- Sanchez-Gonzalez, A. *et al.* Auger electron and photoabsorption spectra of glycine in the vicinity of the oxygen K-edge measured with an X-FEL. *Journal of Physics B: Atomic, Molecular and Optical Physics* **48**, 234004 (2015).
- Liekhus-Schmaltz, C. E. *et al.* Ultrafast isomerization initiated by X-ray core ionization. *Nature Communications* **6**, 8199 (2015).
- Amaya, A. J. *et al.* How Cubic Can Ice Be? *The Journal of Physical Chemistry Letters* **8**, 3216–3222 (2017).
- Stan, C. A. *et al.* Negative Pressures and Spallation in Water Drops Subjected to Nanosecond Shock Waves. *The Journal of Physical Chemistry Letters* **7**, 2055–2062 (2016).
- Stan, C. A. *et al.* Liquid explosions induced by X-ray laser pulses. *Nature Physics* **12**, 966–971 (2016).
- Dao, E. H. , et al. (2015). "Goniometer-based femtosecond X-ray diffraction of mutant 30S ribosomal subunit crystals.", *Struct. Dyn.* **2**, 041706.
- Hunter, M. et al., (2016) "Selenium single-wavelength anomalous diffraction de novo phasing using an X-ray-free electron laser," *Nature Comm.* **7**, 13388.
- Laksmono, H., et al. (2015). "Anomalous behavior of the homogeneous ice nucleation rate in "No-man's land. ", *J. Phys. Chem. Lett.* **6**, 2826.
- Sierra, R. G., et al. (2016). "Concentric-flow electrokinetic injector enables serial crystallography of ribosome and photosystem II." *Nat. Methods* **13**, 59.

SFA: Strong Field AMO Physics

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Project Scope

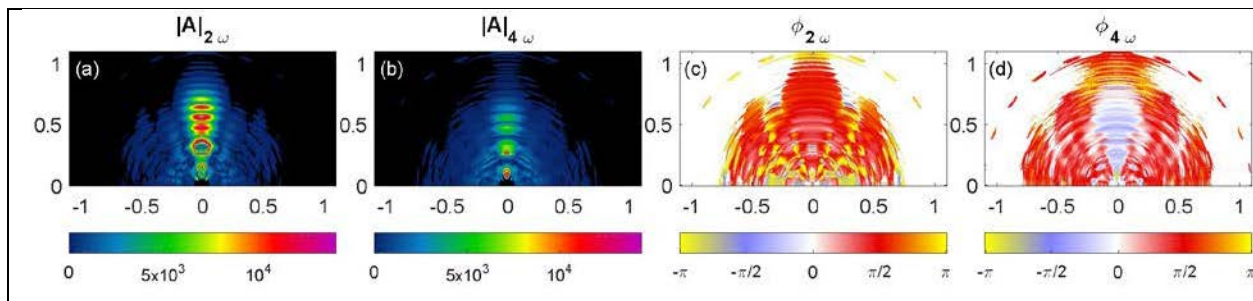
The Strong Field AMO task investigates the dynamics, and control of atoms and molecules in externally applied strong coherent electromagnetic fields, from optical to x-ray frequencies. X-ray free electron lasers are a source of some of the strongest electromagnetic fields available, up to kilovolts per Angstrom. We study strong-field excitation of external and internal quantum coherences in molecules to gain a deeper understanding of strong-field ionization and field-induced changes in symmetry and topology as well as strong-field quantum control.

This year some of the previous scope of SFA moved over to our newly reconstituted non-periodic imaging subtask, which has taken on the challenge of making molecular movies of photoexcited molecules. Dr. Adi Natan, formerly a Research Associate in this subtask, is now the head of the NPI subtask. Matthew Ware, who has been doing his graduate work on molecular movies, has moved to the new subtask. Lucas Zipp graduated, and Ann Wang is a new graduate student hired to continue our work in SFA.

Recent Progress

Imaging electron rescattering momentum amplitudes and phases by 2-Color Phase Contrast Strong Field Photoelectron Spectroscopy: [1] We have demonstrated a method to retrieve and visualize low-energy rescattering signals from the total photoelectron momentum map by Fourier decomposition of angle-resolved two-color strong field photoionization.

The broad structure of strong field ionization of atoms is qualitatively well understood. For the case of linearly polarized intense pulses, field-ionized can gain energies up to $2U_p$, U_p is the ponderomotive energy. In about 0.1% of the cases, the electrons are driven by the laser field and rescatter off their parent ion, gaining energies up to $10 U_p$. Therefore the region between 2 and $10U_p$ contains information about the structure of the system and the ionizing field itself.



The 2ω and 4ω Fourier components of both amplitudes and phases of strong-field ionization and rescattering in the presence of a 2-color field, as described in the text.

Here, we show how a weak probe field at twice the laser frequency, provides information that disentangles direct from rescattered electrons below $2U_p$.

The experimental setup that was used is similar to that found in [2]. Briefly, linearly polarized 800nm, 70 fs laser pulses from a 1 kHz Ti:Sapphire laser is used together with a second harmonic produced in BBO with variable phase delay. We obtained electron VMI images for various delay points of the two-color fields. We then processed the raw images to reconstruct full three-dimensional photoelectron distributions, and filtered the images using Fourier decomposition of the delay at harmonics of the laser frequency. Two frequencies contribute to

most of the observed ionization yield, 2ω and 4ω . The amplitudes and phases for each frequency components are then extracted from the reconstructed VMI images, as seen in Fig 2.

By Fourier filtering the momentum maps and comparing both frequency components, we can disentangle the contribution of rescattered from direct photoelectrons below $2U_p$. We find the following by direct analysis: First, rescattering to a given final momentum generally takes place twice in each half cycles of the ionization field, because recollision happens twice, once from each direction. Thus recollision physics dominates the 4ω Fourier component. Second, the expected relative delay between ionization and rescattering (approximately one-quarter cycle) is consistent with the phase delay found. Third, the 4ω signal is more isotropic than the direct strong-field ionization, as expected for recollision physics.

Imaging the breakdown of molecular frame dynamics through rotational uncoupling [3]: We have observed directly in the time domain the uncoupling of electron motion from the molecular frame due to rotational-electronic coupling in a molecular Rydberg system. In contrast to Born-Oppenheimer dynamics, in which the electron is firmly fixed to the molecular frame, there exists a regime of molecular dynamics known as l-uncoupling where the motion of a non-penetrating Rydberg electron decouples from the instantaneous alignment of the molecular frame. We have imaged this unusual regime in time-dependent photoelectron angular distributions of a coherently prepared electron wave packet in the $4f$ manifold of N_2 . The angular distribution was characterized by a least-squares fit decomposition onto Legendre polynomials, We find that the fitted coefficient values for terms of order higher than to β_8 are negligible, which agrees with the selection rules applying for single-photon ionization from an $L=3$ orbital. Angle-resolved time-domain studies of this uncoupled regime present new opportunities to study the ultrafast dynamics of electron and nuclear motion in a non-Born Oppenheimer setting.

SFA also had several joint experiments with other tasks this year.

Two-photon excitation of a nuclear transition at an Xray FEL: With Andy Kaldun, David Reis, and the NPI task, we have attempted to extend nonlinear optics to the nucleus to generate near-degenerate two-photon excitation of the iron isotope ^{57}Fe $j=1/2-$ to $3/2-$ nuclear transition at about 14.4 keV using the SACLA X-ray FEL. Detection of the excitation was by delayed emission, measured directly in the time domain with nanosecond resolution. The cross-section for the excitation process was such that a detection rate that is well above measured background in recent nonlinear x-ray scattering experiments in SACLA [1]. It also far exceeds the typical 1 per million excitation on synchrotron-based sources. Our theoretical calculations suggest that future high-repetition rate FELs could become attractive sources for Mossbauer spectroscopy. In a first run, we set the x-ray photon energy of BL3 to half the nuclear transition at 14.413 keV (i.e. 7.2065 keV) to excite for the first time by two-photon absorption the nuclear resonance line (see Fig. 1).

X-ray molecular movies in Iodine. With Matt Ware, Dr. Mike Glowina, and Dr. Adi Natan, we are making and studying molecular movies using hard x-rays from LCLS and SACLA. The NPI abstract describes this work.

Attosecond strong fields. With Dr. James Cryan, and Dr. Agostino Marinelli, we are collaborating with ATO and the XLEAP initiative at SLAC in development of a new VMI setup that will use momentum streaking to encode the properties of an attosecond x-ray pulse in the angle resolved photoelectrons.

100 kHz soft x-rays. With Dr. James Cryan, Dr. Thomas Wolf, and Dr. Amy Cordones-Hahn, we are collaborating on commissioning x-ray transient absorption experiments that utilize a 100 kHz HHG source under construction and commissioning.

Future plans:

We can observe above-threshold ionization momentum distributions in small molecules (H_2O , N_2 , O_2 , H_2). These data contain a wealth of information about the strong-field ionization process, which we are trying to extract through a combination of simulations and imaging methods. These include:

- Evidence for quantum interference during rescattering of field-ionized electrons can reveal motion on attosecond timescales from systems that relax following ionization, such as H_2O . We are applying an eikonal model to analyze the interferences in an attempt to retrieve structural information of the molecular sample.
- Structure of ATI peaks show the evolution of Freeman resonances.
- Low-energy structures clearly show double-excitation induced by field ionization that leaves the cation in an excited state.
- Two-color methods can show various aspects of the phase dependence of strong-field phenomena.

We are also collaborating with the Dudovich group from Weizmann and have made progress in explaining fano like phase shifts in photo-electron holography velocity map imaging using two-color fields.

With Dr. James Cryan, Dr. Thomas Wolf, and Dr. Amy Cordones-Hahn, we are collaborating on commissioning x-ray transient absorption experiments that utilize a 100 kHz HHG source under construction and commissioning.

References:

Natan, A., Ware, M. R. & Bucksbaum, P. H. Experimental Signature of Light Induced Conical Intersections in Diatomics. in *Ultrafast Phenomena XIX* (eds. Yamanouchi, K., Cundiff, S., de Vivie-Riedle, R., Kuwata-Gonokami, M. & DiMauro, L.) **162**, 122–125 (Springer International Publishing, 2015).

Sanchez-Gonzalez, A. *et al.* Machine learning applied to single-shot x-ray diagnostics in an XFEL. *arXiv:1610.03378 [physics, stat]* (2016).

Peer-Reviewed Publications Resulting from this Project (2015-2017)

Zipp, L. J., Natan, A. & Bucksbaum, P. H. Imaging the breakdown of molecular-frame dynamics through rotational uncoupling. *Physical Review A* **95**, (2017).

- Natan, A. *et al.* Observation of Quantum Interferences via Light-Induced Conical Intersections in Diatomic Molecules. *Physical Review Letters* **116**, (2016).
- Miyabe, S. & Bucksbaum, P. Transient Impulsive Electronic Raman Redistribution. *Physical Review Letters* **114**, (2015).
- Kamalov, A., Broege, D. W. & Bucksbaum, P. H. Dynamical localization in molecular alignment of kicked quantum rotors. *Physical Review A* **92**, (2015).
- Floß, J., Kamalov, A., Averbukh, I. S. & Bucksbaum, P. H. Observation of Bloch Oscillations in Molecular Rotation. *Physical Review Letters* **115**, (2015).
- Wolf, T. J. A. *et al.* Probing ultrafast $\pi\pi^*/n\pi^*$ internal conversion in organic chromophores via K-edge resonant absorption. *Nature Communications* **8**, (2017).
- Wolf, T. *et al.* Observing Femtosecond Fragmentation Using Ultrafast X-ray-Induced Auger Spectra. *Applied Sciences* **7**, 681 (2017).
- Sanchez-Gonzalez, A. *et al.* Accurate prediction of X-ray pulse properties from a free-electron laser using machine learning. *Nature Communications* **8**, 15461 (2017).
- Glownia, J. M. *et al.* Glownia *et al.* Reply: *Physical Review Letters* **119**, (2017).
- Tenney, I. F., Artamonov, M., Seideman, T. & Bucksbaum, P. H. Collisional decoherence and rotational quasirevivals in asymmetric-top molecules. *Physical Review A* **93**, (2016).
- Marinelli, A. *et al.* Optical Shaping of X-Ray Free-Electron Lasers. *Physical Review Letters* **116**, (2016).
- Lutman, A. A. *et al.* Fresh-slice multicolour X-ray free-electron lasers. *Nature Photonics* **10**, 745–750 (2016).
- Lutman, A. A. *et al.* Polarization control in an X-ray free-electron laser. *Nature Photonics* **10**, 468–472 (2016).
- Kroll, T. *et al.* X-ray absorption spectroscopy using a self-seeded soft X-ray free-electron laser. *Optics Express* **24**, 22469 (2016).
- Hartmann, G. *et al.* Circular dichroism measurements at an x-ray free-electron laser with polarization control. *Review of Scientific Instruments* **87**, 083113 (2016).
- Gorkhover, T. *et al.* Femtosecond and nanometre visualization of structural dynamics in superheated nanoparticles. *Nature Photonics* **10**, 93–97 (2016).
- Glownia, J. M. *et al.* Self-Referenced Coherent Diffraction X-Ray Movie of Ångstrom- and Femtosecond-Scale Atomic Motion. *Physical Review Letters* **117**, (2016).
- Sanchez-Gonzalez, A. *et al.* Auger electron and photoabsorption spectra of glycine in the vicinity of the oxygen K-edge measured with an X-FEL. *Journal of Physics B: Atomic, Molecular and Optical Physics* **48**, 234004 (2015).
- Liekhus-Schmaltz, C. E. *et al.* Ultrafast isomerization initiated by X-ray core ionization. *Nature Communications* **6**, 8199 (2015).
- Kierspel, T. *et al.* Strongly aligned gas-phase molecules at free-electron lasers. *Journal of Physics B: Atomic, Molecular and Optical Physics* **48**, 204002 (2015).

NLX: Nonlinear X-ray Science

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Program Scope:

In the NLX program, we are focused on the nonlinear optics of short-wavelength, ultra-fast coherent radiation. We seek to understand strong-field and multi-photon interactions and exploit them to probe electronic structure at the atomic-scale in space and time. We are interested in fundamental interactions, with a primary focus on coherent non-sequential processes such as wave-mixing and two-photon Compton scattering using hard x rays. In the upcoming funding period, we propose experiments on x-ray and optical wave-mixing to image the strong-field-driven attosecond electronic dynamics responsible for solid-state high-harmonic generation. We will also explore the bound-state contribution to two-photon Compton scattering. The new scattering mechanism holds promise as a nonlinear photons-in/photon-out method of achieving simultaneous chemical specificity and atomic-scale structure in low Z materials. Our program is synergistic with other strong-field investigations in PULSE and makes use of the unprecedented intensities at hard x-ray wavelengths of LCLS and SACLA free-electron lasers. The results could have a profound impact on future light sources such as the LCLS-II.

Recent Progress

Non-sequential two-photon interactions at x-ray wavelengths became possible with the advent of the LCLS free-electron laser. In this program we continue to explore several fundamental nonlinear x-ray processes on the LCLS and SACLA with an emphasis on the hard x-ray regime, where it may be possible to gain simultaneous structure and spectroscopy information. In the past few years, we have performed measurements of phased-matched x-ray second harmonic generation in diamond, x-ray and optical wave-mixing (diamond), and anomalous nonlinear Compton scattering (beryllium) on LCLS as well as two-photon K-shell absorption (zirconium) on the SACLA FEL. In the past year, we have completed several additional beamtimes on LCLS and SACLA aimed at a better understanding of these phenomena, and the limits to the free-electron nonlinearities for non-resonant excitation.

This is important, since far from resonance, the linear x-ray matter interaction can be well approximated by the scattering off a collection of free-electrons. We find that models that treat the solid as a collection of free-electrons are successful at describing both the x-ray second-harmonic generation and the (optically modulated) x-ray susceptibility in x-ray-optical sum frequency generation. However, we found that in nonlinear two-photon Compton scattering, the free-electron model breaks down spectacularly. We find that the spectrum shows an anomalously large broadening and redshift as compared to both the free-electron theory and to the simultaneously measured linear scattering from the weak residual FEL second harmonic generated by the undulators. Our observations are incompatible with kinematics for the ground state electron distribution in the usual impulse approximation (IA). These anomalies are consistent with a novel nonlinear scattering mech-

anism involving bound-state electrons, despite an X-ray energy of approximately two orders of magnitude above the $1s$ binding energy. We have recently extended our original measurements to significantly *larger* red-shift and *smaller* scattering angles; however, recent theoretical work (submitted) with Robin Santra's group predict no such anomalies from the single atom, two-photon response, suggesting an even more exotic mechanism must be at play.

Future Plans (the next three years):

We continue to concentrate our efforts on x-ray nonlinear optics. In collaboration with the Fuchs group at Nebraska, we are still analyzing the new results on two-photon Compton scattering. We have explored in detail x-ray second harmonic generation and set limits for phase-matched nonlinear Compton scattering. We are also analyzing results on two-photon Mossbauer. We have beamtime on LCLS to explore x-ray four wavemixing (transient grating), and x-ray optical wavemixing in the presence of strong-fields, where we will probe the microscopic processes involved in solid-state high harmonics (initially discovered under AMOS support and in collaboration with Ghimire's early career award. Nonlinear x-ray interactions will become more important for LCLS-II and in particular LCLS-II-HE, and we are also exploring possible ways to make use of other multi-color/multi-pulse interactions.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [1] Y. S. You, D. A. Reis, and S. Ghimire. Anisotropic high-harmonic generation in bulk crystals. *Nature Physics*, **13**:345–349, 2017 (collaborative with Ghimire ECA).
- [2] S. Ghimire, M. Fuchs, J. B. Hastings, S. Herrmann, Y. Inubushi, J. Pines, S. Shwartz, M. Yabashi, and D. A. Reis. Nonsequential two-photon absorption from the k shell in solid zirconium. *Physical Review A*, **94**, 043418, 2016.
- [3] G. Ndabashimiye, S. Ghimire, M. Wu, D. A. Browne, K. J. Schafer, M. B. Gaarde, and D. A. Reis. Solid-state harmonics beyond the atomic limit. *Nature*, **534**, 520, 2016.
- [4] M. Fuchs, M. Trigo, J. Chen, S. Ghimire, S. Shwartz, M. Kozina, M. Jiang, T. Henighan, C. Bray, G. Ndabashimiye, P. H. Bucksbaum, Y. Feng, S. Herrmann, G. A. Carini, J. Pines, P. Hart, C. Kenney, S. Guillet, S. Boutet, G. J. Williams, M. Messerschmidt, M. M. Seibert, S. Moeller, J. B. Hastings, and D. A. Reis. Anomalous nonlinear x-ray compton scattering. *Nature Physics*, **11**, 964, 2015.
- [5] M. Wu, S. Ghimire, D. A. Reis, K. J. Schafer, and M. B. Gaarde. High-harmonic generation from Bloch electrons in solids. *Physical Review A*, **91**, 043839, 2015.

Electron Dynamics on the Nanoscale

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Project Scope

This component of the SLAC research program examines the ultrafast dynamics of electronic excitations in nanostructures. In particular, the research addresses the behavior of photoexcited electrons in atomically thin two-dimensional (2D) layers of van-der-Waals crystals and heterostructures, with particular emphasis on the behavior of the model system of transition metal dichalcogenide crystals. The investigations make use of complementary experimental techniques based on ultrafast spectroscopy to probe radiative and non-radiative relaxation pathways after photoexcitation, addressing the role of Coulomb and vibrational interactions as manifest in exciton formation, exciton-exciton and exciton-carrier interactions, intervalley scattering, and exciton radiative decay. The research also examines electron dynamics in heterostructures composed of atomically thin 2D van der Waals layers combined with other 2D layers and with 0D structures, such as quantum dots. Because of the unreactive character of 2D van der Waals layers, combinations of a wide variety of structures can be prepared by mechanical assembly, as well as by chemical deposition techniques, and provide a set of designer systems in which to elucidate the principles of ultrafast electron dynamics.

Recent Progress

The ultrafast dynamics of two-dimensional van-der-Waals layers, particularly ultrathin layers of transition metal dichalcogenide materials in the class of MX_2 ($M = \text{Mo}, \text{W}$ and $X = \text{S}, \text{Se}, \text{Te}$) as model 2D semiconductors, continued to be the focus of recent research. In particular, we have investigated the ultrafast dynamics of photoexcited monolayers of transition metal dichalcogenide materials using broadband transient absorption spectroscopy. These measurements revealed the importance not only of changes in electronic populations, as expected, but also the role of excitation of phonons, as reflected in modest, but readily observable spectral shifts of the excitonic transitions. These measurements give us a more complete picture of the dynamical response of these model systems after photoexcitation. Another important aspect of dynamics in these systems that has recently come to the fore is the role of dark exciton states. In previous investigations of monolayer WSe_2 using time-resolved photoluminescence, we obtained a signature of the presence of an intrinsic dark state, lying below the well-studied bright exciton state, through the thermal activation of radiative decay. In recent work, we have directly observed the signature of these spin-forbidden dark states through a magnetic brightening technique that perturbs the spin of the carriers. We have also examined the dynamics of these states through time-resolved photoluminescence measurements, which revealed a dramatic increase in the lifetime of the (magnetically brightened) dark states compared to the radiatively allowed bright exciton states. Below we summarize these findings and their implications.

Exciton and phonon dynamics in photoexcited monolayer WS_2 (Ref. 1): The dynamics of excitons in the direct-gap monolayer transition metal dichalcogenides have attracted much recent attention, both because of the intrinsic interest obtaining a complete understanding of photophysics in this model 2D system and because of potential applications in energy harvesting and optoelectronics. While the role of radiative decay and non-radiative decay through exciton-exciton annihilation (excitonic Auger process) have been examined experimentally, the influence of phonons generated through carrier cooling and the Auger process have not been identified in dynamics experiments.

We have applied femtosecond broadband transient absorption spectroscopy to probe the sequence of dynamical steps following photoexcitation of the transition metal dichalcogenide WS_2 in its monolayer form. Figure 1 displays typical traces of the evolution of the principal (A) excitonic transition at the band gap following excitation with an ultrafast pulse.

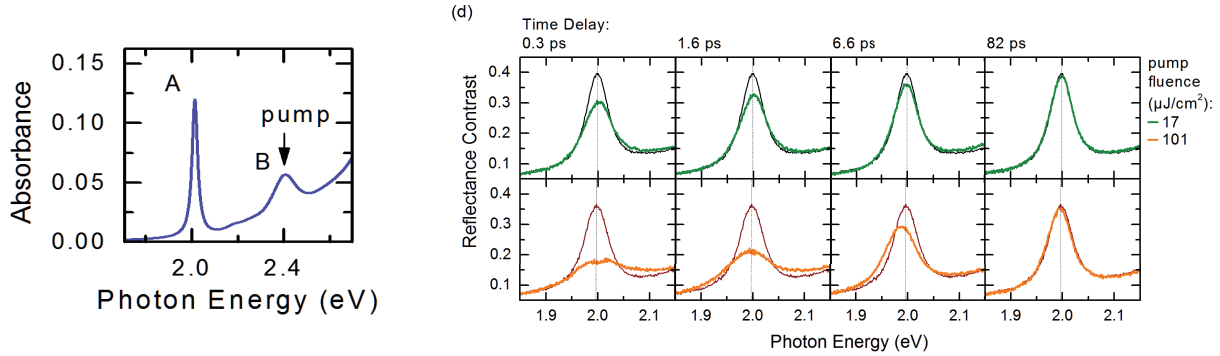


Fig. 1: Spectroscopy and femtosecond transient response of monolayer WS₂. (left) The absorption spectrum of the monolayer, showing the A and B exciton peaks. The area indicates the photon energy of the ultrafast excitation pulse. Peak A is the band-gap exciton state probed in the dynamics measurements. (right) Broadband femtosecond transient absorption spectra of the A exciton peak following ultrafast photoexcitation. The upper line shows the response for a relatively low excitation pump fluence (17 $\mu\text{J}/\text{cm}^2$). In this case, we see modest bleaching of exciton absorption, but little peak shift. At higher excitation pump fluence (101 $\mu\text{J}/\text{cm}^2$), there is more pronounced bleaching, but also a clear broadening and a red-shift in the peak position. These are signatures of excitation of phonons.

The rapid decrease in the area of the absorption feature following pumping is attributed to state-filling effects associated with the prompt creation of band-edge (A) excitons. The ultimate recover corresponds to return to the ground state of the material. We have extracted information on the intervening dynamics by a careful analysis of the temporal evolution of the different spectral features of the response: the area of the absorption feature, the width of the feature, and the central frequency of the feature. We find that the exciton population, reflected in the changes of the area of feature decay rapidly, principally through exciton-exciton annihilation at higher densities. The broadening of the feature arises from exciton-exciton interactions at early times and interactions with phonons at later time. The peak shift has a many-body contribution at early times, but reflects the effect of increased phonon population at later times. The analysis of the spectra yielded information on the time evolution of the layer temperature (after ~ 10 ps) when thermal equilibrium conditions set in. The scheme of the dynamical processes controlling the optical response is summarized in Fig 2.

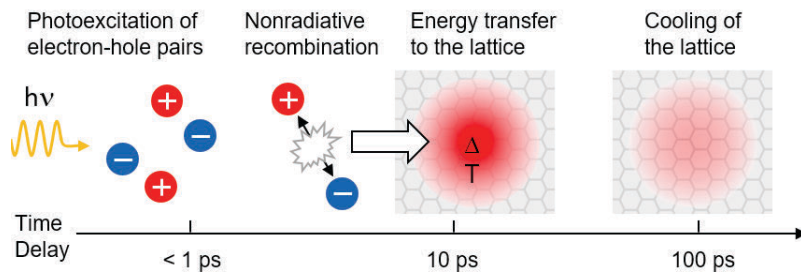


Fig. 2: Overall scheme of ultrafast dynamics following excitation of monolayer WS₂ by an ultrafast pulse. Band-edge excitons are created promptly and undergo exciton-exciton annihilation within a few picoseconds. This leads to excitation of phonons, with system returning to equilibrium on a time scale of ~ 100 ps.

Direct observation of dark exciton states and their dynamics in 2D semiconductors (Ref. 2)

2D semiconductors in the transition metal dichalcogenide family are direct-gap materials in the monolayer limit. At room temperature, they are characterized by bright photoluminescence. However, at reduced temperatures, the emission is quenched in some of the materials, as we have determined in previous experiments. In the WSe₂ system this was attributed to the existence of a dark spin forbidden (triplet-like) exciton located below the spin-allowed band-gap A exciton.

In recent experiments, we have obtained direct proof of the existence of the predicted spin-forbidden dark excitons by means of a magnetic brightening technique. The underlying principle is that by applying a strong magnetic field in the in-plane direction of the layer, the out-of-plane spin orientation of the carriers in the conduction band can be perturbed. This causes the otherwise spin-forbidden

transition to become weakly radiatively allowed. This schema and the emergence of the corresponding dark exciton state with increasing magnetic field are displayed in Fig. 3.

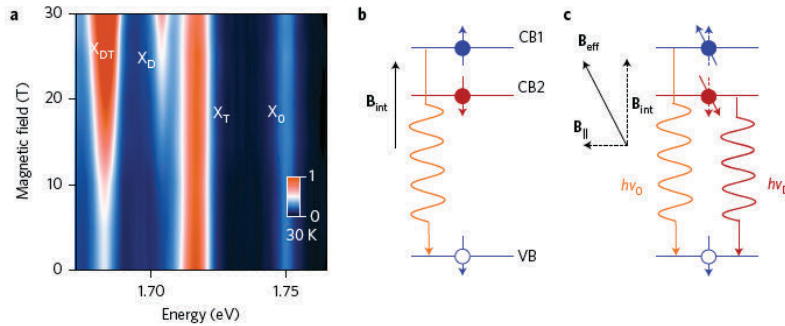


Fig. 3: Magnetic brightening of dark excitons in WSe_2 . (a) Evolution of photoluminescence spectra as a function of magnetic field strength. We see the emergence of new features corresponding to dark neutral (X_D) and charged (X_{DT}) excitons. (b-c) Schema for magnetic brightening of dark excitons

From these spectra, we can determine precise energies for the dark neutral (X_D) and charged (X_{DT}) excitons. Comparison with the corresponding bright excitons, then reveals directly and accurately the dark-bright exciton splitting. These splittings reflect the corresponding splitting of the spin-polarized conduction bands, as shown in Fig.3(b-c). In addition, however, the splittings are also determined by many-body effects in the system, since the observed states are excitons, rather than band-to-band transitions. The principal many-body correction is the exchange interaction, reflecting the fact that the bright and dark excitons have opposite relative electron and hole spins. Analysis of the splitting of the dark-bright neutral and the charged excitons permit accurate estimates of both the conduction spin band splitting and the strength of the exchange interaction.

With respect to dynamics, the bright excitons have very short intrinsic radiative lifetimes, on the order of 1 ps, reflecting the tightly bound character of the excitons. The dark excitons, however, only become weakly allowed under the influence of the magnetic field. Accordingly, the dark exciton radiative lifetimes are expected to be much longer. We verify the long lifetime of the dark exciton by direct measurements of the time-resolved fluorescence, as shown in Fig. 4.

These studies provide detailed information on the band structure of the transition metal dichalcogenide monolayers and their many-body interactions. The time-resolved measurements show that we can create observable states with long radiative lifetimes. This may open the way to create new quantum-correlated states from the tightly bound excitons in these monolayer system

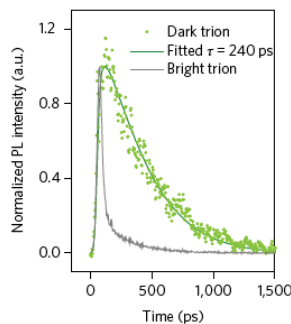


Fig. 3: Dynamics of bright and dark excitons in monolayer WSe_2 . The plot shows time-resolved emission from bright and dark charged excitons (trions, grey curve). The bright state decays within the time resolution of the instrument. The magnetically brightened dark exciton has a radiative lifetime exceeding a few hundred picoseconds (green points).

We have been exploring the nature of these excitonic transitions and of their decay channels. In a recent investigation, we have determined the temperature dependent linewidth of these lowest lying (A) excitonic state as a function of temperature. While the very high radiative emission rates contribute appreciably to the observed linewidth, this factor (as well as inhomogeneous broadening) is expected to be largely independent of temperature. The variation with temperature can be attributed to exciton phonon scattering processes.

In a collaborative study with the Ermin Malic and Andreas Knorr groups in Europe, we have used the measurements of the temperature dependence of the exciton linewidth to evaluation scattering

channels. As indicated in Fig. 2, with increasing temperature, we see a strong activation of different exciton-phonon scattering channels.

Future Plans

In the coming period of time, we wish to further elucidate the dynamics of dark excitons, including the valley and spin degrees of freedom in monolayer transition metal dichalcogenide layers. A further object of study is the lifetime of interlayer excitons produced in transition metal dichalcogenide layers by charge separation, particularly emphasis on the dynamics and efficiency of transfer of the electronic spin and valley degrees of freedom from one layer to the other. This information can be accessed experimentally through the use of time-resolved optical Kerr rotation or circular dichroism measurements following selective excitation of one material with circularly polarized light. These investigations will provide insight into the nature and pathways for interlayer charge separation.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. C. Ruppert, A. Chernikov, H. M. Hill, A. Rigosi, and T. F. Heinz, "The Role of Electronic and Phononic Excitation in the Optical Response of Monolayer WS_2 ," *Nano Lett.* **17**, 644-651 (2017).
2. X.-X. Zhang, T. Cao, Z. Lu, Y.-C. Lin, F. Zhang, Y. Wang, Z. Li, J. Hone, J. A. Robinson, D. Smirnov, S. G. Louie, T. F. Heinz, "Magnetic brightening and control of dark excitons in monolayer WSe_2 ," *Nature Nanotech.* **12**, 883-888 (2017).
3. O. Yaffe, Y. Guo, L. Z. Tan, D. A. Egger, T. Hull, C. C. Stoumpos, F. Zheng, T. F. Heinz, L. Kronik, M. G. Kanatzidis, J. S. Owen, A. M. Rappe, M. A. Pimenta, and L. E. Brus, "Local Polar Fluctuations in Lead Halide Perovskite Crystals," *Phys. Rev. Lett.* **118**, 136001 (2017).
4. C. Schüller, T. Korn, C. Nuckolls, J. Hone, L. E. Brus, T. F. Heinz, D. R. Reichman, and A. Chernikov, "Coulomb engineering of the bandgap in 2D materials," *Nature Commun.* **8**, 15251 (2017).
5. Raja, A. Montoya-Castillo, J. Zultak, X. X. Zhang, Z. Ye, C. Roquelet, D. A. Chenet, A. M. van der Zande, P. Huang, S. Jockusch, J. Hone, D. R. Reichman, L. E. Brus and T. F. Heinz, "Energy transfer from quantum dots to graphene and MoS_2 : absorption versus screening," *Nano Lett.* **16**, 2328 (2016).
6. M. Selig, G. Berghuser, A. Raja, P. Nagler, C. Schuller, T. F. Heinz, T. Korn, A. Chernikov, E. Malic, and A. Knorr. "Excitonic linewidth and coherence lifetime in monolayer transition metal dichalcogenides," *Nature Commun.* **7**, 13279 (2016).
7. X.X. Zhang, Y. You, S. Y. F. Zhao, and T. F. Heinz, "Experimental Evidence for Dark Excitons in Monolayer WSe_2 ," *Phys. Rev. Lett.* **115**, 257403 (2015).
8. H. M. Hill, A. F. Rigosi, C. Roquelet, A. Chernikov, T. C. Berkelbach, D. R. Reichman, M. S. Hybertsen, L. E. Brus, and T. F. Heinz, "Observation of Excitonic Rydberg State in Monolayer MoS_2 and WS_2 by Photoluminescence Excitation Spectroscopy," *Nano Lett.* **15**, 2992 - 2997 (2015).
9. Y. You, X. X. Zhang, T. C. Berkelbach, M. S. Hybertsen, D. R. Reichman, and T. F. Heinz, "Observation of Biexcitons in Monolayer WSe_2 ," *Nature Phys.* **11**, 477-481 (2015)
10. A. F. Rigosi, H. M. Hill, Y. Li, A. Chernikov, T. F. Heinz, "Probing Interlayer Interactions in Transition Metal Dichalcogenide Heterostructures by Optical Spectroscopy: MoS_2/WS_2 and $\text{MoSe}_2/\text{WSe}_2$," *Nano Lett.* **15**, 5033-5038 (2015).
11. A. Chernikov, C. Ruppert, H.M. Hill, A.F. Rigosi, T.F. Heinz, "Population inversion and giant bandgap renormalization in atomically thin WS_2 layers," *Nature Photon.* **9**, 466-470 (2015).
12. G. Jnawali, Y. Rao, J.H. Beck, N. Petrone, I. Kymissis, J. Hone, T.F. Heinz, "Observation of Ground- and Excited-State Charge Transfer at the C_{60} /Graphene Interface," *ACS Nano* **9**, 7175-7185 (2015).
13. O. Yaffe, A. Chernikov, Z. M. Norman, Y. Zhong, A. Velauthapillai, A. van der Zande, J. S. Owen, and T. F. Heinz, "Excitons in Ultrathin Organic-Inorganic Perovskite Crystals," *Phys. Rev. B* **92** 045414 (2015)
14. Chernikov, A. M. van der Zande, H. M. Hill, A. F. Rigosi, A. Velauthapillai, J. Hone, and T. F. Heinz, "Electrical Tuning of Exciton Binding Energies in Monolayer WS_2 ," *Phys. Rev. Lett.* **115**, 126802 (2015).

EIM: Excited States in Isolated Molecules

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Project Scope

Our interest is the investigation of elementary chemical processes in isolated molecules on their natural time scale of femtoseconds and picoseconds. We are especially interested in non-Born-Oppenheimer approximation (non-BOA) dynamics, because of its importance for light harvesting, atmospheric chemistry and DNA nucleobases photoprotection. For this purpose, we use time resolved spectroscopy with extreme ultraviolet (EUV) light from laboratory-based high harmonic generation (HHG) and soft x-rays (SXR) from the Linac Coherent Light Source (LCLS). Those techniques allow a site and element specific access to non-BOA dynamics. We complement spectroscopic investigation methods with gas phase ultrafast electron diffraction (UED).

Recent Progress:

We have recently demonstrated that time-resolved near-edge absorption fine structure spectroscopy (TR-NEXAFS) exhibits exquisite and selective sensitivity to electronic structure changes during ultrafast excited state dynamics of organic chromophores. These molecules show resonances in the vicinity of element K edges like the carbon, oxygen, or nitrogen edges, which are due to transitions from a core electron to empty valence orbitals, e.g. π^* orbitals. It is well known from steady-state NEXAFS spectroscopy that the strength of those resonances is strongly dependent on the overlap between the localized element 1s orbital and the empty and more delocalized valence orbital. We employed this well-established concept to investigate excited state dynamics of the nucleobase thymine. Thymine can be excited at 267 nm to a state with $\pi\pi^*$ electronic character. There is a long-standing discussion about the details of the relaxation mechanism of thymine, in particular, if and when it undergoes internal conversion from the $\pi\pi^*$ state through a conical intersection to the $n\pi^*$ state. In comparison to the ground state, the $\pi\pi^*$ state exhibits an electron hole in the π orbital and an additional electron in the π^* orbital. Therefore, by photoexcitation, an additional NEXAFS resonance e.g. from an oxygen 1s orbital to the π orbital below the energy of the ground state π^* resonance is possible. However, due to the high level of delocalization of the π orbital over the whole molecule, its transition strength is negligible. The $n\pi^*$ state is characterized by an electron hole in an n or lone pair orbital with strong localization at one of thymine's oxygens. The corresponding oxygen 1s to n orbital transition strength therefore is orders of magnitude higher. In our TR-NEXAFS investigation of thymine at linac coherent light source (LCLS), we could exploit this effect and unambiguously show that the $n\pi^*$ state is involved in the relaxation mechanism of thymine. It is populated within 60 fs after photoexcitation by internal conversion through a $\pi\pi^*/n\pi^*$ conical intersection. The selective sensitivity of TR-NEXAFS to changes in the electronic character due to $\pi\pi^*/n\pi^*$ conical intersections has broad applicability to organic chromophores containing heteroatoms like oxygen, nitrogen, or sulfur. We complemented our TR-NEXAFS results on thymine with vacuum ultraviolet time-resolved photoelectron spectroscopy. They exhibit detailed information about the fate of excited state population beyond the $\pi\pi^*/n\pi^*$ internal conversion and are currently being analyzed.

We have investigated the ultrafast photoinduced ring opening reaction of the model system 1,3-cyclohexadiene (CHD) with gas phase ultrafast electron diffraction (UED). CHD has been studied with a number of spectroscopy methods in the gas phase and in solution. Those methods probe the electronic wavefunction of the molecule and are highly sensitive to e.g. dynamics through conical intersections (see above). They are, however, only indirectly sensitive to the nuclear wavepacket dynamics leading to the photoinduced structural change. Only one study directly investigating nuclear wavepacket dynamics of CHD with ultrafast x-ray diffraction has been published so far. The unprecedented combination of momentum transfer range and time resolution of SLAC's UED facility allows for a new and detailed structural dynamics perspective on the ring opening reaction of CHD. The instrument response function of 150 fs permits us to follow the reaction in real time. The large momentum transfer range of $> 8 \text{ \AA}^{-1}$ allows for reliable transformation of the diffraction data from momentum transfer space into real space to yield atomic pair distribution functions (PDFs). The photoinduced ring opening reaction leads to a weakening of PDF intensity in the area of the broken C-C bond at 1.5 Å and of additional C-C distances across the CHD ring, which change considerably during ring opening. We observe a corresponding increase of PDF intensity at C-C distances beyond those occurring in the closed CHD ring, which therefore must stem from open ring hexatriene (HT) molecules. We additionally see a time-dependent broadening of this intensity increase from initially 3.5 Å out to larger distances. This proves that we can resolve broadening of the HT nuclear wavepacket to cover several isomers of HT.

Future Plans:

We plan to investigate additional nucleobases using VUV photoelectron spectroscopy and soft x-ray spectroscopy methods.

We want to extend our studies of ultrafast photochemistry at UED. We are specifically interested in studies on further CHD analogs. In collaboration with theorists from PULSE's UTS subtask, we want to study the influence of substituents on the dynamics and develop the experimental setup towards larger molecules.

References

Probing Molecular Photoexcited Dynamics by Soft X-Rays

M. Gühr in: *Ultrafast Dynamics Driven by Intense Light Pulses*, eds.: M. Kitzler S. Graefe (Springer, Heidelberg, 2016).

Peer-Reviewed Publications Resulting from this Project (2015-2017)

The linac coherent light source single particle imaging road map

A. Aquila, A. Barty, C. Bostedt, S. Boutet, G. Carini, D. dePonte, P. Drell, S. Doniach, K. H. Downing, T. Earnest, H. Elmlund, V. Elser, M. Gühr, J. Hajdu, J. Hastings, S. P. Hau-Riege, Z. Huang, E. E. Lattman, F. R. N. C. Maia, S. Marchesini, A. Ourmazd, C. Pellegrini, R. Santra, I. Schlichting, C. Schroer, J. C. H. Spence, I. A. Vartanyants, S. Wakatsuki, W. I. Weis, and G. J. Williams, *Structural Dynamics* 2, 041701 (2015).

A low-cost mirror mount control system for optics setups

M. Gopalakrishnan and M. Gühr, *American Journal of Physics* 83, 186 (2015).

Self referencing heterodyne transient grating spectroscopy with short wavelength

J. Grilj, E. Sistrunk, J. Jeong, M. Samant, A. Gray, H. Dürr, S. Parkin, and M. Gühr, *Photonics* 2, 392 (2015).

Understanding the modulation mechanism in resonance-enhanced multi-photon probing of molecular dynamics

M. Koch, T. J. A. Wolf, and M. Gühr, *Physical Review A* 91, (2015).

MeV Ultrafast Electron Diffraction at SLAC

S. P. Weathersby, G. Brown, M. Centurion, T. F. Chase, R. N. Coffee, J. Corbett, J. P. Eichner, J. Frisch, A. R. Fry, M. Guehr, N. Hartmann, C. Hast, R. Hettel, K. Jobe, E. N. Jongewaard, J. Lewandowski, R. Li, A. M. Lindenberg, I. Makasyuk, J. E. May, D. McCormick, M. N. Nguyen, A. H. M. Reid, X. Shen, K. Sokolowski-Tinten, T. Vecchione, S. L. Vetter, J. Wu, J. Yang, H. Durr, X. Wang, *Rev. Sci. Instr.* 86, 073702 (2015).

Ultrafast Isomerization Initiated by X-Ray Core Ionization

C. Liekhus-Schmaltz, I. Tenney, T. Osipov, A. Sanchez-Gonzalez, N. Berrah, R. Boll, C. Bomme, Ch. Bostedt, J. Bozek, S. Carron, R. Coffee, J. Devin, B. Erk, K. Ferguson, R. Field, L. Foucar, L. Frasinski, J. Glowia, M. Guehr, A. Kamalov, J. Krzywinski, H. Li, J. Marangos, T. Martinez, B. McFarland, S. Miyabe, B. Murphy, A. Natan, D. Rolles, A. Rudenko, M. Siano, E. Simpson, L. Spector, M. Swiggers, D. Walke, S. Wang, Th. Weber, P. Bucksbaum, V. Petrovic, *Nature Comm.* 6, 8199 (2015).

Auger electron and photoabsorption spectra of glycine in the vicinity of the oxygen K-edge measured with an X-FEL

A. Sanchez-Gonzalez, T. R. Barillot, R. J. Squibb, P. Kolorenč, M. Agaker, V. Averbukh, M. J. Bearpark, C. Bostedt, J. D. Bozek, S. Bruce, S. Carron Montero, R. N. Coffee, B. Cooper, J. P. Cryan, M. Dong, J. H. D. Eland, L. Fang, H. Fukuzawa, M. Guehr, M. Ilchen, A. S. Johnsson, C. Liekhus-Schmaltz, A. Marinelli, T. Maxwell, K. Motomura, M. Mucke, A. Natan, T. Osipov, C. Östlin, M. Pernpointner, V. S. Petrovic, M. A. Robb, C. Sathe, E. R. Simpson, J. G. Underwood, M. Vacher, D. J. Walke, T. J. A. Wolf, V. Zhaunerchyk, J.-E. Rubensson, N. Berrah, P. H. Bucksbaum, K. Ueda, R. Feifel, L. J. Frasinski, J. P. Marangos *J. Phys. A* 48, 234004 (2015).

Femtosecond X-ray-induced fragmentation of fullerenes

N. Berrah, B. Murphy, H. Xiong, L. Fang, T. Osipov, E. Kukk, M. Guehr, R. Feifel, V.S. Petrovic, K.R. Fergusond, J.D. Bozek, C. Bostedt, L.J. Frasinski, P.H. Bucksbaum, J.C. Castagna, *J. Mod. Opt.*, 63, 390 (2015).

Broadband Extreme Ultraviolet Probing of Transient Gratings in Vanadium Dioxide

E. Sistrunk, J. Grilj, J. Jeong, M. G. Samant, A. X. Gray, H. A. Dürr, S. S. P. Parkin, and M. Gühr, *Optics Express* 23, 4340 (2015).

Extreme ultraviolet spectrometer based on a transmission electron microscopy grid

E. Sistrunk and M. Gühr, *Journal of Optics* 17, 015502 (2015).

Ultrafast Dynamics of o-Nitrophenol: An Experimental and Theoretical Study

H. A. Ernst, T. J. A. Wolf, O. Schalk, N. González-García, A. E. Boguslavskiy, A. Stolow, M. Olzmann, A.-N. Unterreiner, *J. Phys. Chem. A* 119, 9225 (2015).

Disentangling formation of multiple-core holes in aminophenol molecules exposed to bright X-FEL radiation

Zhaunerchyk, V., Kamińska, M., Mucke, M., Squibb, R.J., Eland, J.H.D., Piancastelli, M.N., Frasinski, L.J., Grilj, J., Koch, M., McFarland, B.K., Sistrunk, E., Gühr, M., Coffee, R.N., Bostedt, C., Bozek, J.D., Salén, P., Meulen, P. v d, Linusson, P., Thomas, R.D., Larsson, M., Foucar, L., Ullrich, J., Motomura, K., Mondal, S., Ueda, K., Richter, R., Prince, K.C., Takahashi, O., Osipov, T., Fang, L., Murphy, B.F., Berrah, N., Feifel, R., *J. Phys. A* 48, 244003 (2015).

Femtosecond gas phase electron diffraction with MeV electrons

J. Yang, M. Guehr, T. Vecchione, M. S. Robinson, R. Li, N. Hartmann, X. Shen, R. Coffee, J. Corbett, A. Fry, K. Gaffney, T. Gorkhover, C. Hast, K. Jobe, I. Makasyuk, A. Reid, J. S. Robinson, S. Vetter, F. Wang, S. Weathersby, C. Yoneda, M. Centurion, X. Wang, *Faraday Discuss.* 194, 563 (2016).

Monitoring Ultrafast Chemical Dynamics by Time-Domain X-ray Photo- and Auger-Electron Spectroscopy

O. Gessner and M. Gühr, *Acc. Chem. Res.* 49, 138 (2016).

Diffraction imaging of a rotational wavepacket in nitrogen molecules with femtosecond megaelectronvolt electron pulses

J. Yang, M. Guehr, T. Vecchione, M. S. Robinson, R. Li, N. Hartmann, X. Shen, R. Coffee, J. Corbett, A. Fry, K. Gaffney, T. Gorkhover, C. Hast, K. Jobe, I. Makasyuk, A. Reid, J. S. Robinson, S. Vetter, F. Wang, S. Weathersby, C. Yoneda, M. Centurion, X. Wang, *Nature Comm.* 7, 11232 (2016).

Diffraction Imaging of Coherent Nuclear Motion in Isolated Molecules

J. Yang, M. Guehr, X. Shen, R. Li, T. Vecchione, R. Coffee, J. Corbett, A. Fry, N. Hartmann, C. Hast, K. Hegazy, K. Jobe, I. Makasyuk, J. Robinson, M. S. Robinson, S. Vetter, S. Weathersby, C. Yoneda, X. Wang, M. Centurion, *Phys. Rev. Lett.* 115, 173002 (2016).

The Role of Super-Atom Molecular Orbitals in Doped Fullerenes in a Femtosecond Intense Laser Field

H. Xiong, B. Mignolet, L. Fang, T. Osipov, T. J. A. Wolf, E. Sistrunk, M. Gühr, F. Remacle, N. Berrah *Sci. Rep.* 7, 121 (2017).

Emitter-site selective photoelectron circular dichroism of trifluoromethyloxirane

M. Ilchen, G. Hartmann, P. Rupprecht, A. N. Artemyev, R. N. Coffee, Z. Li, H. Ohldag, H. Ogasawara, T. Osipov, D. Ray, Ph. Schmidt, T. J. A. Wolf, A. Ehresmann, S. Moeller, A. Knie, Ph. V. Demekhin *Phys. Rev. A* 95, 053423 (2017).

Probing ultrafast $\pi\pi^*/n\pi^*$ internal conversion in organic chromophores via K-edge resonant absorption

T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch, M. Gühr, *Nature Comm.*, 8, 29 (2017).

Observing Femtosecond Fragmentation Using Ultrafast X-ray-Induced Auger Spectra

T. J. A. Wolf, F. Holzmeier, I. Wagner, N. Berrah, C. Bostedt, J. Bozek, P. Bucksbaum, R. Coffee, J. Cryan, J. Farrell, R. Feifel, T. J. Martinez, B. McFarland, M. Mucke, S. Nandi, F. Tarantelli, I. Fischer, M. Gühr, *Appl. Sci.* 7, 681 (2017).

Soft-x-ray-induced ionization and fragmentation dynamics of Sc₃N@C₈₀ investigated using an ion-ion-coincidence momentum-imaging technique

H. Xiong, R. Obaid, L. Fang, C. Bomme, N. G. Kling, U. Ablikim, V. Petrovic, C. E. Liekhus-Schmaltz, H. Li, R. C. Bilodeau, T. Wolf, T. Osipov, D. Rolles, N. Berrah, *Phys. Rev. A* 96, 033408 (2017).

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Early Career: Strongly-driven attosecond electron-dynamics in periodic media

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Project Scope

Following the discovery of high order harmonic generation (HHG) [Ghimire2011] there has been growing interest in understanding and exploiting condensed phase strong-field physics. Our particular interest is to understand the similarities and differences to the fundamental strong-field response in isolated atoms and molecules, in part because of the prior success in exploiting strong-field dynamics in atoms and molecules. Main fundamental questions we are trying to address in this project are: (i) could harmonics be the atomic-scale probe of generating medium similar to the gas phase, (ii) what is the respective role of high-density and periodicity that may be present in dense optical media, and (iii) how does the temporal structure of HHG look like, focusing on its suitability for attosecond pulse metrology. Unlike the atomic case, HHG from dense optical media involve multiple mechanisms; radiation from pure intraband non-linear current and the emission from interband non-linear current, and there is an escalated debate in the community in determining their relative roles [e.g. Ghimire2012, Vampa2015]. The scope of this project is to provide answers to several key questions on this topic, and test the suitability of high-harmonics from bulk optical media for viewing the condensed phase structure and dynamics with atomic (space and time) resolution.

Recent progress

1. Time-domain investigation of HHG:

We control high-harmonic generation process using strong, two-cycle, near infrared laser pulses, whose carrier-envelope-phase (CEP) offset can be adjusted [You2017b]. This control allows us to probe intrinsic delay between high-order harmonics, which originates in the microscopic generation process. Theory predicts that the generation from single band nonlinear current does not exhibit sub-cycle delay between high harmonics, however inter-band processes would result into phase delayed harmonics [Wu2015]. In order to see this effect directly in the harmonic spectrum one has to use few-cycle driving pulse. In the few-cycle limit, the inter-band emission from subsequent half-cycle would have different spectral phase. Therefore, if the generation mechanism is an inter-band process, we expect that photon energy of harmonic peaks change as a function of the CEP of the driving laser pulse.

In the experiments, high-order harmonics are produced from MgO using two-cycle laser pulses of peak strength $\sim 2 \text{ V/\AA}$ at 1700 nm. As we scan the CEP we find that the photon energy of harmonic peaks increase (called CEP slope from here), as shown in figure 1 at top row. We reproduce the harmonic spectrum and its measured CEP dependence by solving time dependent schrödinger equation (TESE) for strongly driven three-level system that originates at the Gamma point in the important bands (VB, CB1 and CB2 as shown in the DFT results in the right). The harmonic spectrum from single band current would not shift in the photon energy but would rather show a monotonic CEP dependence (as seen in crystalline SiO₂ in section 2). Therefore, our analysis shows strong evidence that the dominating mechanism for generation of high-harmonics from MgO in extreme ultraviolet (XUV) range is the driven inter-band dynamics.

At moderate peak fields only two bands (VB and CB1) couple, giving rise to a primary plateau in harmonic spectrum (Figure 1 a). However, at the highest peak fields higher-lying band (such as CB2) get involved, producing secondary plateau (Figure 1b and 1c), similar to our previous study in condensed phase Ar and Kr [Ndabahimiye2016]. The strong CEP dependence is

seen even in the secondary plateau suggesting that the high-lying conduction bands are also

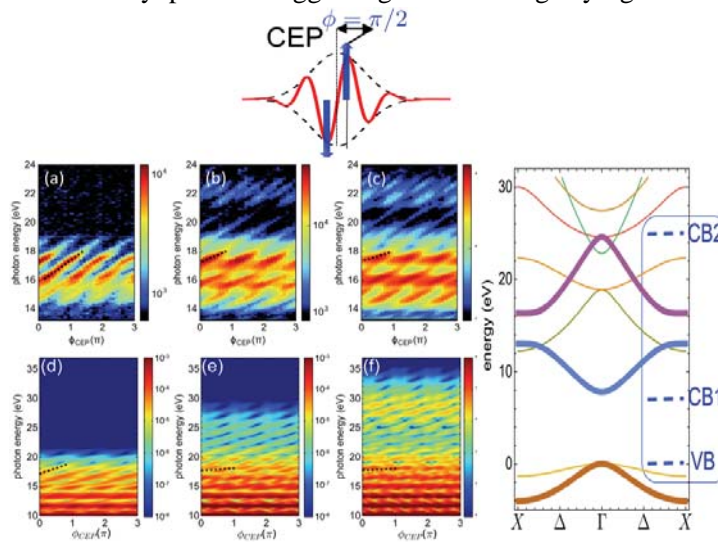


Figure 1 Top sub-figure illustrates carrier-envelope phase (CEP) offset. **a**, **b**, and **c** are measured high harmonic spectra from MgO as a function of CEP setting at 1.2, 1.7 and 2.1 V/Å respectively. Dashed line tracks the photon energy of a harmonic peak, CEP slope. The amplitude of CEP slope decreases with the increase in peak field. **d**, **e**, and **f** are TDSE calculation results using three-levels corresponding to three important bands of MgO labeled VB, CB1 and CB2 in the band-structure on the right.

populated in the sub-cycle time-scale. Therefore, our results show that high harmonics could probe strong-field driven condensed phase, attosecond multi-band dynamics in high-density optical media.

2. Role of atomic-scale periodicity in HHG:

We investigate the fundamental role of atomic-scale periodicity to the strong-field response in dense optical media. The outstanding questions we try to address in this project are; how does the microscopic picture of atomic HHG break down when the atoms are closely packed? And, what happens if the atomic arrangements have any particular order? We excite an amorphous (random collection) and a crystalline (perfectly periodic) SiO₂ using intense, ultra-short, near infrared laser pulses, whose peak intensity is around 10¹⁴ W/cm².

We discovered that both targets produce high-harmonics with spectrum extending to about 25 eV, but with markedly different characteristics. As shown in figure 2a and 2b, they are very different in terms of the generation efficiency, spectral features, and their dependence to the CEP. Amorphous SiO₂ has lower efficiency. It exhibits sub-cycle atto-chirp, as seen from the CEP slope. However, harmonics from crystalline SiO₂ show no apparent shift in the photon energy, but show enhanced generations at particular CEP values, consistent to chirp-free emission. To model our results, we solve time-dependent Schrödinger equations in a multi-level system. For amorphous SiO₂, we consider a simple two-level system, where the separation corresponds to the experimental band gap ~9 eV. Figure 2c and 2d show the simulation results, which reproduce the experimentally observed CEP slope and appropriate CEP periodicity. For crystalline SiO₂, we use a three-level system including a permanent dipole term to account for non-centrosymmetry. We reproduce the dominant monotonic 2π periodicity along with the spectral minima (at around 18 eV) that is independent of the CEP settings.

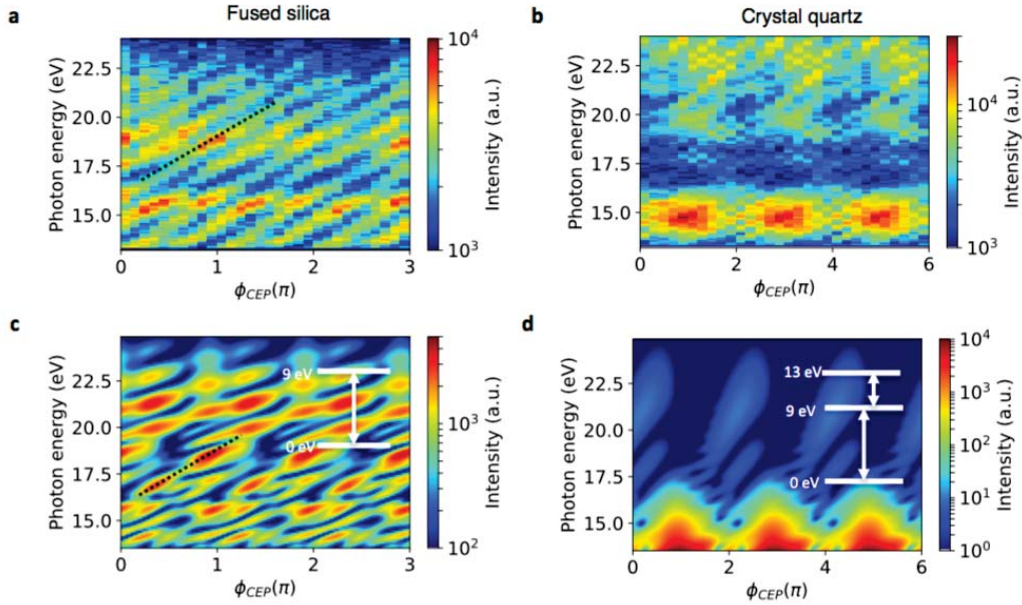


Figure 2 Measured CEP-dependence of high harmonic spectrum from (a) fused and (b) crystalline SiO_2 at 2 V/\AA and 1700 nm . The dashed black line is CEP slope. (c) and (d) show calculated spectrum from a quantum mechanical simulations with insets showing respective energy levels. The simulation results reproduce the periodicity and CEP slope observed in experiments.

The observed differences between amorphous and crystalline SiO_2 indicate strongly that high-harmonics are potentially useful for probing inter-atomic electron scattering processes in the condensed media. At above described laser conditions (1700 nm and 2 V/\AA), we expect that driven electron traverses tens of lattice distances (considering the propagation in vacuum). Therefore, in amorphous SiO_2 electron could decohere quickly, consistent to the lower efficiency. In contrast, at shorter wavelength excitations (such as at 800 nm and 1 V/\AA), the estimated excursion distances are small, just about the size of the unit cell, so the electron would not decohere very quickly even in amorphous SiO_2 . This hypothesis is consistent to our observation of similar efficiencies in crystalline and amorphous SiO_2 at 800 nm . Therefore, our results suggest that electron scattering processes are either coherent (/elastic) or largely incoherent depending on if the generation media exhibits medium and long-range periodicity.

The implications of fundamental response of long-range periodicity are in all-optical approach to image optical media at atomic scales. This is a potentially new type of imaging capability complimentary to the standard, but significantly more complex x-ray diffraction methods. The advantage of utilizing novel strong-field response is the possibility of viewing dynamics (e.g. electron decoherence effects) in the condensed phase with attosecond and femtosecond time resolution. Finally, for XUV photonics, our results show that high-harmonics can be produced even in ordinary glass, the most abundant optical media, which opens up the possibility of potentially easy way of producing attosecond pulses, in fiber based compact table-top setup.

Future Plans

Next items include analysis of polarization of high-harmonics, understanding propagation effects, and time-domain control using a pump probe scheme so multi-step processes can be decoupled. Understanding propagation effects include comparison to HHG in reflection

geometry. One of the goals of time-domain control is to understand detail of electron decoherence effect. Our particular interest on this experiment is to perform comparative measurements between the condensed and the gas phase. Finally, we will control HHG process through mixed rare gas solids such that the potential of high harmonic spectroscopy in the condensed phase can be fully exploited.

We continue to collaborate with *Reis* group, *Heinz* group and *LCLS laser* group in nonlinear x-ray science, nano-scale electron dynamics, and development of high-intensity mid-infrared laser system, respectively. To confirm the results of all-optical experiments from [You2017c], we plan X-ray diffraction experiments at LCLS and SACLA, together with *Reis* group and other PULSE affiliates. For CEP experiments, we benefit from the expertise of *Zenghu Chang* group at UCF. In the future, with help of LCLS laser group, we plan to develop similar capabilities at SLAC.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. [You2017a] Yong Sing You, Yanchun Yin, Yi Wu, Fengjiang Zhuang, Andrew Chew, Xiaoming Ren, Shima Gholam-Mirzaei, Michael Chini, Zenghu Chang, and Shambhu Ghimire, “High-harmonic generation in amorphous solids”, <https://arxiv.org/abs/1705.07854>, accepted by Nature Communications, (2017).
2. [You2017b] Yong Sing You, Mengxi Wu, Yanchun Yin, Andrew Chew, Xiaoming Ren, Shima Gholam-Mirzaei, Dana A. Browne, Michael Chini, Zenghu Chang, Kenneth J. Schafer, Mette B. Gaarde and Shambhu Ghimire, “Laser waveform control of extreme ultraviolet high harmonic generation in solids”, *Optics Letters* **42**, 9, (2017)
3. [You2017c] Yong Sing You, David A. Reis, and Shambhu Ghimire, “Anisotropic high harmonic generation in bulk crystals”, *Nature Physics* **13**, 345-349, (2017)
4. [Liu2017] Hanzhe Liu, Yilei Li, Yong Sing You, Shambhu Ghimire, Tony F. Heinz, and David A. Reis, “Observation of high harmonics from an atomically thin semiconductor”, *Nature Physics* **13**, 262, (2017).
5. [Ndabashimiye2016] Georges Ndabashimiye, Shambhu Ghimire, Mengxi Wu, Dana A. Browne, Kenneth J. Schafer, Mette B. Gaarde, David A. Reis “Solid-state harmonics beyond the atomic limit”, *Nature* **534**, 520, (2016).
6. [Wu2015] Mengxi Wu, Shambhu Ghimire, David A. Reis, Ken J. Schafer, and Mette B. Gaarde. “High-harmonic generation from Bloch electrons in solids” *Physical Review A*, **91**(4):043839, (2015).

References

[Corkum1993] Corkum, P. “Plasma perspective on strong field multiphoton ionization” *Phys. Rev. Lett.* **71**, 1994–1997 (1993). [Ghimire2011] Ghimire, S. *et al.* “Observation of high-order harmonic generation in a bulk crystal” *Nat. Phys.* **7**, 138–141 (2011). [Ghimire2012] Ghimire, S. *et al.* “Generation and propagation of high-order harmonics in crystals” *Phys. Rev. A* **85**, 043836 (2012). [Vampa2015] Vampa, G. *et al.* “Linking high harmonics from gases and solids” *Nature* **522**, 462–464 (2015)

University Research Summaries
(by PI)

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Early Career: Ultrafast Dynamics of Molecules on Surfaces Studied with Time-Resolved XUV Photoelectron Spectroscopy

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Project Scope

The capture and storage of solar energy involves the separation and steering of electrons and holes created by the absorption of light. In dye-sensitized solar cells, electrons are injected from a photo-excited dye molecule into a semiconductor. In heterogeneous photo-catalysis, excitation of the electrons in a solid can cause reactions on the surface, storing the photon's energy in chemical bonds. In both cases, the dynamics of charge separation and subsequent reactions are complex and often involve multiple intermediate states. The objective of this work is to provide important fundamental insight into these dynamics using time-resolved photoelectron spectroscopy to track the motion of electrons, holes, and nuclei at molecule/semiconductor interfaces.

Recent Progress

Photoemission spectroscopy using synchrotron radiation is one of the most important methods for establishing relationships between structural and electronic properties at surfaces, with core and valence level shifts providing information about charge transfer, electronic screening, and the geometrical structure of molecules at surfaces. The quasi-CW nature of synchrotron radiation (~ 100 ps pulses at MHz repetition rates), which produces few photoelectrons per pulse, is essential for surface experiments where electrons emerge from a small volume of space at the surface, and space charge/image charge effects can blur and shift the photoelectron spectrum.

Many attempts to extend XUV photoemission spectroscopy to the ultrafast time domain using either high-order harmonic generation (HHG) from femtosecond lasers or x-ray pulses from free electron lasers have encountered limitations due to low repetition rates, limited average flux, and space charge/image charge effects. The ideal XUV light source for extending photoemission techniques to the time domain would have the flux and duty cycle characteristics of a synchrotron, but with ultrashort pulse durations.

At Stony Brook, we have been working to develop this ideal instrument based on cavity-enhanced high-order harmonic generation and apply it to surface dynamics. An overview of the system appears in our last abstract (fall 2016). We had several setbacks in Fall 2016, such as vacuum pump and electronics failures. Since that time, we restored regular operation of the system and have made progress on the following items:

- We have achieved 7 times higher flux than we reported previously, now delivering to the sample 7×10^{11} photons/second in a single harmonic measured at the exit slit of our time-preserving monochromator.
- We've run our buildup cavity at higher power to achieve HHG in Argon and produced XUV light out to 40 eV photon energies. These higher photon energies help separate the primary photoemission signals of interest from inelastic background and also give better surface sensitivity. Running the HHG system with Argon gas instead of Krypton gas also decreases the operating costs significantly. See figure 1 for a comparison of Argon and Krypton HHG results.

- We have compressed our fiber laser pulses to 70 fs (starting from 155 fs) at high power using a combination of spectral broadening in a sapphire plate and chirped mirrors.
- We completed the installation of our new UHV mirror tank (see 2016 report) with electrically floating toroidal mirror and successfully implemented measuring the mirror photocurrent as a routine beamline diagnostic.
- We have re-positioned and aligned the final toroidal focusing mirror to eliminate coma and achieve a $56 \times 97 \mu\text{m}$ (FWHM) spot size at the sample. See figure 2 for an image of the beam on a Ce:YAG scintillator at the sample plane.
- We upgraded the fiber amplifier protection interlock system to an FPGA-based system for better reliability and easier configuration.
- We installed a heated doser assembly on our surface science chamber for in-situ deposition of films of low vapor pressure molecules.
- The PI has obtained internal funding (Stony Brook Discovery Prize) to implement a new momentum resolving time-of-flight detector on our endstation which will increase the detection efficiency (and thus data rate) for electrons and holes near the Fermi edge by more than three orders of magnitude. The new detector will also have much higher energy and momentum resolution than our current single energy/single angle hemispherical analyzer. We have started a collaboration with another research group specializing in these detectors to develop the system over the next year.

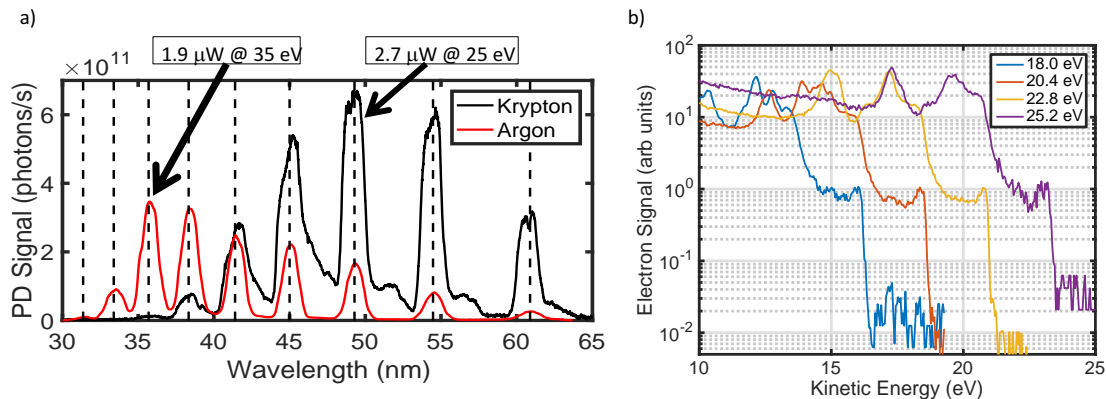


Figure 1: **HHG and photoemission.** a) High-order harmonics between 10 and 40 eV photon energies are generated at the focus of a 6 mirror bow-tie cavity and coupled out of the cavity using a sapphire wafer at Brewster's angle. Shown in the figure are spectra of harmonics generated in Ar and Kr gas jets, recorded using an Al coated XUV photodiode as the monochromator grating angle is rotated. Absolute photon numbers were calculated from the measured photocurrent and the photodiode manufacturer's quantum efficiency. The spectral widths are determined by the low resolution of the time-preserving monochromator. b) Photoelectron spectra recorded from a gold surface using different harmonic orders. The legend indicates the photon energy and the Fermi edge shifts by 2.4 eV for each harmonic order.

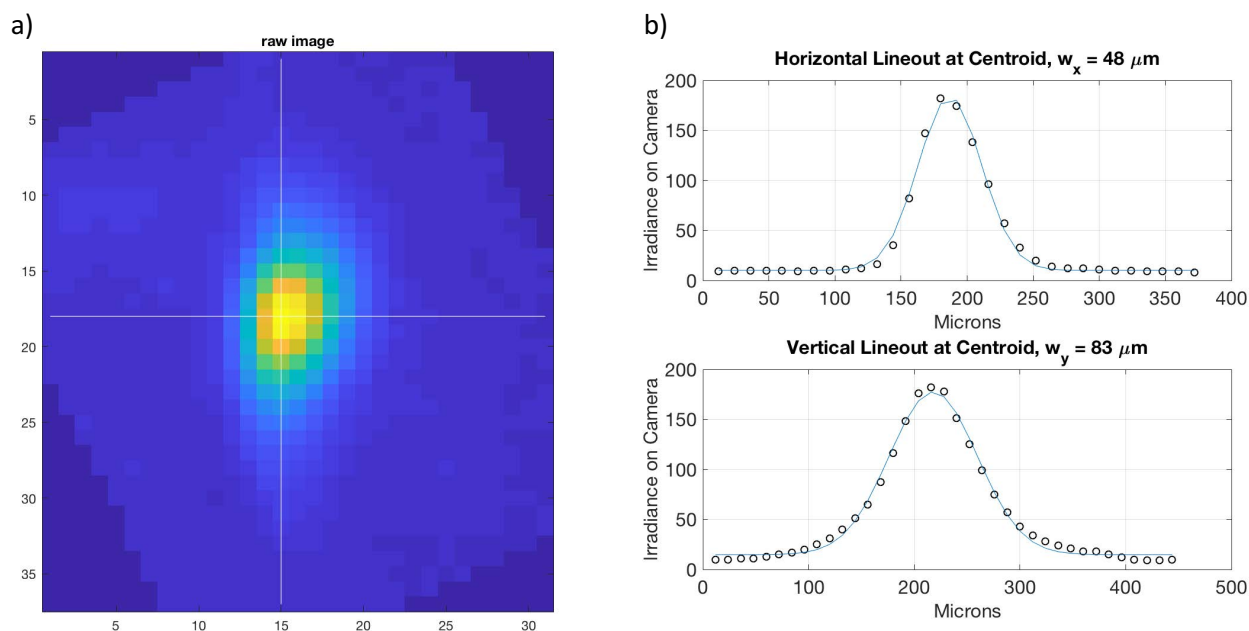


Figure 2: **Optimized spot size.** a) Image of a Ce:YAG scintillator placed at the sample plane illuminated with the 27th harmonic ($h\nu = 32$ eV). b) Lineouts in x and y from the beam centroid using the calibration of $12 \mu\text{m}$ per pixel along with Gaussian fits.

Future Plans

In addition to preparing for the major upgrade to the electron energy analyzer, we are preparing a publication regarding our photoemission instrument to be submitted this fall [1]. In parallel, we are characterizing the deposition of molecular films on Au and TiO_2 surfaces for time-resolved photoemission experiments.

[1] C. Corder, P. Zhao, J. Bakalis, X. L. Li, and T. K. Allison. “Tunable laser-based XUV photoemission without space charge.” In Preparation.

Peer-Reviewed Publications Resulting from this Project (Start Date 07/2016)

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Attosecond dynamics in molecules driven by ultrashort laser pulses

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Project Scope

The application of high intensity laser systems has been closely linked to research in ultrafast science and the development of ultrafast optical techniques since laser pulses have been generated with shorter and shorter pulse durations. Substantial progress in the understanding and controlling of electron dynamics in the highly nonlinear process of harmonic generation throughout the last 15 years has been the gateway to the creation of the shortest pulse durations available today. These controlled electron dynamics over a sub-cycle of the driving laser pulse enables the emission of coherent light at extreme ultraviolet and soft X-ray wavelengths on a sub-optical cycle time scale, i.e. on a sub-femtosecond time scale. With this technological advance comes the ability to shift the frontier of temporal resolution of dynamical processes to the time scale of electron dynamics, which ultimately determines the structure of matter as well as the outcome of chemical reactions. The natural time scale of electron dynamics is given by the atomic unit of time, which is 24 attoseconds ($1 \text{ as} = 10^{-18} \text{ s}$). With our projects, we seek to provide theoretical support related to the establishment of ultrafast optical techniques as a tool to uncover new insights regarding the attosecond electron dynamics in atoms and molecules.

Our research plan is focused on two areas in attosecond science. First, we perform theoretical studies on the application and interpretation of the attosecond streaking technique which enables the retrieval of temporal information of ultrafast processes. Using ab-initio numerical solutions of the time-dependent Schrodinger equation we intend to analyze how temporal aspects of the dynamic coupling between electrons and nuclei can be retrieved from streaking measurements. This includes the task to establish strategies to identify contributions to the measured time delays during different steps of the photoemission process as well as to develop efficient analytical and numerical techniques for the calculations of the time delays. In the second research thrust we aim to study and identify features of the laser induced nonadiabatic electron dynamics in molecules using observables such as high harmonic and photoelectron energy spectra. The response of molecules to a strong electric field is complicated beyond the atomic picture by the addition of rotational and vibrational degrees of freedom, a multi-center nuclear frame, and a more complex electronic energy level structure. Strong field ionization and fragmentation from molecular targets can be significantly altered from expectations informed by quasistatic or cycle-averaged formulations of electron dynamics. We intend to extend with our studies the application of these traditional spectroscopic techniques towards mapping dynamical phenomena occurring within an ultrashort window onto the spectra.

Recent Progress

Recent developments undertaken and accomplishments completed in the research thrusts can be summarized as follows.

A. Application of Attosecond Streaking Technique

Attosecond streaking is one of the popular methods to capture temporal dynamics of ultrafast electronic processes such as photoionization. In the streak camera principle [1] the

photoelectron, liberated into the continuum by an attosecond pulse, experiences a momentum shift due to the presence of a second near-infrared laser pulse. Since the magnitude of the shift depends on the vector potential at the time of ionization and the subsequent propagation of the electron wave packet, spectroscopic and timing information can be retrieved.

A.1 Resonant vs. non-resonant two-photon ionization

We have extended our studies of the streaking of two-photon ionization by determining the absorption time delay [2], which accounts for the delay between the subsequent absorption of the two photons during the transition of the photoelectron from the ground state into the continuum. To this end, we have used perturbation theory to obtain an analytical formula for the absorption delay in the case of a single intermediate resonance [3]. Predictions of the model formula, at central frequencies that are resonant and nonresonant with the first excited state of a target system, are in good agreement with our ab-initio numerical streaking simulations. Furthermore, it is shown that the absorption time delay can accurately be obtained, independent of the parameters of the applied streaking pulse. The results provide new insights into the options how to use the streak camera technique as spectroscopic tool, e.g. concerning the disentanglement and understanding of the different contributions to the streaking time delay in two-photon absorption.

A.2 Effect of attochirp

Recent observations [4] suggest that streaking measurements can be incorrectly interpreted if the chirp of the attosecond pulse used is not taken into account. It is expected that the observed streaking time delay will depend on the contributions from photoelectrons emitted with different energies at different times during the chirped pulse. To study how strong this effect is we have first developed an analytical model for the streaking time delay in photoionization of atoms. In the derivation we have made use of the fact that the time delay depends on the propagation of the photoelectron over a finite range in space [5]. Application of the analytical estimates gave insights into the effect of the streaking field on the short range, Coulomb phase and logarithmic terms in the field-free time delay. Additionally, it provided an alternative justification of the widely used analysis of the streaking time delay as a sum of Wigner-Smith time delay and Coulomb-laser coupling term.

Since the model predictions are found to be in excellent agreement with results of ab-initio numerical calculations [6] we used the model to study the effect of the attochirp on the intrinsic time delay in experiments over a broad range of parameters. Our results show that the effect of the chirp is only significant if the photoionization cross section changes rapidly as a function of the photon energy [7]. On the other hand, if the photoionization cross section of the target subshell varies smoothly, the effect of the attochirp is found negligible. A prominent example for a rapid change is the region around a Cooper minimum in heavier noble gas atoms. Consequently, controlling the attochirp in the experiment can be used to map this effect as a function of photon energy.

B. Single-active-electron calculations: Role of potential and energy spectrum

In the regime of strong-field physics it is common to use the single-active-electron approximation to a multielectron system, in which one electron responds to the influence of the external field while the rest of the electrons are considered as frozen. We have developed and tested a new strategy to obtain so-called single active electron potentials by fitting numerical pseudopotentials, based on DFT calculations (within the so-called Optimized Effective Potential (OEP) approximation), to a concise analytic expression which was physically grounded in the structure of the exchange-correlation component of the full potential. We previously reported that structures, such as the Cooper minimum, in HHG spectra of noble gas atom can be

reproduced. We have extended these studies and found that the position of the minimum and other features in the HHG spectrum strongly depend on the exact form of the potential, the details of the ground as well as excited state wavefunctions within the potential. In simulations of ultrafast processes in heavier atoms (and larger molecules) it is therefore required to represent the numerical solutions of the time-dependent Schrodinger equation on a large grid with fine spacing in time and space. We are in the process to develop mathematical and numerical techniques utilizing higher-order propagation schemes and propagation on non-uniform grids to perform efficient calculations for atoms, which include the resolution of population in highly excited states during the pulse.

C. High-Harmonic Spectroscopy of Nonadiabatic Electron Dynamics

We have extended our studies on how nonadiabatic electron dynamics in molecules [DOE4] effects observables in strong-field processes in two directions [DOE5]: First, we have asked the question what form the previously determined effects of transient electron localization upon the structure of the high harmonic spectrum [DOE3] has in the time domain of the process. We have found that the generated attosecond pulse train shows deep amplitude modulations in form of a double peak structure, while the overall width of each pulse remains unchanged. Consequently, nonadiabatic electron dynamics can be also read from the structure of the attosecond pulses emitted from systems undergoing transient localization. Second, we have studied to which extent the previously analyzed structural changes (minimum and interference structure) in the high energy part of the harmonic spectrum can be detected in a realistic experimental scenario. To this end, we have investigated the phase mismatch accumulated in a macroscopic gas jet. The results show that the coherence lengths, both for longitudinal and transversal phase matching, are sufficient to enable the detection of the transient localization signatures.

Future Plans

Looking forward, we plan to continue our efforts concerning the theoretical studies of the physics and application of ultrafast spectroscopic techniques using ab-initio numerical simulations and analytical models. It is our goal to apply our advanced understanding of the different contributions to the streaking time delay for two-photon ionization. It is anticipated that our analysis of the temporal resolution of resonant and nonresonant transitions will allow us to understand how to obtain and interpret the full spectroscopic information from a streaking delay simulation (measurement) in different atoms and simple molecules. Numerical calculations of streaking time delay simulations for helium atom and hydrogen molecular ion have been performed and the so-called absorption time delay, which contains the relevant information, has been retrieved. As outlined previously, few-photon transitions as well as the extension to molecular photoionization including nuclear motion will be undertaken as the following next steps.

Our studies concerning the observation of nonadiabatic electron dynamics have revealed several features in high harmonic spectra as well as the formation of attosecond pulses that reflect not only the effects but also the option to detect changes on an ultrafast time scale. We therefore intend to continue to shift our focus towards the study of other spectroscopic tools in the time domain (such as transient absorption spectroscopy, or Fourier transform spectroscopy [DOE6]) via ab-initio simulations. Our special attention will be on the application in the heavier noble gas atoms, which on the one hand are relevant regarding experimental observations and on the other hand offer the impulse to overcome challenges in time-dependent ab-initio calculations on a large space-time grid along the lines outlined above.

References

- [1] J. Itatani et al., Phys. Rev. Lett. **88**, 173903 (2002).
- [2] J. Su, H. Ni, A. Jaron-Becker, and A. Becker, Phys. Rev. Lett. **113**, 263002 (2014).
- [3] C. Goldsmith, A. Jaron-Becker and A. Becker, submitted for publication.
- [4] M. Sabbar et al., Phys. Rev. Lett. **115**, 133001 (2015).
- [5] J. Su, H. Ni, A. Becker and A. Jaron-Becker, Phys. Rev. A **88**, 023413 (2013).
- [6] C. Goldsmith, A. Becker and A. Jaron-Becker, submitted for publication.
- [7] C. Goldsmith, A. Jaron-Becker and A. Becker, submitted for publication.
- [8] N. Takemoto and A. Becker, Phys. Rev. Lett. **105**, 203004 (2010).

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [DOE1] D.D. Hickstein, F.J. Dollar, P. Grychtol, J.L. Ellis, R. Knut, C. Hernández-García, D. Zusin, C. Gentry, J.M. Shaw, T. Fan, K.M. Dorney, A. Becker, A. Jaron-Becker, H.C. Kapteyn, M.M. Murnane, and C.G. Durfee, *Noncollinear generation of angularly isolated circularly polarized high harmonics*, Nature Photonics **9**, 743 (2015).
- [DOE2] D. Popmintchev, C. Hernández-García, F. Dollar, C. Mancuso, J.A. Pérez-Hernández, M.-C. Chen, A. Hankla, X. Gao, B. Shim, A. Gaeta, M. Tarazkar, D. Romanov, R. Levis, J.A. Gaffney, M. Ford, S.B. Libby, A. Jaron-Becker, A. Becker, L. Plaja, M.M. Murnane, H.C. Kapteyn, and T. Popmintchev, *Efficient soft X-ray high harmonic generation in multiply-ionized plasmas: the ultraviolet surprise*, Science **350**, 1225 (2015).
- [DOE3] M.R. Miller, A. Jaron-Becker, and A. Becker, *High-harmonic spectroscopy of laser driven nonadiabatic electron dynamics in the hydrogen molecular ion*, Physical Review A **93**, 013406 (2016).
- [DOE4] M.R. Miller, Y. Xia, A. Becker and A. Jaron-Becker, *Laser driven nonadiabatic electron dynamics in molecules*, Optica **3**, 259-269 (2016).
- [DOE5] M.R. Miller, A. Jaron-Becker and A. Becker, *Signatures of transient electron localization in high-order harmonic generation*, Molecular Physics **115**, 1758 (2017).
- [DOE6] A. Jaron-Becker and A. Becker, *Attosecond Spectroscopy*, Encyclopedia of Modern Optics (in press).

Molecular Dynamics Imaging from Within at the Femto- and Atto-Second Timescale using FELs

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Project Scope

The goal of our research program is to investigate *fundamental interactions between photons and molecular systems* to advance our quantitative understanding of electron correlations, charge transfer and many body phenomena. Our research investigations focus on probing, on femtosecond time-scale, multi-electron interactions, and tracing nuclear motion in order to understand and ultimately control energy and charge transfer processes from electromagnetic radiation to matter. Most of our work is carried out in a strong partnership with theorists.

Our current interests include: **1)** The study of non-linear and strong field phenomena, particularly in the soft x-ray and x-ray regime using free electron lasers (FELs), such as the ultrafast linac coherent light source (LCLS) x-ray FEL facility at the SLAC National Laboratory. We have also recently used IR lasers to prepare our FELs experiments with the added benefit of comparing multi-photon ionization dynamics in the IR and x-ray regimes. **2)** Time-resolved molecular dynamics investigations using pump-probe techniques. Our experiments probe physical and chemical processes that happen on femtosecond time scales. This is achieved by measuring and examining both electronic and nuclear dynamics subsequent to the interaction of molecules with LCLS pulses of various (4-80 fs) pulse duration and intensities.

We present below results completed and in progress this past year and plans for the immediate future.

Recent Progress

1) X-ray Pump-Probe Investigation of Charge and Dissociation Dynamics in Methyl Iodine Molecule

We have investigated the photoionization and nuclear dynamics in methyl iodine (CH_3I) molecule using an x-ray pump x-ray probe instrument we built in collaboration with LCLS. The pump-probe experiment was carried out with the soft x-ray, two-mirror x-ray split and delay apparatus [15]. Time-of-flight mass spectra at various x-ray pump-probe delay times were recorded to obtain the time profile for the creation of high atomic iodine charge states via sequential multi-photon ionization and for molecular dissociation. We observed high charge states of atomic iodine up to $29+$, and we visualized the evolution of creating these high atomic ion charge states, including their population suppression and enhancement as the arrival time of the second x-ray pulse was varied. We also determined the evolution of the kinetics of the high charge states upon the timing of their

creation during the ionization-dissociation coupled dynamics [8]. Our work demonstrated the implementation of x-ray pump–probe methodology for investigating x-ray induced molecular dynamics with femtosecond temporal resolution. Our results reveal the footprints of the ionization that lead to high charge states, probing the long-range potential curves of the high charge states [8, 15].

2) The Role of Super-Atom Molecular Orbitals in Doped Fullerenes in a Femtosecond Intense Laser Field

We explored a non-linear physics experiment by investigating the photoionization of a complex target, an endohedral fullerene, in a strong IR laser field as a preparatory work for an FEL experiment. We used the prototype, $\text{Ho}_3\text{N}@C_{80}$, interacting with intense ($0.1\text{--}5 \times 10^{14}$ W/cm²), short (30 fs), 800 nm laser pulses giving rise to multiply charged parent ions as well as fragment ions. We measured and theoretically explained with Françoise Remacle's theory group, the power law for singly ionized $\text{Ho}_3\text{N}@C_{80}$ yields, and we compared our findings to C_{60} results carried out under similar conditions [a]. We distinguished two regions in the ion yield spectra with respect to field strength corresponding to different ionization mechanisms and power laws. For low field strengths, multiphoton ionization dominates, while for higher field strengths, tunneling and ionization over the barrier are the main ionization processes. The power law dependence of $\text{Ho}_3\text{N}@C_{80}^{q+}$, $q=1\text{--}2$, was found to be different from that of C_{60} . Our time-dependent density functional theory computations revealed different light-induced ionization mechanisms. In doped fullerenes, unlike in C_{60} , the breaking of the cage spherical symmetry makes super atomic molecular orbital (SAMO) states optically active. Theoretical calculations suggest that the fast ionization of the SAMO states in $\text{Ho}_3\text{N}@C_{80}$ is responsible for the measured $n=3$ power law for $\text{Ho}_3\text{N}@C_{80}^+$ at intensities lower than 1.2×10^{14} W/cm². The measured C_{60}^+ power law was found to be $n=5$ [a]. For C_{60} , both super atomic molecular orbitals (SAMO) and Rydberg states played important roles when exposed to a strong laser field [b]. Both kinds of states can be indirectly populated by vibronic coupling but because the density of Rydberg states is higher than that of SAMO states, Rydberg state ionization in C_{60} dominates the ionization at laser intensities $>10^{13}$ W/cm² [b]. Our theory demonstrated that the SAMO states play a more important role in doped fullerenes than in C_{60} . Our work demonstrated that endohedral fullerenes respond differently to intense near-infrared femtosecond laser fields compared to C_{60} , and this is reflected by the measured and calculated different slope of the power law for low field strengths [9].

Future Plans.

The principal areas of investigation planned for the coming year are:

1) We have carried out an x-ray pump x-ray probe experiment using 20fs, 645 eV, LCLS pulses to study the time resolved ionization dynamics of C_{60} . We are finishing the analysis of the data and we are waiting for our theorist collaborators from the group of R. Santra to finish their time-resolved molecular dynamic model so we can compare our data with the model. **2)** We plan to write two publications from the LCLS time resolved experiments in C_{60} ; one manuscript will be centered on the ionization of C_{60} with high

LCLS fluence while the second publication will be centered on the ionization of C_{60} with low fluence. **3)** We have started to write the publications related to the single-photon absorption experiments carried out last year on endohedral fullerenes. These x-ray based experiments using the ALS synchrotron provide us the baseline data for our x-ray LCLS proposals and experiments. We plan to have this work completed by next year. **4)** We will carry out a high resolution experiment of the ultrafast photodynamics in nucleobases at the FERMI FEL in Italy since it is the only FEL so far that provides high (meV) resolution. These experiments will be precursors to the future work we will carry out at LCLSII. **5)** We will carry out in September an imaging C_{60} experiment using hard x-rays at the LCLS. This is a collaborative follow up experiment using diffraction technique. This work will be compared to the spectroscopy C_{60} experiments led by the PI. **6)** We have carried out the past two years experiments to understand the single-photon dynamics of highly correlated anions with vuv-soft x-rays from the Advanced Light Source (ALS) at Lawrence Berkeley Laboratory. We are in the process of writing up the manuscripts since the analysis of the data is finished.

References

- [a] I. Shchatsinin *et al.*, *J. Chem. Phys.* 125, 194320, (2006).
 [b] H. Li *et al.* *The Journal of Physical Chemistry Letters* 7, 4677-4682, (2016).

Peer-Reviewed Publications Resulting from this Project (2015-2017).

1. Nora Berrah, “A Perspective for Investigating Photo-Induced Molecular Dynamics from Within with Femtosecond Free Electron Lasers” *Physical Chemistry Chemical Physics*, Royal Society of Chemistry, **19**, 19536 – 19544 (2017).
2. T. J. A. Wolf, R. H. Myhre, J. P. Cryan, S. Coriani, R. J. Squibb, A. Battistoni, N. Berrah, C. Bostedt, P. Bucksbaum, G. Coslovich, R. Feifel, K. J. Gaffney, J. Grilj, T. J. Martinez, S. Miyabe, S. P. Moeller, M. Mucke, A. Natan, R. Obaid, T. Osipov, O. Plekan, S. Wang, H. Koch, M. Gühr, “Probing ultrafast $\pi\pi^*/n\pi^*$ internal conversion in organic chromophores via K-edge resonant absorption”, *Appl. Sci.* (in press) 2017, arXiv:1610.084982017.
3. Carlo Callegari, *et al.*, “Application of Matched-Filter Concepts to Unbiased Selection of Data in Pump-probe Experiments with Free Electron Lasers” *Appl. Sci.*, **7**(6), 621; doi:10.3390/app7060621 (2017).
4. Kasra Amini, *et al.*, “Alignment, Orientation, and Coulomb Explosion of Difluoriodobenzene Studied with the Pixel Imaging Mass Spectrometry (PImMS) Camera” *Journal of Chemical Physics* **147**, 013933 (2017).
5. Evgeny Savelyev, *et al.*, “Jitter-Correction for IR/UV-XUV Pump-Probe Experiments at the FLASH Free-Electron Laser” *New Journal of Physics*, **19**, 043009 (2017).
6. A. Sanchez-Gonzalez, *et al.*, “Accurate prediction of x-ray pulse properties from a free-electron laser using machine learning” *Nature communications* **8**, 15461 (2017).
7. Utuq Ablikim, Cedric Bomme, Evgeny Savelyev, Hui Xiong, Rajesh Kushawaha, Rebecca Boll, Kasra Amini, Timur Osipov, David Kilcoyne, Artem Rudenko, Nora Berrah and Daniel Rolles, “Isomer-dependent fragmentation dynamics of inner-shell photoionized difluoriodobenzene, *Physical Chemistry Chemical Physics* **19**, 13419-13431 (2017).
8. Li Fang, Hui Xiong, Edwin Kuk and Nora Berrah “X-ray Pump-Probe Investigation of Charge and Dissociation Dynamics in Methyl Iodine Molecule”, *Appl. Sci.*, **7**, 529 (2017).
9. Hui Xiong, Benoit Mignolet, Li Fang, Timur Osipov, Thomas J. A. Wolf, Emily Sistrunk, Markus Gühr, Françoise Remacle and Nora Berrah, “The Role of Super-Atom Molecular Orbitals in Doped Fullerenes in a Femtosecond Intense Laser Field” *Scientific Reports (Nature)* **7**, 121 (2017).

10. T. Takanashi, et al., “Time-Resolved Measurement of Interatomic Coulombic Decay Induced by Two-Photon 3 Double Excitation of Ne₂”, *Phys. Rev. Lett.* **118**, 033202 (2017).
11. D. Iablonskyi, et al., “Slow Interatomic Coulombic Decay of Multiply Excited Neon Clusters” *Phys. Rev. Lett.* **117**, 276806 (2017).
12. Utuq Ablikim, et al., “Identification of absolute geometries of cis and trans molecular isomers by Coulomb Explosion Imaging” *Scientific Reports* **6**, 38202 (2016).
13. Iberto A. Lutman, Timothy J. Maxwell, James P. MacArthur, Marc W. Guetg, Nora Berrah, Ryan N. Coffee, Yuantao Ding, Zhirong Huang, Agostino Marinelli, Stefan Moeller & Johann C. U. Zemella “Fresh-slice multicolour X-ray free-electron lasers” *Nat. Photonics* **1**, 745 (2016).
14. C. S. Lehmann, A. Picon, C. Bostedt, A. Rudenko, A. Marinelli, D. Moonshiram, T. Osipov, D. Rolles, N. Berrah, C. Bomme, M. Bucher, G. Doumy, B. Erk, K. Ferguson, T. Gorkhover, P. J. Ho, E. P. Kanter, B. Krassig, J. Krzywinski, A. A. Lutman, A. M. March, D. Ray, L. Young, S. T. Pratt, and S. H. Southworth, “Ultrafast measurements for molecular nuclear dynamics using two x-ray pulses”, *Phys. Rev. A* **94**, 013426 (2016).
15. Nora Berrah, Li Fang, Brendan F Murphy, Edwin Kukk, Timur Y. Osipov, Ryan Coffee, Ken R Ferguson, Hui Xiong, Jean-Charles Castagna, Vlad S Petrovic, Sebastian Carron Montero, and John D. Bozek , “A two mirrors x-ray pulse split and delay instrument for femtosecond time resolved investigations at the LCLS free electron laser facility” *Optics Express* **24** (11), 11768-11781 (2016).
16. A. Picon, et al., “Hetero-site-specific ultrafast intramolecular dynamics”, *Nature Com.* **7**, 11652 (2016).
17. Liu, Ji-Cai, Berrah, Nora; Cederbaum, Lorenz; Cryan, James; Glowina, James; Schafer, Kenneth; Buth, Christian “Rate equations for nitrogen molecules in ultrashort and intense x-ray pulses ” *J. Phys. B: Atomic, Molecular and Optical Physics* **49**, 075602 (2016).
18. Nora Berrah, “Molecular Dynamics Induced by Short and Intense X-rays Pulses from the LCLS” *Physica Scripta*, **T169**, (2016) (Article based on an invited talk at the Nobel Symposium, Stiguna, Stockholm, Sweden, June 15, 2015).
19. P. Bolognesi, et al., “A study of the dynamical energy flow in uracil”, *Journal of Physics: Conference Series* **635**, 112062 (2015).
20. Sanchez-Gonzalez, et al., “Auger electron and photoabsorption spectra of glycine in the vicinity of the oxygen K-edge measured with an X-FEL” *J. Phys. B: At. Mol. Opt. Phys.* **48**, 234004 (2015).
21. V. Zhaunerchyk, et al., “Disentangling formation of multiple-core holes in aminophenol molecules exposed to bright XFEL radiation”, *J. Phys. B: At. Mol. Opt. Phys.* **48**, 244003 (2015).
22. N. Berrah and P. H. Bucksbaum, “The Ultimate X-ray Machine” *Scientific American Special Collector’s edition*, **54**, (2015).
23. N. Berrah, B. Murphy, H. Xiong, L. Fang, T. Osipov, E. Kukk, M. Guehr, R. Feifel, V. S. Petrovic, K. R. Ferguson, J. D. Bozek, C. Bostedt, L. J. Frasinski, P. H. Bucksbaum and J. C. Castagna , “Femtosecond x-ray induced fragmentation of fullerenes” *J. of Mod. Opt.*, **63**, No. 4, 390–401 (2015).
24. P. Bucksbaum & N. Berrah, “Brighter and faster: The promise and challenge of the x-ray free-electron laser”, *Physics Today*, **68** (7), 26 July (2015).
25. N. Berrah and L. Fang “Chemical Analysis: Double Core-Hole Spectroscopy with Free-Electron Lasers” *J. Electr. Spect. and Rel. Phenom.* **204**, 284–289 (2015).
26. C. E. Liekhus-Schmaltz et al., “Ultrafast Isomerization Initiated by X-Ray Core Ionization” *Nature Comm.*, **6**, 8199, (2015).
27. M. Mucke, et al., “Covariance mapping of two-photon double core hole states in C₂H₂ and C₂H₆ produced by an X-ray free electron laser”, *New Journal of Physics*, **17**, 073002, (2015).
28. F. Penent, et al., “Double core hole spectroscopy with synchrotron radiation” *J. Electr. Spect. and Relat. Phenom.* **204**, 303–312, (2015).
29. A. Dubrouil, et al., “Two-photon resonant excitation of interatomic Coulombic decay in neon dimers”, *J. Phys. B: At. Mol. Opt. Phys.* **48** 204005, (2015). doi:10.1088/0953-4075/48/20/204005.
30. L. Fang, Z. Jurek, T. Osipov, B. F. Murphy, R. Santra, and N. Berrah, “Investigating Dynamics of Complex System Irradiated by Intense X-ray Free Electron Laser Pulses”, *Journal of Physics*, **601**, 012006 (2015).

Ultrafast Electron Diffraction from Aligned Molecules

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Project Scope

This project aims to investigate photochemical reactions at the molecular level by observing how the molecular structure changes upon light absorption. The project relies on ultrafast electron diffraction to image photo-induced reactions in isolated molecules with atomic resolution. A sample of molecules in the gas phase is excited by a femtosecond laser pulse, and the structure is probed by a femtosecond electron pulse. The scattering pattern of the probe electrons contains information on the structure of the molecule, and under certain conditions an image of the molecule can be retrieved with atomic resolution. Additional information can be extracted if the molecules are aligned, either selectively through the photoexcitation or actively through an alignment laser pulse before excitation.

Introduction

In photo-induced molecular reactions light can be converted into chemical and kinetic energy on femtosecond time scales. Observing the motion of atoms and the resulting transient structures during these processes is essential to understand them. Diffraction methods are an ideal tool because they are directly sensitive to the spatial distribution of charge, and are thus complementary to spectroscopic methods that probe the energy landscape. We have implemented ultrafast electron diffraction (UED) with femtosecond temporal resolution to observe structural dynamics in isolated molecules.

A gas-phase diffraction experiment comprises four major parts: i) An electron gun that delivers short pulses on a target, ii) a laser that triggers both the electron gun and the photochemical reaction, iii) a sample delivery system that creates a gas jet target in a vacuum environment, and iv) a detection system. Two different systems will be used in this project. The first is the MeV electron gun at the ASTA test facility at SLAC National Lab. This RF photoelectron gun produces femtosecond electron pulses in an energy range between 2 MeV and 5 MeV, with a repetition rate of 120 Hz. We have designed and constructed an experimental chamber for gas phase diffraction experiments, in collaboration with the group of Xijie Wang at SLAC. The main advantage of using MeV electrons is that they are relativistic, which minimizes the velocity mismatch between laser and electrons and also the pulse spreading due to Coulomb forces. The velocity mismatch has been a major limitation in the temporal resolution of UED experiments with sub-relativistic pulses. Experiments will also be performed in the PI's lab at UNL using a photoelectron gun that combines a DC accelerator with an RF compression cavity. Electrons are accelerated to an energy of 90 keV and then temporally compressed at the target position by a small RF cavity, at a repetition rate of 5 kHz. This setup includes an optical system to deliver laser pulses with a tilted intensity front on the sample. The tilted pulses will serve to compensate the velocity mismatch of laser and electrons through the sample to reach femtosecond resolution. The setup at SLAC is expected to reach better temporal resolution due to the use of relativistic electron pulses, while the setup at UNL is expected to reach a better spatial resolution due to the higher average beam current that will allow for capturing the scattering at larger angles.

Recent Progress

After the success of the first run of experiments in 2015, we performed a second run of experiments at the SLAC MeV UED facility. The PIs group is currently involved in the data analysis for three experiments, photodissociation of CF_3I , photodissociation of $\text{C}_2\text{F}_4\text{I}_2$ and isomerization of cis-Stilbene. The CF_3I data analysis has been completed and we are preparing a manuscript for submission, we have some preliminary data analysis to report for the photodissociation of $\text{C}_2\text{F}_4\text{I}_2$, while we have just started the data analysis for Stilbene and there is not yet anything to report. The experiments are supported by theory from the group of Todd Martinez.

UV-Photodissociation of CF_3I . The absorption of a single UV photon leads to the dissociation through breaking of the CI (carbon-iodine) bond. Using UED, we have captured the photodissociation and a second reaction channel that is resonantly excited by two UV-photons into a Rydberg state. We were able to resolve the dynamics in both channels. In the dissociation channel, we have observed the recoil of the carbon atom when the bond breaks, and the ensuing vibrational motion of the CF_3 fragment. In the second channel, we have observed the return of a fraction of the wavepacket to the original position after 500 fs. Based on numerical simulations, this revival is made possible by a non-adiabatic coupling between the Rydberg state and an ion pair state, which then couples back to the ground state.

Figure 1 summarizes the dynamics observed in the dissociation channel. When the CI bond breaks, there is initially a strong recoil of the carbon atom and little movement of the heavier iodine atom. This results in a faster change in the CI distance relative to the FI distance, as shown in Figure 1a, due to the CF_3 fragment becoming more planar due to the carbon recoil. The inset in Figure 1a shows a cartoon picture of the recoil motion leading planarization of the CF_3 fragment. Figure 2b shows the changes in the CF distance and the FCF angle in the CF_3 fragment after dissociation, which are consistent with excitation of CF vibrations and umbrella motion. The data is in good agreement with CASSCF and CASCI simulations

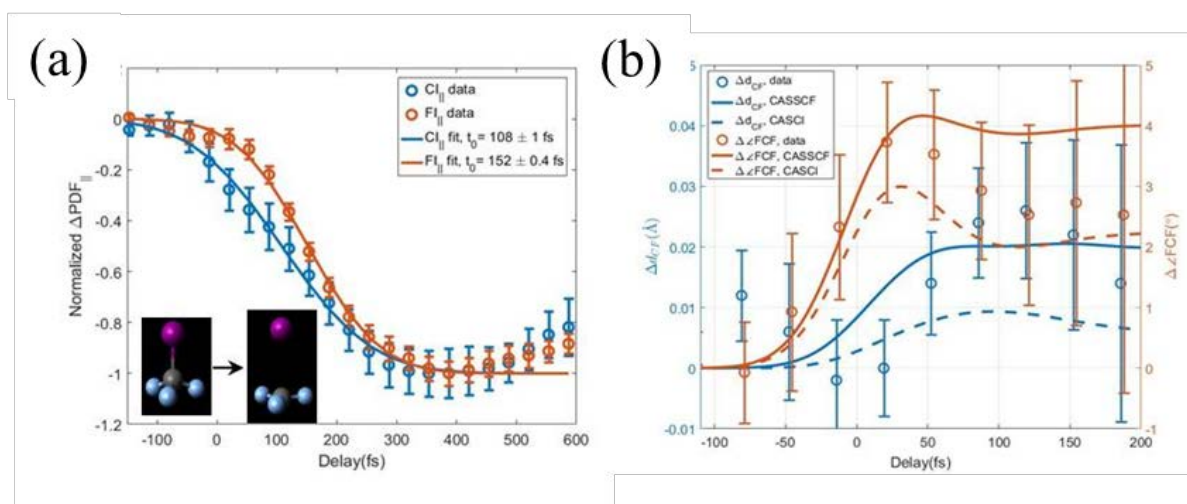


Figure 1. Photodissociation dynamics of the CF_3I molecule. a) Changes in the amplitude of the peak corresponding to the CI distance (blue) and the FI distance (red). The dots represent the data points and the solid line is a fit. There is a delay in the appearance of the signal in the FI distance relative to the CI distance. b) Changes in the structure of the CF_3 fragment. The CF distance is shown in blue, and the FCF angle shown in red. Circles with error bars are the data, and the solid and dashed lines are CASSCF and CASCI simulations.

performed by the group of Todd Martinez.

We have also captured the dynamics following the two-photon excitation into the 7s Rydberg state. This is a perpendicular excitation, meaning that molecules get excited with a higher probability if they are oriented perpendicularly to the laser polarization. Contrast this with the dissociative state, which is a parallel excitation. We have used this to separate the changes in the CI and FI distance corresponding to the two reaction channels by angularly resolving the changes in the diffraction patterns. The dynamics captured here are faster than the rotation of the CF₃I and the CF₃ fragment, so the two directions remain well separated. This reaction channel involves non-adiabatic coupling through a series of conical intersections.

UV Photodissociation of C₂F₄I₂. The UV excitation of C₂F₄I₂ results in the sequential breaking of the two CI bonds: C₂F₄I₂ → C₂F₄I + I → C₂F₄ + 2I. In previous mass spectrometry experiments, the first reaction step takes has been measured to take place in approximately 200 fs, while the second step takes place on a time scale of approximately 20 ps, depending on the excitation wavelength. Here we use UED to capture the first step of the reaction with femtosecond resolution. Previously, the radical was found to have a non-bridged structure by the Zewail group using UED with 5 picosecond time resolution. Here we analyze the same reaction with 150 fs resolution in order to answer some important remaining questions: 1) Does the bridged structure exist on a femtosecond time scale? 2) It is expected that the C₂F₄I will be vibrationally hot, what are the main vibrational modes? 3) Are there any other dynamics that were not seen on the picosecond experiments? These questions can only be answered now that femtosecond resolution is available.

The data analysis is still ongoing, but we can already answer some of these questions. Figure 2 shows the changes in the radial distribution function as a function of time after laser excitation. The changes in the interatomic distances, from the early times are consistent with the non-bridged structure. So we can answer the first question, that the bridged structure does not appear on a times scale of ~ 150 fs and only the non-bridged structure is formed. We also observed that there are modulations on the amplitude of the peaks corresponding to several of the interatomic distances. These may be caused by large vibrations and rotation in the intermediate. Further data analysis is ongoing to answer the two remaining questions.

Characterization of the setup at UNL.

The construction of the new 90 keV setup with RF bunching in Nebraska has been completed. The temporal resolution was measured to be 350 fs using a home made streak camera. The resolution is limited mostly by timing jitter between the laser and electrons. We are currently performing measurements of the phase stability to see if we can further reduce the timing jitter. We have successfully recorded

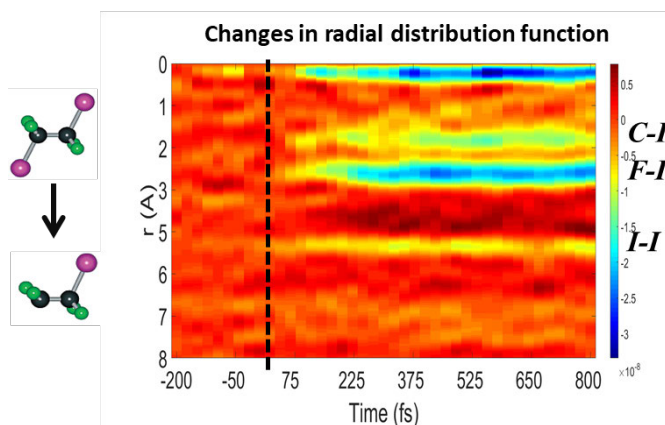


Figure 2. Changes in the radial distribution function of C₂F₄I₂ vs time. A cartoon of the first reaction step is shown on the left hand side. A few of the internuclear distances are labeled on the right hand side of the figure.

static diffraction patterns of CF₃I and Nitrogen with 10⁵ electrons per pulse at a repetition rate of 5 kHz, an increase by a factor of 100 in beam current compared to our previous setup that did not include pulse compression. We have also set up an optical system to deliver tilted laser pulses to compensate for the group velocity mismatch. We had problems with the initial setup and have since installed additional optics to characterize the tilted pulses in situ.

Future plans

The data analysis for C₂F₄I₂ and cis-stilbene will continue in close collaboration with the theory group of Todd Martinez. We are also planning the next run of experiments at SLAC, where we expect to reach a temporal resolution around 100 fs. We also plan to make some improvements on the gas delivery setup for molecules with low vapor pressure. The first time-resolved experiments with the 90 keV high-repetition rate setup are expected to take at the end of this year and beginning of next year.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. S. P. Weathersby, G. Brown, M. Centurion, T. F. Chase, R. Coffee, J. Corbett, J. P. Eichner, J. C. Frisch, A. R. Fry, M. Gühr, N. Hartmann, C. Hast, R. Hettel, R. K. Jobe, E. N. Jongewaard, J. R. Lewandowski, R. K. Li, A. M. Lindenberg, I. Makasyuk, J. E. May, D. McCormick, M. N. Nguyen, A. H. Reid, X. Shen, K. Sokolowski-Tinten, T. Vecchione, S. L. Vetter, J. Wu, J. Yang, H. A. Dürr, and X. J. Wang, "Mega-electron-volt ultrafast electron diffraction at SLAC National Accelerator Laboratory", *Rev. Sci. Instr.* **86**, 073702 (2015).
2. J. Yang, M. Centurion, "Gas phase electron diffraction from laser-aligned molecules" *Struct. Chem.* **26** 1513–20 (2015)
3. J. Yang, J. Beck, C. J. Uiterwaal, M. Centurion, "Imaging of alignment and structural changes of carbon disulfide molecules using ultrafast electron diffraction" *Nature Commun.* **6**, 8172 (2015).
4. M. Centurion, "Ultrafast imaging of isolated molecules with electron diffraction (Topical Review)", *J. Phys. B.* **49**, 062002 (2016).
5. J. Yang, M. Guehr, T. Vecchione, M. S. Robinson, R. Li, N. Hartmann, X. Shen, R. Coffee, J. Corbett, A. Fry, Ke. Gaffney, T. Gorkhover, C. Hast, K. Jobe, I. Makasyuk, A. Reid, J. Robinson, S. Vetter, F. Wang, S. Weathersby, C. Yoneda, M. Centurion, X. Wang, "Diffractive imaging of a rotational wavepacket in nitrogen molecules with femtosecond megaelectronvolt electron pulses" *Nature Commun.* **7**, 11232 (2016).
6. J. Yang, M. Guehr, X. Shen, R. Li, T. Vecchione, R. Coffee, J. Corbett, A. Fry, N. Hartmann, C. Hast, K. Hegazy, K. Jobe, I. Makasyuk, J. Robinson, M. S. Robinson, S. Vetter, S. Weathersby, C. Yoneda, X. Wang, M. Centurion, "Diffractive Imaging of Coherent Nuclear Motion in Isolated Molecules" *Phys. Rev. Lett.* **117**, 153002 (2016).
7. J. Yang, M. Guehr, T. Vecchione, M. S. Robinson, R. Li, N. Hartmann, X. Shen, R. Coffee, J. Corbett, A. Fry, Ke. Gaffney, T. Gorkhover, C. Hast, K. Jobe, I. Makasyuk, A. Reid, J. Robinson, S. Vetter, F. Wang, S. Weathersby, C. Yoneda, X. Wang, M. Centurion, "Femtosecond gas phase electron diffraction with MeV electrons" *Faraday Discuss* **194**, 563 (2016).
8. Omid Zandi, Kyle J. Wilkin, Yanwei Xiong, and Martin Centurion, "High current table-top setup for femtosecond gas electron diffraction" *Structural Dynamics* **4**, 044022 (2017).

Atomic and Molecular Physics in Strong Fields

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Project Scope

In this research program, we address the fundamental physics of the interaction of atoms and molecules with intense ultrashort laser fields. The main objectives are to develop new theoretical formalisms and accurate computational methods for *ab initio* nonperturbative investigations of multiphoton quantum dynamics and very high-order nonlinear optical processes of one-, two-, and many-electron quantum systems in intense laser fields. Particular attention will be paid to (i) the exploration of the effects of electron correlation and multi-electron response on high-harmonic generation (HHG) and multiphoton ionization (MPI) processes of atoms, and diatomic, and small polyatomic molecules; (ii) Development of new time-frequency transform to facilitate the exploration of dynamical origin of near- and below- threshold harmonic generation of atomic and molecular systems in mid-IR laser fields; and (iii) Coherent control of HHG processes for the generation of shorter and stronger attosecond laser pulses, etc.

Recent Progress

1. Coherent Control of the Generation of Single Ultrashort Attosecond Laser Pulse

The investigation of attosecond (*as*) physics in intense ultrashort laser fields is a forefront subject of much current interest and significance in ultrafast science and technology. Attosecond pulses can be produced by means of high-harmonic generation (HHG) of atoms or molecules in intense laser fields, and the time profile of the attosecond pulses can be controlled by tuning the laser pulse shape. The generation of ever-shorter attosecond pulses has continued to attract much interest. It has been demonstrated experimentally that, by superposing the supercontinuum harmonic spectrum, one can obtain a train of attosecond pulses (ATP) or an isolated pulse. The shortest isolated pulse being generated today is 53 attoseconds.

In the last few years, we have initiated a series of *ab initio* studies to investigate new mechanisms for the coherent control of the quantum pathways for efficiently generating ultrashort attosecond (*as*) pulses. We report a new mechanism and experimentally realizable approach for the coherent control of the generation of an isolated attosecond (*as*) laser pulse from atoms by means of the optimization of the two-color and three-color laser fields with proper time delays. Optimizing the laser pulse shape allows the control of the electron quantum paths and enables HHG from the long- and short-trajectory electrons to be enhanced and split near the cutoff region. Then we further investigated the effect of macroscopic propagation on the supercontinuum harmonic spectra and the subsequent attosecond-pulse generation. The effects of macroscopic propagation are investigated in near and far field by solving Maxwell's equation. Further we propose an efficient method for the generation of ultra-broadband supercontinuum spectra and isolated ultrashort attosecond laser pulses from He atoms with two-color mid-IR laser fields [R1]. We found that the optimization of two-color mid-IR laser pulse allows the HHG cutoff to be significantly extended, leading to the production of an ultra-broadband supercontinuum. As a result, an isolated 18-*as* pulse can be generated directly by the superposition of the supercontinuum harmonics.

More recently, we have presented an efficient *optimal control scheme* for the generation of the ultrabroad supercontinuum spectrum and an isolated ultrashort attosecond pulse in gases with a two-color mid-IR laser field [1]. The optimal control scheme is implemented using a derivative-free unconstrained optimization algorithm called NEWUOA (NEW Unconstrained Optimization Algorithm). It is shown that the optimally shaped laser waveforms can greatly enhance and extend the HHG plateau and efficiently generate an isolated ultrashort attosecond pulse. Furthermore, the optimized pulse can produce a single ultrashort pulse that is not only much shorter but also more intense, by two orders of magnitude, than that produced by the initial un-optimized laser pulse. In a latest work in this

direction, we have further found that optimally shaped *inhomogeneous* two-color mid-infrared laser fields can greatly enhance and extend the HHG plateau. Wavelet time-frequency analysis and classical simulations show that the superposition of resulting hydrogen HHG supercontinuum effectively gives rise to a robust isolated 5-*as* pulse [2].

On a different route, we also pursue the exploration of the generation of isolated ultrashort attosecond pulses by coherent control of the population of excited states [3]. The population of the first two low-lying excited states of He^+ ions is selectively controlled by adding low intensity, high frequency laser pulses to a two color mid-IR laser field. Although the intensity of the added field is weak, its high frequency makes the subsequent ionization probability from excited states become much larger than for the case of many photons (mid-IR field), even though the intensity is smaller. We found that the intensity of the attosecond pulse generated by superposing a range of synchronized high harmonics is significantly enhanced by 20 orders of magnitude. Similar calculations have been performed for the neutral He atoms. We found that an intense and ultra-short isolated 18 *as* can be generated directly [3].

2. Subcycle Transient HHG Dynamics and Ultrafast Spectroscopy in the Attosecond Time Domain

The recent development of attosecond metrology has enabled the real-time experimental observation of ultrafast electron dynamics and transient sub-cycle spectroscopy in atomic and molecular systems. While they are a number of recent experimental and theoretical studies of subcycle transient absorption, there has been little study of the subcycle transient behavior of the harmonic emission. We have recently initiated such a direction and performed the first *ab initio* study of the subcycle HHG dynamics of He atoms [R2]. We extend the *self-interaction-free* time-dependent density functional theory (TDDFT) [R2] with proper exchange-correlation (xc) energy functional, allowing the correct long-range asymptotic behavior, and the TDDFT equations are solved accurately and efficiently by means of the time-dependent generalized pseudospectral (TDGPS) method [R3]. We explored the dynamical behavior of the subcycle HHG for transitions from the excited states to the ground state and found oscillation structures with respect to the time delay between the single XUV attosecond pulse and near-infrared (NIR) fields. The oscillatory pattern in the photon emission spectra has a period of ~ 1.3 fs which is half of the NIR laser optical cycle, similar to that recently measured in the experiments on transient absorption of He [R4]. We present the photon emission spectra from 1s2p, 1s3p, 1s4p, 1s5p, and 1s6p excited states as functions of the time delay. We explore the sub-cycle a. c. Stark shift phenomenon in NIR fields and its influence on the photon emission process. Our analysis reveals several novel features of the subcycle HHG dynamics for the first time and we identify the mechanisms responsible for the observed peak splitting in the photon emission spectra. See Figure 1 for an example. More recently, we have further extended the study to subcycle dynamics of HHG in valence-shell and virtual states of Ar atoms [4].

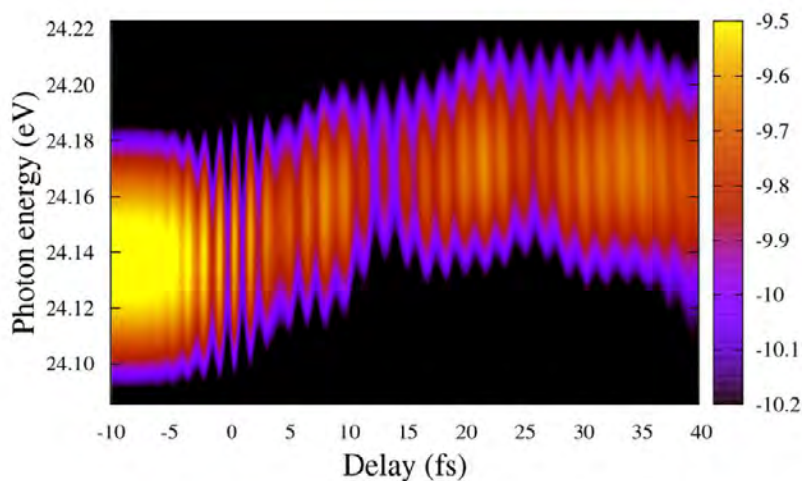


Figure 1. Subcycle photon emission energy spectrum of the $1s4p$ excited state of He as a function of the time delay between the NIR pulse and SAP. The yellow color indicates the highest energy emitted. The color bars are represented by the $\log_{10} S(\omega)$ of the spectral density. Negative delays indicate the NIR pulse arrives on target before the SAP.

3. Dynamical Origin of Near- and Below-Threshold Harmonic Generation of in an Intense Mid-IR Laser Field

Near- and below- threshold harmonic generation provides a potential approach to achieve a high conversion efficiency of VUV and EUV sources for the advancement of spectroscopy [R5]. However, the dynamical origin of these lower harmonics is less understood and largely unexplored. Recently we perform an *ab initio* TDDFT quantum study of the near- and below- threshold harmonic generation of cesium (Cs) atoms in an intense 3,600-nm mid-infrared laser field [5]. By means of the *synchrosqueezing transform* (SST) [R6] of the quantum time-frequency spectrum we have recently developed along with an extended semiclassical analysis, the roles of multiphoton and multiple rescattering trajectories on the near- and below- threshold harmonic generation processes are investigated in details. We find that the multiphoton-dominated trajectories only involve the electrons scattered off the higher part of the combined atom-field potential followed by the absorption of many photons in near- and below- threshold regime. Furthermore, only the near-resonant below-threshold harmonic is exclusive to exhibit phase locked features. Our results uncover the dynamical origin of near- and below- threshold harmonics as well as the role of multi-rescattering trajectories to the resonance-enhanced below-threshold harmonics for the first time. More recently, we have further extend the atomic study to probe multi-rescattering dynamics and electron quantum paths for below- and near- threshold harmonic generation for diatomic H_2^+ [6] and H_2 [7] systems.

Furthermore, in a different but related direction, we have explored the enhancement of VUV and EUV generation by field-controlled resonance structures of diatomic Molecules (CO and N_2) [8]. We find that with the use of different driving laser pulse shapes, one can control and enhance HHG through the excited-state resonance structures. Depending on the pulse shape, the enhancement can reach five to seven orders of magnitude as compared to the reference sine-squared laser pulse of the same duration.

4. Exploration of the Electron Multiple Recollision Dynamics in Intense Laser Fields with Bohmian Quantum Trajectories

Recently it has been found that electron-nucleus multiple rescattering process plays a major role to the resonance-enhanced below-threshold harmonic generation [R7]. We initiate a study of electron multiple recollision dynamics under intense mid-infrared laser fields by means of the de Broglie–Bohm framework of Bohmian mechanics [9]. Bohmian trajectories contain all the information embedded in the time-dependent wave function. This makes the method suitable to investigate the coherent dynamic processes for which the phase information is crucial. In this study, the appearance of the subpeaks in the high-harmonic-generation time-frequency profiles and the asymmetric fine structures in the above-threshold ionization spectrum are analyzed by the comprehensive and intuitive picture provided by Bohmian mechanics. The time evolution of the individual electron trajectories is closely studied to address some of the major structural features of the photoelectron angular distributions.

5. A Graph-Theoretical Representation and Floquet Formulation for Probing Multiphoton Quantum Interference in Superconducting Quantum Circuits

We introduce a new graph-theoretical representation and Floquet formalism to study generic circuit quantum electrodynamics systems consisting of a two-level qubit coupled with a single-mode resonator in arbitrary coupling strength regimes beyond rotating-wave approximation [10]. We define colored-weighted graphs, and introduce different products between them to investigate the dynamics of superconducting qubits in transverse, longitudinal, and bidirectional coupling schemes. The intuitive and predictive picture provided by this method, and the simplicity of the mathematical construction, are demonstrated with some numerical studies of the multiphoton resonance processes and quantum interference phenomena for the superconducting qubit systems driven by intense ac fields.

Future Plans

In addition to continuing the ongoing researches discussed above, we plan to initiate the following several new project directions: (a) Extension of the TDGPS method in momentum space [R8] to the study of HHG/ATI processes in

intense free electron x-ray laser fields. (b) Development of Bohmian mechanics approach [11] for the exploration of the electron quantum dynamics associated with HHG/MPI processes. (c) Extension of the new time-frequency method, the *synchrosqueezing transform* (SST) [R6], for the exploration of the novel quantum dynamics for below- and near-threshold harmonics of diatomic molecules. (d) Exploration of HHG dynamics of vibrating diatomic molecules [12].

Peer-Reviewed Publications Resulting from this Project (2015-2017):

- [1] Y. Chou, P.-C. Li, T.S. Ho, and S.I. Chu, Optimal control of high-order harmonics for the generation of an isolated ultrashort attosecond pulse with two-color midinfrared laser fields, *Phys. Rev. A* **91**, 063408 (2015).
- [2] Y. Chou, P.-C. Li, T.S. Ho, and S.I. Chu, Generation of an isolated few-attosecond pulse in optimized inhomogeneous two-color fields, *Phys. Rev. A* **92**, 023423 (2015).
- [3] H.Z. Jooya, P.-C. Li, S.-L. Liao, and S.I. Chu, Generation of isolated ultra-short attosecond pulses by coherent control of the population of excited states, *Phys. Lett. A* **380**, 316 (2016).
- [4] J. Heslar, D.A. Telnov, and S.I. Chu, Subcycle dynamics of high-harmonic generation in valence-shell and virtual states of Ar atoms: A self-interaction-free time-dependent density-functional-theory approach, *Phys. Rev. A* **91**, 023420 (2015).
- [5] P.-C. Li, Y.L. Sheu, C. Laughlin, and S.I. Chu, Dynamical origin of near- and below-threshold harmonic generation of Cs in an intense mid-infrared laser field, *Nat. Commun.* **6**, 7178 (2015).
- [6] J. Heslar and S.I. Chu, Unravelling the dynamical origin of below- and near-threshold harmonic generation of H_2^+ in an intense NIR laser field, *Sci. Rep.* **6**, 37774 (2016).
- [7] J. Heslar and S.I. Chu, Probing multi-rescattering dynamics and electron quantum paths for below- and near-threshold harmonic generation of H_2 in an intense laser field, *Phys. Rev. A* **95**, 043414 (2017).
- [8] J. Heslar, D.A. Telnov, and S.I. Chu, Enhancement of VUV and EUV generation by field-controlled resonance structures of diatomic molecules, *Phys. Rev. A* **93**, 063401 (2016).
- [9] H.Z. Jooya, D.A. Telnov, and S.I. Chu, Exploration of the electron multiple recollision dynamics in intense laser fields with Bohmian trajectories, *Phys. Rev. A* **93**, 063405 (2016).
- [10] H.Z. Jooya, K. Reihani, and S.I. Chu, A graph-theoretical representation of multiphoton resonance processes in superconducting quantum circuits, *Sci. Rep.* **6**, 37544 (2016).
- [11] H.Z. Jooya, D.A. Telnov, P.-C. Li, and S.I. Chu, Investigation of the characteristic properties of high-order harmonic spectrum in atoms using Bohmian trajectories, *J. Phys. B* **48**, 195401 (2015).
- [12] D.A. Telnov, J. Heslar, and S.I. Chu, High harmonic generation of vibrating H_2^+ and D_2^+ , *Phys. Rev. A* **95**, 043425 (2017).

References:

- [R1] P. C. Li, C. Laughlin, and S. I. Chu, Generation of isolated sub-20-attosecond pulses from He atoms by two-color Mid-infrared laser fields, *Phys. Rev. A* **89**, 023431 (2014).
- [R2] J. Heslar, D.A. Telnov, and S.I. Chu, Subcycle dynamics of high-order-harmonic generation of He atoms excited by attosecond pulses and driven by near-infrared laser fields: A self-interaction-free time-dependent density-functional-theory approach, *Phys. Rev. A* **89**, 052517 (2014).
- [R3] X. M. Tong and S. I. Chu, Theoretical study of multiple high-order harmonic generation by intense ultrashort pulsed laser fields: A new generalized pseudospectral time-dependent method, *Chem. Phys.* **217**, 119 (1997).
- [R4] M. Chini, X. Wang, Y. Cheng, Y. Wu, D. Zhao, D. A. Telnov, S. I. Chu, and Z. Chang, Sub-cycle Oscillations in Virtual States Brought to Light, *Sci. Rep.* **3**, 1105 (2013).
- [R5] M. Chini, X. Wang, Y. Cheng, H. Wang, Y. Wu, E. Cunningham, P.-C. Li, J. Heslar, D.A. Telnov, S.I. Chu, and Z. Chang, Coherent phase-matched VUV generation by field-controlled bound states, *Nat. Photonics* **8**, 437 (2014).
- [R6] Y. L. Sheu, L.Y. Hsu, H.T. Wu, P. -C. Li, and S.I. Chu, A new time-frequency method to reveal quantum dynamics of H atoms in intense laser pulses: Synchrosqueezing transform, *AIP Advances* **4**, 117138 (2014).
- [R7] P.-C. Li, Y.L. Sheu, C. Laughlin, and S.I. Chu, Role of laser-driven electron-multirescattering in resonance-enhanced below-threshold harmonic generation in He atoms, *Phys. Rev. A* **90**, 041401(R) (2014).
- [R8] Z.Y. Zhou and S.I. Chu, Precision calculation of above-threshold multiphoton ionization in intense short-wavelength laser fields: The momentum-space approach and time-dependent generalized pseudospectral method, *Phys. Rev. A* **83**, 013405 (2011).

Optical Two-Dimensional Spectroscopy of Disordered Semiconductor Quantum Wells and Quantum Dots

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Project Scope: The goal of this program has been to implement optical 2-dimensional coherent spectroscopy and apply it to electronic excitations, including excitons, in semiconductors. Specifically of interest are epitaxially grown quantum wells that exhibit disorder due to well width fluctuations and quantum dots. In both cases, 2-D spectroscopy provides information regarding coupling among excitonic localization sites.

Recent Progress: During the last year, we extended the previously reported studies of excitonic spectral diffusion in disordered quantum wells to lower temperature, where the strong redistribution approximation (SRA) fails and the process cannot be described as simple frequency-frequency correlation function. We have also made significant progress in studying colloidal quantum dots using 2D spectroscopy at low temperature, which will allow the effects of phonons to be distinguished from those due to biexcitons and higher electronic states.

The transport of optically created excitations in nanostructures is critical for optoelectronics applications such as light-harvesting, light-emitting diodes, optical modulators and switches. Transport properties are affected by unavoidable structural disorder, which introduces varying local potentials that spatially confine charge carriers, resulting in a decrease in carrier mobility. For example, carriers can be localized due to the interface roughness of a quantum well (QW) confining a two-dimensional electron gas (2DEG), surface trap states in colloidal quantum dot (CQD) and perovskite films, or crystal impurities in transition metal dichalcogenides (TMDs). Understanding the carrier localization dynamics in heterogeneous solid-state systems is critical for the aforementioned applications, but isolating these dynamics from other physical phenomena can be difficult. In the case of 2DEGs, the effect of surface roughness is obscured by strong Coulomb interactions between electrons. In CQD and perovskite films, the surface trap states are optically dark, inhibiting the ability to probe the trapping dynamics.

Excitons in disordered QWs are a model system to study localization without being constrained by the limitations mentioned above. The exciton resonance is inhomogeneously broadened by spatial variations in the confinement potential due to spatial disorder in the width or chemical composition of the QW. Spatial motion of excitons results in dynamic fluctuations of their energy, which is known as spectral diffusion. Low-energy excitons are spatially localized in the lateral direction while high-energy excitons are delocalized in the plane of the QW. The exciton energy at which the transition from localized to delocalized states occurs is dubbed the mobility edge. Thus, the dynamic localization of high-energy “mobile” excitons will decrease their transition energy. Unlike the trap states in CQDs, both localized and delocalized excitons are optically bright, which facilitates measurement of their energy change. As neutral quasiparticles, they are less susceptible to Coulomb scattering compared to carriers in a 2DEG. A disordered QW is also an excellent system to model exciton diffusion in layered materials such as TMDs and perovskites, which exhibit similar excitonic phenomena and are more susceptible to interactions with the surrounding environment.

We present measurements of spectral diffusion of excitons in disordered QWs using two-dimensional coherent spectroscopy (2DCS). Spectrally resolved exciton diffusion dynamics are measured for the entire

inhomogeneously broadened distribution simultaneously. We observe that the SRA fails for a sample temperature around 5 K due to preferential relaxation of more delocalized excitons to the lower-energy localized states. This dynamic localization occurs over a timescale of tens of picoseconds. A transition to spectral diffusion that is well-described with the SRA is observed as the sample temperature is increased, which is attributed to an increase in the population of acoustic phonons.

Figure 1 shows the measured absolute-value 2D spectra with T ranging from 0.2 – 30 ps for a sample temperature of 5 K. The peak is elongated along the dashed diagonal line due to inhomogeneous broadening of the exciton resonance due to the disordered confinement potential. The absence of off-diagonal features indicates that the contribution from a doubly-excited state, formed due to interactions between two excitons in different states, can be neglected. The decay of the total signal strength due to population relaxation is accompanied by a change in the peak shape as T increases. The peak shape for a delay T tell us about the population distribution of the excitons. Thus the change in the peak shape reflects evolution in the population distribution due to spectral diffusion caused by exciton-phonon scattering between the different localized and delocalized 1s exciton states. As delay T increases, signal appears below the diagonal in the circled region in Fig. 1(d) due to a preferential relaxation of excitons from the high-energy, more delocalized states to the low-energy, more localized states. Energy conservation requires that this dynamic localization is accompanied by stimulated or spontaneous emission of acoustic phonons. This data shows that the dynamic localization occurs over a timescale longer than 10 ps, which is consistent with the time scale of exciton-phonon induced decay of delocalized exciton states close to the mobility edge. The influence of processes, which increase the exciton energy due to absorption of phonons, is weaker due to the small phonon population at this temperature. The SRA, which assumes equal probability of increase and decrease in exciton energy, is not valid in this case. We emphasize that it is not possible to observe the timescale associated with this dynamic localization in either frequency-domain or time-domain FWM experiments that were previously used to study spectral diffusion in heterogeneous systems.

We have measured the spectral diffusion of excitons in QWs, over the entire inhomogeneous distribution, using 2DCS for sample temperatures in the range 5 – 20 K (higher temperature data not shown here, see Singh et al., Phys. Rev. B, listed below). We find that the dynamic localization of excitons through emission of phonons is the dominant process at 5 K, and occurs over timescales of tens of picoseconds. At higher sample temperatures, redistribution of the exciton energy occurs uniformly to higher and lower energies due to an increase in the population of phonons. We also found that the dynamic localization is more important for samples with higher disorder correlation length. These results suggest that qualitatively similar exciton dynamics can be expected in other disordered semiconductors such as layered TMDs and perovskites. Interestingly, the exciton diffusion coefficient in atomically thin TMDs, which exhibit significantly larger inhomogeneous broadening and an order-of-magnitude larger many-body interactions, is comparable to that for excitons in a GaAs QW despite the fundamental difference in the nature of exciton localization. 2DCS

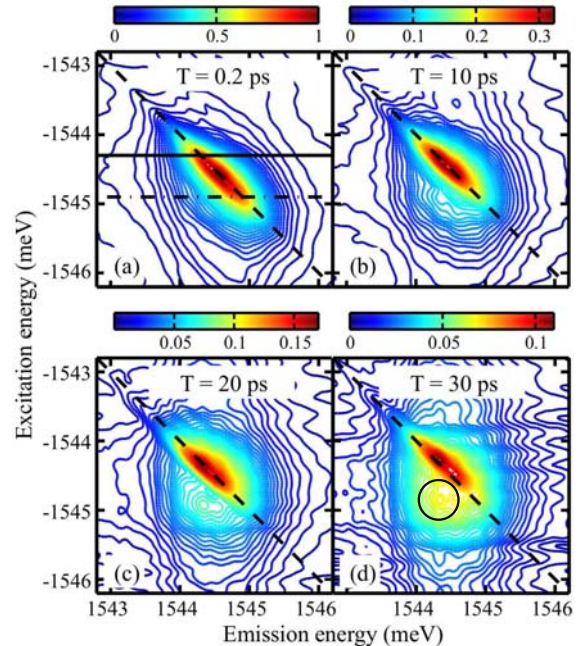


Figure 1: (a) - (d) Experimental 2D spectra for $T = 0.2, 10, 20,$ and 30 ps, respectively, with the sample at a temperature of 5 K. All the spectra are normalized by the maximum of the peak of the spectrum for $T = 0.2$ ps.. Note the relative increase in the signal within the circled region in (d).

experiments may shed light on the limitations of exciton diffusion in these novel materials.

Colloidal quantum dots (CQDs), due to their relative easiness to synthesise and therefore control of their optoelectronic properties, have applications in several fields and are also potential candidates for components in single photon sources, quantum information devices and solar cells. For these applications, knowledge of the charge carriers dynamics, specifically the dephasing mechanisms of the excitons, is essential.

Due to quantum confinement, CQDs can have intricate intraband structures and phonon assisted transitions are central in the dynamics of these structures. Hence, the vibrational modes play a central whole in the CQD states dephasing times.

Using 2DCS, we are able to identify the zero-phonon line, Acoustic and LO phonon sidebands of CdSe/ZnS CQDs ensembles. These features are revealed by taking cross diagonal slices of the 2D plots, which also have the feature of being energy (size) selective.

The size distribution of CQD ensembles add inhomogeneous broadening to their spectra and make it more challenging to identify the fine structure components. Although TFWM experiments have been important for the study of exciton physics, the technique has shortcomings such as: interpreting the correct behavior from oscillatory signal in the time domain can be challenging; any spectral (i.e. size) dependence properties is averaged for an ensemble of oscillators. Two-dimensional coherent spectroscopy (2DCS) overcomes these shortcomings. As for TFWM, it also can probe the homogeneous response even in the presence of large static size inhomogeneity, but with the advantage that this 2D method can be used to directly measure coupling strengths between quantum states because the signal now is spectrally resolved.

Fig. 2 shows a 2D rephasing spectrum at a temperature of 15K. The excitation pulses are 90 fs in duration with an average power of about 110 mW per beam and a 250 kHz repetition rate and are collinearly polarized. The sample is an ensemble of CdSe/ZnS core-shell dots suspended in heptamethylnonane and held in a liquid helium cryostat. The CQDs have an average core diameter of about 4 nm and a shell thickness of 2.5 nm. In this 2D spectrum, the diagonal elongation of the peak represents the inhomogeneous broadening, while cross-diagonal slices represent the homogeneous lineshape.

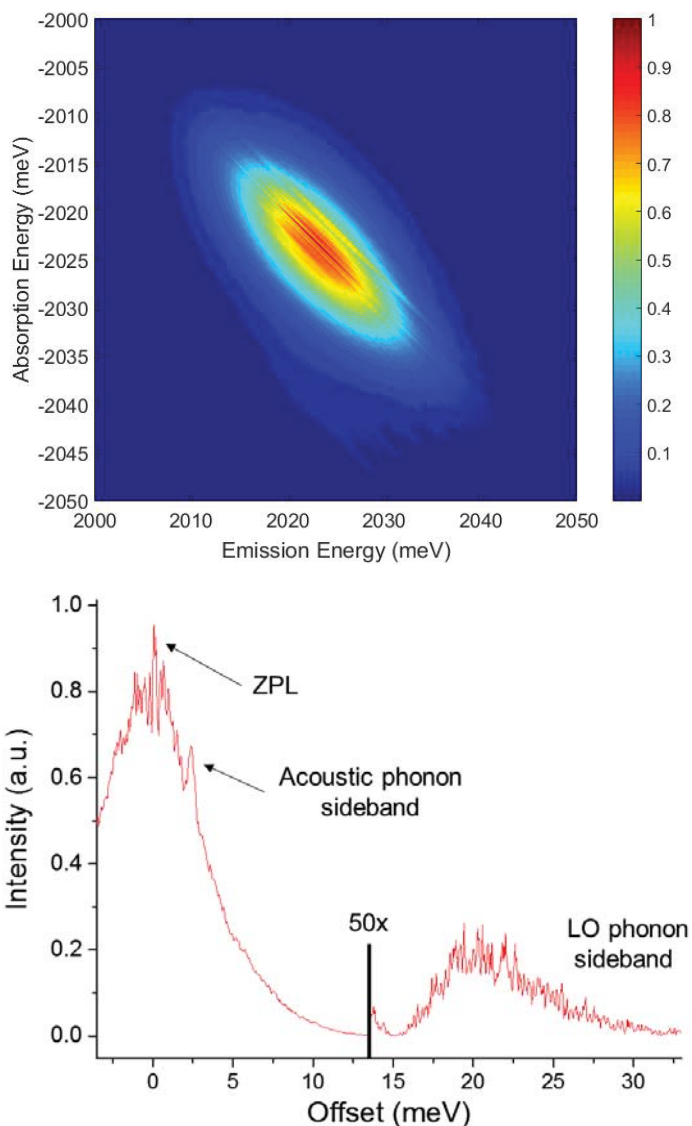


Figure 2: (CQDs 2D rephasing spectrum at 15K (top). Cross-diagonal slice from the 2D plot. the ZPL, Acoustic and LO phonon features are highlighted (bottom)

A cross-diagonal slice from the 2D plot is shown in the lower part of Fig. 2. The cold temperature ($\approx 20\text{K}$) and the long τ scan (60ps) were able to capture multiple dephasing features that, in the energy domain, and with the help of the spectral selectivity of the technique, present distinct features consistent with the ZPL, acoustic and LO phonon sidebands. The large central curve is the acoustic phonon pedestal, connected with the fast dephasing component of the probed quantum levels.

Future plans: During the next year we will continue to focus on exploiting the ability of 2DCS to make size resolved measurements on an ensemble sample to study size dependent effects in both self-organized epitaxially grown quantum dots and colloidal quantum dots. Previously, size dependent phenomena could only be explored by single dot studies, which are challenging to perform. In addition, the process of isolating a single dot may modify the results, either through sample preparation or by choosing to work on an outlier because it is easier to isolate. Furthermore, determining trends, such as size dependence, is challenging because it requires a series of difficult measurement, thus the data sets are often small.

In general, quantum dots show strong inhomogeneous broadening due to size dispersion because the size variation leads to variation in the quantization energy of the electronic states. The inhomogeneous broadening means that linear measurements on ensembles, such as absorption or luminescence, do not measure the properties of individual dots, but rather the properties of the ensemble. For example the width of the linear spectra are completely determined by the size fluctuations, not the linewidth of the individual dots. Furthermore, the individual dots may have multiple transitions, for example exciton and biexciton or fine-structure splitting, that is completely obscured by the inhomogeneity.

We are currently finalizing a project that uses methods for “deblurring” images to extract the underlying dynamics from 2D spectra by removing the effects of the optical response. This approach should make the 2D coherent spectroscopy more useful in a broad context.

Using a so-called “zero-quantum” scan, first demonstrated under support by the AMOS program about 8 years ago, we have been studying the evolution of the side-band due to the LO phonons in colloidal quantum dots. The side bands do not appear for $\tau = 0$, i.e., no delay between the first and second pulses. If the LO phonons were described by a simple model, there side bands should be present for $\tau = 0$ and exponentially decay. We are currently trying to determine if the observe devolution is due to coherence transfer or being in the non-Markovian regime for the phonon-exciton coupling.

Peer-Reviewed Publications resulting from this project (2015-2017):

1. G. Nardin, T.M. Autry, G. Moody, R. Singh, H. Li and S.T. Cundiff, “Multi-Dimensional Coherent Optical Spectroscopy of Semiconductor Nanostructures: Collinear and Non-collinear Approaches,” *J. Appl. Phys.* **117**, 112804 (2015).
2. R. Singh, G.M. Moody, H. Li, M. Siemens and S.T. Cundiff, “Quantifying Spectral Diffusion by Direct Measurement of the Correlation Function for Excitons in Semiconductor Quantum Wells,” *J. Opt. Soc. Am. B* **33**, C137 (2016).
3. R. Singh, T. Suzuki, T. M. Autry, G. Moody, M. E. Siemens, and S. T. Cundiff, “Polarization Dependent Exciton Linewidth in Semiconductor Quantum Wells a Consequence of Bosonic Nature of Excitons,” *Phys. Rev. B* **94**, 081304(R) (2016).
4. T. Suzuki, R. Singh, M. Bayer, A. Ludwig, A. D. Wieck, and S. T. Cundiff, “Coherent Control of the Exciton/Biexciton System in an InAs Self Assembled Quantum Dot Ensemble,” *Phys. Rev. Lett.* **117**, 157402 (2016).
5. R. Singh, M. Richter, G. Moody, M.E. Siemens, H. Li and S.T. Cundiff, “Localization dynamics of excitons in disordered semiconductor quantum wells,” *Phys. Rev. B* **95**, 235307 (2017).

SISGR: Understanding and Controlling Strong-Field Laser Interactions with Polyatomic Molecules

DOE Grant No. DE-SC0002325

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1. Project Scope

When intense laser fields interact with polyatomic molecules, the energy deposited leads to fragmentation, ionization, and electromagnetic emission. The objective of this project is to determine to what extent these processes can be controlled by modifying the phase and amplitude characteristics of the laser field according to the timescales for electronic, vibrational, and rotational energy transfer. Controlling these processes will lead to order-of-magnitude changes in the outcome from laser-matter interactions, which may be both of fundamental and technical interest. The proposed work is unique because it seeks to combine knowledge from the field of atomic, molecular-optical physics with knowledge from the fields of analytical and organic ion chemistry. This multidisciplinary approach is required to understand to what extent the shape of the field affects the outcome of the laser-molecule interaction and to which extent the products depend on ion stability. The information resulting from these systematic studies will be used to construct a theoretical model that tracks the energy flow in polyatomic molecules following interaction with an ultrafast pulse.

2. Recent Progress

(a) Discovery of neutral H₂ roaming chemistry occurring under strong fields

Nagitha Ekanayake, Muath Nairat, Balram Kaderiya, Peyman Feizollah, Bethany Jochim, Travis Severt, Ben Berry, Kanaka Raju P., Kevin D. Carnes, Shashank Pathak, Daniel Rolles, Artem Rudenko, Itzik Ben-Itzhak, Christopher A. Mancuso, B. Scott Fales, James E. Jackson, Benjamin G. Levine, and Marcos Dantus “Mechanisms and time-resolved dynamics for trihydrogen cation (H₃⁺) formation from organic molecules in strong laser fields,” *Nature Scientific Reports*, 7, 4073 (2017)

Strong-field laser-matter interactions often lead to exotic chemical reactions. H₃⁺ formation from organic molecules is one such case that requires multiple bonds to break and form. In this study, conducted in collaboration with James R. Macdonald Laboratory at Kansas State University, we present evidence for the existence of two different reaction pathways for H₃⁺ formation from organic molecules irradiated by a strong-field laser. The existence of two pathways, their mechanistic details and timescales for H₃⁺ formation from organic molecules in a strong laser field have been experimentally determined by femtosecond time-resolved time-of-flight mass spectroscopy and photoion-photoion coincidence momentum measurements carried out on methanol isotopomers, ethylene glycol, and acetone. *Ab initio* molecular dynamics simulations suggest that H₃⁺ formation occurs via a two-step mechanism in which a neutral H₂ molecule is formed, and then roams about the doubly charged intermediate until it abstracts a proton from the remaining CHOH²⁺ fragment. This reaction, proton abstraction by the roaming H₂ molecule, is reminiscent of the well-known Hogness and Lunn reaction for H₃⁺ formation in the universe. These exotic chemical reaction mechanisms, involving roaming H₂ molecules, are found to occur in the ~100 fs timescale. Roaming molecule reactions may help to explain unlikely chemical processes, involving dissociation and formation of multiple chemical bonds, occurring under strong laser fields.

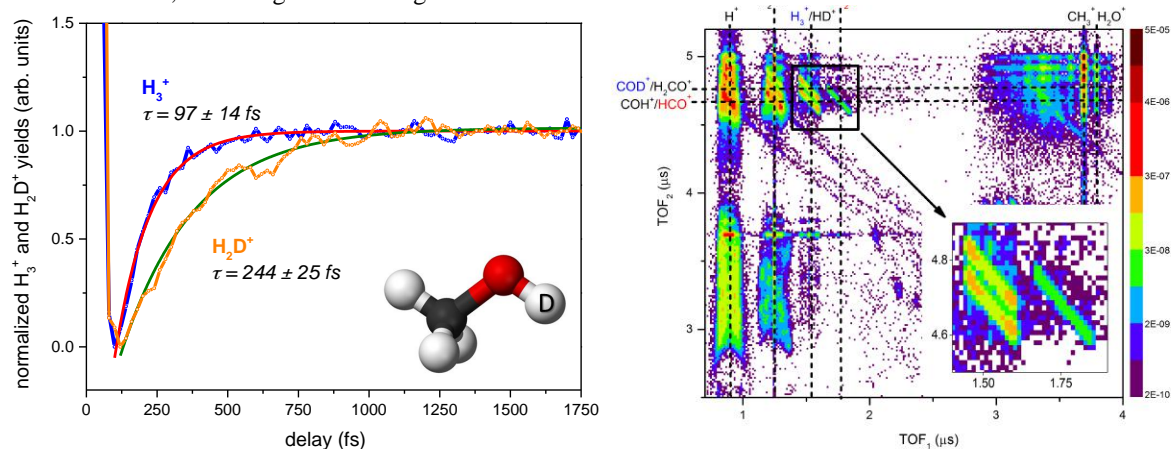


Fig. 1 (Left), Time resolved data used to determine the time for H₃⁺ formation for two distinct pathways. (Right) Photoion-photoion coincidence data confirming the two different pathways.

(b) Additional chemical reactions implying H₂ roaming chemical reactions under strong fields (alcohols and thiols)

Nagitha Ekanayake, Nicholas Weingartz, Vadim V. Lozovoy, James E. Jackson, Marcos Dantus, in collaboration with JRML Itzik Ben-Itzhak “H₂ roaming chemistry and the formation of H₃⁺ from organic molecules in strong laser fields,” to be submitted to Nature Chemistry (Fall 2017).

We have studied the formation of H₃⁺ following strong-field excitation for a number of alcohols. We have measured the quantum yield for this roaming neutral-hydrogen molecule reaction product for the different alcohols. We find that methanol has the highest efficiency while isopropanol has the lowest. We explain the observed reaction timescales and yields with the aid of molecular dynamics simulations.

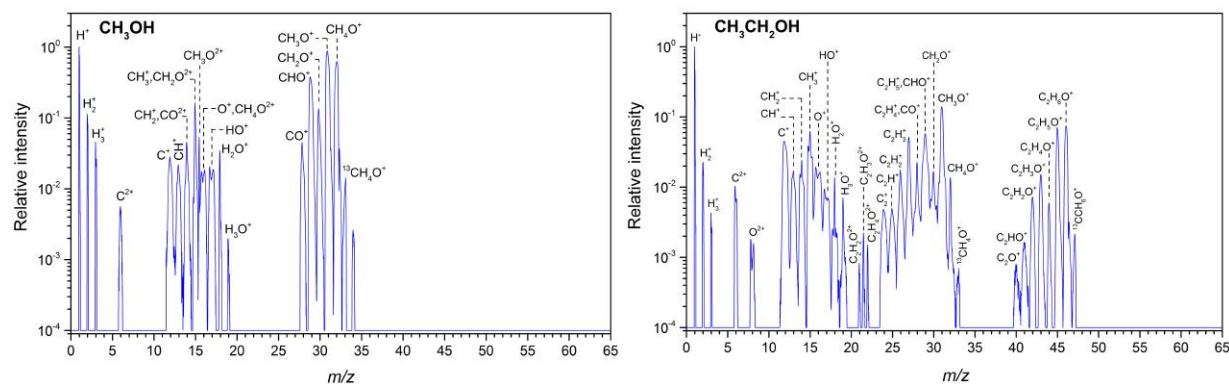


Fig. 2 (Left) Mass spectrum obtained at 10^{14} W/cm² for methanol showing significant H₃⁺ formation. (Right) Mass spectrum obtained at 10^{14} W/cm² for ethanol showing 10x less H₃⁺ formation under the same conditions.

(c) The lower pre-dissociative excited states of the sodium iodide revisited

Gennady Rasskazov, Muath Nairat, Ilias Magoulas, Vadim V. Lozovoy, Piotr Piecuch, Marcos Dantus, “Femtosecond real-time probing of reactions MMXVII: The predissociation of sodium iodide in the A 0+ state,” Chem. Phys. Letters, 683, 127-127 (2017).

We revisit the femtosecond transition-state spectroscopy of sodium iodide taking advantage of modern lasers and pulse-shaping to better map the low-lying electronic states, some forming predissociative wells through curve crossings. We also carry out high-level *ab initio* multi-reference configuration interaction calculations including spin-orbit coupling terms and using large correlation-consistent basis sets to arrive at accurate ground- and excited-state potential energy curves of NaI. Density matrix calculations employing vibrational wave functions determined from the *ab initio* X 0+ and A 0+ potentials are used to simulate time dependent wave packet dynamics of NaI pumped to the A 0+ state.

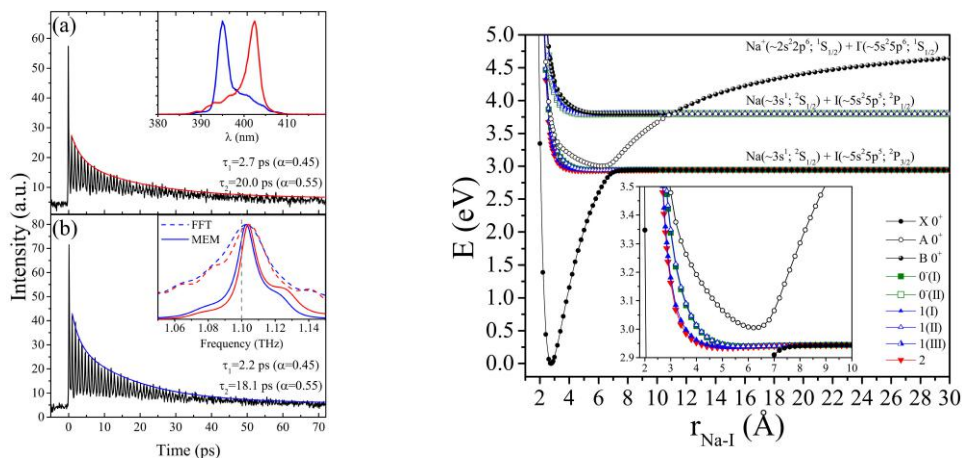


Fig. 3 (Left) Experimental pump-probe transient obtained with (a) 402 nm (red spectrum in the inset of (a)) and (b) 395 nm (blue spectrum in the inset of (a)) pump wavelengths and 798 nm probe laser wavelengths with exponential fitting. The inset of (b) shows the FFT (dashed) and MEM (solid) from the 402 nm (red) and the 395 nm (blue) pump wavelength. (Right) Potential

energy curves of NaI obtained in the MRCI/AV5Z+SO calculations. The inset shows the zoomed in region of the lower-energy avoided crossing.

(d) Re-thinking femtosecond pulse compression:

V. V. Lozovoy, M. Nairat, and M. Dantus, “Binary phase compression of stretched pulses,” J. Optics 19, 105506 (2017).

Pulse stretching and compression are essential for the energy scale-up of ultrafast lasers. Here, we consider a radical approach using spectral binary phases, containing only two values (0 and π) for stretching and compressing laser pulses. We numerically explore different strategies and present results for pulse compression of factors up to a million back to the transform limit and experimentally obtain results for pulse compression of a factor of one hundred, in close agreement with numerical calculations. Imperfections resulting from binary-phase compression are addressed by considering cross-polarized wave generation filtering, and show that this approach leads to compressed pulses with contrast ratios greater than ten orders of magnitude. This new concept of binary-phase stretching and compression, if implemented in a multi-layer optic, could eliminate the need for traditional pulse stretchers and more importantly, expensive compressors.

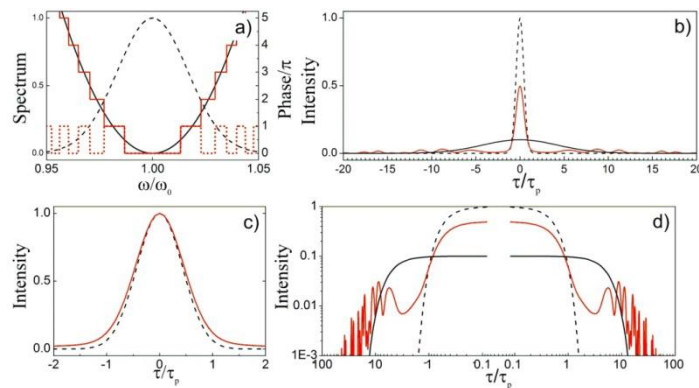


FIG. 4 (left). Principle of binary phase compression. a) (x axis – is relative to carrier frequency) dash – spectrum, black – parabolic phase dispersion to stretch the pulse, red solid and dotted – phase to compensate back to TL duration. b) (x-axis is ratio of time to the duration of the pulse) on y axis are intensity of TL (dash), chirped (black) and red (compressed) pulses. c) Intensities of TL (dash) and compressed (red) pulses normalized on max. d) Plots of the same intensities as on b) but log-log scales to show how energy of laser pulse stretched to the long times.

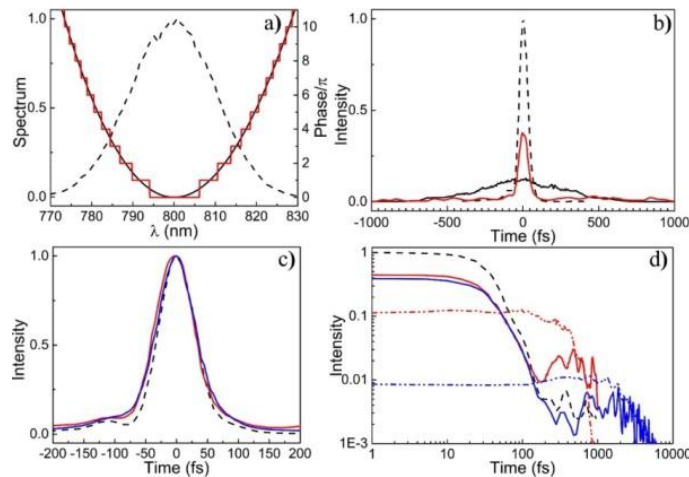


FIG. 5. Experimental results (a) Spectrum and phases used to stretch the pulse 10 times using a chirp value of $10,000 \text{ fs}^2$ (black) and binary (red) phase added to compress it back to have FWHM as for TL pulse. (b) Cross-correlation functions of TL pulse (dash) 10 times stretched (black) and binary compressed pulse (red) (c) Cross-correlation functions of TL pulse (dash) binary compressed pulse that is originally 10 times stretched (red) and 100 times stretched (blue) normalized on maximum and at short times. (d) long time behavior of TL (black dash), chirped at 10 (red dash) and 100 (blue dash) times, and binary compressed pulses that were originally chirped at 10 times (red) and 100 times (blue) in log-log scales for positive delay times.

(e) Polyatomic molecules in strong (10^{14}W/cm^2) fields:

1. M. Nairat, J. Lantis, V. V. Lozovoy, and M. Dantus, "Order of Magnitude Dissociative Ionization Enhancement Observed for Pulses with High Order Dispersion", *J. Phys. Chem. A* **120**, 8529–8536 (2016)

While the interaction of atoms in strong fields is well understood, the same cannot be said about polyatomic molecules. We consider how dissociative ionization of molecules depends on the quality of the femtosecond laser pulses, in particular the presence of third- and fourth-order dispersion (TOD and FOD). We find that high-order dispersion (HOD) unexpectedly results in order-of-magnitude enhanced ion yields, along with factor of three greater kinetic energy release compared to transform-limited (TL) pulses with equal peak intensities. The magnitude of these effects is not caused by increased pulse duration. We evaluate the role of pulse pedestals produced by HOD and other pulse shaping approaches, for a number of molecules, and discuss our findings in terms of processes such as pre-alignment, pre-ionization, and bond softening. We conclude, based on the quasi-symmetric temporal dependence of the observed enhancements, that cascade ionization is likely responsible for the large accumulation of charge prior to the ejection of energetic fragments along the laser polarization axis.

3. Future Plans

The proposed research addresses Grand Challenge questions related to quantum control of electrons in matter, and in particular coherent control of excited electronic states, optimal control, and control pushed to higher energy, broader bandwidth and shorter times. Last year we set out to determine the timescale and mechanism for the formation of H_3^+ , and this led us to discovering neutral hydrogen roaming chemistry. Following a new round of experiments on a series of alcohols, it is now clear that hydrogen roaming is essential to understand the dissociative ionization of organic molecules under strong laser fields. What is even more exciting is that roaming hydrogen chemistry likely plays an important role in astrochemistry (leading to organic compounds in the universe), in combustion, and perhaps in condensed phase. We are planning a number of additional projects to discover the extent of roaming chemistry under strong laser fields (formation of H_2O^+ and H_3O^+) and its possible control through pulse shaping. Recent measurements with alkane-thiols continue the trends observed for the alcohols, however, these compounds are more susceptible to yield multiply ionized species which coulomb explode prior to H_3^+ formation. We plan to complete our work on electronic coherence observed in dicyclopentadiene, and we want to start getting data from our PEPICO instrument.

5. Peer Reviewed Publications Resulting from this Project (2015-2017) (one year under NCE)

1. A. Konar, V.V. Lozovoy, and M. Dantus, "Electronic dephasing of molecules in solution measured by nonlinear spectral interferometry," *ScienceJet* 4, 141 (2015)

2. R. Mittal, R. Glenn, I. Saytashev, V. V. Lozovoy and M. Dantus, "Femtosecond Nanoplasmonic Dephasing of Individual Silver Nanoparticles and Small Clusters," *J. Phys. Chem. Lett.* 6, 1638–1644 (2015)

3. M. Nairat, J. Lantis, V. V. Lozovoy, and M. Dantus, "Order of Magnitude Dissociative Ionization Enhancement Observed for Pulses with High Order Dispersion", *J. Phys. Chem. A* **120**, 8529–8536 (2016)

4. Nagitha Ekanayake¹, Muath Nairat¹, Balram Kaderiya², Peyman Feizollah², Bethany Jochim², Travis Severt², Ben Berry², Kanaka Raju P.², Kevin D. Carnes², Shashank Pathak², Daniel Rolles², Artem Rudenko², Itzik Ben-Itzhak², Christopher A. Mancuso¹, B. Scott Fales¹, James E. Jackson¹, Benjamin G. Levine¹, and Marcos Dantus^{1,3} "Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields," *Nature Scientific Reports*, 7, 4073 (2017)

5. Gennady Rasskazov, Muath Nairat, Ilias Magoulas, Vadim V. Lozovoy, Piotr Piecuch, Marcos Dantus, "Femtosecond real-time probing of reactions MMXVII: The predissociation of sodium iodide in the A 0+ state," *Chem. Phys. Letters*, 683, 127-127 (2017)

6. V. V. Lozovoy, M. Nairat, and M. Dantus, "Binary phase compression of stretched pulses," *J. Optics* 19, 105506 (2017)

PROGRAM TITLE: ATTOSECOND, IMAGING AND ULTRA-FAST X-RAY SCIENCE

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1.1 PROJECT SCOPE

This grant aims at exploring the realm of ultrafast dynamics using different complementary tools. In one thrust, fundamental aspects of generation and measurement of high harmonic and attosecond pulses are explored and exploited to access fundamental atomic and molecular processes. A second thrust provides a natural link to our attosecond effort via the same underlying strong field physics, laboratory infrastructure and technical approach. The strong field driven “self-imaging” method uses elastic scattering of field-driven electron wave packets as an alternative route for spatial-temporal imaging in the gas phase. In 2012, the viability of this approach for achieving femtosecond timing and picometer spatial resolution was demonstrated by a collaboration between OSU and KSU groups. A third scope is the implementation of an AMO science program using the ultra-fast, intense x-rays available at LCLS XFEL. The objective is the study of fundamental atomic processes involving multiple inner-shell ionization, x-ray nonlinear optics and the development of new methods for time-resolved x-ray physics. Our overall objective is advancing these methods as robust tools for imaging and probing electron dynamics thus producing the complete molecular movie.

Progress over the past year includes the completion of two projects: (1) the measurement of the spectral phases near threshold for different inert gas atoms and (2) a precise measure of the complex recombination dipole in the molecular frame. A number of project are underway including (1) an attosecond simulator of strong-field e - $2e$ ionization and (2) dynamical spatial-temporal imaging of the C_{60} fullerene. Two runs are scheduled for the Fall 2017 and Winter 2018: (1) real time streaking of the Auger decay in atoms and molecules and (2) diffractive imaging at the LCLS of pumped C_{60} fullerene.

1.2 PROGRESS IN FY17: THE ATTOSECOND PROGRAM

The technical approach of the Ohio State University (OSU) group is the use of long wavelength ($\lambda > 1 \mu\text{m}$) driving lasers for harmonic and attosecond generation, and imaging. Through support of this program, the long wavelength approach has been successful and adopted by many groups world-wide. Our program over the last several years has turned towards using these long wavelength generated harmonics for measurements, ultimately of dynamics. We are interested in addressing two basic questions related to attosecond physics. First, can high harmonic and attosecond spectroscopy extract atomic/molecular structure and second, what is really being measured.

Probing Electronic Binding Potentials with Attosecond Photoelectron Wavepackets. In the field of Attosecond Physics, pump-probe techniques, such as Attosecond Streaking and Reconstruction of Attosecond Beating by Interference of Two-photon Transitions (RABBITT) [1], employ short extreme-ultraviolet radiation pulses synchronized with a near-infrared dressing field to clock electronic processes in atoms, molecules, and solids down to the exceptionally short timescales over which they occur. The Simpleman model provides the basic understanding of how the energy-transfer processes between the ionized electron and the dressing field yields a direct energy-to-time mapping. Many experiments exploit

the simplicity of this model to uncover and understand the underlying physical processes from their results.

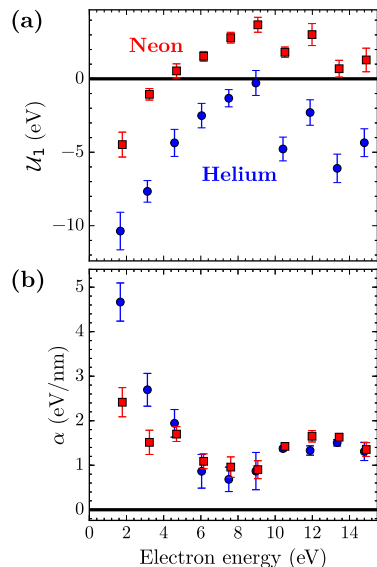


Figure 1: RABBITT+ analysis.

our experimental method, which we dub RABBITT+. The technique is a combination of a RABBITT phase measurement with additional amplitude information and an additional low-ionization-energy reference target (argon). We extract coarse information about the host's potential: the average effective potential (Fig. 1[a]) and average slope (Fig. 1[b]) of the effective potential experienced by slow-moving, low-energy electrons in the first 1.4 femtoseconds after ionization from helium and neon atoms.

From the results shown in the figure, we infer for helium a deep effect potential near the core with a rapid slope, a qualitatively expected result. The results for neon are considerably different, even though the ionization-energy is similar. Not only is the effective potential much shallower and less steep, but there is a change of sign in the average effective potential value as the electron energy changes. For slightly higher-energy electrons, the close-range effective potential becomes repulsive on average. These results are qualitatively comparable to a previous simulated experiment that used pseudopotentials for the atoms [3]. The work was a collaboration with Prof. Bob Jones (UVa) and accepted for publication [7A].

Harmonic spectroscopy: a precise measure of the complex recombination dipole in the molecular frame. We measured the amplitude and group delay of high harmonics generated in nitrogen with 1.3 μm and 2 μm laser pulses up to 70 eV for several angles between the driving field polarization and the molecular ensemble axis of symmetry. The goal of this experiment is to evaluate more precisely than previous studies the contribution of structural and dynamical properties of the nitrogen molecular system to high harmonic generation. This technique of high harmonic spectroscopy has been proposed for molecular orbital tomography [4]. Our experimental results feature several major improvements, such as high degree of molecular alignment and use of mid-infrared driver pulses to

However, the Simpleman model assumes that the host atom has no influence on the outgoing photoionized electron, an approximation that ignores well-known spectroscopic features, such as auto-ionizing resonances and Cooper minima, and that becomes increasing worse as the electron's energy approaches zero. Removing the effects of this influence by the host in these measurements has been an active area of research [2], leading to an improved understanding of specific continuum features and intrinsic effects caused by the measurement technique itself. Working to apply this understanding to experimental results is difficult, requiring significant theoretical input that can be limited by the approximations required, notably, for our experiment, when the electron's energy is near zero.

We approach this problem from a different angle by experimentally extracting from the measured photoelectrons information about the host's effective potential, including multi-electron effects. We concentrate on the lowest-energy electrons, those most difficult to theoretically study, because they spend more time near the host's potential and therefore feel the largest effect. Using a simple, analytical reformulation of the Simpleman model applied to

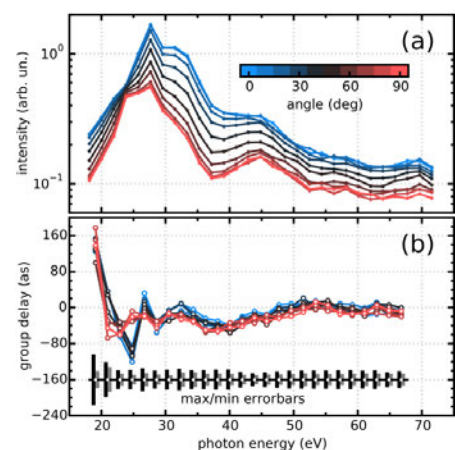


Figure 2: 1.3 μm N₂ (a) high harmonic intensity and (b) group delay as a function of photon energy.

extend the available spectral range and increase the sampling density.

Comparison of the measurement with calculated angle-averaged photoionization scattering-wave dipole (collaboration with Prof. Robert Lucchese [TAMU]) results in quantitative agreement above 30 eV and qualitative agreement over the whole spectrum. Figure 2 shows the results from 19 to 45 eV for alignment angles between 0 and 90 degrees. The amplitude emphasizes a shape resonance at 30 eV. The group delay shows well reproducible narrow and large range features in general good agreement with simulations based on angle-averaged scattering-wave photoionization dipole of the nitrogen Highest Occupied Molecular Orbital [5]. These results highlight the benefit of long wavelengths in efficiently separating the contribution from several molecular orbitals, as well as the influence of electron scattering and resonances on HHG and the need to account for these processes to establish a correct procedure for molecular orbital tomography reconstruction. The work is published in Phys. Rev. Letters (see [4A]).

1.3 PROGRESS IN FY17: THE MOLECULAR IMAGING PROGRAM

Ultrafast dynamical imaging of C₆₀ fullerene. The 1985 discovery of C₆₀ by Kroto, Smalley and Curl marked the beginning of fullerene research in nanoscience. Fullerenes are the third allotrope of carbon next to graphite and diamond. Widespread in nature from soot to interstellar clouds, their world is comprised of a wide variety of nanoscale-size closed shapes from simple spheres to tubules, onions, rods, ribbons etc. each possessing interesting, specific and yet useful properties. Since its discovery, the soccer ball shaped C₆₀ - the archetypical fullerene - remains the focus of most ongoing scientific studies.

The interaction of C₆₀ with strong femtosecond lasers has been the object of numerous studies which revealed that at photon energies comparable with the first excited state (~2.1 eV), the laser energy is efficiently transferred into C₆₀'s internal degrees of freedom. This extra energy is subsequently "evaporated" via C-C pair "boil off" fragmenting the molecule. However, at lower photon energy (less than 2.1 eV/3) fragmentation is not observed and multiple ionization of the intact cage is possible even at high intensities (10¹⁴ W/cm²).

Cage fragmentation suppression at long wavelengths (< 1.8 μm) does not imply a rigid molecule. Indeed, previous theoretical models have shown that collective effects lead to periodic cage deformations along the laser polarization, with h_g(1) the dominant active mode. We have successfully extended the laser-driven self-imaging electron diffraction techniques for visualized a C₆₀ cage elongation of ~5% under irradiation with 80 TW/cm², 100 fs, 3.6 μm, pulses. The observed deformation is verified by density functional theory (DFT) calculations of the nuclear dynamics on time-dependent adiabatic states. This result is the first step towards visualizing and studying the complex real time molecular dynamics of macromolecular structures. The work is a collaboration with Dr. Matthias Kling (LMU) and Prof. Hirohiko Kono (Tohoku U). A manuscript is in preparation.

1.4 FUTURE PLANS

Strong field e-2e simulator: Double ionization is a paradigm for understanding many-body effects. As part of near term plans, we will use a tunneling simulator to time-resolved double ionization of helium atoms. Figure 3 illustrates the basic concept. In the experiment, attosecond pulses will photoionize helium above the 1e threshold (>24 eV) in the presence of an intense dressing field. The linearly polarized dressing field will quiver the electron in a manner similar to the second step (field-driven electron wave packet) in the rescattering model. In this scenario, the attosecond photoionization replaces tunnel ionization in a strong low-frequency field while the dressing field acts as the driver of the electron wave packet (EWP). Subsequent interaction of the EWP with the helium core will promote, among others, the (e,2e) process. The requirement is that 3U_p ≥ 54 eV (He⁺ ionization potential) and that the dressing field alone does not ionize helium. Simple estimates show that this is only possible with mid-infrared dressing fields. If successful, the tunnel simulator will allow exquisite control over the (e,2e) process.

In FY2017, a new attosecond beamline has been modified to incorporate an e^- ion coincidence end station. The apparatus is operational, significant trouble shooting performed and preliminary data collection is in progress. We expect our first helium results by the end of 2017. The work is a collaboration with Robert Jones (UVa) and Ken Schafer (LSU).

Imaging: The goal for FY17 is the application of LIED/FABLES to study ultrafast molecular dynamics using pump-probe geometries. (1) Work will continue on hydrocarbons. Our recent 3 μm static images of butane were captured in ~ 15 minutes with good S/N which makes a pump-probe measurement feasible. The initial investigations will time-resolve dissociation of the carbon chains following VIS/UV excitation; (2) extend the hydrocarbon studies to image aromatic compounds (benzene and its derivative); (iii) examine molecular grating effects in linear hydrocarbons; (iv) continue the work on fullerenes, including planning a second campaign in Barcelona for visualizing the breathing mode of C_{60} .

LCLS: A paper on “Femtosecond profiling of shaped X-ray pulses” that resulted from a previous LCLS on streaking has been submitted to New J. Physics. We have been awarded LCLS time at the end of September 2017 to perform dynamical x-ray imaging of C_{60} . A second LCLS beam time has been awarded in February 2018 for “Attosecond interrogation of relaxation dynamics in highly excited atoms and molecules”. This is a continuation of our attempts to time-resolve Auger decay using a low-frequency streaking field with the LCLS x-ray beam.

1.5 REFERENCES CITED

- [1] H. G. Muller, Appl. Phys. B 74 S17 (2002).
- [2] J. M. Dahlström, A. L’Huillier and A. Maquet, J. Phys. B 45 183001 (2012).
- [3] J. Mauritsson, M. B. Gaarde, and K. J. Schafer, Phys. Rev. A 72, 013401 (2005)
- [1] J. Itatani *et al.*, Nature **432**, 867-871 (2004).
- [2] R. R. Lucchese *et al.* Phys. Rev. A **25**, 2572 (1982).

1.6 PUBLICATION RESULTING FROM THIS GRANT FROM 2015-2017

- 1A. “Numerical simulation of the double-to-single ionization ratio for the helium atom in strong laser fields”, Zhangjin Chen *et al.*, Phys. Rev. A **92**, 063427 (2015). doi: 10.1103/PhysRevA.92.063427.
- 2A. “Time-resolved molecular imaging”, Junliang Xu, C. I. Baga, P. Agostini and L. F. DiMauro, J. Phys. B **49**, 112001 (2016). doi:10.1088/0953-4075/49/11/112001.
- 3A. “Synthesis and characterization of attosecond light vortices in the extreme ultraviolet”, R. Gèneaux *et al.*, Nat. Comm. doi: 10.1038 (2016).
- 4A. “Precise access to the molecular-frame complex recombination dipole through high-harmonic spectroscopy”, S. Schoun *et al.*, Physical Review Letters **118**, 033201 (2017)..
- 5A. “Radial index of Laguerre-Gaussian modes in high-order-harmonic generation”, R. Geneaux *et al.*, Phys. Rev. A **95**, 051801 (2017). doi: 10.1103/PhysRevA.95.051801.
- 6A. “Tunable orbital angular momentum in high-harmonic generation”, D. Gauthier *et al.*, Nat. Comm. doi: 10.1038/ncomms14971.
- 7A. “Probing Electronic Binding Potentials with Attosecond Photoelectron Wavepackets”, D. Kiewewetter *et al.*, Nat. Phys., accepted.

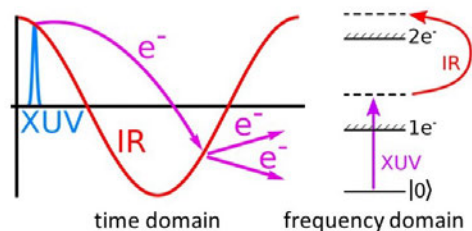


Figure 3: In the time domain, a photoelectron is excited to the $1e$ helium threshold by an XUV attosecond pulse (see frequency domain). The electron accelerated by a phased locked low-frequency field can recollide with the He^+ core, freeing a second electron.

Extended Numerical Detector Theory and Electron Correlation

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Project Scope

High-field effects of recent and current interest in AMO science are triggered by laser pulses with intensities in the range $I \geq 0.1 \text{ PW/cm}^2$. We are interested to understand how such laser pulses excite electrons in atoms, leading to high-correlation effects ranging from multi-electron ejection to high-harmonic generation to the emergent area of atto-science. The combination of phase-coherent character and short-time nature of laser irradiation creates substantial challenges to theoretical study in this high-field domain.

We have listed the challenges and mentioned successes and discussed areas needing future study in an invited review [1] and have recently begun to provide fundamental quantitative information about the ionization event itself, which is usually described in a model calculation based on a tunneling approximation. In contrast, our approach is distinguished by its basis in *ab initio* electron dynamics. The goal is many-sided because one wants to come as close as possible to a theoretical description that starts with a correct electrodynamic treatment of the laser photons, allows for key atomic features, and pursues time-dependent evolution without making perturbative approximations. Our work has been invited for inclusion in a Special Issue of Journal of Physics B coordinated by M. Vrakking (MPI-Erlangen). I mention below future plans, and refer to recent reports [2, 3, 4, 5] of studies of electron momenta near to an ionization event. They build on earlier results [6, 7] and outline the way to the improvements of our SENE method that are outlined below.

Recent Progress

Two avenues of *ab initio* evolution have enabled recent progress, and our calculations have followed both, leading in 2017 to two peer-reviewed publications [3, 4]. One approach is partially analytical via extension of the “Simpleman” model [8, 9], and the other is purely numerical.

We have been engaged in an extended collaboration with the Biegert experimental group in Barcelona. The current project [4] deals with the intriguing transition zone between non-sequential and sequential double ionization in multi-electron systems, previously largely overlooked. This provides an example of our ability to follow longer-than-optical wavelength experiments used to uncover new phenomena or enable more detailed studies. Our *ab initio* semi-classical approach is essentially an extension of the “Simpleman” theory.

The other example [3] is the incorporation of Coulomb effects that have captured attention in single-electron ionization experiments in the past 3-5 years (see [10, 11, 12, 13, 14, 15]). What has been missing is the ability to attend to the nature of electron behavior in the near neighborhood of the legendary (or mythical) “tunnel exit”, which plays an important role in the standard tunneling-based “strong field approximation” (SFA) originating with Keldysh [16] and extended by Reiss and

others (see [1]). A need for attention to this point has existed since it was described a decade earlier by Ivanov, Spanner and Smirnova [17] where they said:

“Identifying the wavepacket dependence on v_x is much harder. The crucial difficulty stems from the fact that the laser field accelerates the electron while it tunnels out. The velocity distribution along the field is changed continuously during tunneling. ... Uncertainty in the moment of tunneling, which is responsible for the uncertainty in the initial velocity, also means that it is virtually impossible to separate the initial velocity distribution from the distortions caused by the electric field during this temporal uncertainty.”

Most recent work with the *ab initio* SENE approach (see [2, 3, 5]), shows that an outgoing wave packet will be accelerated and stretched in the direction of the laser field. In an adiabatic tunneling model, the electron cannot gain energy during the tunneling process. This assumption is correct for transverse momenta, but may reach misleading conclusions for longitudinal momentum distributions. For example, as we have shown, effects of temporal oscillations will be missed.

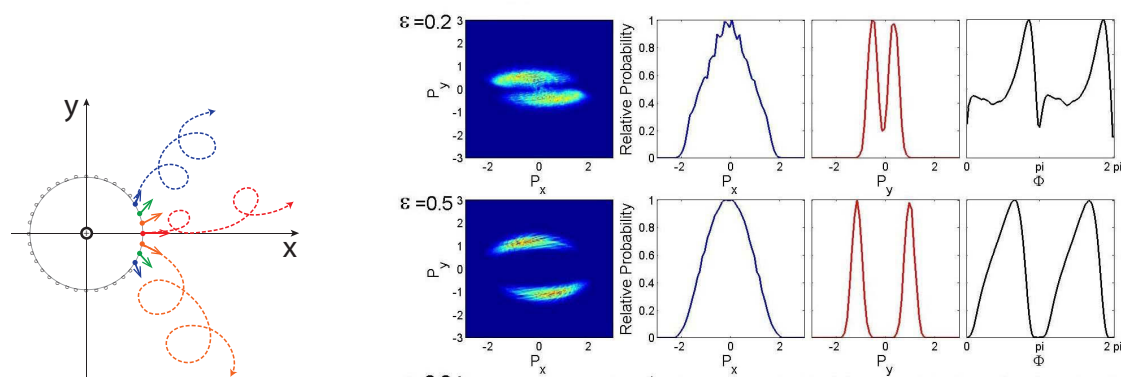


Figure 1: (left) Ionized electron momenta are sketched departing from the numerical detector ring. (right) Their TDNE evolution gives far-field electron momentum distributions consistent with data reported by Pfeiffer, et al. [12].

Future Plans

The top priority for future work is extension of our SENE application (see J. Tian, Ph.D. thesis [2]) of the Feuerstein-Thumm idea [18]. To summarize briefly: the SENE method solves the Schrödinger Equation (SE) numerically exactly in a small region near the ion. Then it makes “virtual” detection of the expanding quantum wave function of the electron by a purely numerical recording of its quantum phase over a sphere around the ion. In cases of elliptically polarized irradiation only a two-dimensional detector ring has been used. From this record a distribution of electron momenta is extracted from the gradient of the wave function’s phase at each point on the ring (or sphere). Then those momenta are used to initiate classical Newtonian Evolution (NE) into the far field, as shown in the left panel of Fig. 1. In the right panel we note the SE + NE = SENE result for $\epsilon = 0.2$. Its asymmetry is consistent with the similar asymmetry in the experimental record on helium (see experimental Fig. 2b of Pfeiffer, et al. [12]).

The numerical detector SENE method has demonstrated attractive features. The successes to date of the two-staged SENE approach [3, 6] strongly mandate extended work. Current results have been satisfactory, but were obtained from detector ring radii in the neighborhood of $10 a_0$ or larger. Several directions for improvement are available. One is to extend from a two-dimensional ring

to a three-dimensional detector surface. However, first we intend to improve the two-dimensional detector ring to allow it to be placed closer to the ion. The ring is composed of a finite number of calculational cells in the grid. This cell-size discreteness naturally contradicts the smoothness desired for the outgoing directional distribution of momenta, and compromises attempts to compare calculated momenta with experimental far-zone momenta. As the detector ring will be made smaller, each of the numerical cells making up the ring will then be responsible for a larger solid angle of wave function emergence. The wave function's phase gradient is then angularly less smooth from cell to cell. This means interruption of directional smoothness of the initial conditions for the subsequent Newtonian propagation and cannot be corrected later "in flight".

Thus our immediate task will be to solve the directional smoothness issue. Possible approaches include the following: (i) We make a brute-force code reconstruction to embed the ring in a narrow computational zone with a finer-grained grid. This is an unattractive and lengthy but probably straightforward prospect. (ii) We will try to avoid this by other means such as design of a phase gradient algorithm that employs a higher number of cells numerically associated to each small outgoing solid angle. (iii) A related alternative is to replace the ring with an "onion" type detector that accepts information from more than one layer of cells.

Publications supported in the two most recent grant periods are marked with * in the listing.**

References

- [1] ***W. Becker, X.J. Liu, P.J. Ho and J.H. Eberly, "Theories of Photo-Electron Correlation in Laser-Driven Multiple Atomic Ionization," *Rev. Mod. Phys.* **84**, 1011 (2012). [ISI Highly Cited Paper]
- [2] ***Justin Tian, "Theory of Strong-Field Atomic Ionizations", Ph.D. Dissertation, Department of Physics and Astronomy, University of Rochester (2017).
- [3] ***J. Tian, X. Wang, and J.H. Eberly, "Numerical Detector Theory for the Longitudinal Momentum Distribution of the Electron in Strong Field Ionization," *Phys. Rev. Lett.* **118**, 213201 (2017).
- [4] *** Michael G. Pullen, Benjamin Wolter, Xu Wang, Xiao-Min Tong, Michele Sclafani, Matthias Baudisch, Hugo Pires, Claus Dieter Schrter, Joachim Ullrich, Thomas Pfeifer, Robert Moshhammer, J. H. Eberly and Jens Biegert, "Transition from nonsequential to sequential double ionization in many-electron systems", *Phys. Rev. A* **96**, 033401 (2017). DOI: 10.1103/PhysRevA.96.033401 .
- [5] *** J.H. Eberly, "Where Do the Electrons Come From?", Invited Plenary Lecture, International Conference on Matter and Radiation at Extremes (ICMRE), Beijing CHINA, June 26-30, 2017; and to be published.
- [6] ***X. Wang, J. Tian and J.H. Eberly, "Extended Virtual Detector Theory for Strong-Field Atomic Ionization," *Phys. Rev. Lett.* **110**, 243001 (2013).
- [7] ***Justin Tian, Xu Wang and J.H. Eberly, "Extended Breakdown of the Simpleman Approximation," *Chin. Opt. Lett.* **11**, 010001 (2013).
- [8] H.B. van Linden van den Heuvell and H. G. Muller, in *Multiphoton Processes*, S. J. Smith and P. L. Knight, eds., vol. 8 of Cambridge Studies in Modern Optics (Cambridge University Press, Cambridge, 1988), p. 25
- [9] *** Xu Wang, Justin Tian and J.H. Eberly, "Angular correlation in strong-field double ionization under circular polarization," *Phys. Rev. Lett.* **110**, 073001 (2013).

- [10] A.S. Landsman, C. Hoffman, A.N. Pfeiffer, C. Cirelli, and U. Keller, *Phys. Rev. Lett.* **111**, 263001 (2013).
- [11] M. Li, Y. Q. Liu, H. Liu, Q. C. Ning, L. B. Fu, J. Liu, Y. K. Deng, C. Y. Wu, L. Y. Peng, and Q. H. Gong, *Phys. Rev. Lett.* **111**, 023006 (2013).
- [12] A.N. Pfeiffer, C. Cirelli, A.S. Landsman, M. Smolarski, D. Dimitrovski, L.B. Madsen and U. Keller, *Phys. Rev. Lett.* **109**, 083002 (2012).
- [13] D. Shafir, H. Soifer, C. Vozzi, A. S. Johnson, A. Hartung, Z. Dube, D. M. Villeneuve, P. B. Corkum, N. Dudovich, and A. Staudte, *Phys. Rev. Lett.* **111**, 023005 (2013).
- [14] C. Hofmann, A. S. Landsman, C. Cirelli, A. N. Pfeiffer, and U. Keller, *J. Phys. B* **46**, 125601 (2013).
- [15] X. F. Sun, M. Li, J. Z. Yu, Y. K. Deng, Q. H. Gong, and Y. Q. Liu, *Phys. Rev. A* **89**, 045402 (2014).
- [16] L.V. Keldysh, *Zh. Eksp. Teor. Fiz.* **47**, 1945 (1964) [Engl. translation: *Sov. Phys. JETP* **20**, 1307 (1965)].
- [17] M. Y. Ivanov, M. Spanner, and O. Smirnova, *J. Mod. Opt.* **52**, 165 (2005).
- [18] B. Feuerstein and U. Thumm, *J. Phys. B* **36**, 707 (2003).

Peer-reviewed Publications Resulting from this Project (2015-2017)

“Numerical Detector Theory for the Longitudinal Momentum Distribution of the Electron in Strong Field Ionization,”

J. Tian, X. Wang, and J.H. Eberly,
Phys. Rev. Lett. **118**, 213201 (2017).

“Transition from nonsequential to sequential double ionization in many-electron systems”,
Michael G. Pullen, Benjamin Wolter, Xu Wang, Xiao-Min Tong, Michele Sclafani, Matthias Baudisch, Hugo Pires, Claus Dieter Schrter, Joachim Ullrich, Thomas Pfeifer, Robert Moshhammer, J. H. Eberly and Jens Biegert,

Phys. Rev. A **96**, 033401 (2017). DOI: 10.1103/PhysRevA.96.033401 .

Image Reconstruction Algorithms

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Division of Chemical Sciences, Geosciences, and Biosciences
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Program Scope

The many-orders-of-magnitude gains in X-ray brightness achieved by free-electron laser sources such as the LCLS are driving a fundamental review of the data analysis methods in X-ray science. It is not just a question of doing the old things faster and with greater precision, but doing things that previously would have been considered impossible. Recently this definition has expanded to include structure determination from synchrotron data that currently is judged infeasible because of noise. Our group works closely with experimental groups at LCLS and elsewhere to develop data analysis tools that exploit the full range of opportunities made possible by new light sources and new algorithms.

Recent Progress

Sparse data crystallography

We are nearing completion of a full structure determination from microcrystals delivered by lipid-gel column for “serial crystallography” at a synchrotron source (APS beamline 23-ID-D). Though still a proof-of-concept demonstration, the data are now taken in the same experimental conditions as a proposed structural biology pipeline. Because of the large background from the lipid-gel, and the small crystal sizes, about 120,000 data frames — about 40% of the total collected — did not have discernible Bragg peaks that could be indexed and used to orient the data in 3D. In an earlier analysis of the data [5UVJ] these very sparse frames — originating from very small crystals — were simply discarded. Our analysis, led by Ti-Yen Lan, used *only* the discarded frames and had to rely on the Expand-Maximize-Compress [EMC] algorithm to recover the crystal orientations. Currently the resolution of our reconstruction is at 4Å, but we are hopeful that with improvements in our algorithm the reconstructed Bragg peaks will extend to the 2Å resolution of the measurements. An example of a reconstructed plane of Bragg peaks and a plot showing the agreement between all Bragg intensities and those obtained from the larger crystal data set [5UVJ] is shown in Figure 1.

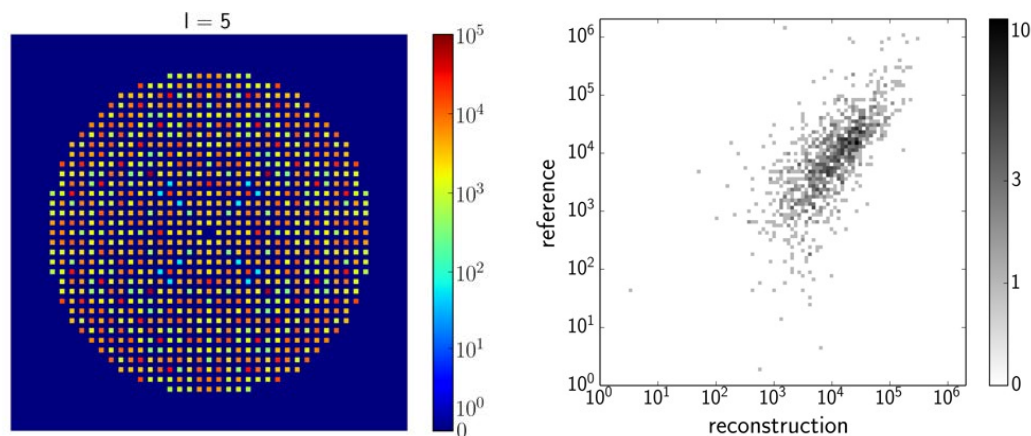


Figure 1: *Left*: Plane of Bragg intensities reconstructed by the [EMC] algorithm from very small crystals. *Right*: Agreement between the reconstructed intensities (horizontal) and reference intensities obtained from large crystal data (vertical).

Electron ptychography

We continue to work with the group of David Mueller to improve and automate tomographic (3D) reconstructions of solid state materials. Our contribution, led by Yi Jiang, is a ptychographic imaging system. Ptychography is an enhanced mode of scanning-probe transmission microscopy, where contrast is recorded not just by the total number of electrons scattered into the detector for each scan position, but by the 2D diffraction patterns that are produced. High spatial frequency information is captured in these images and can be accurately interpreted because consistency among the diffraction patterns allows for the precise reconstruction of the electron focus, the “probe function”. Figure 2 shows the reconstruction of a MoS₂ monolayer that is able to resolve individual sulfur atom vacancies [PTYCHO].

Theoretical phase retrieval

Two theoretical projects, one published [8] and one in the final stages of preparation [BENCH], were undertaken to build a bridge between phase retrieval as practiced by two communities: physicists and crystallographers on the one hand, and applied mathematicians on the other. One paper uses a simple 2-valued signal model to show how periodicity fundamentally increases the difficulty of phase retrieval while the other describes a collection of synthetic, simply-defined benchmark problems with graded difficulty for evaluating algorithms.

Future Plans

We will continue developing the ptychographic imaging system and are rewriting the EMC software for the benefit of “sparse-data” crystallographers to run on Amazon Web Services.

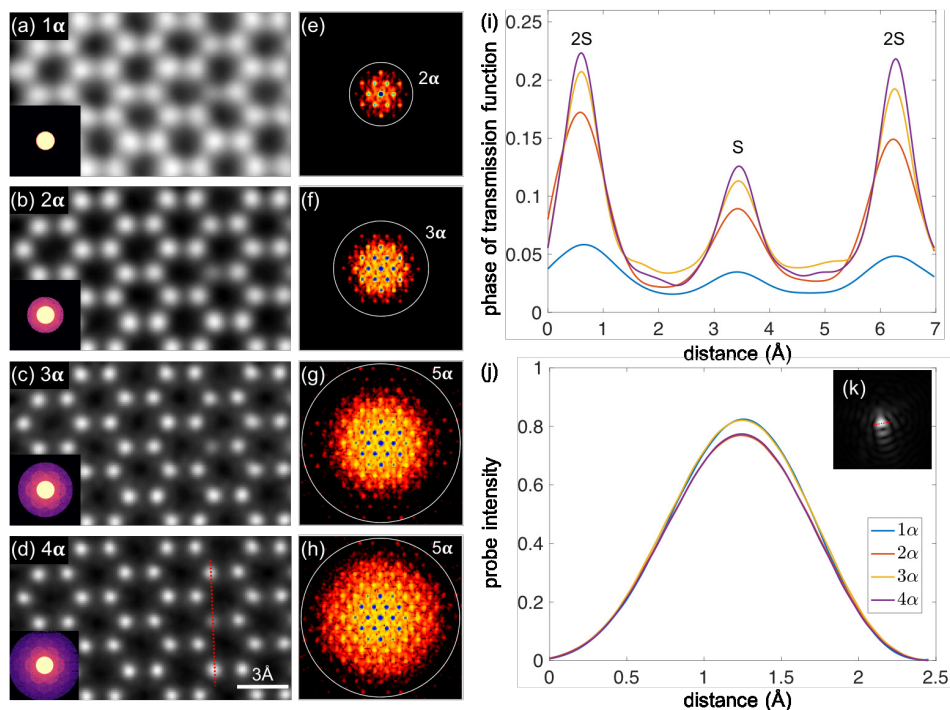


Figure 2: Ptychography reconstructions [PTYCHO] using data with different cutoff angles. (a-d) Reconstructions using electrons collected with cutoffs at multiples 1-4 of the aperture size (α). The averaged diffraction patterns are shown in the lower-left corners and false-color diffractograms (on a log-scale) of the reconstructions are shown in (e-h). (i) Line profiles across three sulfur columns, as indicated by the dashed line in (d). (j) Line profiles across the reconstructed probe function at different cutoffs. (k) Probe intensity reconstructed by ptychography using the data set with the 4α cutoff.

References

- [5UVJ] J. M. Martin-Garcia, et al., *Serial millisecond crystallography of membrane and soluble protein microcrystals using synchrotron radiation*, IUCRJ **4**, 439-454 (2017).
- [EMC] D. Loh & V. Elser, *Reconstruction algorithm for single-particle diffraction imaging experiments*, Phys. Rev. E **80**, 026705 (2009).
- [PTYCHO] Y. Jiang, Z. Chen, Y. Han, V. Elser & D. A. Muller, *Deep sub-angstrom and dose-efficient imaging via full-field electron ptychography*, in preparation.
- [BENCH] V. Elser, T.-Y. Lan & T. Bendory, *Benchmark problems for phase retrieval*, in preparation and arXiv:1706.00399.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [1] K. Ayer, H.T. Philipp, M.W. Tate, J.L. Wierman, V. Elser & S.M. Gruner, *Determination of crystallographic intensities from sparse data*, IUCrJ **2**, 29-34 (2015).
- [2] A. Aquila *et al.*, *The linac coherent light source single particle imaging road map*, Structural Dynamics **2**, 041701 (2015).
- [3] J.L. Wierman, T.-Y. Lan, M.W. Tate, H.T. Philipp, V. Elser & S.M. Gruner, *Protein crystal structure from non-oriented, single-axis sparse x-ray data*, IUCrJ **3**, 43-50 (2016).
- [4] A. Munke *et al.*, *Coherent diffraction of single Rice Dwarf virus particles using hard x-rays at the Linac Coherent Light Source*, Scientific Data **3**, (2016).
- [5] B.D.A. Levin *et al.*, *Nanomaterial datasets to advance tomography in scanning transmission electron microscopy*, Scientific Data **3**, (2016).
- [6] K. Ayer, T.-Y. Lan, V. Elser & N.D. Loh, *Dragonfly: an implementation of the expand-maximize-compress algorithm for single particle imaging*, J. App. Cryst. **49**, 1320-1335 (2016).
- [7] T.-Y. Lan, J.L. Wierman, M.W. Tate, H.T. Philipp, V. Elser & S.M. Gruner, *Reconstructing three-dimensional protein crystal intensities from sparse unoriented two-axis X-ray diffraction patterns*, J. App. Cryst. **50**, 985-993 (2017).
- [8] V. Elser, *The complexity of bit retrieval*, IEEE Transactions on Information Theory, published online DOI: 10.1109/TIT.2017.2754485.

NONLINEAR X-RAY OPTICS

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Project Scope

The scope of the project is the investigation of fundamental nonlinear X-ray - matter interactions. We are interested in studying the mechanism of coherent *non*-sequential multi-photon nonlinearities at X-ray wavelengths including novel effects and methods to increase their efficiency. X-ray free-electron lasers (XFELs) are capable of producing radiation with unprecedented properties. Specifically, their ultrashort coherent X-ray pulses can generate extreme peak intensities where ordinary rules of light-matter interaction may no longer apply and nonlinear processes start to become important. XFELs have made it possible to observe some of the most important coherent *non*-sequential nonlinearities, including X-ray - optical sum frequency generation (SFG)^[1], X-ray second harmonic generation (XSHG)^[2], nonlinear two-photon Compton scattering (2PCS)^[3] and two-photon absorption (TPA)^[4]. In particular, the 2PCS experiment has led to unexpected results, namely the observation of a substantial anomalous red shift in the energy of photons generated by nonlinear two-photon X-ray Compton scattering in beryllium. The energy shift is in addition to the predicted nonlinear Compton shift and was neither expected from extrapolations from linear X-ray interactions nor from nonlinear effects at optical wavelengths. Our results suggest a novel nonlinear scattering mechanism that can only be observed at high fields at X-ray wavelengths, where the photon energy is a significant fraction of the electron rest mass (and thus a significant momentum transfer to the electron occurs during the scattering) and where the interaction is not dominated by the quiver motion of the electron in the field (ponderomotive potential) as is usually the case at longer (optical) wavelengths.

Recent Progress

Nonlinear Two-Photon Compton Scattering

In a recent campaign at the LCLS XFEL we were able to investigate the process of two-photon inelastic Compton scattering in more detail. Additions and improvements to the experimental setup (fig.1) allowed us to further investigate the anomaly in the scattering process. As targets we used Be and diamond in order to extend the observation of the effect into another class of materials, namely metals and dielectrics. The preliminary analysis of the data indicates the observation of the effect in diamond as well. However, the comparison of the nonlinear scattering from the different materials requires a more detailed analysis due to the limited statistics of the data from diamond. More importantly, we were able to infer the electronic temperature of the sample during the interaction by performing spectroscopic measurements of the linear Compton scattering of the FEL fundamental. From our previous data, we could not conclusively exclude that the broadening of the nonlinear Compton profile is due to an extremely hot plasma temperature ($kT > 320$ eV). From the preliminary analysis of the linear Compton scattering data we do not see any significant heating of either the bulk electrons or a supra thermal population, neither in the Be nor the diamond sample (fig. 2a). This rather surprising result indicates that there is no appreciable heating ($kT < 10$ eV) during the interaction. This can be explained by simulations that show that the main energy deposition by the FEL pulse occurs outside the focal volume mediated by the propagation of mobile (~ 10 keV) photo-electrons that are generated inside the focus. Furthermore, we

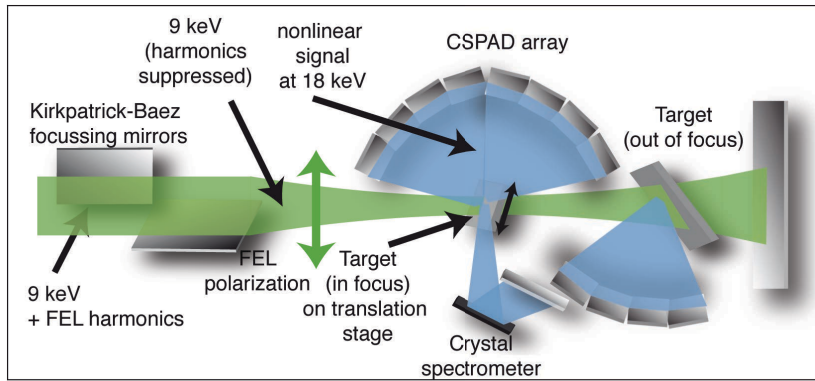


Fig.1: Experimental Setup. The XFEL beam (green) is focused to a spot size of ~ 100 nm onto the sample. The nonlinear scattering (blue) is observed using 2D detectors over a wide angular range. A crystal spectrometer was used to measure the linear Compton scattering from which the electronic temperature during the interaction can be inferred. A second sample placed in a low-intensity region was used to determine the background.

have observed the emission over a wider angular range including forward scattering. In combination with also using a higher FEL photon energy, we were able to determine an even higher value for the lower bound of the red-shift in photon energy from the expected Compton wavelength of up to 2.1 keV (at a photon energy of 10 keV) due to the smaller Compton shift closer to forward direction. The observed emission pattern (fig. 2b) has a double-peaked shape with an asymmetry in intensity towards higher (backward) scattering angles. The asymmetry is increasing with increasing intensity. The position of the peaks and the minimum cannot be explained by a free-electron model. However, it also cannot be explained by a simple model that uses the scattering from a virtual intermediate electronic state following photo-ionization. Despite this progress, the detailed mechanism of this fundamental scattering process is still not fully understood. We can further investigate the process by performing additional experiments including a complete measurement that has the ability to observe of not only the scattered photons but also the momentum distribution of the electrons and ions involved in the process.

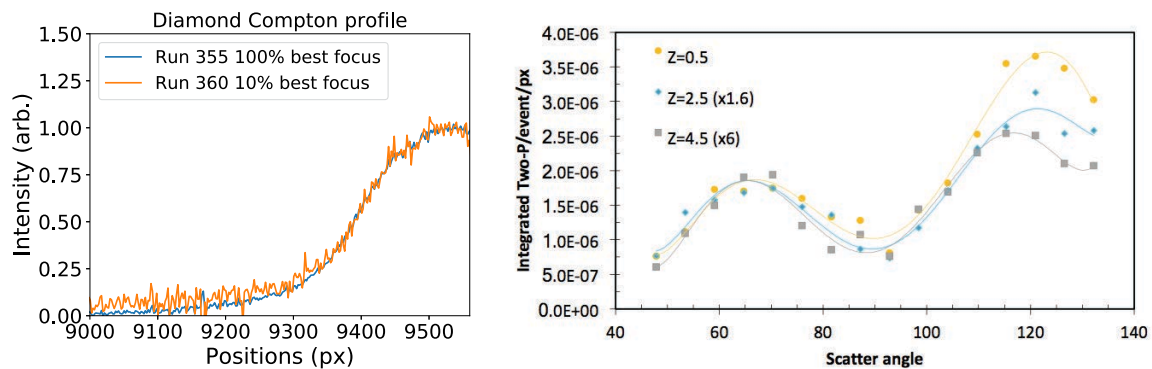


Fig.2: Preliminary experimental results: (a) shows the measured linear Compton scattering from diamond at full FEL intensity (blue) and with an attenuated FEL beam at 10% transmission (orange). The spectral range of the spectrometer was set up to observe the tail of the linear Compton profile. The FEL photon energy was 9800 eV. (b) shows the angular emission pattern of the nonlinear Compton scattering for different positions of the sample relative to the FEL focus, i.e. for different intensities while keeping the photon number on the sample the same. The graphs are scaled such that they can be overlapped. The lines are plotted to guide the eye.

Phase-matching of Nonlinear Compton Scattering

In another campaign at the LCLS XFEL we have measured an upper bound of the phase-matched generation of two-photon Compton scattering. Our recent results suggest a previously unobserved scattering process in which the bound state of the interacting electron plays an important role, despite the fact that the photon energy is significantly above any atomic resonances. If our proposed mechanism can be confirmed, there is the possibility to significantly increase the yield through phase matching. In this mechanism, the phase-matching condition can be fulfilled over a broad angular and energy range, where the energy of the emitted photon for a given angle depends on the crystal orientation. We have experimentally explored the possibility of phase-matching nonlinear Compton scattering in diamond. We have investigated several different phase-matching geometries. However, so far we were only able to observe an upper limit to the process.

X-ray Second Harmonic Generation

Using the LCLS XFEL, we have also extended our measurement of phase-matched X-ray second harmonic generation in order to further investigate the physics behind the nonlinearity for elastic scattering. To this end, we have performed an experiment to observe XSHG using higher-order Bragg reflections as phase-matching condition and to obtain more statistics. In contrast to the nonlinear Compton scattering described above, this process can be observed at lower intensities without damage to the crystal due to the possibility of phase-matching using the crystal lattice. The preliminary analysis of the data shows clear signals well above background. In particular, we have measured the shapes of crystal rocking curves for different higher-order and asymmetric scattering geometries. From these observations, we expect to get a more detailed understanding of the underlying process. In particular, we want to better understand the shapes of the rocking curves and the detailed origin of the nonlinearity including the different contributions to the induced second order current. To this end, we have measured XSHG at different angles including forward and backward scattering. In particular from the emission at a scattering angle close to 90° (parallel to the FEL polarization) we expect that the emission is mainly governed by a different component (Lorentz term) of the nonlinear current than in case of forward or backscattering geometries, which are mainly due to the Doppler term of the current. In order to get more insights into the generation mechanism, we are currently working on a simulation that will allow us to compare to the experimental observations and from which we will be able to find out the contributions for each scattering geometry.

Future Plans

As these processes are typically weak, part of this research is the exploration of more efficient nonlinear X-ray processes by studying novel mechanisms including solid-state effects and the assistance of optical radiation. These experiments require extremely large X-ray field strengths, that can only be produced by XFELs. Nonlinear X-ray effects can lead to important applications in many research fields. For example, it could lead to instantaneous plasma diagnostics for materials in extreme conditions, as a method for combining atomic-scale structural sensitivity with chemical specificity, or as a probe of electron dynamics in solids on the attosecond ($1 \text{ as} = 10^{-18} \text{ s}$) time- and Ångstrom (10^{-10} m) length scales. We will investigate higher-order nonlinear effects, such as third-harmonic generation, self-phase modulation and self-focusing. We plan to investigate two-photon Compton scattering at different wavelength regimes and with a complete measurement that will allow us to measure the angular and momentum distribution of all scattered particles.

A detailed understanding of nonlinear X-ray matter interactions is crucial for understanding and extending the limits of structural determination at high intensity such as in serial femto-crystallography. If one can find a robust X-ray nonlinearity to exploit, the potential applications are numerous spanning from

atomic physics, chemistry, materials science, to plasma physics and other disciplines. The results could have a profound impact on future light sources such as the LCLS-II.

References

- [1] Glover, T.E., Fritz, D. M., Cammarata M., *et al.* X-ray and optical wave mixing. *Nature* **488**, 603–608 (2012).
- [2] Shwartz, S., Fuchs, M., Hastings, J. B *et. al.* X-Ray Second Harmonic Generation. *Phys. Rev. Lett.* **112**, 163901 (2014).
- [3] Fuchs, M., Trigo, M., Chen, J. *et. al.* Anomalous nonlinear X-ray Compton scattering. *Nat Phys* **11**, 964-970 (2015).
- [4] Ghimire, S., Fuchs, M., Hastings, J., *et al.* Nonsequential Two-photon Absorption from the K-shell in Solid Zirconium. *Phys. Rev. A* **94** (2016).

Studies of Autoionizing States Relevant to Dielectronic Recombination

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Project Scope

Originally this research program was focused on laser spectroscopy of doubly excited autoionizing states of alkaline earth atoms, with the goal of providing a better understanding of dielectronic recombination (DR), the recombination of an ion and an electron via an intermediate autoionizing state.^{1,2} In DR an electron colliding with a ground state ion excites the ion and is itself captured. If the resulting autoionizing state decays radiatively to a bound state, DR has occurred. The most important pathway for DR is through the autoionizing Rydberg states converging to the lowest lying excited states of the parent ion. Because Rydberg states are involved, DR rates are profoundly influenced by charged particle collisions and small electric and magnetic fields.^{2,3-5} DR is important in that it provides an efficient recombination mechanism for ions and electrons in astrophysical and laboratory plasmas.⁶⁻⁸

Our approach to this problem is laser excitation from bound Rydberg states to their autoionizing analogs, for example driving the Sr $5snd$ to $5pnd$ transition. In this excitation the nd Rydberg electron is a spectator while the ion core is excited, and the process is termed isolated core excitation (ICE).^{9,10} ICE is precisely the inverse of DR and provides excellent insight into the physics of DR. The major thrust of this program has been understanding how autoionization rates, and thus DR rates, are affected by collisions and external fields. We began to use a microwave field to mimic electron collisions, but the experiments are, in essence, laser photoionization of atoms in the presence of a strong microwave field. A Rydberg atom in the presence of a strong microwave field is analogous to a ground state atom in a strong laser field, and many similarities have been observed. One of the most striking is that in both cases not only ionization but the production of atoms in very highly excited states is observed.¹¹⁻¹³ In the microwave case we have shown that the high lying states are formed by a resonant process. Furthermore, our experiments in which we excite Rydberg atoms in the presence of both a strong microwave field and a visible laser field are analogous to those in which a ground state atom is exposed to an intense infrared (IR) field and the field of an attosecond pulse train (APT) of xuv pulses, a problem under investigation by several research groups.¹⁴⁻¹⁸

Although our primary interest is exploring the interaction of Rydberg atoms with strong microwave fields, we can also use microwaves as a weak spectroscopic probe of the Rydberg states. In particular we have used microwave spectroscopy to measure the energy intervals between the bound high angular momentum states of alkaline earth atoms. From these intervals one can determine the polarizability of its ionic core.¹⁹⁻²¹ The ionic polarizability is important since it determines the blackbody frequency shift of a trapped ion, and it is the most important frequency shift in proposed optical clocks based on these ions.²²

Recent Progress

We previously excited Li atoms to the vicinity of the ionization limit in the presence of 14 GHz microwave fields, using a narrowband laser amplitude modulated synchronously with the microwave field.²³ More precisely, it was modulated at 28 GHz, twice the microwave frequency. We detected atoms which were bound after the laser excitation. With the laser tuned above the ionization limit we observed bound atoms when the excitation occurred at the phase of the microwave field such that energy was removed from the photoelectron as it began to leave the ion. With the laser tuned below the limit we observed ionization when the laser excitation occurred at the phase of the microwave field such that energy was given to the photoelectron. The amplitude modulation of the laser must be at twice the microwave frequency since the laser ejects photoelectrons in both the upfield and downfield directions, so the correct phase for recombining or ejecting the electrons occurs twice in a microwave cycle.

In the past year we have explored the same process in the presence of static fields from 0-300 mV/cm and 16 GHz microwave fields of 5 V/cm. When the static field is parallel to the microwave field it destroys the forward-backward symmetry of the problem, and the two half cycles of the microwave field are no longer equivalent. As a result, there is a difference between laser excitation in the two half cycles, which we detect by modulating the laser at the microwave frequency, 16 GHz, not twice the microwave frequency. When the static field is applied perpendicular to the microwave field, it does not destroy the forward-backward symmetry of the microwave field, and, correspondingly, we do not observe a signal when the laser is amplitude modulated at the microwave frequency. Consider the case in which the laser is tuned above the ionization limit with the laser excitation at the microwave phase which produces the maximum signal. As the static field is raised from zero to 300 mV/cm we first observe an increase in the number of recombined atoms, as the symmetry is broken, then a decrease as the static field begins to ionize all the atoms. When the laser is tuned below the zero field limit, with excitation at the same microwave phase as above, as the static field is raised from zero we first observe a decrease in the number of surviving bound atoms, followed by an increase, and finally a decrease to zero. Classical simulations show that the sign reversal is due to the microwave field's forcing atoms ejected in the up field and down field directions to lower energy. We are preparing a report of this work for publication.

Controlling the stray electric fields is a major limitation in these experiments. We currently control them to ~ 1 mV/cm, which may well be the limit in our experiment, which has many fast high voltage pulses due to the pulsed lasers. Raising the microwave frequency allows us to use lower lying Rydberg states, minimizing the stray field problem. For this reason we are implementing a new method of generating the amplitude modulated optical beam. It is based on frequency modulating the laser beam using the same microwave source which generates the microwave field the atoms see. This approach eliminates the need for phase locking and the high frequency photodiode, allowing the use of microwave frequencies up to 40 GHz. We plan to use the two sidebands displaced from the optical carrier by plus or minus the microwave frequency to generate the amplitude modulated beam. As a first experiment we are using the frequency modulated optical beam to excite atomic states which are themselves frequency modulated by the microwave field. We have made preliminary observations of the phase dependence of this excitation, which has not, to our knowledge, been observed previously.

We have completed the examination of ionization of Na atoms by 79 GHz microwave fields. This experiment completes the connection between photoionization and field ionization. For state of high principal quantum number, $n > 200$, the absorption of a single microwave photon ionizes an atom, and it is possible to observe a measurable rate of single photon microwave ionization. The observed rate is linear in the microwave power and matches that calculated using Fermi's golden rule. At lower n , the process is a multiphoton process, and it is no longer useful to describe ionization in terms of a rate calculated by perturbation theory. Instead, it is more useful to describe the process in terms of a threshold field, which is the field at which the ionization rate rapidly increases to an observable value. Not surprisingly, at very low n , where the orbital frequency of the electron vastly exceeds the microwave frequency, the microwave and static fields required for ionization are the same.

We have made microwave measurements of the intervals between the highly excited $6sn\ell$ states of Yb. The high angular momentum bound Rydberg states of Yb are used for cold atom research, and Yb^+ is an atomic clock candidate. By microwave spectroscopy we have connected the $6sns$, $6snd$, $6sng$, and $6snh$ series. We have completed the measurements of the $6sns$ and $6snd$ series, the latter of which is perturbed at $n=26$. While our microwave resonance measurements alone show the perturbation very clearly, after we had finished our analysis we discovered that the group at Laboratoire Aime Cotton in Orsay had done laser spectroscopy of the $6sns$ and $6snd$ series. Combining the two sets of data has led to a better result than the use of either set alone, and we have completed quantum defect theory analyses of the $6sns$ and $6snd$ series. We expect to submit a paper describing this work in October. We have just completed measurements of the Yb $6snd$ - $6sng$ - $6snh$ - $6sni$ intervals, with the object of extracting the Yb^+ polarizability from the energies of the $6snh$ and $6sni$ states. Our measurement should yield the first good measurement of this polarizability.

Future Plans

During the coming period we plan to bring into full operation the new method of amplitude modulating the laser, one based on frequency modulating the laser at a frequency of 40 GHz, and selecting the sidebands displaced by 40 GHz above and below the carrier to excite the atoms. This approach gives a laser beam amplitude modulated at 80 GHz, allowing us to use a 40 GHz microwave field to repeat the zero field experiment described above. The higher the microwave frequency the less susceptible the experiment is to omnipresent stray electric fields. As a result we expect to have a much greater dynamic range and observe more subtle effects. In addition, we plan to finish the microwave experiments with Yb, thus determining the Yb^+ polarizability.

References

1. A. Burgess, *Astrophys. J.* **139**, 776 (1964).
2. A. Burgess and H. P. Summers, *Astrophysical Journal* **157**, 1007 (1969).
3. V. L. Jacobs, J. L. Davis, and P. C. Kepple, *Phys. Rev. Lett.* **37**, 1390 (1976).
4. F. Robicheaux and M. S. Pindzola, *Phys. Rev. Lett.* **79**, 2237 (1997).

5. E. S. Shuman, Y. Wang, and T. F. Gallagher, *Phys. Rev. A* **76**, 031401 (2007).
6. A.L. Merts, R.D. Cowan, and N.H. Magee, Jr., Los Alamos Report No. LA-62200-MS (1976).
7. S. B. Kraemer, G. J. Ferland, and J. R. Gabel, *Astrophys. J.* **604** 556 (2004).
8. N. R. Badnell, M. G. O'Mullane, H. P. Summers, Z. Altun, M. A. Bautista, J. Colgan, T. W. Gorczyca, D. M. Mitnik, M. S. Pindzola, and O. Zatsarinny, *Astronomy and Astrophysics*, **406**, 1151 (2003).
9. W. E. Cooke, T. F. Gallagher, S. A. Edelstein, and R. M. Hill, *Phys. Rev. Lett.* **40**, 178 (1978).
10. N. H. Tran, P. Pillet, R. Kachru, and T. F. Gallagher, *Phys. Rev. Lett.* **29**, 2640 (1984).
11. T. Nubbemeyer, K. Gorling, A. Saenz, U. Eichmann, and W. Sandner, *Phys. Rev. Lett.* **101**, 233001 (2008).
12. U. Eichmann, A Saenz, S. Eilzer, T. Nubbemeyer, and W. Sandner, *Phys. Rev. Lett.* **110**, 203002 (2013).
13. A. Arakelyan and T. F. Gallagher, *Phys. Rev. A* **89**, 053412 (2014).
14. P. Johnsson, R. Lopez-Martens, S. Kazamias, J. Mauritsson, C. Valentin, T. Remetter, K. Varju, M. B. Gaarde, Y. Mairesse, H. Wabnitz, P. Salieres, Ph. Balcou, K. J. Shafer, and A. L'Huillier, *Phys. Rev. Lett.* **95**, 013001 (2005).
15. P. Ranitovic, X. M. Tong, B. Gramkow, S. De, B. DePaola, K. P. Singh, W. Cao, M. Magrakelidze, D. Ray, I. Bocharova, H. Mashiko, A. Sandhu, E. Gagnon, M. M. Murnane, H. C. Kapteyn, I. Litvinyuk, and C. L. Cocke, *New J. Phys.* **12**, 013008 (2010).
16. P. Johnsson, J. Mauritsson, T. Remetter, A. L'Huillier, and K. J. Schafer, *Phys. Rev. Lett.* **99**, 233001 (2007).
17. X. M. Tong, P. Ranitovic, C. L. Cocke, and N. Toshima, *Phys. Rev. A* **81**, 021404 (2010).
18. P. Riviere, O. Uhden, U. Saalmann, and J. M. Rost, *New J. Phys.* **11**, 053011 (2009).
19. J. E. Mayer and M. G. Mayer, *Phys. Rev.* **43**, 605 (1933).
20. J. H. Van Vleck and N. G. Whitelaw, *Phys. Rev.* **44**, 551 (1933).
21. S. R. Lundeen, in *Advances in Atomic, Molecular, and Optical Physics*, edited by P. Berman and C. Lin (Elsevier Academic Press, San Diego, 2005).
22. C. W. Chou, D. B. Hume, J. C. J. Koelmeij, D. J. Wineland, and T. Rosenband, *Phys. Rev. Lett.* **104**, 070802 (2010).
23. V. Carrat, E. Magnuson, and T. F. Gallagher, *Phys. Rev. A* **92**, 063414 (2015).

Peer Reviewed Publications Resulting from this Project (2015-2017)

1. J. Nunkaew and T. F. Gallagher, "Microwave spectroscopy of the Ca $4s_{n\ell} \rightarrow 4s_{(n+1)d}$, $4s_{n\ell}$, $4s_{n\ell}$, $4s_{n\ell}$, and $4s_{n\ell}$ transitions," *Phys. Rev. A* **91**, 042503 (2015).
2. V. Carrat, E. Magnuson, and T. F. Gallagher, "Coherence, ionization, and recombination in a microwave field," *Phys. Rev. A* **92**, 063414 (2015).
3. A. Arakelyan and T. F. Gallagher, "Resonant production of high lying states in the microwave ionization of Na," *Phys. Rev. A* **93**, 013411 (2016).
4. A. Arakelyan, J. Nunkaew, and T. F. Gallagher, "Ionization of Na Rydberg atoms by a 78 GHz microwave field," *Phys. Rev. A* **94**, 053416 (2016).

Physics of Correlated Systems

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Project Scope

A major goal of this project is the development of a theoretical understanding of microscopic chemical transformations, especially those that result in constituent rearrangement and those causing energy transfer from one degree of freedom to another. While such transformations that hinge on the strong coupling or correlation between different degrees of freedom are the most difficult to describe theoretically, they are the most important for describing the making or breaking of chemical bonds. Extensive evidence exists that these processes of chemical transformation and energy flow can be handled by quantum mechanical theory. While quantum theory has advanced tremendously during the past century, each new type of system where it must be applied poses new challenges and difficulties. These require the continual development of new approximations and/or simplified models that can both build qualitative intuition and rules of thumb, while also achieving a quantitative level that is capable of predicting and reproducing the real-world behavior observed in experiments. The hallmark of our previous theoretical studies along these lines has been the development of alternative ways to solve the complicated quantum dynamics at a realistic level that can be tested against experimental phenomena. The methods are in some cases specialized, such as our use of theoretical techniques like the adiabatic hyperspherical representation, multichannel quantum defect theory, and quantal frame transformation theory, but other techniques are adapted from standard tools such as the use of quantum chemistry packages in the Born-Oppenheimer approximation. Among the specific systems intended for study in this project are three-body recombination processes where one of the bodies is a positive or negative ion, a process that can occur in dilute gases or in combustion. Another is the process of interatomic Coulombic decay in weakly bound molecules, an ultrafast process that can produce low energy electrons that cause radiation damage in biological matter. Still another class of problems are processes occurring in an ionized gas that can neutralize the gas, such as dissociative recombination in an electron collision with a molecular ion to form neutral products, and electron-catalyzed mutual neutralization. Our theoretical project has a particular emphasis on bringing theory and calculations to the point that can connect with and encourage new experimental tests and realizations of the phenomena being studied

Recent Progress

(i) Few-body collisions occurring at chemically interesting temperatures

One of the simplest yet challenging collision systems that requires a nontrivial level of sophistication in the theoretical description involves an electron colliding with the diatomic molecular ion HeH^+ . Among the different possible outcomes of such a collision at low temperatures are rotational excitation of the molecule, vibrational excitation, or dissociative recombination. At higher energies, more complex processes such as dissociative ionization or ion-pair formation can also occur. We have implemented a new treatment of the low temperature processes in order to test some conclusions published by another group (Takagi) which presented evidence that the computed cross sections for dissociative recombination depend (unphysically) on the choice one adopts for the origin of coordinates. Our results

confirm reassuringly that equivalent results can be obtained using different coordinate origins, but they also show that faster convergence in the electronic part of the calculation is obtained by choosing the origin to coincide with the center of charge of the molecular ion rather than the center of mass.

The process of associative ionization following Rydberg state excitation has been challenging to understand, even qualitatively in many cases. If one starts from a fairly dilute gas of simple alkali atoms such as rubidium, one normally imagines that it would not be a promising environment for studying chemically reactive processes. However, experimental evidence has shown that occasionally molecular ions such as Rb_2^+ are also formed in an associative ionization reaction. The detailed mechanism by which this reactive process occurs had, not been identified, however, until it was tracked down this year in a collaboration between our theory group and the experimental group of Tilman Pfau in Stuttgart.[5] Specifically, the mechanism that forms these molecular ions turns out, surprisingly, to be triggered by the low energy $^3\text{P}^o$ electron-Rb scattering resonance that was shown in 2002 (independently by our group and by the Fabrikant group in Nebraska) to produce “butterfly molecule” potential curves that can accelerate a ground state atom inward towards the nucleus of a Rydberg atom. Such an implosion can drive the diatomic molecule into the autoionization region of the Born-Oppenheimer potential curves, and the resulting autoionization produces the molecular ions that are observed experimentally. Implementation of this theoretical mechanism explains much of the experimental observations by the Stuttgart group, with some discrepancies at very high quantum numbers that are not yet understood.

In other recent progress, the P.I. worked with postdoctoral associate Jesus Perez-Rios to implement a classical Newtonian description of three-body recombination reactions between an ion and two neutral atoms, which can create molecular ions at a high rate. [4,7] Even though most of the focus of our group over the years has concentrated on developing quantum mechanical theoretical ideas and methods, this ion-atom-atom recombination reaction turns out to be reasonably well described classically, even down to temperatures in the millikelvin regime. Our theoretical work based on this classical picture derived a threshold law that applies in the intermediate temperature range, i.e. low energy but still high enough to have multiple partial waves contributing. Specifically, in the case of the recombination process $\text{Ba}^+ + \text{Rb} + \text{Rb} \rightarrow (\text{BaRb})^+ + \text{Rb}$ this classical threshold behavior has been shown to be valid for energies from 0.2 mK up to at least around 1K and probably higher. Experiments performed by the Ulm group of J. Denschlag have now confirmed aspects of these theoretical predictions in papers [4,7].

(ii) Fano resonances and short-pulse phase control

In the years since a paper co-authored by the P.I. was published in 2013 in *Science*, a paper that grew out of a collaboration with the Heidelberg group of Thomas Pfeifer and others, interest has grown in finding the broader implications of that technique for manipulating the absorption and transmission and dispersion properties of a gas. As part of the present project, we have initiated some explorations in the direction of trying to find other scenarios in collision physics where Fano lineshapes or even more complicated multichannel lineshapes can be modified through ultrafast phase control. This project led to a first publication [2] that formulates and explores a model study of this phenomenon that points to its generality.

(iii) Atomic and molecular electron dynamics in internal and external fields

Recent work by our group in collaboration with F. Robicheaux has resulted in a new development of significant improvements to the atomic Stark effect theory. Tests of the improved theory have been highly promising, as judged by comparison with both experiment and with large computations that are more exact (but more expensive). The resulting theory [6,8,9,10] is a significant improvement over the original Fano-Harmin quantum treatment, which can be applied now with confidence to a wider class of physical systems and regimes. A subsequent goal that will build on our progress will be to ultimately apply the theory to other problems such as strong-field ionization of an atom or molecule by a powerful short pulse laser.

Future Plans

A recent theoretical treatment by the Dresden group of J.M. Rost has demonstrated that nonadiabatic turn-on and turn-off of a laser pulse can result in enhanced ionization. We have begun an exploration of this phenomenon in an attempt to understand its wider applicability as well as its limitations. Another project that is well underway and should be completed within the coming year is a treatment of extreme correlation between electrons that arises in photodetachment of the potassium negative ion in the energy range of high double excitations. If time permits, we also plan to treat single and double ionization of atoms and negative ions with two valence electrons, via short laser pulses. Our exploration of an impulsive interatomic Coulombic decay (ICD) process is also well underway and should be completed within the coming year for the first such system in a fundamental prototype small molecule. A final project that has been started and is expected to get finished within the coming year is a quantitative test of the rovibrational frame transformation theory. While that variant of frame transformation theory has given excellent results, in comparison with other theories as well as experiment, and permitted the solution of some highly challenging problems such as indirect dissociative recombination, its quantitative limitations are still not well understood.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [1] *Inelastic low-energy collisions of electrons with HeH⁺: Rovibrational excitation and dissociative recombination*, R Čurík and C H Greene, *J. Chem. Phys.* **147**, 054307-1 to -11 (2017); DOI: 10.1063/1.4994921
- [2] *Coupled-square-well model and Fano-phase correspondence*, Bin Yan and C H Greene, *Phys. Rev. A* **95**, 032706-1 to -7 (2017). DOI: 10.1103/PhysRevA.95.032706
- [3] *Universal few-body physics and cluster formation*, C H Greene, P. Giannakeas, and J. Pérez-Ríos, *Rev. Mod. Phys.* **89**, 035006-1 to -66 (2017). DOI: 10.1103/RevModPhys.89.035006
- [4] *Energy Scaling of cold atom-atom-ion three-Body recombination*, A. Kruekow, A. Mohammadi, A. Haerter, J. H. Denschlag, J Pérez-Ríos, and C H Greene, *Phys. Rev. Lett.* **116**, 193201-1 to -5 (2016).
- [5] *Ultracold chemical reactions of a single Rydberg atom in a dense gas*, M. Schlagmueller, T. C. Liebisch, F. Engel, K. S. Kleinbach, F. Boettcher, U. Hermann, K. M. Westphal, A. Gaj, R.

Loew, S. Hofferberth, T. Pfau, J Pérez-Ríos, and C H Greene, Phys. Rev. X **6**, 031020-1 to -14 (2016).

[6] *Generalized local-frame-transformation theory for excited species in external fields*, P. Giannakeas, C H. Greene, and F. Robicheaux, Phys. Rev. A **94**, 013419-1 to -9 (2015).

[7] *Communication: Classical threshold law for ion-neutral-neutral three-body Recombination*, J Pérez-Ríos and C H Greene, J. Chem. Phys. **143**, 041105-1 to -3 (2015).

[8] *Photoionization microscopy in terms of local-frame-transformation theory*, P Giannakeas, F Robicheaux, and C H Greene, Phys. Rev. A **91**, 043424-1 to -14 (2015).

[9] *Comment on “Test of the Stark-effect theory using photoionization microscopy”*, P Giannakeas, F Robicheaux, and C H Greene, Phys. Rev. A **91**, 067401-1 to -4 (2015).

[10] *Schwinger-variational-principle theory of collisions in the presence of multiple potentials*, F Robicheaux, P Giannakeas, and C H Greene, Phys. Rev. A **92**, 022711-1 to -21 (2015).

[11] *Hyperspherical asymptotics of a system of four charged particles*, K M Daily, Few Body Systems, **56**, 809–822 (2015), pp 1-14, DOI 10.1007/s00601-015-0979-7.

[12] *Scattering properties of the $2e^-2e^+$ polyelectronic system*, K M Daily, J. von Stecher, and C. H. Greene, Phys. Rev. A **91**, 012512-1 to -7 (2015).

[13] *Two-photon total annihilation of molecular positronium*, J Pérez-Ríos, S T Love, and C H Greene, Europhys. Lett. **109**, 63002-1 to -4 (2015).

[14] *Adiabatic hyperspherical analysis of realistic nuclear potentials*, K. M. Daily, A. Kievsky, and C. H. Greene, Few Body Systems **56**, 753-759 (2015), DOI 10.1007/s00601-015-1012-x.

[15] *Two-photon total annihilation of molecular positronium*, J Pérez-Ríos, S. T. Love, and C. H. Greene, Europhys. Lett. **109**, 63002-1 to -4 (2015).

[16] *Effective single photon decay mode of positronium via electroweak interactions*, J Pérez-Ríos and S. T. Love, J. Phys. B **48**, 244009-1 to -5 (2015).

[17] *Formation of ultracold (LiRb)- ^7Li - ^{85}Rb molecules in the lowest triplet electronic state by photoassociation and their detection by ionization spectroscopy*, A. Altaf, S. Dutta, J. Lorenz, J Pérez-Ríos, Y. P. Chen, and D. S. Elliott, J. Chem. Phys. **142**, 114310-1 to -9 (2015).

Manipulating and Probing Ultrafast Atomic and Molecular Dynamics

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I. Project Scope

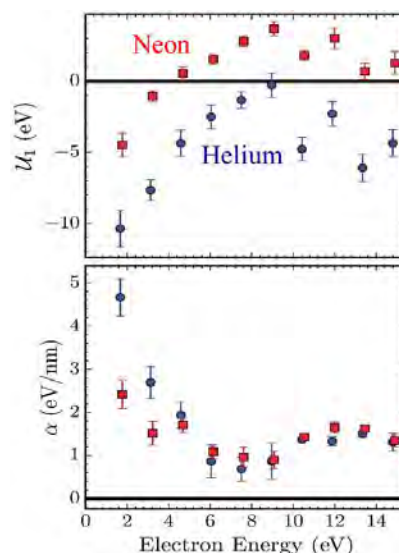
This project focuses on the exploration and control of dynamics in atoms, small molecules, and micro- or nano-structures driven by strong laser fields. Our goal is to exploit strong-field processes to implement novel ultrafast techniques for manipulating and probing coherent electronic and nuclear motion within atoms, molecules, and on surfaces. Ultimately, through the application of these methods, we hope to obtain a more complete picture of correlated multi-particle dynamics in molecules and other complex systems.

II. Recent Progress

This project was on no-cost extension (NCE) from December 2015 until December 2016. Since the small amount of residual funding was completely depleted by August 2016, no students or postdocs were positioned to begin work on the project when new funds became available in mid-February 2017. A search for a postdoctoral researcher is continuing.

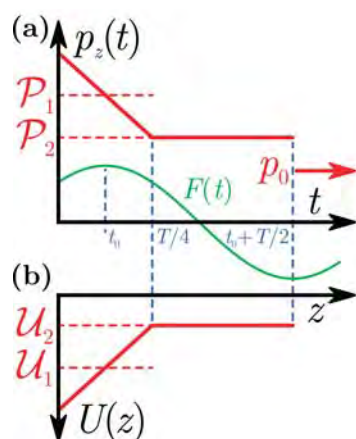
While progress has been substantially slowed due to the NCE, during the current funding year the PI has continued to work in collaboration with the DiMauro/Agostini group at OSU, developing an interferometric method to obtain information about the effective binding potential experienced by low-energy photoelectrons immediately following their release from their parent ions. The method is based on energy transfer to photoelectron wavepackets in a phase-locked infrared dressing field. The photoelectron wavepackets, which are produced by attosecond XUV pulses from high-harmonic generation, experience an energy transfer that depends on their (position-dependent) momentum and the phase of the dressing field at which they are emitted. We have shown that the amount of energy transfer *directly* reflects the coarse characteristics of the effective binding potential experienced by the photoelectrons during the first femtosecond or so after their release. Moreover, those characteristics can be directly extracted from energy transfer vs delay measurements. Importantly, the effective potential which is measured includes both electron-ion and electron-electron interactions.

Figure 1: Average effective potential, \mathcal{U}_1 , and average gradient of that potential, α , as probed by outgoing photoelectrons, as a function of their kinetic energy. The measurement employs an augmented version of RABBITT [1] and utilizes an analytic reformulation of energy transfer in a non-zero potential to extract the coarse characteristics of the effective potential during the first ~ 1 fs after photoionization.



To demonstrate the method, we use an extension of RABBITT (Reconstruction of Attosecond Beating By Interfering Two-photon Transitions), which was developed to characterize attosecond XUV pulse trains [1]. In RABBITT, electrons are photoionized by a discrete XUV harmonic comb, producing a series of "direct" ionization peaks in the photoelectron spectrum. However, in the presence of an additional dressing laser, the direct photoelectrons can absorb/emit infrared photons, generating sidebands in the photoelectron spectrum which appear midway between the "direct" ionization peaks. As the delay between the dressing laser and the harmonic comb is delayed, two-path interference modulates the yield in each sideband N , which is coherently populated by IR emission and IR absorption from electrons with initial energies corresponding to direct ionization peaks $N+1$ and $N-1$, respectively. We augment the standard method, using what we call RABBITT+ to measure both the amplitude (relative to the direct ionization) and phase of the photoelectron sidebands as a function of the dressing laser delay.

Figure 2: Schematic of the pseudo-potential and corresponding time-dependent momentum function we utilize to express classical energy transfer and RABBITT+ sideband amplitudes in terms of the coarse characteristics of the actual potential. Specifically, the relevant characteristics are the average potential and its gradient during the first quarter-cycle of the dressing field, $F(t)$, after emission.



Because the energy transfer process depends only on the coarse characteristics of the true effective potential, we have found that one can use a simple pseudo-potential in combination with a semi-classical WKB-Volkov formalism to derive explicit closed form expressions for the sideband amplitude and phase in terms of the coarse characteristics of the potential. We have used this formulation to extract information on the effective potentials that are relevant to photoionization in Ne and He. We have found significant differences between the effective potentials for those two atoms, suggesting differences in the strength of electron-electron interactions during the first ~ 1 femtosecond after photoionization in those two species. A manuscript describing our results has been accepted for publication in Nature Physics [a].

III. Future Plans

Once the postdoctoral researcher position has been filled, we hope to make rapid progress in several areas. First, we plan to further characterize the high-energy electron field emission we have observed [b] from THz irradiated nano-tips (e.g. angular and temporal distributions), as a potential source of short electron bursts for initiating and probing molecular dynamics. Second, we will explore the possibilities for exploiting enhanced THz fields in the vicinity of micro-structured metals, particularly in razor geometries which offer relatively large enhanced-field volumes, to manipulate laser-driven tunneling ionization and electron recollisions, and perhaps improve THz-based field-free molecular orientation. Third, we will work to improve our

experimental capabilities to revisit a problem that we have been studying for several years, namely the coupled dynamics of electrons and nuclei during asymmetric strong-field multi-electron dissociative ionization. Two recent experiments [2,3] have offered conflicting views as to the importance of multi-electron processes during enhanced ionization. We plan to reduce the duration of the laser pulses available from our hollow-core-fiber compressor to < 7 fs to perform 2-color pump probe experiments in an attempt to resolve that conflict.

IV. References

- [1] P.M. Paul, E.S. Thoma, P. Breger, G. Mullot, F. Audebert, Ph. Balcou, H.G. Muller, and P. Agostini, "Observation of a Train of Attosecond Pulses from High Harmonic Generation," *Science* **292**, 1689 (2001).
- [2] V. Tagliamonti, H. Chen, and G. N. Gibson, "Multielectron Effects in Charge Asymmetric Molecules Induced by Asymmetric Laser Fields," *Phys. Rev. Lett.* **110**, 073002 (2013).
- [3] X. Gong, M. Kunitski, K.J. Betsch, Q. Song, L. Ph. H. Schmidt, T. Jahnke, Nora G. Kling, O. Herrwerth, B. Bergues, A. Senftleben, J. Ullrich, R. Moshhammer, G.G. Paulus, I. Ben-Itzhak, M. Lezius, M.F. Kling, H. Zeng, R.R. Jones, and J. Wu, "Multielectron Effects in Strong-field Dissociative Ionization of Molecules," *Phys. Rev. A* **89**, 043429 (2014).

V. Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [a] D. Kiewewetter, R.R. Jones, A. Camper, S.B. Schoun, P. Agostini, and L.F. DiMauro, "Probing Electronic Binding Potentials with Attosecond Photoelectron Wavepackets," *Nat. Phys.* (accepted for publication).
- [b] S. Li and R.R. Jones, "High-Energy Electron Emission from Metallic Nano-tips Driven by Intense Single-Cycle Terahertz Pulses," *Nat. Comm.* **7**, 13405 (2016).

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Quantum Dynamics Probed by Coherent Soft X-Rays

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Project Scope

The goal of this work is to develop novel short wavelength probes of molecules and to understand the response of atoms, molecules and nanosystems to strong laser fields. We made exciting advances in several areas since 2015. Recent highlights include –

Recent Progress

Helicity-Selective Enhancement and Polarization Control of Attosecond HHG Waveforms [1,2,8–11,15]: High harmonics (HHG) driven by two-color counter-rotating circularly-polarized laser fields are a unique source of bright, circularly-polarized, extreme UV and soft x-ray beams, where the individual harmonics themselves are completely circularly polarized. In recent work,[1] we demonstrated the ability to preferentially select either the right or left circularly polarized HHG simply by adjusting the relative intensity ratio of the bichromatic circularly polarized driving laser field. In the frequency domain, this significantly enhances the harmonic orders that rotate in the same direction as the higher intensity driving laser. In the time domain, this helicity-dependent enhancement corresponds to control over the polarization of the resulting attosecond waveforms. This helicity control enables the generation of circularly-polarized high harmonics with a user-defined polarization of the underlying attosecond bursts. In the future, this technique should allow for the production of bright highly elliptical harmonic supercontinua as well as the generation of isolated elliptically polarized attosecond pulses.

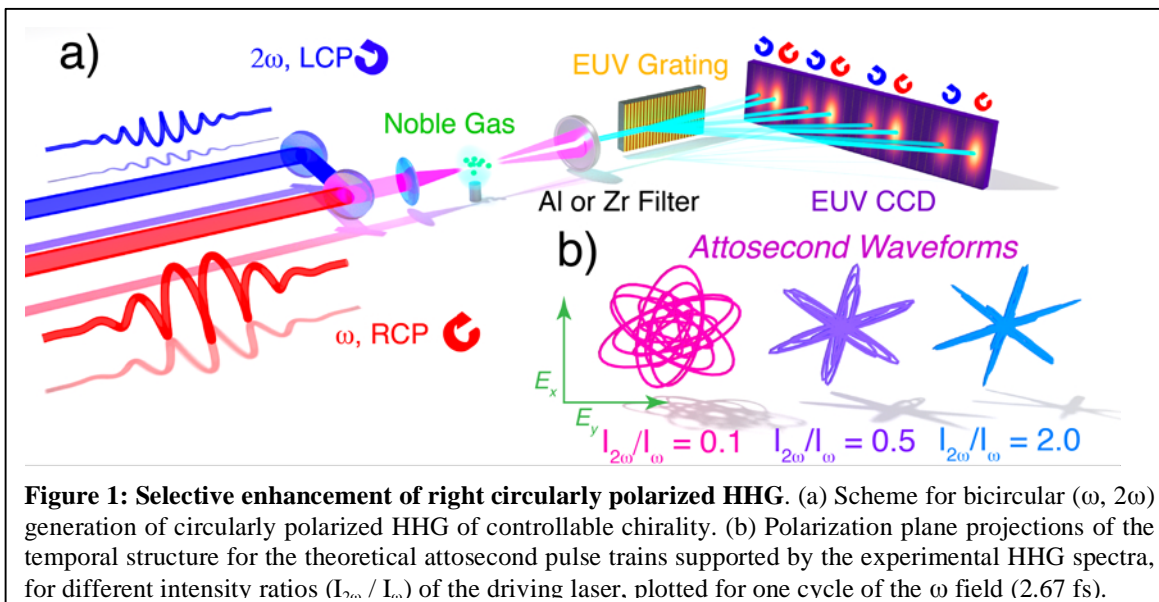


Figure 1: Selective enhancement of right circularly polarized HHG. (a) Scheme for bicircular (ω , 2ω) generation of circularly polarized HHG of controllable chirality. (b) Polarization plane projections of the temporal structure for the theoretical attosecond pulse trains supported by the experimental HHG spectra, for different intensity ratios ($I_{2\omega} / I_{\omega}$) of the driving laser, plotted for one cycle of the ω field (2.67 fs).

In related research,[2] we also found that when atoms are irradiated by two-color circularly polarized laser fields, the resulting strong field processes are dramatically different than when the same atoms are irradiated by a single-color ultrafast laser e.g. electrons can be driven in complex 2D trajectories before rescattering or circularly polarized HHG can be generated as discussed above, which was once thought impossible. We showed that two-color circularly

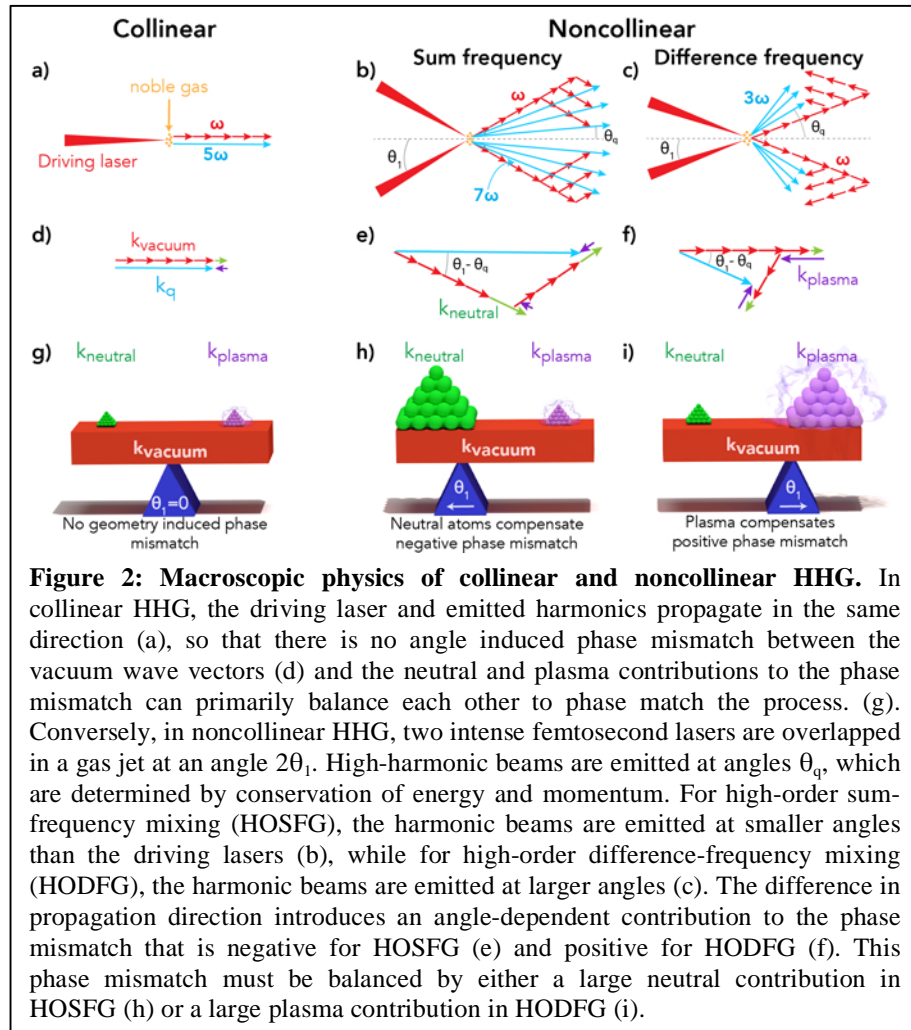
polarized lasers also enable control over the ionization process itself and make a surprising finding: *the ionization rate can be enhanced by up to 700% simply by switching the relative helicity of the two-color circularly polarized laser field.* This enhancement is experimentally observed in He, Ar and Kr, for a wide range of intensity ratios of the two-color field. We use a combination of advanced quantum and fully classical calculations to explain this ionization enhancement as resulting in part due to the increased density of excited states available for resonance-enhanced ionization in counter-rotating fields compared with co-rotating fields. In the future, this effect could be used to probe the excited state manifold of complex molecules.

Phase Matching of Noncollinear Sum and Difference Frequency High-Harmonic Generation [5]:

Noncollinear HHG has the advantage of full control over the polarization state – from linear to circular polarization – as well as making it possible to generate isolated attosecond bursts of circularly polarized high harmonics. Recently we experimentally demonstrated for the first time phase matching of noncollinear high-order-difference-frequency generation at ionization fractions above the critical ionization level, which normally sets an upper limit on the laser intensity that can be used to drive HHG and therefore the achievable cutoff photon energies.

Additionally, we showed that noncollinear high-order-sum-frequency generation requires much higher pressures to phase match than is necessary for single-beam HHG, which mitigates the short interaction region in this geometry. We also dramatically increased the cutoff energy of noncollinear circularly polarized HHG, reaching photon energies of 90eV. Finally, we achieved complete angular separation of HHG orders without using a spectrometer.

Probing how the the mechanical properties of 11-50nm ultrathin films: influence of network connectivity on the Poisson's ratio [6,13,16]: Precise characterization of the mechanical



properties of ultrathin films is important for a fundamental understanding of nanoscale materials and for continued scaling and improvement of nanotechnology. In recent work we used the

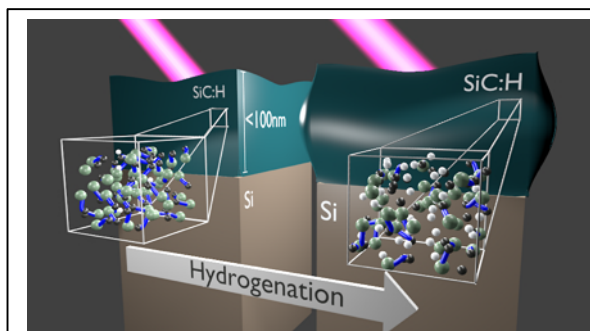


Figure 3: Probing how hydrogenation influences the mechanical properties of ultrathin films. Strong hydrogenation of a film results in bond breaking, lowering the network connectivity and Young’s modulus of the material, while significantly decreasing the compressibility.

exquisite stability and sensitivity of coherent EUV HHG beams to characterize the full elastic tensor of isotropic ultrathin films down to 11 nm in thickness, to probe how doping influenced their properties. Contrary to past assumptions, we found that the Poisson’s ratio of such films is not constant, but rather can significantly increase as the films are hydrogenated. Physically, the strong hydrogenation required to decrease the dielectric constant results in bond breaking, lowering the network connectivity and Young’s modulus of the material, but also decreases the compressibility of the film. This new understanding of ultrathin films demonstrates that coherent EUV beams present

a new nanometrology capability that can probe a wide range of novel complex materials not accessible using traditional approaches.

Molecular dynamics probed using HHG [3,4]: Understanding ultrafast dynamics in highly-excited electronic states of small molecules is critical for a wide variety of phenomena, including atmospheric and astrophysical processes. In highly excited states, nonadiabatic coupling, electron-electron interactions, and the high density of states govern the dynamics. However, these states are computationally and experimentally challenging to access. We used time-resolved photoelectron-photoion coincidence experiments using 8 eV VUV photons to study the highly excited states of acetone. We uncovered for the first time direct evidence that the resulting excited state has a strongly-mixed character, and decays with a time constant of 330 fs.

Future work

We will apply use circularly and linearly polarized high harmonics in the EUV and soft x-ray regions to probe dynamics in molecular, nano and materials systems. We are using ultra-broad bandwidth, ultrafast HHG soft X-rays to capture NEXAFS over hundreds of electron volt energies simultaneously. To implement dynamic NEXAFS, gas, solid and liquid-phase samples will be excited using mid-IR – UV light, and then probed using soft X-ray HHG supercontinua. We will also capture orbital dynamics in molecules and nanosystems using photoelectron spectroscopy.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. K. Dorney, J. Ellis, C. Hernández-García, D. Hickstein, C.A. Mancuso, N. Brooks, T. Fan, G. Fan, P. Grychtol, D. Zusin, C. Gentry, H. Kapteyn, M. Murnane, “Helicity-selective enhancement and polarization control of attosecond high harmonic waveforms driven by bichromatic circularly polarized laser fields”, *Physical Review Letters* **119**, 063201 (2017).
2. C. Mancuso, K. Dorney, D. Hickstein, J. Chaloupka, X-M. Tong, J. Ellis, H. Kapteyn, M. Murnane, “Observation of ionization enhancement in two-color circularly polarized laser fields,” *Physical Review A* **96**, 023402 (2017). DOI: 10.1103/PhysRevA.96.023402

3. W. Peters, D. Couch, R. Fortenberry, H. Kapteyn, M. Murnane, "Uncovering highly-excited state mixing in acetone using ultrafast VUV pulses and coincidence imaging techniques," *J. Phys. Chem. A*, **121**, 2361–2366 (2017). DOI: 10.1021/acs.jpca.7b01112
4. D. Couch, G. Buckingham, J. Baraban, J. Porterfield, L. Wooldridge, G.B. Ellison, H. Kapteyn, M. Murnane, W. Peters, "Tabletop Femtosecond VUV Photoionization and PEPICO Detection of Microreactor Pyrolysis Products," *J. Physical Chemistry* **121** (28), 5280–5289 (2017). DOI: 10.1021/acs.jpca.7b02821
5. J. Ellis, K. Dorney, C. Durfee, C. Hernandez-Garcia, F. Dollar, C. Mancuso, T. Fan, P. Grychtol, D. Zusin, C. Gentry, H. Kapteyn, M. Murnane, D. Hickstein, "Phase Matching of Noncollinear Sum and Difference Frequency High-Harmonic Generation," *Optics Express* **25**(9), 10126-10144 (2017).
6. J. Hernandez-Charpak, K. Hoogeboom-Pot, Q. Li, T. Frazer, J. Knobloch, M. Tripp, S. King, E. Anderson, W. Chao, M. Murnane, H. Kapteyn, D. Nardi, "Full characterization of the mechanical properties of 11-50nm ultrathin films: influence of bond coordination on the Poisson's ratio", *Nano Letters* **17** (4), 2178–2183 (2017). DOI: 10.1021/acs.nanolett.6b04635.
7. J. Ellis, D. Hickstein, W. Xiong, F. Dollar, B. Palm, K. Keister, K. Dorney, C. Ding, T. Fan, M. Wilker, K. Schnitzenbaumer, G. Dukovic, J. Jimenez, H. Kapteyn, M. Murnane, "Materials Properties and Solvated Electron Dynamics of Isolated Nanoparticles and Nanodroplets Probed with Ultrafast EUV Beams", *J. Phys. Chem. Lett.* **7** (4), 609-615 (2016).
8. C. Mancuso, K. Dorney, J. Chaloupka, J. Ellis, F. Dollar, R. Knut, P. Grychtol, D. Zusin, C. Gentry, H. Kapteyn, D. Hickstein, M. Murnane, "Controlling nonsequential double ionization in two-color circularly polarized femtosecond laser fields," *Physical Review Letters* **117**, 133201 (2016).
9. C.A. Mancuso, D.D. Hickstein, K.M. Dorney, J.L. Ellis, E. Hasovic, R. Knut, P. Grychtol, C. Gentry, M. Gopalakrishnan, D. Zusin, F.J. Dollar, X.M. Tong, D.B. Milosevic, W. Becker, H.C. Kapteyn, M.M. Murnane, "Controlling electron-ion rescattering in two-color circularly polarized femtosecond laser fields", *Physical Review A* **93** (5), 053406 (2016). *Also selected as an Editor's Suggestion.*
10. C. Hernández-García, C.G. Durfee, D. Hickstein, T. Popmintchev, A. Meier, M. M. Murnane, H. C. Kapteyn, I. J. Sola, A. Jaron-Becker, A. Becker, "Schemes for generation of isolated attosecond pulses of pure circular polarization", *Physical Review A* **93**, 043855 (2016). *Also selected as an Editor's Suggestion.*
11. D. Hickstein, F. Dollar, P. Grychtol, J. Ellis, R. Knut, C. Hernández-García, C. Gentry, D. Zusin, J. Shaw, T. Fan, K. Dorney, A. Becker, A. Jaroń-Becker, H. Kapteyn, M. Murnane, C. Durfee, "Angularly separated beams of circularly polarized high harmonics," *Nature Photonics* **9**, 743–750 (2015).
12. J. Miao, T. Ishikawa, I. K. Robinson & M. M. Murnane, "Beyond Crystallography: Diffractive Imaging with Coherent X-ray Sources", *Science* **348**, 530 (2015). Featured on cover of *Science*.
13. K.M. Hoogeboom-Pot, J.N. Hernandez-Charpak, T. Frazer, E.H. Anderson, W. Chao, R. Falcone, X. Gu, R. Yang, M.M. Murnane, H.C. Kapteyn, D. Nardi, "A new regime of nanoscale thermal transport: collective diffusion increases dissipation efficiency", *PNAS* **112**, 4846–4851 (2015).
14. Jennifer L. Ellis, Kyle J. Schnitzenbaumer, Daniel Hickstein, Molly B. Beernink, Brett B. Palm, Jose L. Jimenez, Gordana Dukovic, Henry C. Kapteyn, Margaret M. Murnane, Wei Xiong, "Revealing solvent effects on charge transfer between quantum dots and surface adsorbates", *JACS* **137** (11), 3759–3762 (2015).
15. C. Mancuso, D. Hickstein, P. Grychtol, R. Knut, O. Kfir, X. Tong, F. Dollar, D. Zusin, M. Gopalakrishnan, C. Gentry, E. Turgut, J. Ellis, M. Chen, A. Fleischer, O. Cohen, H. Kapteyn, M. Murnane, "Observation of photoelectron distributions resulting from strong field ionization from two-color circularly polarized laser fields using tomographic methods", *Physical Review A* **91**, 031402(R) (2015).
16. D. Nardi, M. Travaglini, M. Murnane, H. Kapteyn, G. Ferrini, C. Giannetti, F. Banfi, "Impulsively Excited Surface Phononic Crystals: a Route towards Novel Sensing Schemes", *IEEE Sensors Journal* **15**, 5142 (2015).

Real-time observation of multi-electron processes in atoms and diatomic molecules

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Project Scope:

The goal of this project is to implement a reliable experimental approach to observe, in real-time, electron dynamics in atoms and molecules at the attosecond time scale. Despite significant efforts that are underway, time-resolved studies at the attosecond time scale are still restricted to a few benchmark systems possessing an electronic structure sufficiently simple to make it possible to isolate a particular electronic process and univocally dissect its dynamic [1-7]. We plan to combine high-repetition-rate attosecond sources and sophisticated multi-particle imaging techniques, such as the well-established reaction microscope or COLTRIMS (Cold Target Recoil Ion Momentum Spectroscopy) [8,9] to investigate in kinematically complete experiments the correlated electron dynamics in atoms and the coupled electron nuclear motion in small molecules. This new capability will offer promising possibilities to yield a deeper insight into atomic and molecular processes and ultimately to identify ways to control them. In addition, we expect that the multi-differential cross section measurements carried out in this project will foster the development of new theoretical models that are essential for a quantitative interpretation of experiments on complex systems.

Recent Progress:

Extreme ultraviolet attosecond pulses provide photons of sufficient energy to initiate electronic processes in most atomic and molecular species through single-photon excitation and ionization. Due to the broad energy bandwidth associated with these attosecond pulses (~10-80eV), a large number of electronic processes are generally simultaneously triggered by the same pulse. As a result, several decay channels are opened up and occurred in the same experiment. In order to disentangle and dissect the time-track of one or several of them, the coincidence measurements of at least a few particles produced in these reactions (electrons, ions or fragments in the case of a molecular target) is required. Because the data integration time for such coincidence measurements are generally much longer than other one-particle measurements, experimental conditions need to be kept stable over an extended period of time. Over the past two years, we have completed the construction of a brand-new laboratory at Auburn University possessing state-of-the-art facilities to perform such highly sensitive attosecond measurements. Our current experimental setup shown in figure 1 is composed of (1) a commercial 1.5-mJ, 35-fs intense femtosecond laser system centered at 800 nm and operating at 10kHz, (2) a hollow core fiber compressor for the generation of laser pulses down to 8 fs, (3) an attosecond pulse source based on high harmonic generation, (4) an optically-stabilized XUV-IR interferometer for pump/probe measurements, and (5) a reaction-microscope for particle coincidence measurements in single event mode.

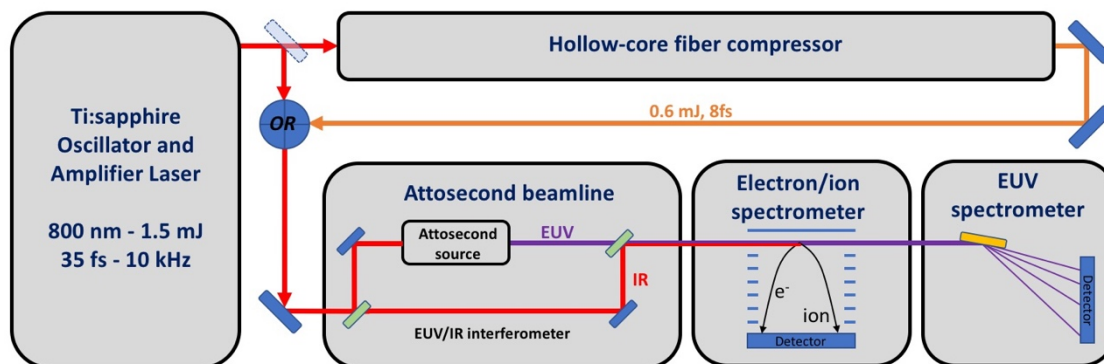


Figure 1: Schematic view of the experimental setup currently operating at Auburn University. The setup is composed of: (1) an intense femtosecond laser system, (2) a hollow core fiber compressor, (3) an attosecond pulses source, (4) an XUV-IR interferometer, and (5) a multi-particle electrons/ions spectrometers.

Future Plans:

During this upcoming year, we plan to complete the assembling of the experimental setup which will be used to perform attosecond studies on atoms and diatomic molecules. In particular, the two main goals are (1) to generate and characterize tailored attosecond pulses of good pulse contrast in the 10-80 eV photon energy range, and (2) to implement and calibrate the multi-coincidence particle's momentum spectrometer in the presence of EUV and IR pulses.

References:

- [1] M. Drescher et al., Nature 419, 803 (2002)
- [2] E. Goulielmakis et al., Nature 466, 739 (2010)
- [3] M. Schultze et al., 328, 1658 (2010)
- [4] K. Klünder et al., Physical Review Letters 106, 143002 (2011)
- [5] M. Uiberacker et al., Nature 446, 627 (2007)
- [6] P. Eckle et al., Science 322, 1525 (2008)
- [7] A. N. Pfeiffer et al., Nature Physics 7, 428 (2011)
- [8] R. Dörner et al., Physics Reports 330, 95 (2000)
- [9] J. Ullrich et al., Reports on Progress in Physics 66, 1463 (2003)

Peer-Reviewed Publications Resulting from this Project (Project start date: 08/2017)

none

Exploiting Non-equilibrium Charge Dynamics in Polyatomic Molecules to Steer Chemical Reactions

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Project Scope

This project aims to control and probe ultrafast electron dynamics in the first few femtoseconds and also explore the coupled nuclear dynamics on longer timescales. In the third funding period, our research teams have made significant progress in both theoretical and experimental effort in probing attosecond charge dynamics and controlling chemical reactions. We are detailing select recent progress in the following.

Recent Progress

1. Development of 3D-2eAS: A general pump-probe attosecond technique capable of probing electron dynamics in the 1st femtosecond of a reaction

Research led by Wayne State University developed a novel 3D coincidence imaging system capable of highly efficient electron-electron coincidence detection.¹⁻³ This new capability has now been duplicated at CU and elsewhere. In recent work, a breakthrough was achieved by combining this new technique with attosecond angular streaking which resulted in a new and general attosecond pump-probe method.

The capability of 3D-2eAS was first demonstrated in probing the attosecond electron correlation dynamics in benzene.⁴ The main result is shown in Fig. 1(a), in which the double ionization yield is plotted against the relative ejection angles between the two electrons in the plane of polarization. Three features are seen at ~25, ~85 and ~170 degrees. Because a multi-cycle laser pulses (30 fs, 800 nm) was used, it is not straightforward to convert the ejection angle (0°-180°) into ionization time delay (0-1.33 fs). An ambiguity of multiples of half laser period (1.33 fs) needs to be considered. We turn to the momentum correlation in the third dimension (perpendicular to the plane of the polarization, *i.e.* X axis). Fig. 1(b) shows the ratios between back-to-back events and side-by-side events along this direction against the relative angles between the electrons in the plane of the polarization. We see a higher than one ratio for small relative angles while it decays to 1 toward larger angles. It is well established that when electrons are ejected in close proximity (spatially and temporally) of each other, Coulomb repulsion in the final states will force electron ejection in the opposite directions and thus back-to-back events are favored over side-by-side events.^{5,6} As the time separation (distance) increases, the Coulomb repulsion becomes weaker and the electrons relative ejection direction loses preference. As shown in Fig. 1(b), the correlation between the small relative angles in the plane and the high back-to-back ejection probability in the perpendicular direction can only be understood in terms of angle-to-time correlation, as in angular streaking. This correlation suggests the first feature (peaked around 25°) in Fig. 1(a) correlates to the double ionization events that take place within the first 500 attoseconds (~70 degrees). This is the first time that such a correlation is observed and it validates the application of 3D-2eAS in probing attosecond dynamics. For the second (85°) and third feature (170°), because of the close to one ratio between back-to-back and side-by-side

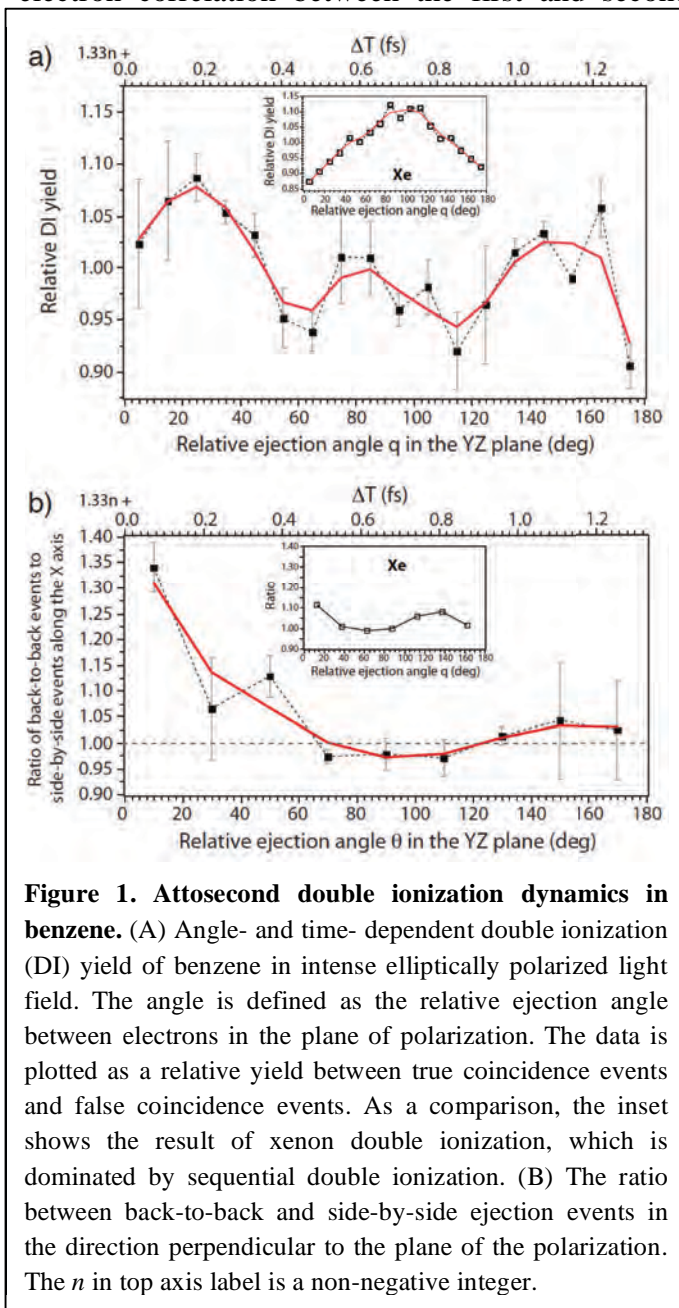
events, they are most likely related to the double ionization at longer time delay possibly over a few laser cycles.

A sequential calculation assuming no electron correlation between the first and second electron, has failed to reproduce the trend of the time-resolved transient and this suggests that a different mechanism is at play in the ionization dynamics at the short time scale (< 500 as) (Fig. 1(a)). The Schlegel group then implemented a classical ensemble calculation to successfully elucidate the nonsequential nature of the attosecond electron dynamics, arising from recollision. The second feature in Fig. 1(a) is due to the orthogonal configuration of the two degenerate HOMO orbitals of the benzene: the first electron is ionized when the electric field is aligned with one HOMO orbital and the second electron is ionized when the electric field rotates 90 degrees and aligns with the second HOMO orbital. Because the ionization rate is high when electric field is aligned with orbital orientation, a peak will occur at 90 degrees. TDCIS-CAP (time dependent configuration interaction singles with complex absorbing potentials) calculation was able to reproduce this feature. The observation of this feature suggests that in addition to the extremely fast time resolution, 3D-2eAS can also provide spatial sensitivity on orbital orientation.

More recent technical developments have further simplified the setup and similar coincidence measurements can now be achieved with a conventional velocity mapping imaging system.⁷

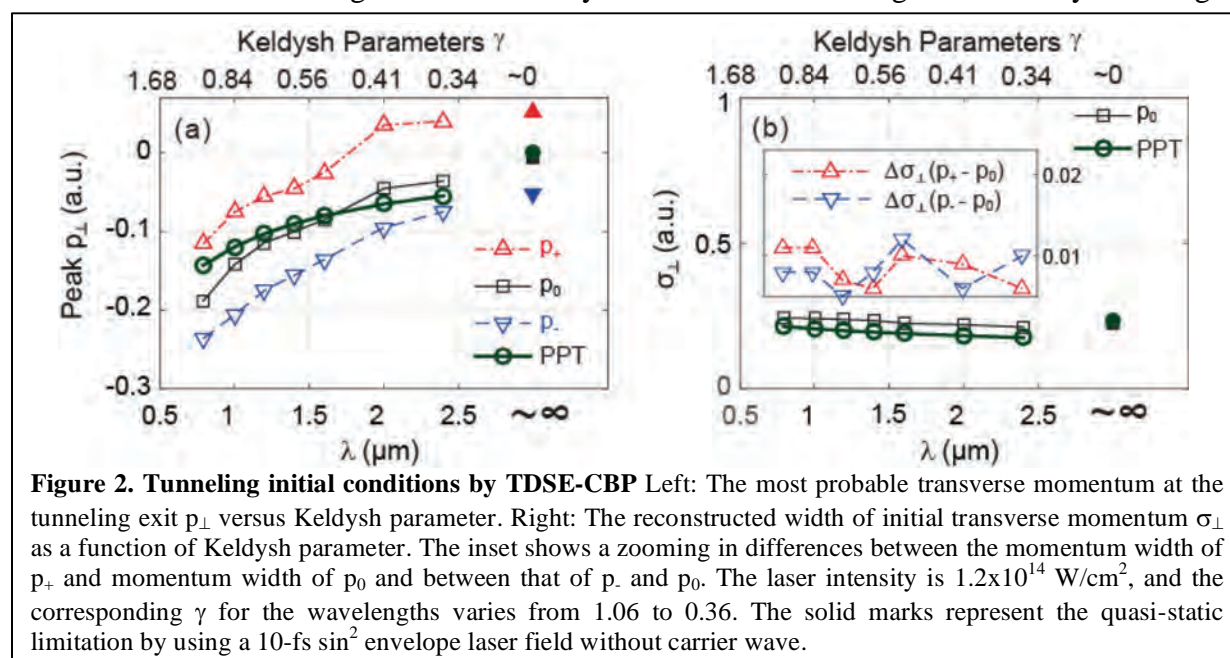
2. Orbital-resolved nonadiabatic tunneling

Tunneling ionization is one of the most fundamental process in strong field atomic and molecular physics, in which the binding potential is strongly suppressed by the laser electric field and the electrons gain a non-zero probability of escaping (tunneling) to the continuum. Because tunneling is a quantum phenomenon and has no direct classical analog, the determination of tunneling exit, initial momentum and time is intensely debated. However, angular streaking principle is strongly dependent on the validity of the concept of tunneling and detailed



characteristics of tunneling processes. The WSU group developed a hybrid quantum (numerical solution of TDSE) and classical (back-propagation of electron trajectories) approach to locate the tunneling exit through virtual detector methods.⁸ Indeed, when the electrons' trajectories are back propagated toward the ionic core using the extracted local momenta, they encounter an impenetrable barrier and “bounced” off from the atoms. This clearly demonstrates the validity of tunneling at the normal strong field experimental conditions and justifies our usage of angular streaking to extract time delay information.

Further results from the TDSE-CFP method (classical forward propagation) show that the different orbitals (p_+ , p_0 and p_-) have slightly different angular shift and energy distributions. Using classical backward propagation, we were able to decide the difference in angular shift mainly arises from different tunneling exit locations and thus different Coulomb effect. Furthermore, it was found that the reason for the different tunneling exit locations for p_+ and p_- orbitals is due to the stronger nonadiabaticity for the counter rotating electrons. By scanning the



wavelengths of the elliptically polarized driving laser, we found significant nonadiabaticity persists beyond Keldysh parameter <0.5 (Fig. 2). These results are critical for providing guidance for selecting experimental conditions in which the principle of angular streaking will work as expected.

3. Probing Ultrafast, 25 fs, nonadiabatic dynamics in methyl azide

Highly excited states of neutral molecules behave qualitatively differently than the lower excited states that are commonly studied in photochemistry. Such states are involved in ionospheric and astrochemical phenomena, as well as in detonation processes. However, highly excited states are poorly understood due to experimental and theoretical challenges in probing their complex dynamics.

In a joint experimental-theory study among WSU, CU Boulder and UCLA/ULg, we applied vacuum-UV (VUV) femtosecond laser sources and an imaging photoelectron-photoion coincidence spectrometer to directly probe the reaction pathways of the model energetic molecule methyl azide (manuscript under revision). Combined with advanced calculations, we

concluded that the electronic relaxation occurs on a surprisingly fast 25 fs timescale, driven by strong nonadiabatic coupling. Population transfer occurs along a seam well above the minimum energy conical intersection.

In this work, ultrafast (10 fs) high harmonic pulses at 8 eV were used to prepare a single highly excited state, that is then probed via multiphoton ionization by an infrared (IR) laser field (see Fig. 3). We found that the vibrational wavepacket is nonadiabatically accelerated (*i.e.* accelerated faster than would adiabatically occur), leading to ultrafast internal conversion through a conical intersection to a dark state at lower energy that cannot be ionized by the probe

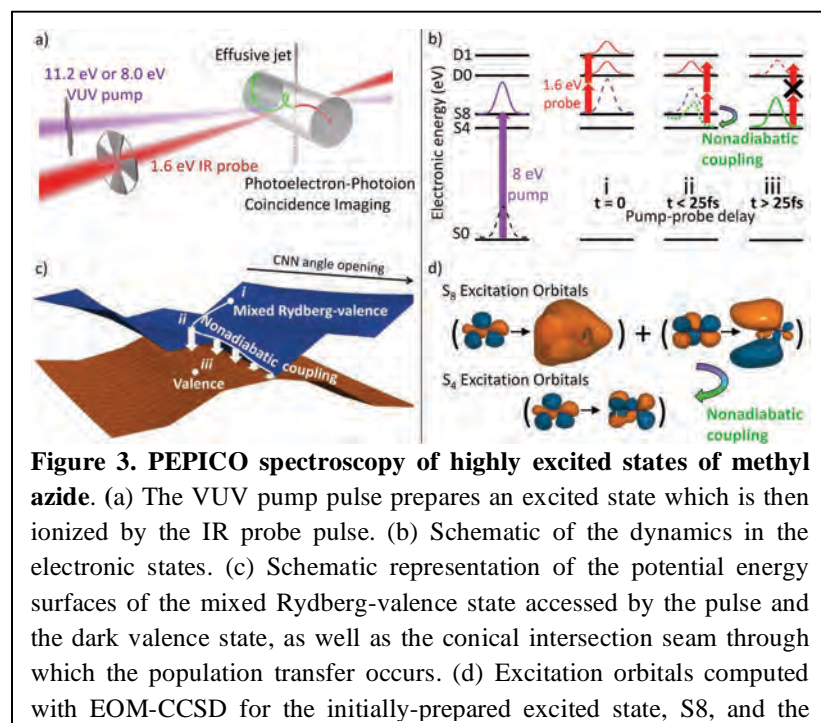


Figure 3. PEPICO spectroscopy of highly excited states of methyl azide. (a) The VUV pump pulse prepares an excited state which is then ionized by the IR probe pulse. (b) Schematic of the dynamics in the electronic states. (c) Schematic representation of the potential energy surfaces of the mixed Rydberg-valence state accessed by the pulse and the dark valence state, as well as the conical intersection seam through which the population transfer occurs. (d) Excitation orbitals computed with EOM-CCSD for the initially-prepared excited state, S8, and the

pulse. This population transfer is complete on a surprisingly fast timescale of 25 fs, which is much faster than the adiabatic vibrational period of 135 fs for the most closely related vibrational mode, the CNN angle bend. These dynamics are directly evidenced by a very rapid increase in vibrational energy in the molecule followed by a fast decrease in ionization signal induced by rapid population transfer to a dark state. This ultrafast relaxation differs from dynamics occurring on lower excited states, where the timescale required for the wavepacket to reach a region of strong

nonadiabatic coupling is typically much longer.

This work benefitted greatly from our combined experimental-theory collaboration to fully interpret the behavior of the molecule in each phase of the measurement. In order to uncover the mechanisms behind this ultrafast relaxation, we implemented a set of complementary advanced theoretical calculations to describe the excited states and resulting dynamics. These calculations showed that the initially prepared excited electronic state is mixed with both Rydberg and valence character. This excited electronic state strongly interacts with neighboring lower excited states through nonadiabatic couplings that drive large changes in the electronic and structural character of the molecule on an ultrafast timescale, ~ 10 fs. The wavepacket is quickly transferred to a lower excited state along one of the conical intersection seams, which leads to a faster relaxation timescale than if the wavepacket had to travel all the way to the minimum energy conical intersection region. In fact these nonadiabatic couplings are already strong in the Franck Condon region, leading to a faster timescale for relaxation than is typical for the lowest excited state, when the time required for the wavepacket to reach a strong nonadiabatic region is typically longer.

These findings are important for understanding the unique strongly-coupled non-Born-Oppenheimer molecular dynamics of VUV-excited energetic molecules. Although such

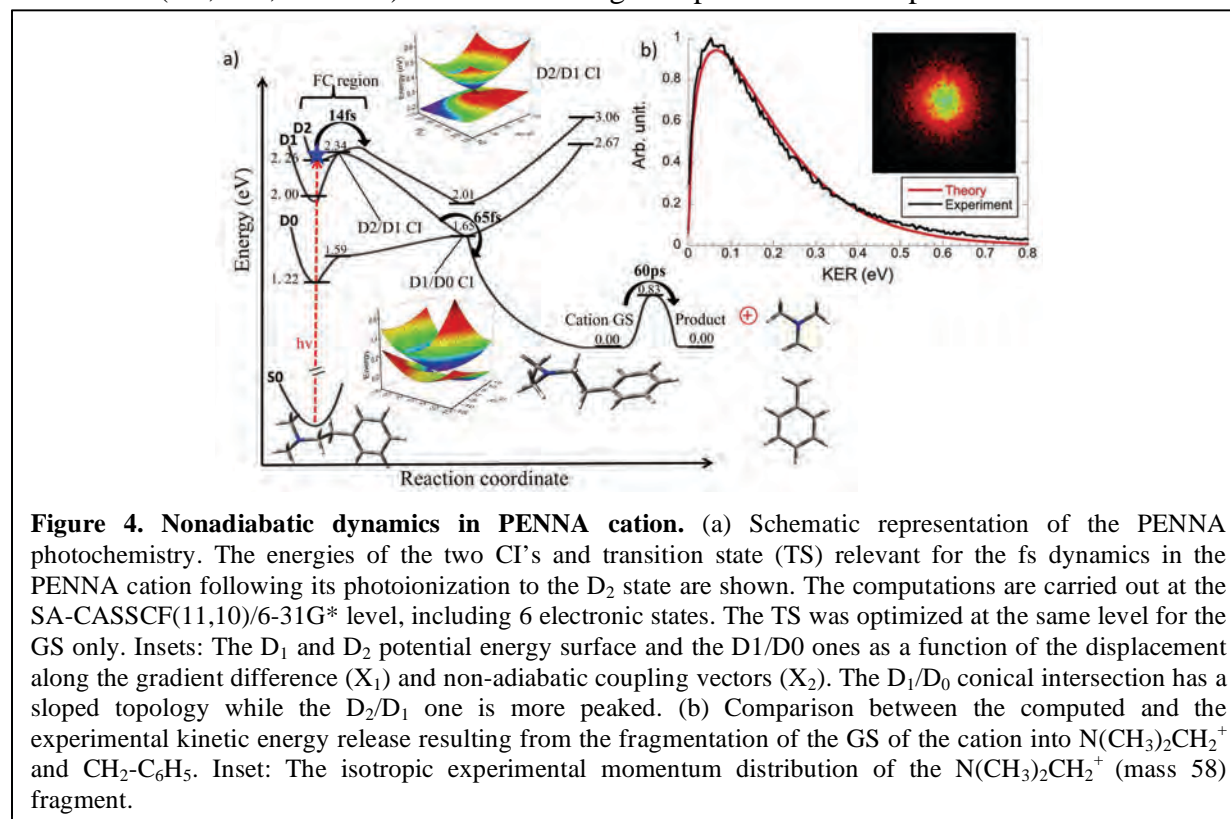
observations have been predicted for many years, this study represents one of the few where such strongly-coupled non-Born-Oppenheimer molecular dynamics of VUV-excited energetic molecules have been conclusively observed directly, making it possible to identify the ultrafast reaction pathways.

4. Multiphoton ionization processes in fullerenes

The UCLA/ULg group collaborated with two fellow PIs of the DOE AMOS program, Matthias Kling at Kansas University and Nora Berrah at the University of Connecticut, to provide theoretical interpretation for their experiments on the multiphoton ionization of C_{60} ⁹ and of the doped $HoN_3@C_{80}$ fullerene¹⁰ by strong IR laser pulses. In both cases, it was found that Super Atomic Molecular Orbital states, which are low Rydberg states with a nanoscale hydrogenic symmetry, contribute significantly to the photoionization process for low field strengths at which this is the dominant mechanism for ionization. The reason is that they possess photoionization widths significantly larger than isoenergetic valence and Rydberg states because of their nanoscale spherical symmetry. As the field intensity increases, Rydberg state strong field ionization over the barrier dominates the ionization process.

5. Ultrafast dynamics in PENNA

The UCLA/ULg group investigated the ultrafast photodissociation of the PENNA ($C_{10}H_{15}N$) cation following multiphoton ionization of the neutral. A comparison was made with the experiments of the WSU group. The ultrafast dynamics on the three lowest electronic states of the cation (D0, D1, and D2) accessed during the photoionization process was studied using



quantum chemistry and surface hopping on the fly. The simulations take into account all the

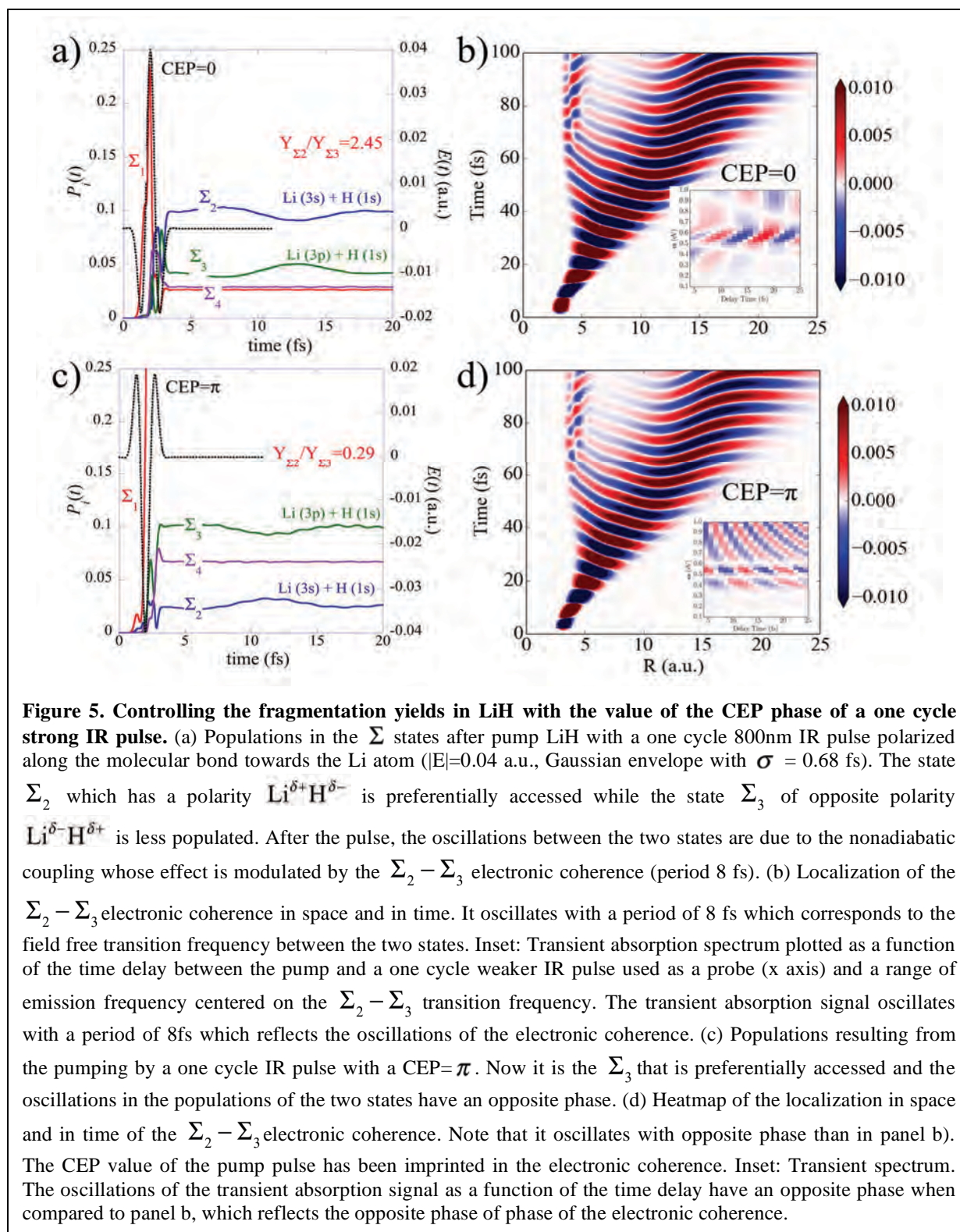
nuclear degrees of freedom and 6 electronic states. The potentials, gradients and nonadiabatic couplings are computed at the State averaged CAS-SCF level. We show that a conical intersection, localized in the Franck–Condon region, between the D0 and the D1 states, leads to an ultrafast charge transfer, computed here to be on a time scale of 65 fs, between the phenyl and the amine charged subunits. Such a charge transfer between different parts of a molecule induced by conical intersections has been reported for other systems.¹¹⁻¹³ On the D0 ground state, the dissociation proceeds on the 60 ps time scale through a 19 kcal/mol late barrier. The computed kinetic energy release is in good agreement with a new experimental measurement of PENNA ionization by an 800 nm 30 fs intense laser pulses by the Li group at WSU, see Fig. 4.¹⁴

6. Non-equilibrium electronic and nuclear dynamics: steering chemical reactivity

The UCLA/ULg group investigated the effect of nuclear motion on the coherent non-equilibrium electronic density built through the excitation by a short few cycle pulse in the diatomic molecules N_2 ^{15,16} and LiH,¹⁷⁻¹⁹ and in HCN.²⁰ The quantum dynamics was computed by solving the nuclear time-dependent Schrodinger equation on a grid on coupled several electronic states, also coupled by dipole interaction with the electric field during the pulse. For N_2 , we work in a basis of diabatic electronic states that diagonalizes the nuclear kinetic energy operator and the coupling between diabatic states is local and efficient.

For LiH and HCN, we work in the adiabatic basis that diagonalizes the electronic Hamiltonian. In this basis set, it is the nuclear kinetic energy term that couples the electronic states. In all three molecules, our quantum dynamical simulations over the first few hundreds of fs show that the coupling between electronic states modulates the temporal and the spatial localization of the electronic coherences but does not dephase it, even for the two dimensional nuclear motion in HCN²⁰. We also showed that transient absorption spectra²¹ recorded as a function of the time delay of a probe pulse as the nuclear dynamics unfolds provide a probe not only of the coherences between the electronic states but also of the coherent vibrational excitation on each potential energy surface.

In the case of the LiH molecule, we showed that one can steer selective fragmentation by controlling the carrier-envelope-phase of the essentially one cycle IR pulse used to pump a non-equilibrium electronic density by multiphoton IR excitation. If there are too many oscillations of the electric field within the pulse envelope, this control is lost. The control is made possible by the fact that the Σ states of LiH are of alternating polarity. For aligned molecules, one cycle pulses with the maximum of the electric field oriented towards the Li or the H atom predominantly selectively excite different electronic states. These states correspond to asymptotes with different excitations of the Li, and therefore can be probed. Our simulations demonstrate a ratio of fragmentation yields for the $\Sigma_2(Li^{\delta+}H^{\delta-})$ and $\Sigma_3(Li^{\delta-}H^{\delta+})$ states of $Y_{\Sigma_2}/Y_{\Sigma_3} = 2.45$ for a maximum of the electric field pointing to the Li atom (CEP=0) and of 0.29 when the electric field points to the H atom (CEP= π), see Fig. 5.



Future Plans

1. 3D-2eAS probing of charge migration and attosecond nuclear dynamics

With the development of the 3D-2eAS, the WSU group is now ready to study detailed electron wavepacket dynamics in the first femtosecond. We will start from small molecules such as CO₂ and HCCI and later move on to PENNA and ABCU and other bigger molecules.

Because 3D-2eAS is also sensitive to orbital geometry, we will implement studies on probing attosecond nuclear dynamics involving hydrogen atom in CH₄ and H₂.

2. Development of TDCI-CAP-Virtual detector for modeling angular streaking dynamics

The Schlegel group will develop a new method based on TDCI-CAP (time-dependent configuration interaction with a complex absorbing potential) and virtual detector to provide a full modeling of the angular streaking experiments on polyatomics.

3. Probing femtosecond charge dynamics in chloroacetone

To explore the possibility of measuring energy partitioning in electronic superposition states, the CU group will perform PEPICO experiments on chloroacetone. The key advantage of chloroacetone is that both the carbonyl group (the carbon-oxygen double bond) and the alkyl chloride group (the carbon-chlorine bond) are expected to have Rydberg states near 8 eV, which matches the 5th harmonic of a Ti:Sapphire laser. The near-degeneracy would be between $n_{\text{O}} \rightarrow 3p$, where the hole in the ionic core is localized on the oxygen atom, and $n_{\text{Cl}} \rightarrow 4s$, where the hole is localized on the chlorine atom; the corresponding cation states in chloroacetone are 1.5 eV apart (vertical ionization energies) and have narrow Franck-Condon widths, so that the electronic character will be easily resolvable and inhomogeneous dephasing will be minimized. In the presence of Rydberg mixing between manifolds, the energies of the photoelectrons from a superposition state will oscillate between the two final cation states.

Importantly, if this oscillation can be observed, it will have real chemical consequences. Rydberg states of carbonyl compounds will, in a few hundred femtoseconds, dissociate by breaking the bond next to the carbonyl group, which in this case is a carbon-carbon bond. On the other hand, Rydberg states of alkyl chlorides break the carbon-chlorine bond on a 100 fs timescale. Thus, as the electronic character oscillates, so too will the reaction products, as the electronic wavefunction controls which reaction pathways are accessible. Our PEPICO instrument is capable of measuring the changes in electronic character, the level of vibrational excitation in the superposition state, and the energy released by each reaction pathway, providing an extraordinarily detailed accounting of coherent energy partitioning in this extremely non-adiabatic process.

The experimental effect will be closely coordinated with the theory groups.

4. Raman-like field induced electronic dynamics

The UCLA/ULg group will develop the theory and the computational tools for understanding Raman-like field induced electron dynamics and producing electronic wavepackets in neutral molecules. In ultrafast time-domain Raman-like processes a non-stationary excited electronic state is first created by the laser. It then rapidly evolves in time, with associated changes in the nuclear coordinates, before reaching a region of phase space from which it can be stimulated, by the laser, to otherwise inaccessible states. Typically, these states cannot be directly pumped because of Franck-Condon limitations. The CU group has already demonstrated experimentally the feasibility of such experiments in simple molecules such as H₂.²² The UCLA/ULg group has

suggested based on work reported during this funding period that HCN could be a good candidate for exploiting such a process in a polyatomic system. In the work reported in this period, the nuclear dynamics was constrained in 2D with a fixed CN bond length. We will extend the dynamics to 3D, and include the vibration of the CN fragment. The inclusion of the photoionization process in the nuclear dynamics code will allow modeling photoionization to probe the dynamics on the GS. We will also explore the case of a Raman excitation when the transition is from the electronic continuum to bound states. The continuum is that of the cation plus the ionized electron. The field that drives the electron away brings it back when it swings its sign after half a cycle. The recollision of an ionized electron is extensively documented in the context of high harmonic generation.²³ But the result of a recombination of the cation and the returning electron is a wavepacket coherently spanning many states.²⁴ We will investigate how to control the produced neutral electronic wavepacket using the recollision process.

5. Control of chemical reactions through specific electronic excitations

In order to control not only bond breaking but also bond making, the UCLA/ULg group will investigate the coupled electronic-nuclei dynamics induced by photoexcitation by a short strong UV or fs pulse in two systems, allene oxide²⁵⁻²⁷ and norbornadiene.²⁸ The allene oxide system was chosen because it exhibits rich dynamics of photoinduced bond breaking and bond making and is a relatively small system. Another advantage is that the excited states of the oxyallyl diradical can be accessed by photodetachment from the anion.²⁵ The electronic structure and pathways on the GS of these two systems were previously studied by the Schlegel group.^{29,30} The photoinduced isomerization of norbornadiene was previously studied by the UCLA group under extreme condition.³¹ It can be described in reduced dimensionality for the nuclear motion.³² The experimental implementation will be carried out by the WSU and CU groups using angular streaking and photoelectron-photoion coincidence spectroscopy.

6. Developing quantum nuclear dynamics on the fly

Computing on the fly the course of chemical reactions and other processes where the nuclei move has been developed primarily to address two issues, the cost of precomputing the potential for the entire configurational space of the nuclei and doing so for several coupled electronic states. These two issues are far more severe for attochemistry. So computing nuclear dynamics on the fly is one possible way to realistically address the control of reactivity of polyatomic molecules by nonequilibrium electron dynamics.

We aim to develop a methodology to compute the nuclear dynamics on several coupled electronic states on the fly on a limited number of grid points, based on computing the matrix elements on the kinetic energy and momentum operators using finite difference instead of the Fourier method, which requires to use precomputed potential energies and coupling terms in the entire configurational space of the nuclei. The grid method uses thin slabs localized at each grid point as nuclear basis functions. These basis functions are orthogonal and not limited to harmonic potentials. This is an advantage over the Gaussian nuclear wave functions that are typically used in semi-classical approaches. We will investigate using an algebraic approach to propagate classically anharmonic nuclear basis functions on coupled electronic states.

Cited References

1. Lee, S. K.; Cudry, F.; Lin, Y. F.; Lingenfelter, S.; Winney, A. H.; Fan, L.; Li, W., Coincidence Ion Imaging with a Fast Frame Camera, *Rev. Sci. Instrum.* **2014**, *85*, 123303.
2. Lee, S. K.; Lin, Y. F.; Lingenfelter, S.; Fan, L.; Winney, A. H.; Li, W., Communication: Time- and Space-Sliced Velocity Map Electron Imaging, *J. Chem. Phys.* **2014**, *141*, 221101.
3. Lin, Y. F.; Lee, S. K.; Adhikari, P.; Herath, T.; Lingenfelter, S.; Winney, A. H.; Li, W., Note: An Improved 3D Imaging System for Electron-Electron Coincidence Measurements, *Rev. Sci. Instrum.* **2015**, *86*, 096110.
4. Winney, A. H.; Lee, S. K.; Lin, Y. F.; Adhikari, P.; Basnayake, G.; Liao, Q.; Schlegel, H. B.; Li, W., Attosecond Electron Correlation Dynamics in Double Ionization of Benzene Probed with Two-Electron Angular Streaking, *Phys. Rev. Lett.* **2017**, *119*, 123201.
5. Weckenbrock, M.; Becker, A.; Staudte, A.; Kammer, S.; Smolarski, M.; Bhardwaj, V. R.; Rayner, D. M.; Villeneuve, D. M.; Corkum, P. B.; Dörner, R., Electron-Electron Momentum Exchange in Strong Field Double Ionization, *Phys. Rev. Lett.* **2003**, *91*, 123004.
6. Weckenbrock, M.; Zeidler, D.; Staudte, A.; Weber, T.; Schöffler, M.; Meckel, M.; Kammer, S.; Smolarski, M.; Jagutzki, O.; Bhardwaj, V. R.; Rayner, D. M.; Villeneuve, D. M.; Corkum, P. B.; Dörner, R., Fully Differential Rates for Femtosecond Multiphoton Double Ionization of Neon, *Phys. Rev. Lett.* **2004**, *92*, 213002.
7. Fan, L.; Lee, S. K.; Tu, Y.-J.; Mignolet, B.; Couch, D.; Dorney, K.; Nguyen, Q.; Wooldridge, L.; Murnane, M.; Remacle, F.; Bernhard Schlegel, H.; Li, W., A New Electron-Ion Coincidence 3D Momentum-Imaging Method and Its Application in Probing Strong Field Dynamics of 2-Phenylethyl-N, N-Dimethylamine, *J. Chem. Phys.* **2017**, *147*, 013920.
8. Zhang, Q.; Basnayake, G.; Winney, A.; Lin, Y. F.; Debrah, D.; Lee, S. K.; Li, W., Orbital-Resolved Nonadiabatic Tunneling Ionization, *Phys. Rev. A* **2017**, *96*, 023422.
9. Li, H.; Mignolet, B.; Wang, Z.; Betsch, K. J.; Carnes, K. D.; Ben-Itzhak, I.; Cocke, C. L.; Remacle, F.; Kling, M. F., Transition from Samo to Rydberg State Ionization in C60 in Femtosecond Laser Fields, *J. Phys. Chem. Lett.* **2016**, *7*, 4677.
10. Xiong, H.; Mignolet, B.; Fang, L.; Osipov, T.; Wolf, T. J. A.; Sistrunk, E.; Gühr, M.; Remacle, F.; Berrah, N., The Role of Super-Atom Molecular Orbitals in Doped Fullerenes in a Femtosecond Intense Laser Field, *Sci. Rep.* **2017**, *7*, 121.
11. Mendive-Tapia, D.; Vacher, M.; Bearpark, M. J.; Robb, M. A., Coupled Electron-Nuclear Dynamics: Charge Migration and Charge Transfer Initiated near a Conical Intersection, *J. Chem. Phys.* **2013**, *139*, 044110.
12. Assmann, M.; Köppel, H.; Matsika, S., Photoelectron Spectrum and Dynamics of the Uracil Cation, *J. Phys. Chem. A* **2015**, *119*, 866.
13. Plasser, F.; Granucci, G.; Pittner, J.; Barbatti, M.; Persico, M.; Lischka, H., Surface Hopping Dynamics Using a Locally Diabatic Formalism: Charge Transfer in the Ethylene Dimer Cation and Excited State Dynamics in the 2-Pyridone Dimer, *J. Chem. Phys.* **2012**, *137*, 22A514.
14. Sun, S.; Mignolet, B.; Fan, L.; Li, W.; Levine, R. D.; Remacle, F., Nuclear Motion Driven Ultrafast Photodissociative Charge Transfer of the Penna Cation: An Experimental and Computational Study, *J. Phys. Chem. A* **2017**, *121*, 1442.
15. Ajay, J.; Šmydke, J.; Remacle, F.; Levine, R. D., Probing in Space and Time the Nuclear Motion Driven by Nonequilibrium Electronic Dynamics in Ultrafast Pumped N₂, *J. Phys. Chem. A* **2016**, *120*, 3335.
16. Šmydke, J.; Jayanth, S. A.; Remacle, F.; Levine, R. D., Electronic and Nuclear Dynamics for a Non-Equilibrium Electronic State: The Ultrafast Pumping of N₂. In *Progress in Theoretical Physics and Chemistry*, Maruani, J., Ed. Springer: Dordrecht, 2016; p 195.
17. Nikodem, A.; Levine, R. D.; Remacle, F., Quantum Nuclear Dynamics Pumped and Probed by Ultrafast Polarization Controlled Steering of a Coherent Electronic State in Lih, *J. Phys. Chem. A* **2016**, *120*, 3343.
18. Nikodem, A.; Levine, R. D.; Remacle, F., Spatial and Temporal Control of Populations, Branching Ratios, and Electronic Coherences in Lih by a Single One-Cycle Infrared Pulse, *Phys. Rev. A* **2017**, *95*, 053404.
19. Nikodem, A.; Levine, R. D.; Remacle, F., Controlling Coherent Quantum Nuclear Dynamics in Lih by Ultra Short Ir Atto Pulses. In *Progress in Ultrafast Laser Science Xiii*, Yamanouchi, K.; Hill, W.; Paulus, F., Eds. Springer: Dordrecht, 2017; Vol. XIII, p accepted.
20. van den Wildenberg, S.; Mignolet, B.; Levine, R.; Remacle, F., Pumping and Probing Vibrational Modulated Coupled Electronic Coherence in Hcn Using Short Uv Fs Laser Pulses: A 2d Quantum Nuclear Dynamical Study, *Phys. Chem. Chem. Phys.* **2017**, *19*, 19837

21. Mengxi, W.; Shaohao, C.; Seth, C.; Kenneth, J. S.; Mette, B. G., Theory of Strong-Field Attosecond Transient Absorption, *J. Phys. B* **2016**, *49*, 062003.
22. Ranitovic, P.; Hogle, C. W.; Rivière, P.; Palacios, A.; Tong, X.-M.; Toshima, N.; González-Castrillo, A.; Martin, L.; Martín, F.; Murnane, M. M.; Kapteyn, H., Attosecond Vacuum Uv Coherent Control of Molecular Dynamics, *Proc. Natl. Acad. Sci. U. S. A.* **2014**, 10.1073/pnas.1321999111.
23. Corkum, P. B., Plasma Perspective on Strong Field Multiphoton Ionization, *Phys. Rev. Lett.* **1993**, *71*, 1994.
24. Ferré, A.; Boguslavskiy, A. E.; Dagan, M.; Blanchet, V.; Bruner, B. D.; Burgy, F.; Camper, A.; Descamps, D.; Fabre, B.; Fedorov, N.; Gaudin, J.; Geoffroy, G.; Mikosch, J.; Patchkovskii, S.; Petit, S.; Ruchon, T.; Soifer, H.; Staedter, D.; Wilkinson, I.; Stolow, A.; Dudovich, N.; Mairesse, Y., Multi-Channel Electronic and Vibrational Dynamics in Polyatomic Resonant High-Order Harmonic Generation, *Nat. Commun.* **2015**, *6*, 5952.
25. Ichino, T.; Villano, S. M.; Gianola, A. J.; Goebbert, D. J.; Velarde, L.; Sanov, A.; Blanksby, S. J.; Zhou, X.; Hrovat, D. A.; Borden, W. T.; Lineberger, W. C., Photoelectron Spectroscopic Study of the Oxyallyl Diradical, *J. Phys. Chem. A* **2011**, *115*, 1634.
26. Hess, B. A.; Eckart, U.; Fabian, J., Rearrangements of Allene Oxide, Oxyallyl, and Cyclopropanone, *J. Am. Chem. Soc.* **1998**, *120*, 12310.
27. Mozhayskiy, V.; Goebbert, D. J.; Velarde, L.; Sanov, A.; Krylov, A. I., Electronic Structure and Spectroscopy of Oxyallyl: A Theoretical Study, *J. Phys. Chem. A* **2010**, *114*, 6935.
28. Antol, I., Photodeactivation Paths in Norbornadiene, *J. Comp. Chem.* **2013**, *34*, 1439.
29. Hebert, S. P.; Cha, J. K.; Brash, A. R.; Schlegel, H. B., Investigation into 9(S)-Hpode-Derived Allene Oxide to Cyclopentenone Cyclization Mechanism Via Diradical Oxyallyl Intermediates, *Org. Biomol. Chem.* **2016**, *14*, 3544.
30. Bach, R. D.; Schilke, I. L.; Schlegel, H. B., The Energetics of Valence Isomerization in the Norbornadiene–Quadricyclane System, *J. Org. Chem.* **1996**, *61*, 4845.
31. Raz, T.; Levine, R. D., Four-Center Reactions: A Computational Study of Collisional Activation, Concerted Bond Switching, and Collisional Stabilization in Impact Heated Clusters, *J. Phys. Chem.* **1995**, *99*, 7495.
32. Blancafort, L.; Jolibois, F.; Olivucci, M.; Robb, M. A., Potential Energy Surface Crossings and the Mechanistic Spectrum for Intramolecular Electron Transfer in Organic Radical Cations, *J. Am. Chem. Soc.* **2001**, *123*, 722.

Peer-Reviewed Publications Resulting from this Project (2015-2017) with Institutional Contribution

1. L. Fan, S. K. Lee, Y. J. Tu, B. Mignolet, D. Couch, K. Dorney, Q. Nguyen, L. Wooldridge, M. Murnane, F. Remacle, H. B. Schlegel, W. Li, “A new electron-ion coincidence 3D momentum-imaging method and its applications in probing strong field dynamics of PENNA”, *J. Chem. Phys.*, **147**, 013920 (2017) (WSU-ULg-CU)
2. S. Sun, B. Mignolet, L. Fan, W. Li, R. D. Levine, F. Remacle, “Nuclear motion driven ultrafast photodissociative charge transfer of PENNA cation”, *J. Phys. Chem. A*, **121**, 1442 (2017) (ULg-UCLA-WSU)
3. J. Hollett, W. Li, “The relative momentum of electron pairs and the effect of static field”, *J. Phys. Chem. A* (accepted) (WSU)
4. A. Winney, S. Lee, Y. Lin, P. Adhikari, G. Basnayake, Q. Liao, H. Schlegel, W. Li, “Attosecond electron correlation dynamics in double ionization of benzene probed with two-electron angular streaking”, *Phys. Rev. Lett.* **119**, 123201 (2017) (WSU)
5. Q. B. Zhang, G. Basnayake, A. Winney, Y. F. Lin, D. Debrah, S. K. Lee, W. Li, “Orbital-resolved nonadiabatic tunneling ionization”, *Phys. Rev. A*, **96**, 023422 (2017) (WSU)
6. D. E. Couch, H. C. Kapteyn, M. M. Murnane, William K. Peters, “Uncovering highly-excited state mixing with in acetone ultrafast VUV pulses and coincidence imaging techniques”, *J. Phys. Chem. A*, **121**, 2361 (2017) (CU)

7. A. Nikodem, R. D. Levine, and F. Remacle, "Spatial and temporal control of populations, branching ratios, and electronic coherences in LiH by a single one-cycle infrared pulse", *Phys. Rev. A*, **95**, 053404 (2017) (UCLA-ULg)
8. V. Schwanen, F. Remacle, "Photoinduced Ultrafast Charge Transfer and Charge Migration in Small Gold Clusters Passivated by a Chromophoric Ligand", *Nano Letters*, *in press*, 10.1021/acs.nanolett.7b02568 (ULg)
9. S. van den Wildenberg, B. Mignolet, R. Levine, and F. Remacle, "Pumping and probing vibrational modulated coupled electronic coherence in HCN using short UV fs laser pulses: a 2D quantum nuclear dynamical study", *Phys. Chem. Chem. Phys.*, **19**, 19837 (2017) (UCLA-ULg)
10. H. Xiong, B. Mignolet, L. Fang, T. Osipov, T. Wolf, E. Sistrunk, M. Gühr, F. Remacle, N. Berrah, "The Role of Super-Atom Molecular Orbitals in Doped Fullerenes in a fs Intense Laser Field", *Sci. Rep.* **7**, 121 (2017). (UCLA-ULg)
11. X. Shi, W. Li, H. B. Schlegel, "Computational Simulations of Hydrogen Circular Migration in Protonated Acetylene Induced by Circularly Polarized Light", *J. Chem. Phys.*, **145**, 084309 (2016) (WSU)
12. Q. Liao, W. Li, H. Schlegel, "Angle-Dependent Strong Field Ionization of Triple Bonded Systems Calculated by Time-Dependent Configuration Interaction, with an Absorbing Potential", *Can. J. Chem.*, **94**, 989, (2016) (WSU)
13. X. Shi, B. Thapa, W. Li, H. B. Schlegel, "Controlling chemical reactions by short, intense mid-infrared laser pulses: comparison of linear and circularly polarized light in simulations of ClCHO⁺ fragmentation", *J. Phys. Chem. A*, **120**, 1120 (2016) (WSU)
14. Ajay, J. Šmydke, F. Remacle, and R. D. Levine, "Probing in Space and Time the Nuclear Motion Driven by Non-equilibrium Electronic Dynamics in Ultrafast Pumped N₂", *J. Phys. Chem. A*, **120**, 3335 (2016) (UCLA-ULg)
15. H. Li, B. Mignolet, Z. Wang, K. J. Betsch, K. D. Carnes, I. Ben-Itzhak, C. L. Cocke, F. Remacle, and M. F. Kling, "Transition from SAMO to Rydberg State Ionization in C₆₀ in Femtosecond Laser Fields", *J. Phys. Chem. Lett.* **7**, 4677 (2016) (ULg)
16. A. Nikodem, R. D. Levine, and F. Remacle, "Quantum Nuclear Dynamics Pumped and Probed by Ultrafast Polarization Controlled Steering of a Coherent Electronic State in LiH", *J. Phys. Chem. A*, **120**, 3343 (2016). (UCLA-ULg)

Early Career: First-Principles Tools for Nonadiabatic Attosecond Dynamics in Materials

DOE Award Number: DE-SC0017868

Report Date: September 2017

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Project Scope

The ultrafast response of materials to intense electromagnetic radiation underpins a wide range of important applications such as time-resolved spectroscopy, radiation damage, light harvesting, and high-density capacitors and electronics. At the atomistic level, however, the mechanisms are still poorly understood, especially concerning the attosecond dynamics immediately following excitation, and the downstream electron/lattice couplings.

The objective of this project is to develop quantum chemistry techniques for simulating strong-field attosecond electron/nuclear dynamics in semiconductors and insulators using a single theoretical framework. This will consist of real-time time dependent density functional theory (TDDFT) with hybrid functionals, and bulk-mimicking clusters using covalent and electrodynamic embedding. Electron/nuclear coupling will be captured using an Ehrenfest band hopping scheme.

These tools will be validated against ultrafast experiments and enable computation of key properties such as: electron/lattice couplings, excited state lifetimes, “photochemistry” around defects/dopants, and the ultrafast origins of non-thermal materials damage. This will form the basis for interpreting ultrafast time-resolved experiments on materials, and motivate new directions as the drive towards faster time resolution continues. Finally, all resulting software will be released as part of the free/open source NWChem package, where they will be broadly applicable to ongoing DOE ultrafast efforts spanning molecular and materials systems.

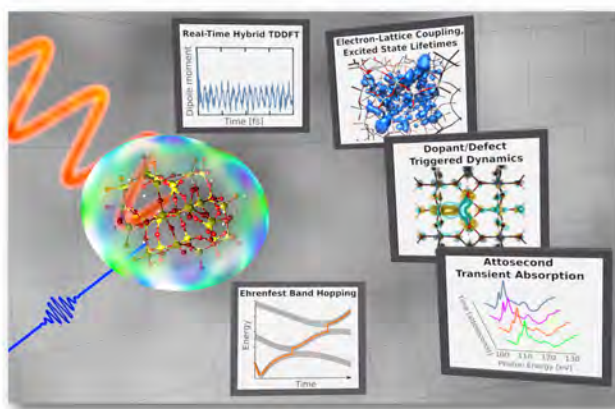


Figure 1: Schematic of attosecond electron/nuclear dynamics simulations of solid-state materials. These simulations will facilitate interpretation of ultrafast experiments and help elucidate the mechanisms of transient electronic shifts, energy/lattice coupling, and dopant/defect centered dynamics.

Recent Progress

DOE funding for this project started in September 2017. There is no progress to report yet.

Future Plans

The coming year is the first year of this project. Initially, work will proceed along three interrelated directions. First, TDDFT tools for *simulating attosecond transient X-ray absorption* in insulators will be developed. These include embedded bulk-mimicking finite clusters [1] for use of atom-centered basis sets [2], spectral acceleration techniques for high density of states systems [3], and validation of DFT functionals. Here, finite clusters allow for all electron simulations which are natural for core-level response and enable efficient use of hybrid of DFT functionals, which typically have improved band gaps and reduced self-interaction. Since core-holes can be easily prepared via SCF techniques, there is no need for resonant excitation. Thus, these simulations can circumvent the peak-shifting errors that results from using DFT functionals that are local-in-time [4].

Next, as a first step towards non-adiabatic electron/lattice coupling, we will develop *Ehrenfest approaches* where the nuclei move on a mean-field potential arising from the time-dependent electron density. This approach is natural for the high energy, parallel, nearly-degenerate, and electronically smeared states found in strong-field excited materials. Future work will expand to include band hopping processes.

Finally, work will begin on *embedding TDDFT in a classical electrodynamics background* treated with finite-difference time-domain (FDTD) [5]). Work in the first year will focus parallel implementation of FDTD in the NWChem software package, and application to spatially varying external fields. Non-uniform fields enable beyond dipole coupling, which is essential for simulations involving hard X-rays, which can have wavelengths on the order of bonds or shorter. Results will be validated against XANES spectra for molecules and materials. Next, these techniques will be extended to electrodynamics embedding of finite clusters to include a background with the correct frequency-dependent response.

References

- [1] R. G. Fernando, M. C. Balhoff, and K. Lopata, "X-ray absorption in insulators with non-Hermitian real-time time-dependent density functional theory", *J. Chem. Theory Comput.* **11**, 646 (2015).
- [2] K. Lopata and N. Govind, "Modeling fast electron dynamics with real-time time-dependent density functional theory: application to small molecules and chromophores", *J. Chem. Theory Comput.* **7**, 1344 (2011).
- [3] A. Bruner, D. LaMaster, and K. Lopata, "Accelerated broadband spectra using transition dipole decomposition and Pade approximants", *J. Chem. Theory Comput.* **12**, 3741 (2016).
- [4] A. Bruner, S. Hernandez, F. Mauger, P. M. Abanador, D. J. LaMaster, M. B. Gaarde, K. J. Schafer, and K. Lopata, "Attosecond charge migration with TDDFT: Accurate dynamics from a well-defined initial state", *J. Phys. Chem. Lett.* **8**, 3991 (2017).
- [5] H. T. Smith, T. E. Karam, L. H. Haber, and K. Lopata, "Capturing plasmon-molecule dynamics in dye monolayers on metal nanoparticles using classical electrodynamics with quantum embedding", *J. Phys. Chem. C* **121**, 16932 (2017).

Peer-Reviewed Publications Resulting from this Project (Project Start Date: 09/2017)

None

Complexity and Correlated Motion of Electrons in Free and Confined Atomic Systems

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Project Scope

The goals of this research program are: to further our understanding of the interaction of radiation with matter; to provide theoretical support to, and collaboration with, various experimental programs that employ latest generation light sources, particularly ALS, APS and LCLS; and to study the properties (especially photoionization) of confined atoms and ions. Specifically, calculations are performed using and upgrading state-of-the-art theoretical methods to help understand the essential physics of the experimental results; to suggest future experimental investigations; and seek out new phenomenology, especially in the realm of confined systems, attosecond time delay in photoionization, and outer-shell photoionization in the vicinity of inner-shell thresholds. The primary areas of programmatic focus are: nondipole and relativistic effects in photoionization; photoabsorption of inner and outer shells of atoms and atomic ions (positive and negative); dynamical properties of atoms endohedrally confined in buckyballs, primarily C₆₀; studies of Wigner time delay on the attosecond scale in photoionization of free and confined atomic systems. Flexibility is maintained to respond to opportunities as they arise.

Recent Progress

The study of confined atoms is a rapidly growing field. Theoretical investigations of various atoms endohedrally confined in C₆₀ [1,2] abound, but experimental studies are sparse [3-5]. Our theoretical program, at various levels of approximation, is aimed at mapping out the properties of such systems, especially photoionization, to guide experiment and uncover new phenomena. Among our major results, we have found that a huge transfer of oscillator strength from the C₆₀ shell, in the neighborhood of the giant plasmon resonance, to the encapsulated atom for both Ar@C₆₀ [6] and Mg@C₆₀ [7]. And confinement resonances [8], oscillations in the photoionization cross section of an endohedral atom due to interferences of the photoelectron wave function for direct emission with those scattered from the surrounding carbon shell, were predicted in a broad range of cases; and their existence has been confirmed experimentally [4,5]. Further, in the photoionization of endohedral atoms within nested fullerenes, as a result of the multi-walled confinement, the confinement resonances become considerably more complicated [9]. In addition, spin-orbit induced confinement resonances in photoionization have been found owing to interchannel coupling between inner-shell spin-orbit split channels in high-Z endohedral atoms [10], an effect which occurs solely owing to relativistic interactions. We have also explored the interatomic Coulomb decay (ICD) phenomenon in confined atoms and found, owing to hybridization between atomic and shell orbitals, that ICD occurs both ways, from atom to shell and shell to atom, and the rates (widths) are often much larger than the ordinary Auger rates [11-14]; the widths

of these resonances makes them excellent candidates for experimental study of endohedral atoms.

A number of aspects of attosecond time delay in the photoionization process were explored. Time delay of photoemission from valence subshells of noble-gas atoms were theoretically scrutinized within the framework of the dipole relativistic random phase approximation [15] with a focus on the variation of time delay in the vicinity of the Cooper minima where the corresponding dipole matrix element changes its sign while passing through a node. It was found that the presence of the Cooper minimum in one photoionization channel has a strong effect on time delay in other channels owing to interchannel coupling, and that relativistic effects strongly affect the time delay in regions of Cooper minima; it is likely that relativistic effects will be even more important as one goes to heavier and heavier elements. A study of Wigner time delay in Mn photoionization in the region of the $3p \rightarrow 3d$ giant resonance showed the dramatic effect of the resonance on the time delay of photoemission from the $3d$ and $4s$ valence subshells of the Mn atom [16]. Similar features are expected to emerge in photoionization time delays of other transition-metal and rare-earth atoms with half-filled subshells that possess giant autoionization resonances as well. It was shown that photoionization time delay in the autoionizing resonance region is explicitly associated with the resonance lifetime, which can, thus, be directly measured in attosecond time-delay experiments. We also conducted a systematic study of the dipole phase and the Wigner time delay in inner-shell photoionization of noble gas atoms from Ne to Xe [17] using both the relativistic and the nonrelativistic versions of the random-phase approximation and found that the time delay, as a function of photoelectron energy, follows more or less a universal shape. And the angular distribution of Wigner time delay was investigated and it was found that strong angular anisotropy of the time delay in photoemission occurs near Cooper minima while the spin-orbit splitting affects the time delay near threshold [18]. Since Wigner time delay near the photoionization threshold is dominated by the long-range Coulomb interaction between the photoelectron and residual ion [17,18], we have initiated studies of attosecond time delay in negative ion photodetachment in Cl^- , Br^- , I^- and Tm^- (which are isoelectronic to Ar, Kr, Xe and Yb, respectively) where the problem of the long-range Coulomb interaction is obviated and the effects of near-threshold shape resonances are emphasized in the time-delay spectrum [19].

It has also been found that confinement resonances in the photoionization of endohedral atoms induce rather significant resonances in the attosecond time delay of photoelectron emission [20], which suggests that time-domain spectroscopy might be efficacious in studying endohedral systems and clusters. And in high- Z atoms, it was found that spin-orbit induced confinement resonances [10] also induce rather significant structures in the Wigner time delay, in the vicinity of these induced resonances, another domain that is ripe for experimental investigations. Also, a study of the angular-dependence of Wigner time delay has been performed on the $4d$ subshell of $\text{Xe}@C_{60}$ and various new phenomena have been uncovered including a new kind of Cooper-line minima in certain of the photoionization channels which can lead to huge time delays and great sensitivity to the details of the confinement [21]; confined Xe $4d$ was chosen because its cross section has already been studied experimentally [3-5], thereby suggesting the possibility of experimental investigation of the Wigner time delay of $\text{Xe}@C_{60}$.

Future Plans

Our future plans are to continue on the paths set out above. In the area of confined atoms, expand on our studies of interatomic Coulomb decay (ICD) of resonances. We will also work on ways to enhance the time-dependent local-density approximation to make it more accurate in our calculations of confined atoms. In addition, we shall work towards upgrading our theory to include relativistic interactions to be able to deal with heavy endohedrals with quantitative accuracy. In addition, we shall focus upon calculations taking into account the full molecular symmetry of free and endohedral C_{60} to understand the limits of utility of simple potential models representing the C_{60} cage, and to deal with off-center endohedral confinement in a realistic manner. We will also continue investigations into the attosecond time delay in photoionization that has been found in various experiments, including a particular focus on how electron-electron correlation effects become important in the vicinity of inner-shell thresholds (interchannel coupling), and we will work to further our understanding of how confinement might affect this time delay. To provide a “road map” for experimental investigations at various synchrotron facilities, we will perform exploratory calculations of atomic photoionization at high energies (tens of keV) to predict where interchannel coupling alters the simple behavior of cross sections that is the present conventional wisdom; preliminary indications are that this can be a very significant phenomenon. In addition, the search for cases where nondipole effects are likely to be significant, as a guide for experiment, and quadrupole Cooper minima, will continue. And we shall respond to new experimental capabilities as they are developed, and new experimental results as they come up.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- “Fano shape analysis of autoionization resonances in neon isoelectronic sequence using relativistic multichannel quantum defect theory,” M. Nrisimhamurty, G. Aravind, P. C. Deshmukh and S. T. Manson, *Phys. Rev A* **91**, 013404-1-12 (2015).
- “Attosecond time delay in the photoionization of Mn in the $3p \rightarrow 3d$ giant resonance region,” V. K. Dolmatov, A. S. Kheifets, P. C. Deshmukh and S. T. Manson, *Phys. Rev. A* **91**, 053415-1-7 (2015).
- “Photoabsorption studies of some closed-shell ions in the La isonuclear sequence,” S. Kalyadan, H. R. Varma, P. C. Deshmukh, J. T. Costello, P. Hayden and S. T. Manson, *Phys. Rev. A* **91**, 053422-1-8 (2015).
- “Photoionization of Endohedral Atoms: Molecular and Interchannel Coupling Effects” A. Ponzi, P. Decleva and S. T. Manson, *Phys. Rev. A* **92**, 023405-1-7 (2015).
- “Jellium Model Potentials for the C_{60} Molecule and the Photoionization of Endohedral Atoms, $A@C_{60}$,” A. S. Baltenkov, S. T. Manson S. T. and A. Z. Msezane, *J. Phys. B* **48**, 185103-1-8 (2015).
- “Dipole phase and photoelectron group delay in inner shell photoionization,” A. S. Kheifets, S. Saha, P. C. Deshmukh, D. A. Keating, and S. T. Manson, *Phys. Rev. A* **92**, 063422-1-9 (2015).
- “Coherence of Auger and inter-Coulombic decay processes in the photoionization of $Ar@C_{60}$ versus $Kr@C_{60}$,” M. Magrakvelidze, R. De, M. H. Javani, M. E. Madjet, S. T. Manson, and H. S. Chakraborty, *Eur. Phys. J. D* **70**, 96-1-7 (2016).
- “Correlation Study of Endohedrally Confined Alkali Earth Atoms ($A@C_{60}$),” M. F. Hasoğlu, H.-L. Zhou, and S. T. Manson, *Phys. Rev. A* **93**, 022512-1-5 (2016).
- “First prediction of inter-Coulombic decay of C_{60} inner vacancies through the continuum of confined atoms,” R. De, M. Magrakvelidze, M. E. Madjet, S. T. Manson and H. S. Chakraborty, *J. Phys. B* **49**, 11LT01-1-5 (2016).
- “Relativistic calculations of angular dependent photoemission time delay,” A. Kheifets, A. Mandal, P. C. Deshmukh, V. K. Dolmatov, D. A. Keating and S. T. Manson, *Phys. Rev. A* **94**, 013423-1-7 (2016).
- “Wigner photoemission time delays from endohedral anions,” A. Kumar, H. R. Varma, P. C. Deshmukh, S. T. Manson, V. K. Dolmatov and A. S. Kheifets, *Phys. Rev. A* **94**, 043401-1-9 (2016).

- “Wigner time delay and spin-orbit-activated confinement resonances,” D. A. Keating, P. C. Deshmukh and S. T. Manson, *J. Phys. B* **50**, 175001-1-9 (2017).
- “Photoionization of atomic barium subshells in the 4*d* threshold region using the relativistic multi-configuration Tamm-Dancoff approximation,” A. Ganesan, P. C. Deshmukh, and S. T. Manson, *Phys. Rev. A* **95**, 033417-1-8 (2017).

References

- [1] V. K. Dolmatov, A. S. Baltenkov, J.-P. Connerade and S. T. Manson, *Radiation Phys. Chem.* **70**, 417 (2004) and references therein.
- [2] V. K. Dolmatov, *Advances in Quantum Chemistry*, **58**, 13 (2009) and references therein.
- [3] A. Müller *et al*, *Phys. Rev. Lett.* **101**, 133001 (2008).
- [4] A. L. D. Kilcoyne, A. Aguilar, A. Müller, S. Schippers, C. Cisneros, G. Alna'Washi, N. B. Aryal, K. K. Baral, D. A. Esteves, C. M. Thomas, and R. A. Phaneuf, *Phys. Rev. Lett.* **105**, 213001 (2010).
- [5] R. A. Phaneuf, A. L. D. Kilcoyne, N. B. Aryal, K. K. Baral, D. A. Esteves-Macaluso, C. M. Thomas, J. Hellhund, R. Lomsadze, T. W. Gorczyca, C. P. Ballance, S. T. Manson, M. F. Hasoglu, S. Schippers, and A. Müller, *Phys. Rev. A* **88**, 053402-1-7 (2013).
- [6] M. E. Madjet, H. S. Chakraborty and S. T. Manson, *Phys. Rev. Letters* **99**, 243003 (2007).
- [7] M. E. Madjet, H. S. Chakraborty, J. M. Rost and S. T. Manson, *Phys. Rev. A* **78**, 013201 (2008).
- [8] V. K. Dolmatov and S. T. Manson, *J. Phys. B* **41**, 165001 (2008).
- [9] V. K. Dolmatov and S. T. Manson, *J. Phys. Rev. A* **78**, 013415 (2008).
- [10] D. A. Keating, P. C. Deshmukh and S. T. Manson, *J. Phys. B* **50**, 175001-1-9 (2017).
- [11] H. S. Chakraborty, M. E. Madjet, T. Renger, J.-M. Rost and S. T. Manson, *Phys. Rev. A* **79**, 061201(R) (2009).
- [12] M. H. Javani, J. B. Wise, R. De, M. E. Madjet, H. S. Chakraborty, and S. T. Manson, *Phys. Rev. A* **89**, 063420 (2014).
- [13] M. Magrakvelidze, Ruma D., M. H. Javani, M. E. Madjet, S. T. Manson, and H. S. Chakraborty, *Eur. Phys. J. D* **70**, 96 (2016).
- [14] R. De, M. Magrakvelidze, M. E. Madjet, S. T. Manson and H. S. Chakraborty, *J. Phys. B* **49**, 11LT01-1-5 (2016).
- [15] S. Saha, A. Mandal, J. Jose, H. R. Varma, P. C. Deshmukh, A. S. Kheifets, V. K. Dolmatov and S. T. Manson, *Phys. Rev. A* **90**, 053406 (2014).
- [16] V. K. Dolmatov, A. S. Kheifets, P. C. Deshmukh and S. T. Manson, *Phys. Rev. A* **91**, 053415 (2015).
- [17] A. S. Kheifets, S. Saha, P. C. Deshmukh, D. A. Keating, and S. T. Manson, *Phys. Rev. A* **92**, 063422 (2015).
- [18] A. Kheifets, A. Mandal, P. C. Deshmukh, V. K. Dolmatov, D. A. Keating and S. T. Manson, *Phys. Rev. A* **94**, 013423 (2016).
- [19] S. Saha, J. Jose, P. C. Deshmukh, V. K. Dolmatov, A. Kheifets and S. T. Manson, *Bull. Am. Phys. Soc.* **6**(8), 206 (2017).
- [20] P. C. Deshmukh, A. Mandal, S. Saha, A. S. Kheifets, V. K. Dolmatov and S T Manson, *Phys. Rev. A* **89**, 053424 (2014).
- [21] A. Mandal, P. C. Deshmukh, A. S. Kheifets, V. K. Dolmatov and S. T. Manson, *Phys. Rev. A* (submitted); A. Mandal, P. C. Deshmukh, V. K. Dolmatov, A. Kheifets and S. T. Manson, *J. Phys. Conf. Ser.* **875**, 022022 (2017).

ELECTRON/PHOTON INTERACTIONS WITH ATOMS/IONS

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PROJECT SCOPE

The project's primary objective is to gain a fundamental understanding of the near-threshold electron attachment mechanism in low energy electron elastic scattering from complex atoms and fullerenes through the calculation of integral and differential cross sections. The complex angular momentum (CAM) methodology [1], wherein is embedded the crucial electron-electron correlations and the core polarization interaction, is used for the investigations. Regge trajectories allow us to probe electron attachment at its fundamental level near threshold, thereby uncovering new manifestations, including the mechanism of nanocatalysis, and determine reliable electron affinities (EAs). The recently revealed characteristic correlation and polarization induced dramatically sharp resonances manifesting long-lived metastable negative ion formation in fullerenes are explored. These are important in nanocatalysis, organic solar cells and chemical sensor technology. The time-dependent-density-functional theory is utilized to investigate the photoabsorption spectra of encapsulated atoms, focusing on the confinement resonances. Standard codes are used to generate sophisticated wave functions for investigating CI mixing and relativistic effects in atomic ions. The wave functions are also used to explore correlation effects in dipole and non-dipole studies as well as in R-matrix calculations of photoionization of inner-shell CI.

RECENT PROGRESS

Recently, a theoretical breakthrough was achieved in low-energy electron scattering from fullerenes through our robust Regge pole methodology [1], wherein is fully embedded the electron-electron correlations and the vital core-polarization interaction. Entirely new in the field of electron-cluster/fullerene collisions, the Regge pole methodology was benchmarked on the measured electron affinity of the C_{60} fullerene [2, 3]. Consequently, the current report focuses on the unprecedented accomplishments of the Regge pole methodology in low-energy electron elastic scattering from fullerenes and heavy complex atoms, demonstrated in the following:

Ground state fullerene negative ion formation

A robust potential wherein is embedded the crucial core-polarization interaction is used in the Regge-pole methodology to calculate low-energy electron elastic scattering total cross section (TCS) for the C_{60} fullerene in the electron impact energy range $0.0 \leq E \leq 10.0$ eV. The energy position, binding energy (BE) of the characteristic dramatically sharp resonance appearing at the second Ramsauer–Townsend (R-T) minimum of the TCS representing stable C_{60}^- negative ion formation agrees excellently with the measured EA of C_{60} [2, 3]. The benchmarked potential and the Regge-pole methodology are then used to calculate electron elastic scattering TCSs for selected fullerenes, from C_{54} through C_{240} [1]; a theoretical feat that has never been accomplished before. The TCSs are found to be characterized generally by R-T minima, shape resonances (SRs) and dramatically sharp resonances representing long-lived ground state fullerene negative ion formation. The match between the extracted anionic BEs of the very sharp resonances in the TCSs of C_{70} , C_{76} , C_{78} , and C_{84} and the measured EAs [3, 4] is outstanding. Additionally, we compare our extracted energy positions of the resultant fullerene anions from our calculated TCSs of the C_{86} , C_{90} and C_{92} fullerenes with the estimated EAs ≥ 3.0 eV by the experiment [4] obtaining excellent agreement. Ground state negative ion BEs of other fullerenes, including C_{180} and C_{240} are also obtained. Most of the TCSs presented in the paper [1] are the first and only; our novel approach is general and should be applicable to other fullerenes as well and complex heavy atoms, such as the lanthanide atoms.

The paper [1] concludes with a remark on the catalytic properties of the fullerenes through their anions and fullerene application in organic solar cells.

Long-lived metastable anions in fullerene molecules C_{60} through C_{92}

A strong motivation for the exploration is the availability of high quality measured EAs for the fullerenes from C_{60} through C_{92} [2-4] and the experimental observation that electron scattering cross sections from fullerenes are characterized by long lived metastable anionic formation [5]. Also, in [1] correlation and polarization induced resonances were revealed for the first time in the electron scattering TCSs for C_{92} . Indeed, the TCSs are found to be characterized by sharp resonances manifesting both ground and metastable anionic formation. Importantly, the metastable anionic states could be mistaken for the ground state anions and the impact of the size is drastic as the fullerene size increases from C_{76} through C_{82} to C_{92} ; it induces additional metastable resonances in the ground TCS of the C_{92} fullerene [6].

Large fullerenes for nanocatalysis, sensor technology and organic solar cells

We report here on first low-energy electron elastic scattering total cross sections for the large C_{94} , C_{96} , C_{98} , C_{112} and C_{120} fullerenes, whence we extract the binding energies (BEs) of the resultant anions formed during the collision. The TCSs, obtained using our robust Regge pole methodology, are found to be characterized by correlation and polarization induced dramatically sharp resonances manifesting long-lived metastable negative ion formation [7, 8]. The results demonstrate that when subjected to varying gentle electron impact energy the investigated fullerenes respond through rich resonance structures, representing doorway states to stable ground state negative ion formation. These results significantly widen the selection scope of tunable fullerenes for multiple functionalization through their anions in *inter alia* nanocatalysis, organic solar cells and sensor technology. In particular the series of resonances could provide an essential mechanism for dumping out the hot-carriers thereby eliminating/minimizing their liability in the efficient operation of robust organic solar cells.

Finally, these results are expected to impact new materials design and creation significantly through the fundamental understanding of gentle electron processes at the atomic and nano scales. And the robust Regge pole methodology, representing a theoretical breakthrough in electron-cluster collision will certainly continue to be used to identify suitable fullerenes for various applications, including in organic solar cells and nanocatalysis.

New insights in low-energy electron-fullerene interactions

The internal region of zero potential provided by the hollow cage structure of fullerenes is conducive to metastable anionic states formation during the gentle electron-fullerene collisions. Using our Regge-pole methodology we probe for long-lived metastable anionic formation in C_n ($n=20, 24, 26, 28, 44, 70, 92$ and 112) through the calculated elastic scattering total cross sections. All the TCSs are found to be characterized by Ramsauer-Townsend minima, shape resonances and dramatically sharp resonances manifesting metastable anionic formation during the collisions [9, 10]. The energy positions of the anionic ground states resonances are found to match the measured electron affinities (EAs).

Additional to producing first time anions in C_n ($n=20, 24, 26, 28, 44, 70, 92$ and 112) through low-energy electron scattering TCSs, here we also investigated the size-effect through the induced metastable resonances as the fullerene size varied from C_{20} through C_{112} . The C_{20} TCSs exhibit atomic behavior consistent with the view [11] while the C_{112} TCSs demonstrate strong departure from atomic behavior due to the size effect; it impacts significantly the polarization interaction inducing a series of long-lived metastable C_{112}^- anions [9, 10]. Surprisingly, the small C_{24} , exhibiting mild atomic behavior, has the largest EA, 3.79 eV among the investigated fullerenes. It is therefore suitable for use in organic solar cells to counter the rate of irreversible polymer photobleaching in blend films (polymer: fullerene) and to resist fullerene degradation by the photo-oxidation mechanism [12]. The large fullerenes C_{92} and C_{112} and the small fullerene C_{24} could be used to catalyze the oxidation of water to peroxide through their first metastable anions as well as serve as an inexpensive single nanocatalyst for water purification in the

developing world [13]. These metastable anions could also be used in the oxidation of methane to methanol without C_2O emission, with vast implications for the environment.

Indeed, the delineated anionic resonances should facilitate considerably the fundamental understanding of the interactions of gentle electrons with fullerenes and the latter's functionalization.

Conundrum in measured electron affinities of heavy, complex atoms

Recently, the EA of atomic Eu was measured to be 0.116 ± 0.013 eV [14]. This value is in outstanding agreement with the values of the Regge pole [15] and MCDF-RCI [16] methods. Previously, the EA of Eu was measured to be 1.053 ± 0.025 eV [17], which agrees excellently with the Regge pole value of 1.085 eV. Here we have a conundrum because an atom can have only a single EA value. Although correct, neither of the measured values corresponds to the EA of Eu. Also, a recent experiment [18] measured the EA of Nb and obtained generally good agreement with existing theoretical EAs. However, our Regge pole calculated value of 0.905 eV, although in good agreement with the measured EA (0.917 eV) [18], corresponds to the BE of an excited state of Nb^- ; we calculated its ground state BE to be 2.48 eV. The quandary requires that the measured EAs above be reinterpreted.

Low-energy electron elastic scattering from Tb, Tm, Dy, Gd and Nd atoms have also been explored through the TCSs calculations. The TCSs are found to be characterized by dramatically sharp resonances manifesting negative ion formation in these systems. The extracted BEs for the resultant anions match excellently the measured EAs. Save for Nd, where our ground state BE matches the measured EA [19], our calculated anionic BEs for the above referenced atoms are for metastable anions formed during the collisions and not for the ground state anions [20]. These results clarify standing inconsistencies among measurements and suggest the reinterpretation of the many measured EAs for the heavy complex atoms.

FUTURE PLANS

We continue with the theoretical investigations of low-energy electron scattering from simple and complex atomic systems including fullerenes to identify possible negative ion nanocatalysts, chemical sensors and organic solar cells materials. Photoabsorption of endohedral fullerenes, strongly correlated systems and atomic structure energy levels are currently being investigated. Sophisticated and elaborate wave functions will be constructed for fullerenes for use in R-matrix calculations. New accurate EAs for complex atoms and large fullerenes will be obtained and nanocatalysts for various chemical reactions will be investigated and identified as well.

It is noted here that once the anionic ground, metastable and excited states of the fullerenes (and complex atoms) are reliably determined as has been accomplished for the many fullerenes using our robust Regge pole methodology, sophisticated elaborate CI wave functions can be generated using standard structure types methods.

References

1. "Simple method to calculate binding energies of fullerene negative ions", Z. Felfli and A.Z. Msezane, Euro Phys. J. D, Submitted (June 2017); "Resonances in low-energy electron elastic scattering from Fullerenes", Z. Felfli and A.Z. Msezane, J. Phys.: Conf. Ser. **875**, 062011 (2017).
2. D. -L. Huang *et al*, *J. Chem. Phys.* **140**, 224315 (2014)
3. C. Brink *et al*, *Chem. Phys. Lett.* **233**, 52 (1995)
4. O. V. Boltalina *et al*, *J. Rapid Commun. Mass. Spectrom.* **7**, 1009 (1993)
5. O. Elhamidi *et al*, *J. Phys. B* **30**, 4633 (1997)
6. "Long-lived metastable anions in fullerene molecules", Z. Felfli and A.Z. Msezane, Phys. Lett. A, Submitted (2017)
7. "Large fullerenes for nanocatalysis, sensors and organic solar cells", A.Z. Msezane, Z. Felfli, V.R. Shaginyan and M. Ya. Amusia, ChemChem, Submitted (2017)
8. "Negative ion formation in C_{94} , C_{96} , C_{98} , C_{112} and C_{120} fullerenes", A.Z. Msezane, Z. Felfli, V.R. Shaginyan and M. Ya. Amusia, Proc. ISACC 8 (2017)

9. “New insights in low-energy electron-fullerene interactions”, A.Z. Msezane and Z. Felfli, *Phys. Chem. Chem. Phys.*, Submitted (August 2017)
10. A.Z. Msezane and Z. Felfli, *J. Phys.: Conf. Ser.* **875**, 062009 (2017)
11. M. Ya. Amusia, *Chem. Phys.* **414**, 168 (2013)
12. E. T. Hoke *et al*, *Adv. Energy Mat.* **2**, 1351 (2012)
13. S. J. Freakley *et al*, *Science* **351**, 959 (2016)
14. S. -B. Cheng and A. W. Castleman, *Sci. Rep.* **5**, 12414 (2015)
15. Z. Felfli *et al*, *Phys. Rev. A* **79**, 012714 (2009)
16. S. M. O’Malley *et al*, *Phys. Rev. A* **78**, 012510 (2008)
17. V. T. Davis and J. S. Thompson, *J. Phys. B* **37**, 1961 (2004)
18. Z. Luo *et al*, *Phys. Rev. A* **93**, 020501(R) (2016)
19. V. T. Davis *et al*, *Nucl. Instrum. Methods Phys. Res. B* **241**, 118 (2005)
20. “Binding energies of fullerene and complex atomic negative ions”, Alfred Msezane and Zineb Felfli, *J. Phys.: Conf. Ser.* **875**, 062010 (2017)

PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2015-2017)

- [1] “Photoabsorption spectra of Xe atoms encapsulated inside fullerenes,” Zhifan Chen and Alfred Z Msezane, *Eur. Phys. J. D* **69**, 88 (2015)
- [2] “Heavy fermion spin liquid in herbertsmithite,” V. R. Shaginyan, M. Ya. Amusia, A. Z. Msezane, K. G. Popov, V. A. Stephanovich, *Phys. Lett. A* **379**, 2092-2096 (2015)
- [3] “Jellium Model Potentials for the C60 Molecule and the Photoionization of Endohedral Atoms, A@C60,” Baltenkov, Arkadiy; Manson, Steven; Msezane, Alfred, *J. Phys. B: At. Mol. Opt. Phys.* **48**, 185103 (2015)
- [4] “Doubly-charged Negative Ion of C60 Molecule,” A. S. Baltenkov and A. Z. Msezane, *Proceedings of Dynamic Systems and Applications* **7**, 239–245 (2016)
- [5] “Model Potentials for a C60 Shell,” S. T. Manson, A. S. Baltenkov and A. Z. Msezane, *Proceedings of Dynamic Systems and Applications* **7**, 275–281 (2016)
- [6] “Scaling behavior of the thermopower of the archetypal heavy-fermion metal YbRh2Si2,” V. R. Shaginyan, A. Z. Msezane, G. S. Japaridze, K. G. Popov and V. A. Khodel, *Front. Phys.* **11**(2), 117101 (2016).
- [7] “Strongly correlated Fermi systems as a new state of matter,” V. R. Shaginyan, A. Z. Msezane, G. S. Japaridze, K. G. Popov, and V. A. Khodel, *Front. Phys.* **11**(5), 117103 (2016).
- [8] “Electronic Quantum Confinement in Cylindrical Potential Well,” A. S. Baltenkov and A. Z. Msezane, *Euro Phys. J. D* **70**, 81 (2016).
- [9] Comment on "Correlated impurities and intrinsic spin liquid physics in the kagome material Herbertsmithite" (T. H. Han, M. R. Norman, J. J. Wen, J. A. Rodriguez-Rivera, J. S. Helton, C. Broholm, and Y. S. Lee, arXiv:1512.06807, V.R. Shaginyan, M.Ya. Amusia, J.W. Clark, G.S. Japaridze, A.Z. Msezane, K.G. Popov, <http://arxiv.org/abs/1602.03330>)
- [10] “Topological grounds for challenging behavior of the heavy-fermion metal *beta*-YbAlB4 under the application of magnetic field and pressure”, V. R. Shaginyan, A. Z. Msezane, K. G. Popov, J. W. Clark, V. A. Khodel, and M. V. Zverev, *Phys. Rev. B* **93**, 205126 (2016)
- [11] “Strongly correlated Fermi systems as a new state of matter”, V. R. Shaginyan, A. Z. Msezane, G. S. Japaridze, K. G. Popov, and V. A. Khodel, *Front. Phys.* **12**(1), 127101 (2017)
- [12] “New State of Matter: Heavy Fermion Systems, Quantum Spin Liquids, Quasicrystals, Cold Gases, and High-Temperature Superconductors”, V. R. Shaginyan, V. A. Stephanovich, A. Z. Msezane, P. Schuck, J. W. Clark, M. Ya. Amusia, G. S. Japaridze, K. G. Popov, and E. V. Kirichenko, *J. Low Temp. Phys.*; DOI: 10.1007/s10909-017-1801-3 (2017)
- [13] “The influence of topological phase transition on the superfluid density of overdoped copper oxides”, Vasily R. Shaginyan, Vladimir A. Stephanovich, Alfred Z Msezane, George Japaridze and Konstantin Popov, *Phys. Chem. Chem. Phys.*, **19**, 21964 (2017)

Theory and Simulation of Nonlinear X-ray Spectroscopy of Molecules

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Project Scope

Nonlinear X-ray spectroscopy experiments which use sequences of coherent broadband X-ray pulses are made possible by new ultrafast X-ray free electron laser (XFEL) and high harmonic generation (HHG) sources. These techniques provide unique windows into the motions of electrons and nuclei in molecules and materials and offer novel probes for electron and energy transfer in molecular complexes. This program is aimed at the design of X-ray pulse sequences for probing core and valence electronic excitations, and the development of effective simulation protocols for describing multiple-core excited state energetics and dynamics. Applications are made to time-resolved photoelectron spectroscopy, detecting strongly coupled electron-nuclear dynamics in molecules through electronic coherence observed in multidimensional broadband stimulated X-ray Raman and diffraction signals, and investigating multiple core excitations in molecules by X-ray double-quantum coherence signals.

Recent Progress

The monitoring of nonadiabatic avoided-crossing dynamics in molecules by ultrafast X-ray diffraction was investigated. Time-resolved X-ray diffraction signals from molecules in the gas phase which undergo nonadiabatic avoided-crossing dynamics involving strongly coupled electrons and nuclei were simulated. Several contributions to the signal were identified, representing (in decreasing strength) elastic scattering, contributions of the electronic coherences created by nonadiabatic couplings in the avoided crossing regime, and inelastic scattering. The former probes the charge density and delivers direct information on the evolving molecular geometry. The latter two contribu-

tions are weaker and carry spatial information through the transition charge densities (off-diagonal elements of the charge-density operator). Simulations were carried out for the nonadiabatic harpooning process in the excited state of sodium fluoride. The signal contains signatures of the created electronic coherence on top of the dominant ground- and excited-state population wavepacket motions. It depends on the ground- and the excited-state charge densities as well as the transition charge density that causes the inelastic contribution (v). These densities depend on time through the interatomic distance, which can be extracted directly from the diffraction signal. The shape of the nuclear wavepacket can be qualitatively retrieved without further phase reconstruction. For diatomic molecules, this allows to create a molecular movie out of the diffraction data. The coherence contributions do not merely indicate that a coherence has been created but also reveal where it has been created. Its contribution is significantly weaker than elastic scattering processes and appears as a rapid oscillation on top of the diffraction pattern. Our results contradict a recent XFEL diffraction study of molecular iodine in gas phase (Glownia et al. Phys. Rev. Lett., **117**,

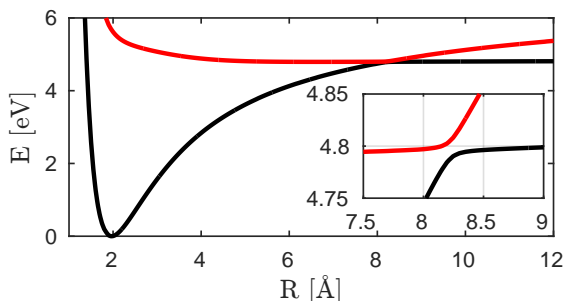


FIG. 1: Adiabatic potential energy surfaces for the electron harpooning in NaF (ionic $X^1\Sigma |g\rangle$ black, covalent $A^1\Sigma, |e\rangle$ red). The inset displays a close up of the avoided crossing region [P1].

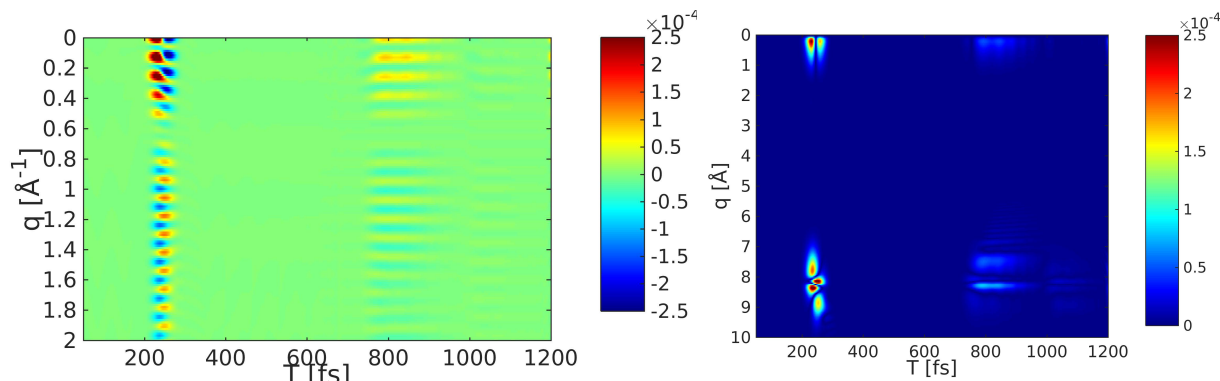


FIG. 2: Contributions of electronic coherences to the diffraction pattern [P1]. The left panel shows the momentum transfer vs. the probe delay. At approx. 200 fs the nuclear wave reaches the avoided crossing (see Fig. 1) and creates a short lived coherence between the ionic and the covalent state. The right panel shows the real space representation of the signal (inverse Fourier transform of the left panel). The coherence signal appears at around 8 \AA , which corresponds to the position of the avoided crossing.

153003 (2016)) which claimed that the ground and excited state diffraction amplitudes interfere to form a holographic pattern.

Photoinduced molecular chirality probed by ultrafast resonant X-ray spectroscopy was studied. Recently developed circularly polarized X-ray light sources can probe ultrafast chiral electronic and nuclear dynamics through spatially localized resonant core transitions. We have presented simulations of time-resolved circular dichroism signals given by the difference of left and right circularly polarized X-ray probe transmission following an excitation by a circularly polarized optical pump with a variable time delay. Application was made to formamide which is achiral in the ground state and assumes two chiral geometries upon optical excitation to the first valence excited state. Probes resonant with various K-edges (C, N, and O) provide different local windows onto the parity breaking geometry change thus revealing the enantiomer asymmetry dynamics.

Core-resonant circular dichroism (CD) signals are induced by molecular chirality and vanish for achiral molecules and racemic mixtures. The highly localized nature of core excitations makes them ideal probes of local chirality within molecules. Simulations of the circular dichroism spectra of several molecular families illustrate how these signals vary with the electronic coupling to substitution groups, the distance between the X-ray chromophore and the chiral center, geometry, and chemical structure. Clear insight into the molecular structure is obtained through analysis of the X-ray CD spectra.

Future Plans

Novel nonlinear optical signals where the coherence contribution is more pronounced and possibly background-free will be explored. By including additional nuclear coordinates, our approach may be used to predict signatures of conical intersections in polyatomic molecules. The ring opening reaction of cyclohexadiene (CHD) will be used as test case. We will compare our three nonlinear techniques and demonstrate the simulated signals: First, the TRUECARs technique (Kowalewski et al. Phys. Rev. Lett. **115**, 193003 (2015)) will be applied to CHD and required pulse parameter regimes will be predicted. While TRUECARs is an off-resonant technique we will also consider X-Ray transient absorption, its resonant counterpart. Second, photoelectron based techniques, like time resolved photoelectron spectroscopy [3] and streaking [P8] will be applied. Third, we will simulate the time resolved diffraction patterns [P1] and investigate the signal for signatures of the CoIn.

The time resolved diffraction techniques investigated so far are based on homodyne detection. We will investigate the heterodyne detection technique, which allows to overcome the phase reconstruction problem. Non-linear excitation schemes combined with diffraction pulses will interrogate electron dynamics by means of a molecular movie focusing on the valence electrons. Standard diffraction is dominated by the high charge densities of the core electrons. This challenge may be overcome by employing non-linear diffraction techniques.

Core ionization dynamics computed by real-time time-dependent density functional theory (RT-TDDFT) has been implemented and will be used to keep track of the hole evolution. We will include multiple pulses nonpertubatively within the RT-TDDFT propagation scheme. In order to extract signals of a given nonlinear order and a given interaction pathway, we will use the phase-cycling protocol.

We will explore new families of signals to gain structural information on chirality. We will study the vis/UV preparation - X-ray diffraction technique. This technique is analogue to sum frequency generation (SFG) but the X-ray pulse is off-resonant with the cores. Just like SFG, this signal vanishes in isotropic samples making it a good probe of molecular chirality. The SFG X-ray diffraction signal can also monitor time-evolving transition charge densities in oriented samples. Diffraction of circularly polarized pulses will be considered as well. We will examine Raman optical activity signals in the X-ray regime by calculating the diffraction intensity difference between a left and right polarized X-ray pulses.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- P1. M. Kowalewski, K. Bennett, and S. Mukamel, “Monitoring Nonadiabatic Avoided Crossing Dynamics in Molecules by Ultrafast X-Ray Diffraction”, *Struct. Dynam.*, **4**, 054101 (2017).
- P2. K. Bennett, M. Kowalewski, and S. Mukamel, “Comment on Self-Referenced Coherent Diffraction X-ray Movie of Angstrom-and Femtosecond-Scale Atomic Motion”, *Phys. Rev. Lett.*, **119**, 069301 (2017).
- P3. J. R. Rouxel, M. Kowalewski, and S. Mukamel, “Current vs charge density contributions to nonlinear x-ray spectroscopy”, *J. Chem. Theor. Comput.*, **12**, 3959 (2016).
- P4. J. R. Rouxel, M. Kowalewski, and S. Mukamel, “Photoinduced molecular chirality probed by ultrafast resonant X-ray spectroscopy”, *Struct. Dynam.*, **4**, 044006 (2017).
- P5. L. Monacelli, G. Batignani, G. Fumero, C. Ferrante, S. Mukamel, T. Scopigno, “Manipulating Impulsive Stimulated Raman Spectroscopy With a Chirped Probe Pulse”, *J. Phys. Chem. Lett.*, **8**, 966 (2017).
- P6. K. Bennett, V.Y. Chernyak, and S. Mukamel, “Discriminating Cascading Processes in Non-linear Optics; A QED Analysis Based on Their Molecular and Geometric Origin”, *Phys. Rev. A*, **95**, 033840 (2017).
- P7. F. Schlawin, Konstantin E. Dorfman, and Shaul Mukamel, “Pump-probe spectroscopy using quantum light with two-photon coincidence detection”, *Phys. Rev. A*, **93**, 023807 (2016).
- P8. M. Kowalewski, K. Bennett, J. R. Rouxel, and S. Mukamel, “Monitoring nonadiabatic electron-nuclear dynamics in molecules by attosecond streaking of photoelectrons”, *Phys. Rev. Lett.*, **117**, 043201 (2016).

- P9. K. Bennett, Y. Zhang, M. Kowalewski, W. Hua, and S. Mukamel, “Multidimensional Resonant Nonlinear Spectroscopy with Coherent Broadband X-ray Pulses”, *Phys. Scr.*, **91**, 083004 (2016).
- P10. J.R. Rouxel, V.Y. Chernyak, and S. Mukamel, “Non-local real space analysis of chiral optical signals with nanoshaped fields”, *Chem. Sci.*, **7**, 6824 (2016).
- P11. Y. Zhang, J.R. Rouxel, J. Autschbach, N. Govind and S. Mukamel, “X-ray Circular Dichroism Signals: A Unique Probe of Local Molecular Chirality”, *Chem. Sci.*, **8**, 5969 (2017).

Revealing Nanoscale Energy Flow Using Ultrafast THz to X-ray Beams

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Program Scope

We are developing novel spectroscopic methods and making use of them to study energy flow and material properties on nanometer length scales and ultrafast time scales. Access to short length scales is provided through the use of light beams with short wavelengths (EUV through hard x-ray spectral ranges) and/or fabricated structural elements with nanometer dimensions. Recent advances in tabletop high harmonic generation of extreme ultraviolet (EUV) pulses are exploited to measure thermal transport and acoustic vibrations using time-resolved diffraction from photoexcited periodic nanostructures, revealing new physics that arises at length scales of tens to hundreds of nm. The tabletop EUV sources as well as the FERMI free electron laser at FERMI-Elettra in Trieste can be used to generate as well as measure nanoscale thermoelastic responses without the need for patterned nanostructures, with the short length scale coming from optical interference patterns formed by crossing pairs of beams in transient grating experiments. We also use EUV and optical sources to excite and monitor ultrahigh-frequency acoustic waves (coherent phonons) at ultraflat interfaces and multilayer structures, extending our recent measurements of the highest-frequency coherent acoustic waves observed to date. Our measurements of acoustic properties allow direct calculation of thermal conductivities which can be compared with our measurements of thermal transport and with first-principles calculations. Terahertz-frequency acoustic measurements can also be used to reveal complex relaxation dynamics in glass-forming liquids and partially disordered solids. Acoustic measurements are also used to investigate the confinement effect in ultrathin liquid layers and to characterize mechanical properties of ultrathin solid layers. The methods we develop have broad fundamental applications and may also enable new practical metrology for use in nanoelectronics, just as earlier methods we developed have found commercial applications in microelectronics metrology.

Recent Progress

Thermal transport in and coherent phonons investigated by EUV transient grating spectroscopy

During two recent beamtimes at the FERMI free electron laser (FEL), in experiments led by MIT with participation from JILA, significant progress has been achieved in the development of the EUV transient grating (TG) measurements. In experiments with the EUV excitation (12.7 nm) and optical probe (400 nm) at the DiproI beamline, improvements in the setup and data analysis, as well as the stable operation of the FEL at 50 Hz, enabled us to obtain data of greatly improved quality compared to earlier measurements [1]. We also implemented measurements in reflection mode which enabled experiments with opaque samples. In the most recent experiment at the TIMER beamline, we succeeded in the first all-EUV four-wave mixing experiment, using crossed excitation pulses of 53.4 nm wavelength and a third-harmonic probe of 17.8 nm wavelength. Figure 1 shows the response from a silicon nitride membrane dominated by acoustic oscillations at a wavelength equal to the 112 nm TG period.

In the TG experiment at the DiproI beamline we made the first experimental observation of thermal transport dynamics initiated by EUV excitation (wavelength 12.7 nm). We monitored the decay of a sinusoidal temperature profile with a period of 280 nm which corresponds to a thermal transport distance of ~ 100 nm (the effective heat transfer distance is equal to the TG period divided by π). The TG period was still limited by the 400 nm optical probe, but it was almost an order of magnitude smaller than in our earlier experiments on non-diffusive thermal transport at room temperature. At this distance scale, thermal

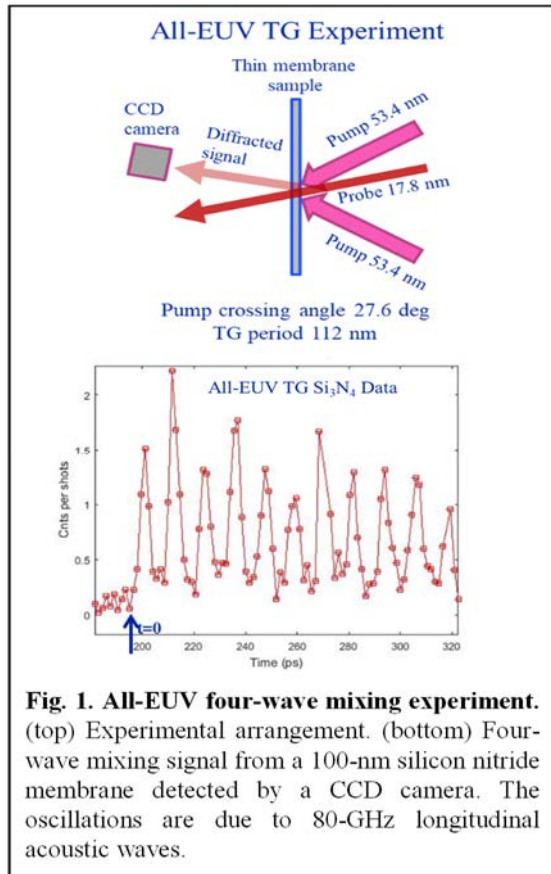


Fig. 1. All-EUV four-wave mixing experiment. (top) Experimental arrangement. (bottom) Four-wave mixing signal from a 100-nm silicon nitride membrane detected by a CCD camera. The oscillations are due to 80-GHz longitudinal acoustic waves.

transport becomes strongly non-diffusive in many materials. The simplicity of the experimental geometry enabled, for the first time, a rigorous comparison of thermal transport measurements in the non-diffusive regime with first-principles theoretical calculations based on the Boltzmann transport equation for phonons. The results obtained on single crystal diamond are particularly striking, as the observed thermal decay time is 25 times longer than predicted by the heat equation, and the speed of the heat transfer is approaching the speed of sound. Diamond presents a challenge for theoretical analysis because of the failure of the single-mode relaxation time approximation (RTA) owing to diamond's high Debye temperature. Our experimental results stimulated the development of theoretical methods for analyzing nanoscale thermal transport beyond the RTA currently underway in the G. Chen group at MIT. We have also observed strongly non-diffusive transport in SiGe, an important thermoelectric material. Recent work at JILA also probed thermal transport in the deep nanoscale regime, with periods <30 nm, to uncover new regimes of thermal transport.

We also made the first experimental observation of the EUV excitation of acoustic waves in a number of materials such as diamond, silicon, SiGe, SiC, $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO), and BK-7 glass. Both longitudinal and Rayleigh surface waves were observed. An EUV transient grating

represents an ultimate source of tunable hypersound: with the 4-80 nm wavelength range of the FERMI FEL, the acoustic wavelength can be tuned between a few μm and a few nm, covering a large part of the Brillouin zone in most solids and providing a frequency range from several GHz to several THz. In our first experimental run, the shortest acoustic wavelength we could detect was still limited by the use of the optical probe; however, at an acoustic wavelength of 280 nm we already generated the highest frequency surface acoustic waves (40 GHz) ever produced without periodic nanostructures. In the latest all-EUV experiment illustrated in Fig. 1, the acoustic wavelength was 112 nm, and much shorter acoustic wavelengths are now within reach. We also observed the EUV TG excitation of the optical phonon mode at 2.7 THz in BGO. This is the first observation of coherent optical phonons produced by EUV light. It offers unique prospects for study of optical phonon properties deep into the Brillouin zone.

Optical measurements of GHz-THz acoustic waves in solids and glass forming liquids

An alternative to employing EUV light for generating high-wavevector acoustic phonons is using a periodic structure such as a semiconductor superlattice (SL) to define the acoustic wavevector. We designed a sample with two GaN/InGaN SLs separated by a 2.3 μm -thick GaN spacer; THz acoustic wavepackets at frequencies 1-1.4 THz (depending on the SL period) were generated simultaneously in both SLs and detected simultaneously after they crossed the spacer layer. This is the first observation of the propagation of acoustic wavepackets above 1 THz at room temperature. Our approach will enable experiments with coherent THz phonon wavepackets at thermal phonon frequencies which hitherto were only possible in molecular dynamics simulations.

We have continued linear and nonlinear acoustic studies of glass-forming liquids [2-4]. In a joint study with the group of J. Dyre (Roskilde University, Denmark) [2] we provided a comprehensive validation of the two scaling relations that are central to the fundamental question of whether supercooled liquid dynamics can be described universally. We conducted ultrabroadband acoustical/mechanical measurements covering

a frequency range of 13 decades over a temperature range spanning liquid to glassy states. In another joint work with researchers from Universite du Maine (France) [3] we showed that time-domain Brillouin scattering can be used as a sensitive local probe of temperature gradients in glass-forming liquids such as glycerol and octamethylcyclotetrasiloxane (OMCTS). Our results demonstrated that acoustic signatures can be used to measure thermal diffusion in complex multilayer systems involving thin liquid and solid layers. The results obtained on OMCTS are particularly valuable as a first step in studying confinement effects in this liquid and others, with a versatile setup that allows a controllable nanometer dimension.

Microscale granular crystals and surface acoustic waves

In a recently completed study [6] we employed our optical TG setup to investigate acoustic waves in a self-assembled monolayer of micron-sized polystyrene spheres on a solid substrate. Acoustics of “granular crystals,” i.e. ordered arrays of particles interacting via Hertzian contacts, is a rapidly growing area of research, with experiments conducted mainly with macroscopic (cm- or mm-sized) particles. Our experiment [6] is the first acoustic study of a fully-ordered microscale granular crystal. Our data revealed the presence of multiple acoustic modes including low-frequency contact-based modes, high-frequency modes originating from spheroidal vibrations of the microspheres, and Rayleigh surface waves in the substrate. We observed a number of hitherto unexplored phenomena such as the dispersion of contact-based and spheroidal modes due to sphere-sphere interactions and the avoided crossing of a spheroidal mode and the Rayleigh wave, well accounted for by our analytical model. From our acoustic data, we were able to determine both particle-particle and particle-substrate contact stiffness thus getting insight into nanoscale contact mechanics. A separate study pertaining to surface acoustic waves (results recently submitted for publication) has demonstrated that so-called “supersonic surface waves” exemplifying bound states in the radiation continuum are encountered in simple planar waveguides such as a solid layer on a solid substrate without periodic structures, in contrast to the optical case, where such bound states in the continuum can only exist in photonic crystal slabs.

Probing thermal and elastic properties of nanoscale materials

A broad range of materials science and nanotechnology relies on the fabrication of nanostructured materials such as ultrathin films that can now be deposited with single-atom layer precision. However, how the elastic

properties change with film thickness, doping or structural changes in the deep nanoscale regime <100 nm is not yet understood, since full characterization techniques only work for dimensions >100 nm. Fortunately, laser-like beams at very short wavelengths can now be routinely generated using the process of high harmonic (HHG) upconversion of femtosecond laser pulses. These new quantum light sources are providing powerful new tools for probing and understanding nanoscale material properties. The short wavelengths of EUV beams are sensitive to picometer-scale displacements of the surface, while the femtosecond duration of HHG pulses is fast enough to capture thermal and acoustic dynamics in few-nm scale structures. Recent work using coherent HHG

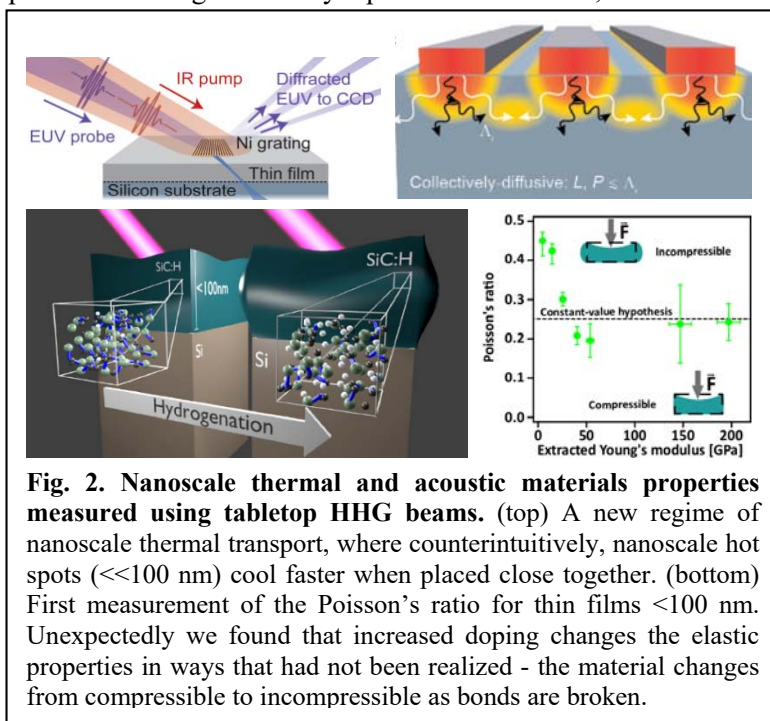


Fig. 2. Nanoscale thermal and acoustic materials properties measured using tabletop HHG beams. (top) A new regime of nanoscale thermal transport, where counterintuitively, nanoscale hot spots ($\ll 100$ nm) cool faster when placed close together. (bottom) First measurement of the Poisson's ratio for thin films <100 nm. Unexpectedly we found that increased doping changes the elastic properties in ways that had not been realized - the material changes from compressible to incompressible as bonds are broken.

beams has uncovered new nanoscale materials properties, including how thermal transport changes

dramatically at dimensions on the order of the phonon mean free path, and how the mechanical properties of sub-5-nm films dramatically change from bulk, even when the density does not [8-11].

Future Plans

We are very excited to have done the first measurements of thermal transport and coherent phonons with EUV excitation. The all-EUV setup at FERMI will now allow us to generate transient gratings with periods down to single digit nanometers which will be a great advance in studying both nanoscale thermal transport and ultrahigh-frequency coherent phonons. At the same time, both the MIT and JILA research groups are continuing complementary experiments in their home labs, at JILA using fabricated patterns and planning EUV transient grating to reach the deep nanoscale regime <100 nm as described above but on a tabletop; and at MIT extending our optical TG measurements into the near-UV (~ 266 nm wavelengths) and using “solid immersion” prism couplers (to shorten the wavelength by a factor of the prism refractive index) to shorten the TG period down to almost 100 nm. We are also applying for beamtime at the LCLS to attempt preliminary TG measurements using hard x-rays. This will open the door to wide-ranging x-ray four-wave mixing measurements. Finally, we have been approved for beamtime at the LCLS for March 2018, in which we will use hard x-rays to probe “squeezed” thermal phonon populations in SiGe, in collaboration with Stanford Professor David Reis who pioneered this technique. This experiment will provide direct measurements of acoustic phonon lifetimes in SiGe across the entire Brillouin zone, expected to yield insights into the fundamentals of thermal transport in this important thermoelectric material. On the theory side, JILA is finishing the development of complete models of nanoscale heat flow in 1D and 2D systems. Better fundamental models are needed for deep understanding and predictive designs, particularly for nanostructured materials that are key to applications in energy-efficient technologies. JILA is also analyzing data and writing up a paper that compares heat flow in nanostructures with the same linewidth but with different periods that directly provides evidence of the new collectively-diffusive regime.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. F. Bencivenga et al., “Four-wave-mixing experiments with seeded free electron lasers,” *Faraday Discuss.* **194**, 283 (2016).
2. T. Hecksher, D. H. Torchinsky, C. Klieber, J. A. Johnson, J. C. Dyre, and K. A. Nelson, “Toward broadband mechanical spectroscopy,” *PNAS* **114**, 8710 (2017).
3. I. Chaban, D. Shin, C. Klieber, R. Busselez, V. Gusev, K. A. Nelson, T. Pezeril, “Time-domain Brillouin scattering for the determination of laser-induced temperature gradients in liquids,” *Rev. Sci. Instrum.* **88**, 074904 (2017).
4. C. Klieber, V.E. Gusev, T. Pezeril, and K.A. Nelson, “Nonlinear acoustics at GHz frequencies in a viscoelastic fragile glass former,” *Phys. Rev. Lett.* **114**, 065701 (2015).
5. V. V. Temnov, I. Razdolski, T. Pezeril, D. Makarov, D. Seletskiy, A. Melnikov, and K. A. Nelson, “Towards the nonlinear acousto-magnetoplasmonics,” *J. Opt.* **18**, 093002 (2016).
6. A. Vega-Flick, R. A. Duncan, S. P. Wallen, N. Boechler, C. Stelling, M. Retsch, J. J. Alvarado-Gil, K. A. Nelson, and A. A. Maznev, “Vibrational dynamics of a two-dimensional micro-granular crystal,” *Phys. Rev. B* **96**, 024303 (2017).
7. P. H. Otsuka, S. Mezil, O. Matsuda, M. Tomoda, A. A. Maznev, T. Gan, N. Fang, N. Boechler, V. E. Gusev and O. B. Wright, “Time-domain imaging of GHz surface waves on an acoustic metamaterial,” *New J. Phys.*, accepted for publication.
8. J. Hernandez-Charpak, K. Hoogeboom-Pot, Q. Li, T. Frazer, J. Knobloch, M. Tripp, S. King, E. Anderson, W. Chao, M. Murnane, H. Kapteyn, D. Nardi, “Full characterization of the mechanical properties of 11-50nm ultrathin films: influence of bond coordination on the Poisson’s ratio,” *Nano Letters* **17**, 2178–2183 (2017).
9. D. Nardi, M. Travagliati, M. Murnane, H. Kapteyn, G. Ferrini, C. Giannetti, F. Banfi, “Impulsively Excited Surface Phononic Crystals: a Route towards Novel Sensing Schemes,” *IEEE Sensors Journal* **15**, 5142 (2015).
10. K. Hoogeboom-Pot, J. Hernandez-Charpak, T. Frazer, X. Gu, E. Turgut, E. Anderson, W. Chao, J. Shaw, R. Yang, M. Murnane, H. Kapteyn, M. Nardi, “Mechanical and thermal properties of nanomaterials at sub-50nm dimensions characterized using coherent EUV beams,” *Proc. SPIE* **9424**, 942417 (2015).
11. J. Hernandez-Charpak, T. Frazer, J. Knobloch, K. Hoogeboom-Pot, D. Nardi, W. Chao, L. Jiang, M. Tripp, S. King, H. Kapteyn, and M. Murnane, “Reliable characterization of materials and nanostructured systems $<<50$ nm using coherent EUV beams,” *Proc. SPIE* **9778**, 97780I (2016).

“Low-Energy Electron Interactions with Complex Molecules and Biological Targets”

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Project Scope: The primary objectives of this program are to investigate the fundamental physics and chemistry involved in low-energy (1-250 eV) electron and soft x-ray interactions with complex targets. There is a particular emphasis on understanding correlated electron interactions and energy exchange in the deep valence and shallow core regions of the collision targets. The energy loss channels associated with these types of excitations involve ionization/hole exchange and negative ion resonances. Thus, the energy decay pathways are extremely sensitive to many body interactions and changes in local potentials. Our investigations should help determine the roles of hole exchange via inter-atomic and inter-molecular Coulomb decay (ICD), electron transfer mediated decay (ETMD) and energy exchange via localized shape and Feshbach resonances in the non-thermal damage of weakly interacting heterogeneous interfaces. We also seek to understand the primary mechanisms of secondary electron induced damage of complex bio-molecules such as DNA and RNA.

Recent Progress: We have worked on three main tasks. The first focused on inter-atomic coulomb decay (ICD) and dissociative electron attachment (DEA) at weakly interacting interfaces. The second probed the role of secondary electrons and substrate interactions in x-ray induced DNA and RNA nucleotide damage and the third explores the use of laser-induced acoustic desorption to produce cold molecular beams of biomolecules. These beams will be generally useful for future attosecond ionization dynamics and angle-resolved velocity mapped gas-phase DEA studies of molecules of biological relevance.

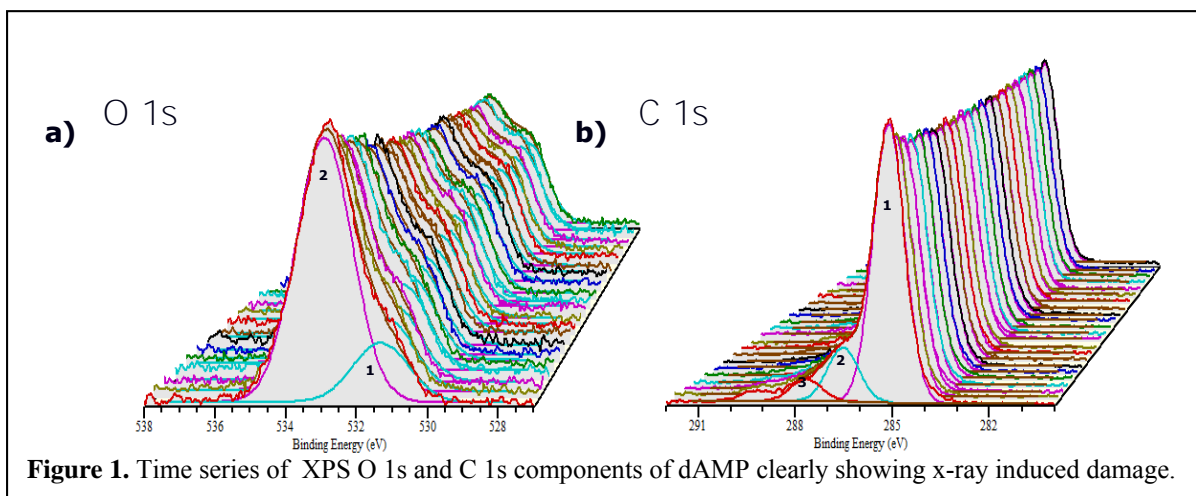
Task 1. Investigating intermolecular Coulomb decay (ICD) and dissociative electron attachment (DEA) at weakly interacting interfaces.

We have continued studies of intermolecular Coulomb decay (ICD) and have begun studies of dissociative electron attachment (DEA) at condensed interfaces composed of weakly interacting rare gases and/or polyatomic molecules. Specifically, we probe ICD in mixed rare gas (50%Ar: 50%Xe) samples condensed at 25K on graphite surfaces by monitoring the ejected ion masses and kinetic energies as a function of incident electron energy. The low-energy electron-induced threshold for the formation and desorption of rare gas cluster ions and mixed dimer ions likely correlates with the ionization of the Ar 3s level. We are also working on the ICD of C₂H₂ co-adsorbed with water. This system involves an ultrafast proton transfer channel which complicates the simple Coulomb ejection process. In addition, the first excited states of both water and acetylene are nearly degenerate. Quantum interference effects in these coupled states may be observable in the DEA yields and cross sections.

Task 2. X-ray induced damage of DNA and RNA nucleotides.

We have extended our collaboration on x-ray induced damage of adsorbed DNA¹⁻³ and completed a second set of experiments at the Advanced Photon Source at Argonne National Laboratory. Specifically, we examined the cross sections and rates of secondary electron induced damage of 5'-deoxyadenosine monophosphate (5'-dAMP) and 5'-adenosine monophosphate (5'-rAMP) using tunable x-rays. A 950 eV synchrotron x-ray beam was used

to take snapshot spectra of the C 1s and O 1s transitions. The integrated areas in Figure 1 are fit to a simple decay curve yielding a dAMP damage cross of $2.0 \pm 0.2 \times 10^{-17} \text{ cm}^2$. Though not shown, the C 1s and O 1s decay constants and cross section for rAMP are very similar. This indicates that there is no discernable difference in dAMP and rAMP nucleotide survival when using x-rays as both the probe and source of slow electron.



Task 3. Developing a cold molecular beam source for biomolecules.

A technique known as laser induced acoustic desorption (LIAD) has been recently exploited to introduce liable biomolecules into the gas-phase for ultrafast ionization dynamics studies. Though the acronym implies that acoustic waves drive the desorption event, this is not correct and somewhat misleading. We are therefore unraveling the physics of this desorption process using state-resolved laser detection schemes. We are also exploiting this technique using different substrates such as graphene to produced well defined molecular beams of nucleotides, nucleosides and short oligomers. Initial work using microplasmas under ambient atmospheric conditions proved the initial viability of this LIAD approach.⁴

Future Plans.

- We will complete the ICD studies of mixed rare gas overlayers as well as water clusters adsorbed on weakly coupled molecular solids such as ethane (C_2H_6), acetylene (C_2H_2), and/or formaldehyde (HCHO). This series has been chosen since it spans the regime of essentially no coupling (C_2H_6), to weak π -interactions (C_2H_2), and hydrogen bonding (HCHO). We will also continue to examine potential quantum interference effects in DEA resonances involving mixtures of C_2H_2 and D_2O .
- Low energy electron damage of DNA and RNA strands as well as DNA and RNA nucleosides (i.e. dAMP, rAMP, dCMP, and rCMP) adsorbed on graphene coated Au thin-films or substrates that have been functionalized with amino acids will be examined using Raman micro-spectroscopy and atomic force microscopy. This information will ultimately be valuable to ongoing studies regarding targeted treatment of cancer using radiotherapies and gold nanoparticles.

- We will continue the state-resolved LIAD measurements to probe the physics governing this process. We will also utilize substrates used in the low-energy electron induced damage of nucleoside studies in LIAD production to use this as another tool to assess damage.
- We also plan to screen LIAD active substrates such as graphene for use in generating cold molecular beams of biomolecules such as amino acids, nucleobases, nucleotides. And short oligomers of DNA and RNA. If viable, collaborative studies on attosecond ionization and DEA of nucleotides will be carried out.
- Apply for beam-time to continue work on near-edge x-ray absorption fine structure spectroscopy (NEXAFS) on dAMP, rAMP, dCMP and rCMP thin-films.

References:

1. R. A. Rosenberg, J. M. Symonds, K. Vjayalakshmi, D. Mishra, T. M. Orlando, and R. Naaman, "The relationship between interfacial bonding and radiation damage of adsorbed DNA" *Phys. Chem. Chem. Phys.* **16**, 15319-15325 (2014).
2. R. A. Rosenberg, J. M. Symonds, V. Kalyanaraman, T. Z. Markus, T. M. Orlando, R. Naaman, E. a. Medina, F. A. Lopez and V. Muijca, "Kinetic Energy Dependence of Spin Filtering of Electrons Transmitted through Organized Layers of DNA", *J. Phys. Chem. C.* **117**, 22307-22313, (2013).
3. R. Rosenberg, J. M. Symonds, T. Z. Markus, T. M. Orlando and R. Naaman, "The lack of spin selectivity in low-energy electron induced damage of DNA films", *J. Phys. Chem. C.* **117**(43), 22307-22313 (2013).
4. K. Benham, R. Hodyss, F. Fernandez, and T. M. Orlando, "Laser-Induced Acoustic Desorption Atmospheric Pressure Photoionization via VUV-Generating Microplasmas", *J. of Amer. Soc. for Mass Spectrom.* **27** (11), 1805-1812 (2016).

Peer-reviewed publications resulting from this project (2015-2017)

1. A. N. Sidorov and T. M. Orlando, Correction to "Monolayer Graphene Platform for the Study of DNA Damage by Low-Energy Electrons" *J. Phys. Chem. Lett.* **7**, 2168, (2016).
2. E. Alizadeh, T. M. Orlando and L. Sanche, "Biomolecular damage induced by ionizing radiation; The direct and indirect effects of low-energy electrons on DNA", *Ann. Rev. of Phys. Chem.* **66**, 379-98 (2015).

Presentations acknowledging support from this program

1. Invited, T. M. Orlando, "Very low energy (<5 eV) electron induced damage of complex biomolecules", "Miller Conference on Radiation Chemistry", Oct. 7- 11, Sicily 2017.
2. Invited, T. M. Orlando, "Low energy (<5 eV) electron interactions with DNA and RNA nucleotides", XIX International symposium on electron-molecule collisions and swarms", July 17-20, Lisboa, Portugal 2015.
3. Invited, T. M. Orlando, "Very low energy electron-induced damage of DNA", Dept. of Physics, Auburn University, March 21, 2015.

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SISGR - Structure from Fleeting Illumination of Faint Spinning Objects in Flight

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Project Scope

The advent of the X-ray Free Electron Laser (XFEL) has made it possible to interrogate molecules and their assemblies “in flight” with intense short pulses of radiation, and record “snapshots” before they are destroyed. We are developing a new generation of powerful algorithms to recover structure and dynamics from such ultra-low-signal sightings. Combining concepts from machine learning, differential geometry, general relativity, graph theory, and diffraction physics, these techniques promise to revolutionize our understanding of ultrafast dynamics in molecular systems, and key processes in biological machines, such as viral infection, and water-splitting in photosystem II.

Recent Progress

Conformational Dynamics of a Virus by Single-particle X-ray Scattering

With A. Hosseinizadeh, G. Mashayekhi, J. Copperman, P. Schwander, A. Dashti, R. Sepehr, R. Fung, M. Schmidt, C.H. Yoon, B.G. Hogue, G. Williams, A. Aquila

Using experimental diffraction snapshots from the LCLS XFEL, we have determined the three-dimensional (3D) structure and conformational dynamics of the PR772 virus to a detector-limited resolution of 9 nm, the highest reported value for 3D single-particle imaging by XFEL (Fig. 1). Our results show a single conformational coordinate controls the reorganization of the genome, the growth of a tubular structure from a portal vertex, and the release of the genome (Fig. 2). These results demonstrate that single-particle X-ray scattering has the potential to shed new light on key macromolecular processes.

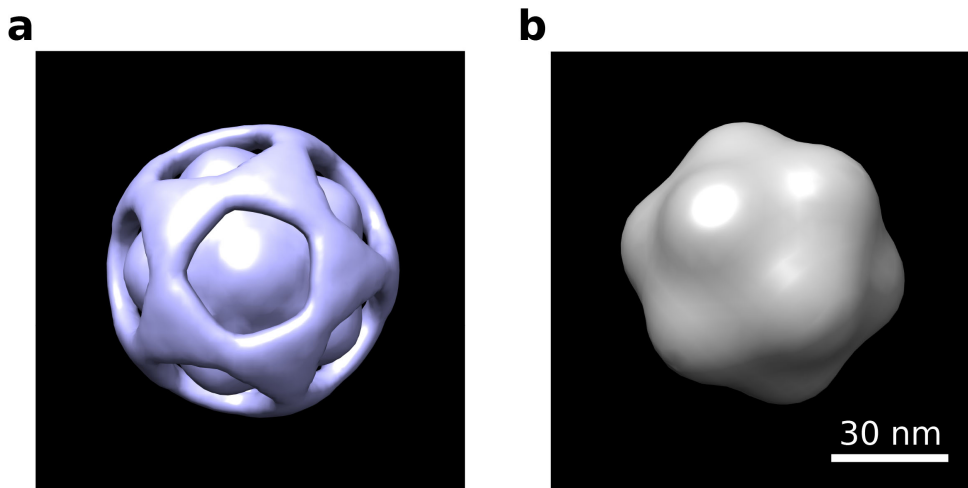


Fig. 1: (a) Diffraction volume, and (b) 3D structure of the PRD772 virus extracted from ~40,000 experimental XFEL data without conformational analysis. The resolution is limited to 9 nm by detector geometry.

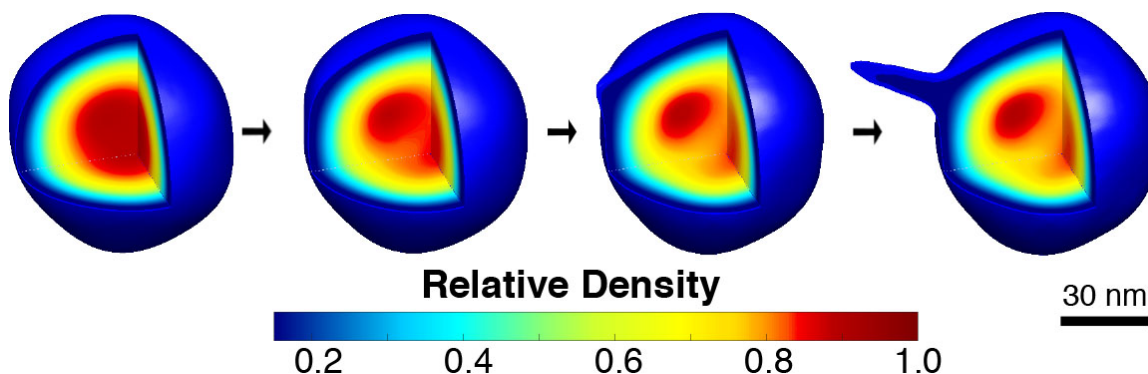


Fig. 2: Frames from a 3D movie obtained by conformational analysis of experimental XFEL data. Note the reorganization of the genome and the emergence of a tubular structure from a five-fold portal. These processes are controlled by a single parameter (“reaction coordinate”).

This work represents:

1. **The first three-dimensional (3D) reconstruction of the structure of a biological entity by X-ray lasers to detector-limited resolution.** The resolution of a reconstructed 3D structure depends critically on the number of 2D snapshots. Previous reconstructions stem from at most 200 snapshots, carefully selected from collections of a million or more snapshots to minimize heterogeneities. We have shown a 3D reconstruction from ~40,000 snapshots can reach the maximum resolution allowed by the detector (Fig. 1).
2. **The first 3D movie of the continuous conformational dynamics of a virus by any technique.** Although it has long been known that critical biological processes, including viral infection and replication, depend on conformational changes, our work represents the first mapping of the continuous conformational changes in a virus (Fig. 2).
3. **The first demonstration that a single reaction coordinate controls the formation of a tubular structure, and the reorganization and release of the genome.** Although the formation of a tubular structure and the release of genome have been observed before, this is the first evidence that these important processes are controlled by a single reaction coordinate.

More generally, the combination of our approach and the emerging generation of high repetition-rate X-ray Free Electron Lasers promises unprecedented access to the conformations and energy landscapes of fleetingly occupied, rate-limiting transition states with energies comparable with that released by ATP hydrolysis.

Future Plans

We plan to extend our data-analytical approach to other important domains, including ultrafast structural dynamics from incomplete data. Success in this challenging endeavor would constitute a decisive advance; in a wide range of important applications, the

available dynamical information represents only a small fraction (~1%) of that needed by traditional data-analytical approaches.

Peer-reviewed Publications Resulting from this Project (2015-2017)

1. Conformational landscape of a virus by single-particle X-ray scattering, A. Hosseinizadeh, G. Mashayekhi, J. Copperman, P. Schwander, A. Dashti, R. Sepehr, R. Fung, M. Schmidt, C.H. Yoon, B.G. Hogue, G. Williams, A. Aquila, and A. Ourmazd, **Nature Methods** (accepted).
2. Machine-learning routes to dynamics, thermodynamics, and work cycles of biological nanomachines, Book Chapter in “X-ray Free Electron Lasers”, U. Bergmann, J. Yano, V. Yachandra (editors), **Royal Society of Chemistry** (accepted).
3. Laser control over the ultrafast Coulomb explosion of N_2^{2+} after Auger decay: A quantum mechanical investigation, A.M. Hanna, O. Vendrell, A. Ourmazd, and R. Santra, **Physical Review A** **95**, 043419 (2017).
4. Structural enzymology using X-ray free electron lasers, C. Kupitz et al., **Structural Dynamics** **4**, 044003 (2017).
5. Femtosecond structural dynamics drives the trans/cis isomerization in photoactive yellow protein, K. Pande et al., **Science** **352**, 725 (2016).
6. Coherent soft X-ray diffraction imaging of the coliphage PR772 at the Linac Coherent Light Source, H.K.N. Reddy et al., **Scientific Data** **4**, 170079 (2017).
7. Coherent diffraction of single Rice Dwarf virus particles using hard X-rays at the Linac Coherent Light Source, A. Munke et al., **Scientific Data** **3**, 160064 (2016).
8. Dynamics from noisy data with extreme timing uncertainty, R. Fung, A.M. Hanna, O. Vendrell, S. Ramakrishna, T. Seideman, R. Santra, and A. Ourmazd, **Nature** **532**, 471 (2016).
9. Single-particle structure determination by X-ray free electron lasers: Possibilities and challenges (Invited Perspective), A. Hosseinizadeh, A. Dashti, P. Schwander, R. Fung, and A. Ourmazd, **Structural Dynamics** **2**, 041601 (2015).
10. The Linac Coherent Light Source Single-particle Imaging Roadmap, A. Aquila et al., **Structural Dynamics** **2**, 041701 (2015).

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Control of Molecular Dynamics: Algorithms for Design and Implementation

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A. Project Scope:

This research considers the conceptual and algorithmic developments addressing control over molecular dynamics phenomena. The research is theoretical and computational in nature, but its ultimate significance lies in the associated implications and applications in the laboratory. The goal of the research is to develop a good understanding of the principles of quantum control to enhance the laboratory control capabilities, as well as to extract greater information from these efforts.

B. Recent Progress:

In the past year, several research studies were carried out in the general area of controlling quantum dynamics phenomena. These activities are summarized below.

(1) How to make distinct dynamical systems appear spectrally identical²²: We showed that a laser pulse can always be found that induces a desired optical response from an arbitrary dynamical system. As illustrations, driving fields were computed to induce the same optical response from a variety of distinct systems (open and closed, quantum and classical). Thus, it was found that the observed induced dipolar spectra without detailed information on the driving field were not sufficient to characterize atomic and molecular systems. The formulation may be applied to design materials with specified optical characteristics. These findings revealed unexplored flexibilities of nonlinear optics.

(2) Pareto-front shape in multi-observable quantum control²³: This study analyzed the Pareto-front shape for the problem of quantum multi-observable control, i.e., optimizing the expectation values of multiple observables in the same quantum system. Analytic and numerical results demonstrated that with two commuting observables the Pareto front is a convex polygon consisting of flat segments only, while with non-commuting observables the Pareto front includes convexly curved segments. We also assessed the capability of a weighted-sum method to continuously capture the points along the Pareto front. Illustrative examples with realistic physical conditions were presented,

(3) Control landscapes are almost always trap free: a geometric assessment²⁴: We presented a proof showing that almost all closed, finite dimensional quantum systems have trap free (i.e. free from local optima) landscapes for a large and physically general class of circumstances. This result offers an explanation for why gradient-based methods succeed so frequently in quantum control. The role of singular controls was analyzed using geometric tools in the case of the control of the propagator, as well as in the case of observables. It was shown that a control being singular is not sufficient to cause control optimization progress to halt, and sufficient conditions for a trap free landscape are presented. It was further shown that the local surjectivity (full rank) assumption of landscape analysis can be refined to the condition that the end-point map is transverse to each of the level sets of the fidelity function.

(4) Searching for an optimal control in the presence of saddles on the quantum-mechanical observable landscape²⁵: We performed simulations to show that both the

detailed topology of the control landscape and the parameters of the system Hamiltonian influence whether the searches are attracted to a saddle. Specifically, for some circumstances with a special initial state and target observable, optimizations may approach a saddle very closely, reducing the efficiency of the gradient algorithm. Encounters with such attractive saddles were found to be quite rare. Neither the presence of a large number of saddles on the control landscape nor a large number of system states increases the likelihood that a search will closely approach a saddle. Even for applications that encounter a saddle, well-designed gradient searches with carefully chosen algorithmic parameters will readily locate optimal controls.

(5) Time-local equation for the exact optimized effective potential in time-dependent density functional theory²⁶: We formulated an exact, Sturm-Liouville-type, time-local time-dependent optimized effective potential (TDOEP) equation for orbital-dependent xc functionals in terms of time-dependent Kohn-Sham and effective memory orbitals. The many-electron dynamics of a hydrogen chain was successfully solved to show the applicability of the time-local TDOEP equation. The numerical simulations show that the time-local TDOEP rigorously obeys the zero-force theorem. This new reformulation is intended to expedite the construction of the TDOEP in real time and to facilitate studies on various orbital-dependent functionals beyond the adiabatic approximation.

(6) Conductance and activation energy for electron transport in series and parallel intramolecular circuits¹⁹: We presented a study of electron transport through intramolecular circuits from tunneling to thermally activated hopping. Specifically, we explored intramolecular circuits based on monomers (or molecules) bonded to each other. The simulations and asymptotic analyses both gave the result that the series and parallel circuits based on the same molecular units should have nearly the same decay constants. In the high-temperature regime, the temperature dependence of conductance exhibits Arrhenius behavior, and the series and parallel circuits based on the same type of monomer show nearly the same activation energies.

(7) Theory of molecular conductance using a modular approach²⁰: We probed the correlation between the conductance of a molecular wire (the property of a whole system) and its constituent backbone units (modules). By using a tight-binding Hamiltonian combined with single-particle Green's functions, we developed an approach that enables an estimate of a conductance decay constant in terms of the Hamiltonians of the molecular backbone units and the couplings between two nearest-neighbor units in the off-resonant tunneling regime. As a demonstration, we examined several representative molecular systems in a framework of the Huckel model. Based on the proposed approach, we showed the correspondence between the complete destructive quantum interference and an infinite injection gap and derived the preconditions of the modified Simmons equation and the rule of intramolecular series circuits.

(8) Dirac open-quantum-system dynamics: Formulations and simulations²¹: We introduced the density matrix formalism for relativistic quantum mechanics as a generalization of the spinorial description of the Dirac equation. This formalism was employed to describe interactions with an environment. Moreover, we presented concise and effective numerical algorithms for the density matrix as well as the relativistic Wigner function propagation. Employing these instruments, we gain important insights into the effect of quantum dephasing for relativistic systems in many branches of physics.

(9) Relationship between sensitivity indices defined by variance- and covariance-based methods²⁷: We analyzed the validity of the extension of the sensitivity indices for the main and

total effects defined by the variance- based method to correlated variables. We proved that the extension of the main effect is valid. However, the extension of the sensitivity index of the total effect is questionable. We further established the relationship between the sensitivity indices defined by the variance- and the covariance-based structural correlative analysis methods.

C. Future Plans:

The research in the coming year will include the following:

(1) We plan to develop a new so-called Hartree Propagator toolkit (HPT, or H-FPT in the extension to Hartree-Fock) technique, which promises to greatly accelerate quantum dynamical simulations of complex polyatomic systems under control, especially with increased efficiency when considering multiple objectives for similar molecular systems. Our prime interest in this regard, in analogy with common practice in traditional chemistry, is to explore control, based on optimal control theory (OCT), over large families of *homologous* molecules seeking patterns in their behavior, including bond-breaking. We will initially focus upon control occurring on ground state potential energy surfaces, but even there, the many body quantum dynamics can be highly complex.

(2) We plan to extend the monotonically convergent constrained optimal control framework to general quantum control optimal problems subject to an arbitrary number of equality constraints in both the time and frequency domains, either separately or simultaneously. This extension aims at potential applications in quantum physics including multi-objective optimal control problems.

(3) We are continuing the study of control landscape structure by now extending it to classical molecular control landscape structure through steering the phase space coordinates of classical systems to given target landscape values and examining underlying metric defined as the ratio of the gradient-based optimization path length of the control field evolution to the Euclidean distance between a given initial control field and the resultant optimal control field, which corresponds to a yield that lies at the top of the landscape.

(4) We are exploring two opposing optimal control scenarios of orientation/entanglement involving couplings between multiple coupled molecular rotors. Preliminary studies have been performed for two identical rotors coupled via a distance-dependent dipole-dipole interaction.

(5) We are continuing our study (in collaboration with Dr. Yuzuru Kurosaki in Japan) to obtain a more elaborate assessment of the prospects of performing ozone isomerization by executing OCT calculations to include rotation under the sudden approximation in order to reveal more general nature of the field resonances necessary for a learning control experiment.

D. Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [1] Systematically altering the apparent topology of constrained quantum control landscapes, A. Donovan and H. Rabitz, *Math. Chem.* **53**, 718–736 (2015).
- [2] Exploring the complexity of quantum control optimization trajectories, A. Nanduri, O. M. Shir, A. Donovan, T.-S. Ho, and H. Rabitz, *Phys. Chem. Chem. Phys.*, **17**, 334 (2015).
- [3] Constrained Control Landscape for Population Transfer in a Two-Level System, K. M. Tibbetts and H. Rabitz, *Phys. Chem. Chem. Phys.*, **17**, 3164 (2015).
- [4] Topology of classical molecular optimal control landscapes for multi-target objectives, C. Joe-Wong,

- T.-S. Ho, H. Rabitz, and R. Wu, *J. Chem. Phys.* **142**, 154115 (2015).
- [5] Hessian facilitated analysis of optimally controlled quantum dynamics of systems with coupled primary and secondary states, C.-C. Shu, M. Edwalds, A. Shabani, T.-S. Ho, and H. Rabitz, *Phys. Chem. Chem. Phys.*, **17**, 18621 (2015).
- [6] Searching for quantum optimal controls under severe constraints, G. Riviello, K. M. Tibbetts, C. Brif, R. Long, R. Wu, T.-S. Ho, and H. Rabitz, *Phys. Rev. A* **91**, 043401 (2015).
- [7] Experimental observation of saddle points over the quantum control landscape of a two-spin system, Q. Sun, I. Pelczer, G. Riviello, R. Wu, and H. Rabitz, *Phys. Rev. A* **91**, 043412 (2015).
- [8] Measuring the distance from saddle points and driving to locate them over quantum control landscapes, Q. Sun, G. Riviello, R.-B. Wu, and H. Rabitz, *J. Phys. A: Math. Theor.* **48**, 465305 (2015).
- [9] Quantum control and pathway manipulation in rubidium, F. Gao, Y. Wang, R. Rey-de-Castro, H. Rabitz, and F. Shuang, *Phys. Rev. A* **92**, 033423 (2015).
- [10] Efficient method to generate time evolution of the Wigner-function for open quantum systems, R. Cabrera, D. I. Bondar, K. Jacobs, and H. Rabitz, *Phys. Rev. A* **92**, 042122 (2015).
- [11] Coherent revival of tunneling, L.-Y. Hsu and H. Rabitz, *Phys. Rev. B* **92**, 035410 (2015).
- [12] The role of dissociation channels of excited electronic states in quantum optimal control of ozone isomerization: A three-state dynamical model, Y. Kurosaki, T.-S. Ho, and H. Rabitz, *Chem. Phys.* **469-470**, 115, (2016).
- [13] On choosing the form of the objective functional for optimal control of molecules, C. Joe-Wong, T.-S. Ho, and H. Rabitz, *J. Math. Chem.* **54**, 1 (2016).
- [14] Wigner-Lindblad Equations for Quantum Friction, D. I. Bondar, R. Cabrera, A. Campos, S. Mukamel, and H. Rabitz, *J. Phys. Chem. Lett.* **7**, 1632 (2016).
- [15] Frequency domain quantum optimal control under multiple constraints, C.-C. Shu, T.-S. Ho, X. Xing, H. Rabitz, *Phys. Rev. A* **93**, 033417 (2016).
- [16] Identifying a cooperative control mechanism between an applied field and the environment of open quantum systems, F. Gao, R. Rey-de-Castro, Y. Wang, H. Rabitz, and F. Shuang, *Phys. Rev. A* **93**, 053407 (2016).
- [17] Monotonic convergent quantum optimal control method with exact equality constraints on the optimized control fields, C.-C. Shu, T.-S. Ho, H. Rabitz, *Phys. Rev. A* **93**, 053418 (2016).
- [18] Efficient computations of quantum canonical Gibbs state in phase space, D. I. Bondar, A. Campos, R. Cabrera, and H. Rabitz, *Phys. Rev. E* **93**, 063304 (2016).
- [19] Conductance and Activation Energy for Electron Transport in Series and Parallel Intramolecular Circuits, L.-Y. Hsu, N. Wu, and H. Rabitz, *Phys. Chem. Chem. Phys.* **18**, 32087 (2016).
- [20] Theory of molecular conductance using a modular approach, L.-Y. Hsu and H. Rabitz, *J. Chem. Phys.* **145**, 234702 (2016).
- [21] Dirac open-quantum-system dynamics: Formulations and simulations, R. Cabrera, A. G. Campos, D. I. Bondar, and H. Rabitz, *Phys. Rev. A* **94**, 052111 (2016).
- [22] How to Make Distinct Dynamical Systems Appear Spectrally Identical, A. G. Campos, D. I. Bondar, R. Cabrera, and H. Rabitz, *Phys. Rev. Lett.* **118**, 083201 (2017).
- [23] Pareto-front shape in multiobservable quantum control, Q. Sun, R.-B. Wu and H. Rabitz, *Phys. Rev. A* **95**, 032319 (2017).
- [24] Control landscapes are almost always trap free: a geometric assessment, B. Russell, H. Rabitz, and R.-B. Wu, *J. Phys. A: Theor.* **50**, 205302 (2017).
- [25] Searching for an optimal control in the presence of saddles on the quantum-mechanical observable landscape, G. Riviello, R.-B. Wu, Q. Sun, and H. Rabitz, *Phys. Rev. A* **95**, 063418 (2017).
- [26] Time-Local Equation for the Exact Optimized Effective Potential in Time-Dependent Density Functional Theory, S.-L. Liao, T.-S. Ho, S.-I. Chu and H. Rabitz, *Phys. Rev. Lett.* **118**, 243001 (2017).
- [27] Relationship between sensitivity indices defined by variance- and covariance-based methods, G. Li and H. Rabitz, *Reliability Engineering and System Safety* **167**, 136 (2017).

“Atoms and Ions Interacting with Particles and Fields”

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Program Scope

This theory project focuses on the time evolution of systems subjected to either coherent or incoherent interactions represented by fields and particles, respectively. This study is divided into three categories: (1) coherent evolution of highly excited quantum states, (2) incoherent evolution of highly excited quantum states, and (3) the interplay between ultra-cold plasmas and Rydberg atoms. Some of the techniques we developed have been used to study collision processes in ions, atoms and molecules. In particular, we have used these techniques to study the correlation between two (or more) continuum electrons and electron impact ionization of small molecules.

Recent Progress 10/2016-9/2017

Imaging Transfer: The postdoc Hua-Chieh Shao, supported by this grant, led a study [13] proposing the use of ultrafast electron diffraction to image a controllable, laser-driven coherent electron population transfer. Using the proposed atom, lithium, calculations suggest the imaging should be possible with currently available femtosecond electron pulses. Detailed simulations demonstrated the ability of ultrafast electrons to image an electronic population transfer, validating ultrafast electron diffraction as a direct means of investigating electron dynamics. Provided the incident electron pulses have sufficient temporal resolution, the diffraction images can resolve the relative phases of the target electronic wave functions.

Monochromatic electron beams: In Ref. [14], we studied Rydberg ionization in an electric field with the goal of producing monochromatic ion and electron beams. Cs atoms were used as the source and the Rydberg excitation occurred with a single photon from the $7s$ state in the presence of a uniform electric field. High Rydberg states can exhibit complex ionization behavior, for instance, highly localized growth in the ionization rate due to interference effects. The experimental data were well reproduced by the WKB quantum-defect and frame transformation methods with no adjustable parameters. This shows that large changes in the Rydberg ionization rate from small changes in electric field are possible when a nearly stable state crosses a more unstable one. A fast variation of the ionization rate with electric field allows for the production of beams with very low energy dispersion. We developed a simple two-level model to predict the voltage and spatial resolution that would occur when atoms are prepared in a state with such sharp ionization in electric field. These results confirmed that Rydberg forced ionization in an electric field presents a pathway for the production of high-brightness, highly monochromatic ion and electron beams

Two electron physics: In Ref. [15], we showed the simulated results of using fast single-cycle pulses to detect the properties of double Rydberg wave packets. Fully quantum and classical calculations were performed for a helium atom with two excited, radially localized Rydberg wave packets. The differences between the classical and quantum methods were compared for a wide range of principal quantum numbers to study the validity of the classical method for low-lying states. The effects of fast terahertz single-cycle pulses on an atomic system with one or two

Rydberg wave packets were also studied using classical equations of motion. These results suggested that single-cycle pulses can be used as time-resolved probes to detect motion of the wave packets and to investigate autoionization properties.

Finally, this program has several projects that are strongly numerical but only require knowledge of classical mechanics. This combination is ideal for starting undergraduates on publication quality research. Since 2004, twenty-nine undergraduates have participated in research projects in my group. Most of these students have completed projects published in peer reviewed journals. Two undergraduates, Michael Wall in 2006 and Patrick Donnan in 2012, were one of the 5 undergraduates invited to give a talk on their research at the undergraduate session of the DAMOP meeting. One publication during the past three years had an undergraduate supported by DOE as first author or coauthor.

Future Plans

Basic scattering theory: We will further apply the developments in Refs. [5,12] to perform precision studies of Stark states. Previously, the local-frame-transformation theory gives qualitative agreement with measurements but allows an intuitive method for including the effects from strong fields. We will extend our recent developments to perform calculations for actual atoms including the strong fields, spin-orbit interactions, etc. A successful implementation will confirm that the GLFT can be used both as an intuitive method and as a spectroscopically accurate technique.

Two electron physics: The graduate student Xiao Wang will lead the study of time dependent two electron systems. We will focus on the cases where two electrons are launched successively into Rydberg wave packets as in the joint experiment/calculation with R.R. Jones in 2013. The first studies will probe where the classical and quantum correspondence breaks down. If we can make rapid progress, we will also investigate whether stable wave packet states can be formed by this technique and, if they can, we will study their generic properties. We will also investigate the properties of the recaptured electron when the photo-electron is launched near threshold.

Benchmarking Strong Field Programs: Jens Svensmark and Brett Esry proposed a test problem to benchmark the programs used for calculating the strong laser-atom ionization at 800 nm. They organized this project involving many different theory groups around the world. The goal is to compare the performance of the many different methods being used in the strong field community. The test case they chose was the angular momentum distribution at 0.1 Up and 10 Up for H with the laser at a particular strength and frequency. The calculation was done blind by the different groups and the results sent to Svensmark and Esry to be compared and organized. A paper will be written comparing the different methods.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [1] B.C. Yang and F. Robicheaux, "Field-ionization of Rydberg atoms in a single-cycle pulse," Phys. Rev. A **91**, 043407 (2015).
- [2] P. Giannakeas, F. Robicheaux, and C.H. Greene, "Photoionization microscopy in terms of local-frame-transformation theory," Phys. Rev. A **91**, 043424 (2015).
- [3] P. Giannakeas, F. Robicheaux, and C.H. Greene, "Comment on "Test of the Stark-effect theory using photoionization microscopy"," Phys. Rev. A **91**, 067401 (2015).
- [4] C. Zhong and F. Robicheaux, "Spectrum of quasistable states in a strong infrared field," Phys. Rev. A **92**, 013406 (2015).

- [5] F. Robicheaux, P. Giannakeas, and C.H. Greene, “Schwinger-variational-principle theory of collisions in the presence of multiple potentials,” *Phys. Rev. A* **92**, 022711 (2015).
- [6] B.C. Yang and F. Robicheaux, “Temporal interferences driven by a single-cycle terahertz pulse in the photodetachment dynamics of negative ions,” *Phys. Rev. A* **92**, 063410 (2015).
- [7] C. Zhong and F. Robicheaux, “Coherence and quasistable states in a strong infrared field,” *Phys. Rev. A* **93**, 033410 (2016).
- [8] B.C. Yang and F. Robicheaux, “Closed-orbit theory for photodetachment in a time-dependent electric field,” *Phys. Rev. A* **93**, 053413 (2016).
- [9] H.-C. Shao and F. Robicheaux, “Photodetachment of H^- from intense, short, high-frequency pulses,” *Phys. Rev. A* **93**, 053414 (2016).
- [10] M.S. Pindzola, J. Colgan, F. Robicheaux, T.G. Lee, M.F. Ciappina, M. Foster, J.A. Ludlow, and Sh.A. Abdel-Naby, “Time-dependent close-coupling calculations for ion-impact ionization of atoms and molecules,” *Adv. At. Mol. Opt. Phys.* **65**, 291 (2016).
- [11] S. Cohen, M. M. Harb, A. Ollagnier, F. Robicheaux, M. J. J. Vrakking, T. Barillot, F. Lepine, and C. Bordas, “Photoionization microscopy of the lithium atom: Wave-function imaging of quasibound and continuum Stark states,” *Phys. Rev. A* **94**, 013414 (2016).
- [12] P. Giannakeas, Chris H. Greene, and F. Robicheaux, “Generalized local-frame-transformation theory for excited species in external fields,” *Phys. Rev. A* **94**, 013419 (2016).
- [13] H.-C. Shao and A.F. Starace, “Imaging population transfer in atoms with ultrafast electron pulses,” *Phys. Rev. A* **94**, 030702(R) (2016).
- [14] E. Moufarej, M. Vielle-Grosjean, G. Khalili, A.J. McCulloch, F. Robicheaux, Y.J. Picard, and D. Comparat, “Forced field ionization of Rydberg states for the production of monochromatic beams,” *Phys. Rev. A* **95**, 043409 (2017).
- [15] X. Wang and F. Robicheaux, “Probing double Rydberg wave packets in a helium atom with fast single-cycle pulses,” accepted *Phys. Rev. A* (2017).

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Generation of Bright Soft X-ray Laser Beams

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Project Scope

The great interest in the use of high intensity coherent soft x-ray and x-ray light motivates the development of compact sources of intense coherent short wavelength light that can be readily accessible. The project goals are to explore amplification of atomic transitions in plasma regimes leading to compact soft x-ray lasers emitting high energy ultra-short pulses at shorter wavelengths, and to investigate approaches that can achieve high average powers. This research builds on recent progress in the generation of bright soft x-ray laser beams on a table-top that made use of a diode-pumped laser driver to demonstrated soft x-ray laser operation at 100 Hz repetition rate, producing a record 0.1 mW average power at 13.9 nm. The project studies the amplification of soft x-ray radiation in high plasma density regimes in which collisions broaden the laser transitions to create a gain medium with the increased bandwidth necessary to amplify femtosecond soft x-ray laser pulses. The combination of an increased efficiency with a further increase in repetition rate can be expected to yield soft x-ray laser beams with an unprecedented average power on a table-top high photon flux demanding applications. Recent results include demonstration of an 18.9 nm soft x-ray laser operation at 400 Hz repetition rate, the highest reported today for a soft x-ray laser, and the extension of repetitive gain-saturated plasma-based table-top x-ray lasers to the shortest wavelength to date: 6.9 nm. Laser amplification at wavelengths as short as 5.9 nm was observed by isoelectronic scaling into other Ni-like lanthanide ions.

Recent Progress

Demonstration of compact gain-saturated X-ray lasers down to 6.9 nm and gain down to 5.9 nm

Plasma-based x-ray lasers allow many experiments requiring bright, high energy, x-ray laser pulses to be conducted in compact facilities. These lasers provide extremely monochromatic radiation, typically $\Delta\lambda / \lambda = 3 \times 10^{-5}$, and when injection-seeded can reach full spatial and temporal coherence. The efficient generation of high energy x-ray laser pulses requires operation in the gain-saturated regime. Gain saturation in plasma-based x-ray lasers was previously demonstrated for wavelengths as short as 5.9 nm at large laser facilities. However, this required laser pump pulse energies on target larger than 70 J, which limited their repetition rate to a few shots per hour. In previous work our group obtained soft x-ray amplification down to 7.3 nm using laser pump pulse energies of up to 7.5 J on target to cause transient population inversions. Nevertheless, gain saturated operation was limited to a shortest wavelength of 8.8 nm in Ni-like La. During this report period we have succeeded in extending gain saturated repetitive x-ray lasers down to 6.9 nm in Ni-like Gd. These lanthanide ion-based collisionally pumped lasers generate microjoule pulses which enable for example nano-scale resolution single shot imaging, opening the opportunity to conduct sequential imaging of ultrafast nano-scale phenomena with ultra-high special resolution. Furthermore, in the same experiments we observed gain at even shorter wavelength transitions, down to 5.9 nm in Ni-like Dy. These results, in combination with previous measurements of the optimum angles for lasing in lower Z ions, allowed us to experimentally determine the optimum pump angle for laser operation at wavelengths between 18.9 nm and 5.9 nm, which is closely related to the plasma density at which lasing occurs. The results were useful to bench mark models that can be used to predict the optimum irradiation conditions necessary to further extend table-top gain saturated laser to even shorter wavelengths.

The x-ray lasers were excited irradiating 1–2 mm thick solid slab targets with a sequence of two laser pulses from a $\lambda=800$ nm chirped pulse amplification Ti:Sa laser. The two pulse sequence consisted of a normal-incidence pre-pulse followed by a main sub-picosecond pulse impinging at selected grazing incidence angles with a traveling-wave excitation velocity of (1.0 ± 0.03) c. An acousto-optic programmable dispersive filter (AOPDF) was used after the laser oscillator to tailor the bandwidth of the Ti:Sa pump laser. This gave us the ability to adjust the length of the un-compressed pre-pulse from 45 ps to 300 ps to find the optimal conditions for laser amplification, which was proven critical to obtain the results discussed below. The plasmas were

created by normal-incidence irradiation at an intensity of $I \sim 2 \times 10^{13} \text{ W/cm}^2$ with a 185 ps duration pre-pulse. The pre-pulse was focused onto the target to form a line of approximately $15 \mu\text{m}$ FWHM width and $\sim 9 \text{ mm}$ length using the combination of a spherical and a cylindrical lens. To assist in achieving efficient pumping, we developed a focusing geometry designed to create a plasma column of constant width along the target. The plasma created by the pre-pulse is allowed to expand to reduce the density gradient and subsequently is rapidly heated with a $\sim 7.2 \text{ J}$ pulse of a 0.7 ps FWHM duration. This pre-pulse is shaped into a line focus of approximately $30 \mu\text{m} \times 9 \text{ mm}$ FWHM, corresponding to an intensity of $I \sim 3.6 \times 10^{15} \text{ W/cm}^2$. The target surface was tilted with respect to the axis of the short pulse to define a grazing incidence angle of 35 degrees and 43 degrees for efficient heating in the case of Sm and Gd respectively. Due to the short duration of the gain, the mismatch between the propagation velocities of the pump pulse and the amplified soft x-ray laser pulse significantly reduces the amplification of the x-ray laser pulse. To overcome this limitation, a reflection echelon composed of six adjustable mirror segments was used to obtain traveling wave excitation.

Figure 1 shows a 3 orders of magnitude increase in the intensity of the $\lambda=7.36 \text{ nm } 4d^1S_0-4p^1P_1$ laser transition of Ni-like Sm as the plasma column length increases from 3 mm to 8 mm. Saturation of the gain is observed to have an onset at a plasma-column length of approximately 5.5 mm. A fit of the data with an expression for the gain that takes into account saturation yields a gain coefficient of 27.3 cm^{-1} with a gain-length product of 16.6. The energy of the most intense Sm laser pulses was estimated to be $\sim 1.8 \mu\text{J}$ from the CCD counts, a value that is sufficient to perform nano-scale imaging with a single laser shot. Similar pump pulse conditions were used to obtain a gain-saturated $\lambda=6.9 \text{ nm}$ laser in Ni-like Gd. Fig. 2(a) shows a series of on-axis spectra as a function of the length for a Gd plasma column created by depositing 7.3 J of short-pulse energy and a total of 14.1 J optical pump pulse energy on a polished Gd slab target with the irradiation parameters described above. Fig. 2 (b)

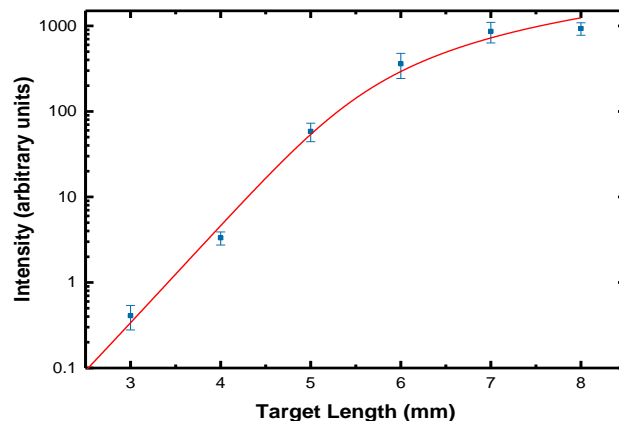


Fig. 1. Intensity of the $\lambda=7.3 \text{ nm}$ Sm laser line as a function of the plasma-column length. The line is a fit of the data that yields a gain coefficient of 27.3 cm^{-1} and a gain-length product of 16.6. The error bar represents one standard deviation.

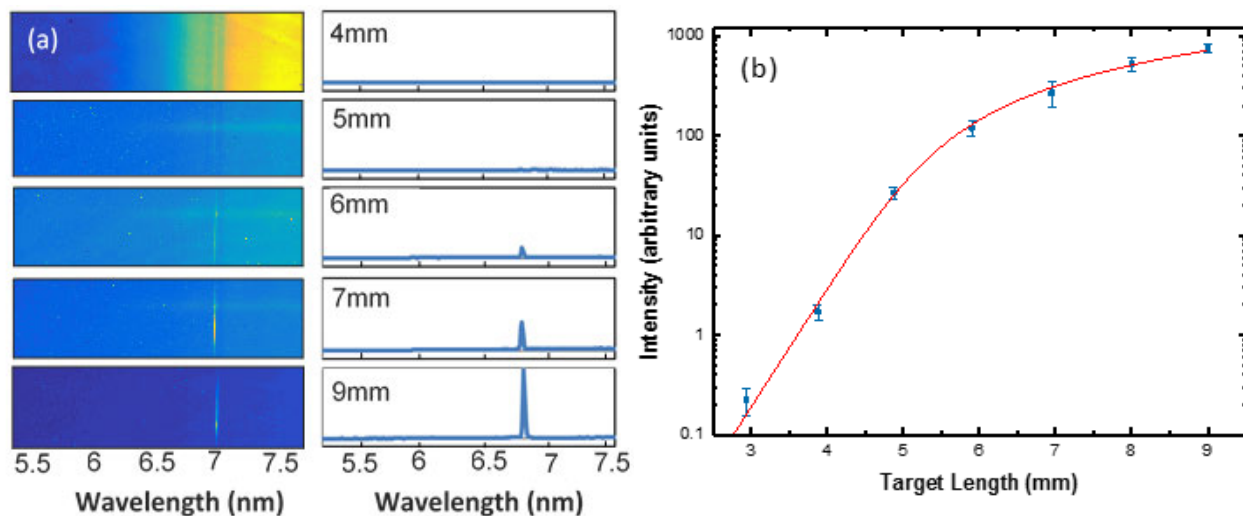


Fig. 2. (a) End-on spectra of a line-focus gadolinium plasma column showing saturated amplification in the $\lambda=6.9 \text{ nm}$ line of Ni-like Gd. (b) Intensity of the $\lambda=6.9 \text{ nm}$ laser line as a function of the plasma-column length. The line is a fit of the data that yields a gain coefficient of 26.3 cm^{-1} and a gain-length product of 16.2. The error bar represents one standard deviation.

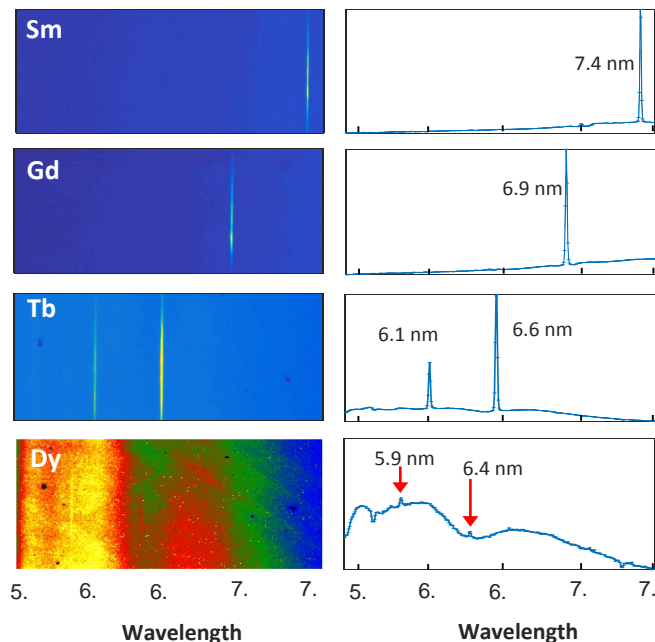


Fig. 3. End-on spectra showing lasing at progressively shorter wavelengths in the $4d^1 S_0-4p^1 P_1$ line of nickel-like lanthanide ions, down to $\lambda=5.9$ nm in Ni-like Dysprosium (Dy).

shows the increase in the 6.9 nm laser line intensity as a function of plasma column length. A fit to the data gives a gain coefficient of 26.3 cm^{-1} and a gain length product of 16.2. The pulse energy for the longest plasma column length is $\sim 1 \mu\text{J}$. Weak amplification was also observed for $\lambda=6.9$ and $\lambda=6.4$ nm of Ni-like Sm and Gd respectively. The results are in good agreement with hydrodynamic/atomic physics simulations.

The demonstration of a gain-saturated tabletop laser at $\lambda=6.9$ nm with reduced pump energy also opens the prospect for bright high-repetition-rate plasma-based lasers at shorter wavelengths. In progress toward this goal we made use of isoelectronic scaling along the elements of the lanthanide series to obtain lasing in several shorter wavelength transitions from Ni-like ions. The spectra of Fig. 3 show that the use of similar irradiation conditions resulted in strong amplification in the $\lambda=6.6$ nm and $\lambda=6.0$ nm transitions of Ni-like Tb. Finally, we have also observed amplification in the $\lambda=5.9$ nm and $\lambda=6.4$ nm lines of Ni-like Dy (Fig. 3) using the same pump conditions. For lasing in all elements the traveling wave excitation was kept constant and near c . The spectra in Fig. 3 show that the intensity ratio of the longer wavelength to the shorter wavelength of the two $J=0-1$ lines becomes smaller as Z increases, with the shortest wavelength line becoming dominant for Ni-like Dy.

Another significant aspect of these amplifiers is the fact that collisional x-ray laser amplification at shorter wavelengths favors higher plasma densities. This is shown by the increase of the grazing incidence angle of the short pump pulse necessary for optimum laser amplification. Adding the experimental data of optimum angle obtained in this work to our previously published data for lower Z Ni-like ions it is possible to experimentally map the dependence of the optimum pump angle and plasma density for a large range of Z and lasing wavelengths, in comparison with simulations. This provides both a benchmark for simulation codes, as well as a prediction of the optimum condition for further scaling these lasers to shorter wavelengths. The increase in irradiation angle was observed to be linear over a broad range of atomic numbers ranging from $Z=42$ (Mo) to $Z=66$ (Dy) (Fig. 4). In this range of Z the optimum short pulse irradiation angle is observed to increase from a grazing incidence

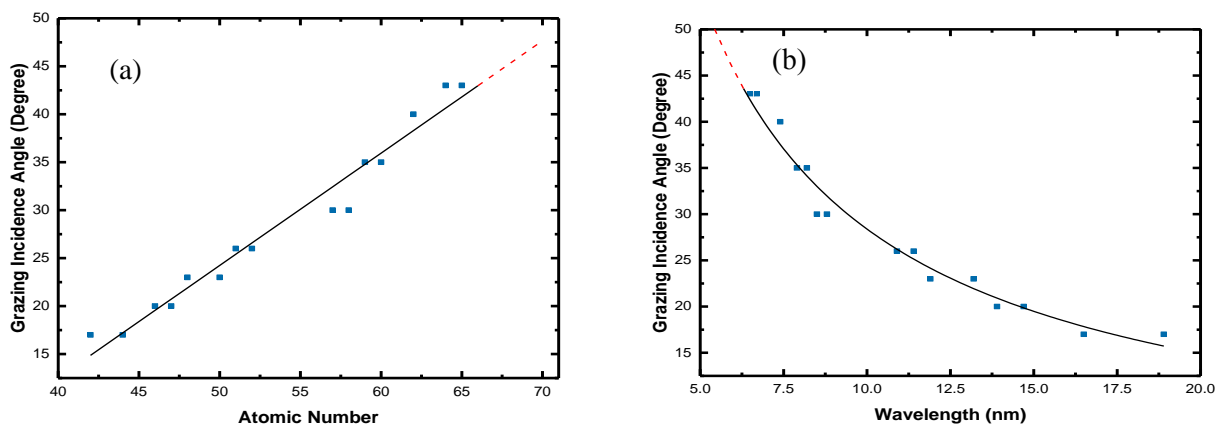


Fig. 4. (a) Optimum grazing incidence angle as a function of atomic number. The dashed line is an extrapolation of the data. (b) The optimum grazing incidence angle as a function of lasing wavelength. The dashed line is an extrapolation of the data.

angle of 17 degrees for Mo to 43 degrees for Dy. This corresponds to an increase in electron density from $1.5 \times 10^{20} \text{ cm}^{-3}$ to $7.9 \times 10^{20} \text{ cm}^{-3}$.

Nanoscale isotopic imaging

Expanding the goals of this project we collaborated with scientists at Pacific Northwest Laboratory (PNNL) in using one of our ultrashort wavelength lasers to map with nano-scale spatial resolution the isotopic composition of uranium micro-dust particles using a new ultrahigh resolution chemical composition imaging technique: Extreme Ultraviolet Time of Flight Laser Ablation mass spectrometry (EUV TOF). Using as benchmark the well-standardized NIST 61x glasses, the results show the EUV TOF spectra contain well defined signatures of U, Th, and their oxides, with far fewer spectral interferences than observed in Time-of-Flight Secondary Ion Mass Spectrometry (SIMS TOF). Furthermore, the method achieved a sample utilization efficiency (SUE), which is a measure of trace analysis sensitivity, of 0.014% for U and Th. This value compares very well with 0.017%, of SIMS TOF in the same mass range. However, in imaging mode EUV TOF is capable to map variations in composition with a superior lateral resolution of 80 nm. Such high lateral resolution enabled us to map the isotopic distribution of ^{238}U and ^{235}U in closely spaced micron-size uranium oxide particles from isotope standard materials (Fig. 5). Trace elemental sensitivity and nanometer spatial resolution gives EUV TOF great potential to dramatically improve the state-of-the-art laser ablation/ionization mass spectrometry and elemental spectro-microscopy for applications such as geochemical, forensic and environmental analysis. The results are discussed in detail in a paper published in the Journal of Analytical Atomic Spectrometry.

Future Plans

We plan to continue our efforts in using transient collisional excitation of atomic transitions in highly ionized ions to develop compact plasma-based soft x-ray lasers at shorter wavelength, with shorter pulse duration, and increased average power. Specifically, during the next year of the project we plan to study amplification in lanthanide ions at sub 6 nm wavelengths, and to investigate plasma gain media with increased bandwidth to allow the amplification of bright soft x-ray pulses of femtosecond duration. Efforts of increasing the average power of table-top soft x-ray lasers will continue using efficient diode-pumped pump laser technology we have developed.

Peer reviewed publications resulting from this project (2015-2017)

T. Green, I. Kuznetsov, D. Willingham, B. E. Naes, G. C. Eiden, Z. Zhu, W. Chao, J. J. Rocca, C. S. Menoni, A. M. Duffin, "Characterization of extreme ultraviolet laser ablation mass spectrometry for actinide trace analysis and nanoscale isotopic imaging", *Journal of Analytical Atomic Spectrometry*, **32**, 1092-1100 (2017).

D. Schiltz, D. Patel, C. Baumgarten, B.A. Reagan, J.J. Rocca, C.S. Menoni, "Strategies to increase laser damage performance of Ta₂O₅/SiO₂ mirrors by modifications of the top layer design," *Appl. Opt.* **56**, C136-C139 (2017).

C. Baumgarten, M. Pedicone, H. Bravo, H.C. Wang, L. Yin, C.S. Menoni, J.J. Rocca, B.A. Reagan, "1 J, 0.5 kHz repetition rate picosecond laser", *Optics Letters* **41**, 3339 (2016).

V. Aslanyan, I. Kuznetsov, H. Bravo, M. R. Woolston, A. K. Rossall, C. S. Menoni, J. J. Rocca, and G. J. Tallents, "Ablation and transmission of thin solid targets irradiated by intense extreme ultraviolet laser radiation", *Applied Physics Letters Photonics*, **1**, 066101 (2016).

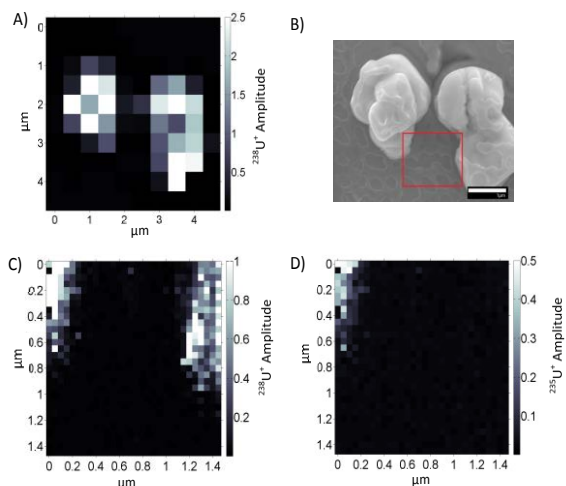


Fig. 5. Isotopic Imaging of U micron size particles. (A) ^{238}U distribution. Pixel size: 200 nm. (B) Scanning electron micrograph of the particles. (C) ^{238}U distribution in the region delineated by the red square. Pixel size: 50 nm. (D) ^{235}U is only present in one of the particles. Pixel size: 50 nm.

Light-induced modification of electronic interactions and electron-nuclear couplings

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Project Scope

Electron-nuclear couplings and electronic correlations play a central role in determining how the charge and energy get distributed inside molecules and materials. For example, immediately following an excitation event, an electron or a hole can migrate across a molecule on attosecond to few-femtosecond timescales, driven by electronic correlations[1,2]. Concurrently, the coupling between electronic and nuclear degrees of freedom[3] leads to exchange of energy, and eventual transfer of the charge between molecular moieties or across an interface. Thus, electronic interactions and electron-nuclear couplings play a fundamental role in physical, chemical, and biological processes. Important examples of many-body interaction mediated, ultrafast charge and energy transfer dynamics can be found in light harvesting, photo-catalysis, interfacial energy storage, DNA stability etc.

By the virtue of unsurpassed time-resolution, attosecond spectroscopy forms an ideal tool to study correlation and coupling driven electron dynamics in molecules and materials. Typical attosecond spectroscopy schemes employ attosecond extreme-ultraviolet (XUV) pulses in combination with strong near-infrared (NIR) laser pulses to extract the pertinent information. However, in such measurements, understanding and disentangling the role of strong-field modification is crucial for uncovering the dynamics of interest. We aim to characterize the strong-field electronic couplings, and use them as a tool to tune the interactions that drive electron dynamics in molecules.

Specifically, we will use a tunable multi-pulse pump-probe schemes to study electronic processes, where attosecond XUV excitation will be implemented along with a wavelength-tunable femtosecond infrared (0.6-1.4 eV) pulse for dressing or control. We plan to conduct two main types of experiments: 1) Study of light-induced couplings and electronic interactions 2) Light-induced modification of electron-nuclear couplings. The first topic will study of how light-induced couplings manifest in the attosecond transient absorption and how they could be used to alter the fast dynamics stemming from interaction between electrons, e.g. in atomic and molecular autoionization. The second topic concerns the light-induced modification of electron-nuclear coupling driven dynamics in small polyatomics, e.g. near conical intersections. We will mainly use electron and ion imaging in the latter studies. In this program, the application of tunable IR fields for systematic study of resonant and non-resonant electronic couplings will also lead to new strategies for control over the electron dynamics governed by many-body interactions.

Recent Progress

Using ultrafast XUV-NIR spectroscopy, PI and coworkers have conducted a number of studies[4–8] at the University of Arizona to investigate atomic and molecular dynamics using Attosecond Transient Absorption Spectroscopy (ATAS) and Velocity Map Imaging (VMI)

techniques. Under the current DoE funded project, we have initiated experiments that employ wavelength adjustable probe pulses for transient absorption studies in atoms. Our first experiments focus on the impact of tunable laser induced couplings on attosecond transient absorption features. The novelty of these studies is that high harmonics and laser photons are non-commensurate, allowing us to investigate the effects of laser dressing vis-à-vis the static electronic resonances, without the additional complication of interferences between various excitation paths stemming from different high harmonics. We have obtained a few interesting preliminary results in Helium, where we observe wavelength dependence of Autler-Townes splitting. We are conducting additional experimental tests and collaborating with Profs. Ken Schafer and Mette Gaarde from LSU to gain insight into the non-linear mechanisms responsible for the fast energy exchange between the atom and light fields.

Future Plans

In the near term, we will employ and advance the strong-field transient absorption technique to study and control electronic interactions. Attosecond transient absorption spectroscopy is inherently a strong-field modification based method[9], where the XUV absorption between two states is modulated by the strong IR pulse acting as a pump to prepare the initial state[10], or as a probe to monitor or alter the excited state dynamics[11–14]. We will employ the latter configuration, where the IR probe pulse induces linear and non-linear couplings between the excited states. Despite many recent studies in this field, the role of IR modification is still not fully understood, and the potential of this approach for the control of electron dynamics is just becoming clear. We will conduct a systematic investigation of this topic by using tunable-wavelength IR pulses to control electronic couplings, and therefore, the energy exchange between XUV pulses and the medium. We will then advance to unique three-pulse experiments to access the dynamics of spectroscopically dark states. Building on the knowledge gained from these studies, we will investigate the light-induced modification of electronic correlations in atoms and molecules.

As mentioned above, we have initiated preliminary study with tunable IR pulses in Helium. We address the 4p state with 15th harmonic, and vary the IR pulse center wavelength from 1.3 to 1.6 μm , holding the peak intensity at 0.5 TWcm^{-2} . This allows us to control the detuning of a one-photon resonance between 4p and 3s states, which in turn provides a knob to control the Autler-Townes splitting of the 4p lineshape. Dependence of this splitting on IR laser intensity will be investigated. The non-linear couplings in the form of four-wave-mixing also lead to XUV emissions, which will be observed as sidebands at two-photon spacing from the 4p line. We will conduct experiments on various atomic systems to acquire multi-parameter data sets, and collaborate with Prof. Ken Schafer and Mette Gaarde to develop detailed understanding of light-induced effects. The variation of light polarization will also be used in these studies to explore additional couplings.

The broader goal here is to study if the IR laser induced modification, and the resulting changes in transient absorption line shapes, can be used to characterize the unknown electronic properties of a fast evolving atomic or molecular system. Systematic and focused investigations, aimed at the light-induced modification of correlated and coupled electron dynamics, will provide means for benchmarking the theoretical calculations, and guide the design of next generation of experiments. The research proposed here will also provide strategies for controlling the charge and energy redistribution in molecules, which can in-turn enable the development of transformative solutions for light harvesting, energy conversion, and catalysis – topics that are clearly of immense importance to the society.

References Cited

- (1) Kuleff, A. I.; Cederbaum, L. S. Ultrafast correlation-driven electron dynamics. *J. Phys. B-Atomic Mol. Opt. Phys.* **2014**, *47*, 124002.
- (2) Sansone, G.; Pfeifer, T.; Simeonidis, K.; Kuleff, A. I. Electron Correlation in Real Time. *ChemPhysChem* **2012**, *13*, 661–680.
- (3) Li, Z.; Vendrell, O.; Santra, R. Ultrafast Charge Transfer of a Valence Double Hole in Glycine Driven Exclusively by Nuclear Motion. *Phys. Rev. Lett.* **2015**, *115*, 143002.
- (4) Shivaram, N.; Timmers, H.; Tong, X. M.; Sandhu, A. Attosecond-resolved evolution of a laser-dressed helium atom: Interfering excitation paths and quantum phases. *Phys. Rev. Lett.* **2012**, *108*, 193002.
- (5) Timmers, H.; Shivaram, N.; Sandhu, A. Ultrafast dynamics of neutral superexcited Oxygen: A direct measurement of the competition between autoionization and predissociation. *Phys. Rev. Lett.* **2012**, *109*, 173001.
- (6) Timmers, H.; Li, Z.; Shivaram, N.; Santra, R.; Vendrell, O.; Sandhu, A. Coherent Electron Hole Dynamics Near a Conical Intersection. *Phys. Rev. Lett.* **2014**, *113*, 113003.
- (7) Liao, C.-T.; Sandhu, A.; Camp, S.; Schafer, K. J.; Gaarde, M. B. Beyond the Single-Atom Response in Absorption Line Shapes: Probing a Dense, Laser-Dressed Helium Gas with Attosecond Pulse Trains. *Phys. Rev. Lett.* **2015**, *114*, 143002.
- (8) Liao, C. T.; Sandhu, A.; Camp, S.; Schafer, K. J.; Gaarde, M. B. Attosecond transient absorption in dense gases: Exploring the interplay between resonant pulse propagation and laser-induced line-shape control. *Phys. Rev. A* **2016**, *93*, 33405.
- (9) Wu, M.; Chen, S.; Camp, S.; Schafer, K. J.; Gaarde, M. B. Theory of strong-field attosecond transient absorption. *J. Phys. B At. Mol. Opt. Phys.* **2016**, *49*, 62003.
- (10) Goulielmakis, E.; Loh, Z.-H.; Wirth, A.; Santra, R.; Rohringer, N.; Yakovlev, V. S.; Zherebtsov, S.; Pfeifer, T.; Azzeer, A. M.; Kling, M. F. Real-time observation of valence electron motion. *Nature* **2010**, *466*, 739–743.
- (11) Wang, H.; Chini, M.; Chen, S. Y.; Zhang, C.-H. H.; He, F.; Cheng, Y.; Wu, Y.; Thumm, U.; Chang, Z. H. Attosecond Time-Resolved Autoionization of Argon. *Phys. Rev. Lett.* **2010**, *105*, 143002.
- (12) Chen, S.; Bell, M. J.; Beck, A. R.; Mashiko, H.; Wu, M.; Pfeiffer, A. N.; Gaarde, M. B.; Neumark, D. M.; Leone, S. R.; Schafer, K. J. Light-induced states in attosecond transient absorption spectra of laser-dressed helium. *Phys. Rev. A* **2012**, *86*, 063408.
- (13) Ott, C.; Kaldun, A.; Raith, P.; Meyer, K.; Laux, M.; Evers, J.; Keitel, C. H.; Greene, C. H.; Pfeifer, T. Lorentz Meets Fano in Spectral Line Shapes: A Universal Phase and Its Laser Control. *Science* **2013**, *340*, 716–720.
- (14) Bernhardt, B.; Beck, A. R.; Li, X.; Warrick, E. R.; Bell, M. J.; Haxton, D. J.; McCurdy, C. W.; Neumark, D. M.; Leone, S. R. High-spectral-resolution attosecond absorption spectroscopy of autoionization in xenon. *Phys. Rev. A* **2014**, *89*, 023408.

Peer-Reviewed Publications Resulting from this Project (Project Start Date: 09/2017)

none

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Transient Absorption and Reshaping of Ultrafast Radiation

DE-SC0010431

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September 2017

Project Scope

Our program is centered around the theoretical study of transient absorption of ultrafast extreme ultraviolet (XUV) radiation by atoms and materials interacting with a precisely synchronized near-to-mid infrared (IR) laser pulse. Transient absorption spectroscopy can in principle provide high spectral resolution and high (attosecond) time resolution simultaneously, by spectrally resolving the light transmitted through a sample as a function of delay between the dressing laser pulse and the broadband attosecond EUV probe. As in all transient absorption calculations/measurements, one of the main challenges we confront is the extraction of time-dependent dynamics from delay-dependent information. In addition, we must also account for the reshaping of the broadband XUV light in the macroscopic medium. We study attosecond transient absorption (ATA) using a versatile theoretical treatment that takes account of both the strong laser-atom interaction at the atomic level via the time-dependent Schrödinger equation (TDSE), as well as propagation of the emitted radiation in the non-linear medium via the Maxwell wave equation (MWE), often in the single-active electron (SAE) approximation [1]. We have also extended our TDSE/MWE treatment in atoms to fully-active two electron calculations in helium, in both full and reduced dimensions. Consistent with our goals in the original proposal, we have built a program that emphasizes both fundamental theoretical research and a close connection with experimental groups doing attosecond physics.

Recent Progress

We have completed a number of research projects in collaboration with experimental groups carrying out attosecond transient absorption (ATA) measurements, see [R1-R3, R5, R7]. We have also recently published an *Invited Topical Review* in *Journal of Physics B* [R6] that summarizes and places in context many of the theoretical results on attosecond transient absorption that we have obtained in the course of our work over the past three years. In this abstract we focus on our most recent collaboration, with the experimental group of Prof. Mauritsson at Lund University, Sweden, which was recently published in *Nature Photonics* [R7].

This collaboration is centered on extending IR-driven spectral and temporal control of ultrafast XUV radiation, which is by now well-known in ATA spectroscopy, to the spatial domain, thereby creating a so-called opto-optical XUV modulator. The control scheme is based on spatially redirecting the long-lived dipole radiation that results from resonantly exciting an ensemble of atoms by an ultrashort XUV pulse and is illustrated in Fig. 1. This dipole emission is often referred to as free induction decay (FID) and has been observed in many different contexts for several decades, originating in studies of nuclear magnetic resonances [2,3]. In the absence of an IR pulse, the XUV excited dipole radiation gives rise to emission which is out of phase with the generating field, and because it has the same spatial properties as the excitation pulse leads to absorption of the light in the forward direction, at the resonance frequency (Fig. 1(a)). The effect of a time-delayed IR pulse on the XUV absorption *spectrum* has been studied by a number of groups [4–6] and can be thought of in terms of the extra time-dependent phase on the XUV dipole moment resulting from the IR-induced Stark shift of the resonant state. In this work, we control the XUV *spatial* properties by shifting the IR beam relative to the XUV beam so that the XUV excited atoms experience a radially varying IR

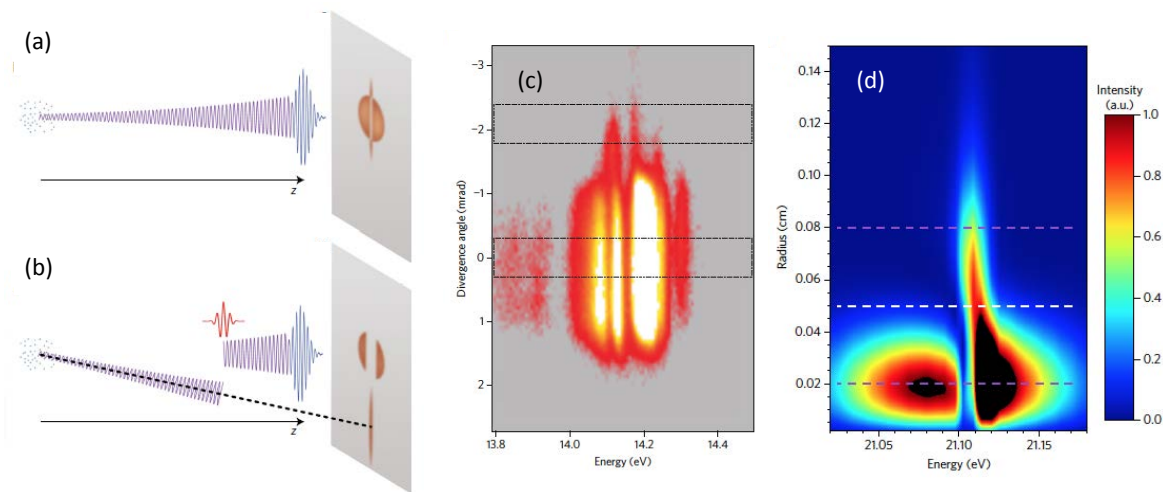


Figure 1: Illustration of space-time control of XUV free induction decay: (a) and (b) illustrate the principle of the spatiotemporal control: A short XUV pulse excites a long-lived resonance in an ensemble of atoms which emits through FID. In the absence of the IR pulse, the FID radiation is exactly out of phase with the exciting XUV, leading to absorption (missing light in the center of far field profile in (a)). An IR pulse with a spatial distribution that varies across the FID beam will give rise to a radially dependent phase shift that rotates the FID wavefront, leading to off-axis XUV emission in the far field (b). (c) Example of experimentally redirecting the FID emission from the 5s and 3d states in argon, manifesting as absorption lines in the on-axis profile, and emission lines off-axis, near -2 mrad. (d) Calculation of FID redirection near the 2p state in helium. Adapted from [R7].

intensity. This causes a radial variation of the IR-induced phase on the FID emission so that its wavefront is rotated, leading to off-axis XUV emission in the far field (Fig. 1(b)). Both the missing XUV light on axis, and the induced XUV emission off axis, can be seen in the experimentally measured far field profile of XUV light near 14 eV which has propagated through argon, and excited the 5s and 3d states (Fig. 1(c)).

The IR-controlled redirection of the FID light is the result of the complex interplay between the microscopic quantum interactions leading to the Stark shift of the excited states and the macroscopic bending of the FID phase front. To reproduce the experimental result it is therefore necessary to solve the coupled TDSE and MWE in the macroscopic medium and thereby calculate the XUV electric field in the far field. Fig. 1(d) shows a calculation of redirecting XUV light in the vicinity of the 2p state in helium which we have been using as an exemplar for the spatiotemporal control. Our calculations are done using cylindrical symmetry in the MWE solver which means that the redirection works slightly differently - instead of the IR beam being displaced vertically from the XUV beam, we adjust the size of the IR beam so that the IR intensity varies substantially across the XUV beam profile. This means that our FID emission is redirected in a cylindrically symmetric "halo" around the XUV beam. Similarly to the experimental result, we see the FID emission both as missing light on axis, and new light off axis (Fig. 1(d)).

The work in [R7] demonstrates that an IR pulse can be used to control both the spatial and temporal properties of resonant emission in the XUV, by sending the FID emission in a direction of our choosing, at a time of our choosing. As a tool in ATA spectroscopy, the opto-optical modulator allows us to study resonant emission in a background-free measurement scheme. More generally, it will also allow for synchronization between X-rays from XFELs and IR pulses at the sub-femtosecond level.

Future Plans

We are currently exploring several different approaches to background-free studies of attosecond transient absorption dynamics:

(i) *Spatio-temporal control of FID emission as initiated in [R7]*: It is clear from the description above that the efficiency of the spatial redirection of the XUV FID emission depends on the magnitude and variation

of the phase shift that is induced on the XUV dipole moment by the interaction with the IR pulse. This means that the dependence of the spatial redirection on the IR and gas parameters can be used to probe the interaction between the excited atom and the IR pulse, *i.e.* the dynamics of the laser-dressed states. As an example of this, we have observed in both theory and experiment that the FID emission associated with the 2p state in helium shifts in one direction at low IR intensity and in the opposite direction at high IR intensity. We have found that this behavior can be traced back, in detail, to how the 2p state interacts with several other excited states in the presence of the IR field. This work is nearing completion and will be submitted soon [7].

(ii) *ATA spectroscopy with a variable-wavelength IR control field*: We have continued our collaboration with the experimental group of Arvinder Sandhu and University of Arizona (*cf.* [8] and [R5]). Dr. Sandhu's group has developed an ATA setup in which the IR probe pulse has been sent through an optical parametric amplifier (OPA) and therefore has a variable wavelength. The XUV excitation field in this setup is in the form of a train of attosecond pulses (in the frequency domain it corresponds to a few harmonics of an 800nm laser), and the gas of interest thus interacts with XUV and IR frequencies that are not commensurate. The variable wavelength IR probe is interesting for several reasons: (a) It allows for the IR interaction of the excited atoms to be scaled by the variable wavelength, sliding excited states in and out of resonances with each other, and (b) it means that the two-IR-photon sidebands of a resonance which has been excited by one of the XUV harmonics is *not* resonant with the neighboring harmonic, so that the two-photon sideband can be studied on its own (*i.e.* background free). In both experiment and theory we have explored a range of phenomena pertaining to the variable IR wavelength, in particular the onset and wavelength dependence of an Autler-Townes structure in the ATA spectrogram. This work is in progress.

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- R1 J. Herrmann, M. Lucchini, S. Chen, M. Wu, A. Ludwig, L. Kasmi, K. J. Schafer, L. Gallmann, M. B. Gaarde, U. Keller, *Multiphoton transitions for delay-zero calibration in attosecond spectroscopy*, **New J. Phys.** 17, 013007 (2015).
- R2 M. Reduzzi, J. Hummert, A. Dubrouil, F. Calegari, M. Nisoli, F. Frassetto, L. Poletto, S. Chen, M. Wu, M. B. Gaarde, K. J. Schafer, G. Sansone, *Polarization-control of absorption of virtual dressed-states in helium*, **Phys. Rev. A** 92, 033408 (2015).
- R3 C.-T. Liao, A. Sandhu, S. Camp, K. J. Schafer, and M. B. Gaarde, *Beyond the single-atom response in absorption line shapes: Probing a dense, laser-dressed helium gas with attosecond pulse trains*, **Phys. Rev. Lett.** 114, 143002 (2015).
- R4 X. Li, D. J. Haxton, M. B. Gaarde, K. J. Schafer, and C. W. McCurdy, *Direct extraction of intense-field-induced polarization in the continuum on the attosecond time scale from transient absorption*, **Phys. Rev. A** 93, 023401 (2016).
- R5 C.-T. Liao, A. Sandhu, S. Camp, K. J. Schafer, and M. B. Gaarde, *Attosecond Transient Absorption in Dense Gases: Exploring the Interplay between Resonant Pulse Propagation and Laser-Induced Line Shape Control*, **Phys. Rev. A** 93, 033405 (2016).
- R6 M. Wu, S. Chen, S. Camp, K. J. Schafer, and M. B. Gaarde, *Topical Review: Theory of strong-field attosecond transient absorption*, **J. Phys.** B 49, 062003 (2016).
- R7 S. Bengtsson, E. W. Larsen, D. Kroon, S. Camp, M. Miranda, C. L. Arnold, A. L'Huillier, K. J. Schafer, M. B. Gaarde, L. Rippe, and J. Mauritsson, *Controlled free-induction decay in the extreme ultraviolet*, **Nature Photonics**, 11, 252 (2017).

References

- [1] Mette B. Gaarde, Christian Buth, Jennifer L. Tate, and Kenneth J. Schafer. Transient absorption and reshaping of ultrafast XUV light by laser-dressed helium. *Phys. Rev. A*, 83(1):013419, January 2011.
- [2] F. Bloch. Nuclear induction. *Phys. Rev.*, 70:460, 1946.

- [3] R. G. Brewer and R. L. Shoemaker. Optical free induction decay. *Phys. Rev. A*, 6:2001, 1972.
- [4] H Wang, M. Chini, S. Chen, C.-H. Zhang, F. He, Y. Cheng, Y. Wu, U. Thumm, and Z. Chang. Attosecond time-resolved autoionization of argon. *Phys. Rev. Lett.*, 105:143002, 2010.
- [5] Christian Ott, A. Kaldun, P. Raith, K. Meyer, M. Laux, J. Evers, C. H. Keitel, C. H. Greene, and T. Pfeifer. Lorentz Meets Fano in Spectral Line Shapes: A Universal Phase and Its Laser Control. *Science*, 340(6133):716–720, 2013.
- [6] Shaohao Chen, Mengxi Wu, Mette B. Gaarde, and Kenneth J. Schafer. Laser-imposed phase in resonant absorption of an isolated attosecond pulse. *Phys. Rev. A*, 88(3):033409, September 2013.
- [7] E. Simpson, S. Bengtsson, S. J. Camp, M. B. Gaarde, K. J. Schafer, and J. Mauritsson. Probing nonlinear Stark shifts with opto-optical phase modulation. *In preparation*, 2017.
- [8] C.-T. Liao, A. Sandhu, S. Camp, K. J. Schafer, and M. B. Gaarde. Beyond the single-atom response in absorption line shapes: Probing a dense, laser-dressed helium gas with attosecond pulse trains. *Phys. Rev. Lett.*, 114:143002, 2014.

Time Resolved High Harmonic Spectroscopy: A Coherently Enhanced Probe of Charge Migration

Science Using Ultrafast Probes: DE-SC0012462

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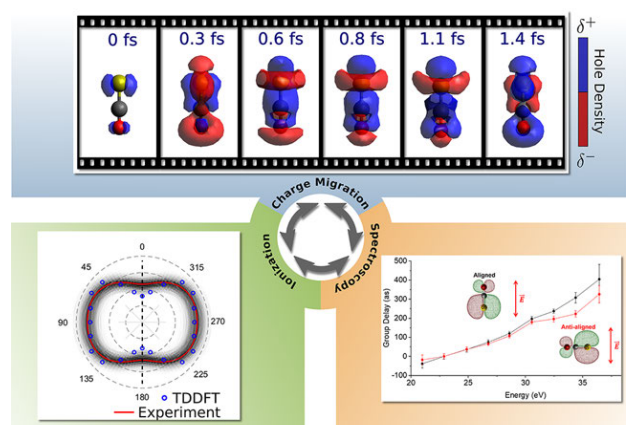


Figure 1: Principal tasks of the ATTO-CM network to observe charge migration with strong laser fields. Each identified component corresponds to one of the main tasks discussed in this abstract, all illustrated for the OCS molecule. (Top) Calculated charge migration, (left) ionization of aligned OCS; (right) group delay of high harmonics from aligned and anti-aligned molecules.

two and many-electron interactions are averaged over. Attosecond studies open a new perspective on these interactions beyond the mean-field picture and without time-averaging. The second motivation is the study of the earliest step of charge transfer reactions. These reactions are among the most fundamental processes in chemistry, e.g., the efficiency at which electrons move around in a molecule is one of the primary regulation mechanisms in biology. As an important example of correlated electron dynamics in many-body systems we study ultrafast charge migration in complex chemical environments. Charge migration refers to the rapid movement (femtosecond or faster) of positively charged holes in a molecule following localized excitation or ionization.

Attosecond charge migration in molecular systems is thought to be driven by a complex interplay between many-electron correlation effects and dephasing/relaxation due to weak coupling with nuclear motion. Understanding the mechanisms of this migration, and developing experimental tools for observing this process, is crucial to advancing ultrafast science. The objective of the ATTO-CM team is to advance ultrafast science in the US, both at small- and large-scale facilities, using a concerted effort of theorists and experimentalist solving these problems side by side, as illustrated in Figure 1. Our emphasis is to

Project Scope

Understanding the quantum transport of electrons and holes, and the correlations between them, provides an avenue toward improving the efficiency of chemical processes including energy conversion and catalysis. The relevant electron dynamics evolve on exceedingly fast time scales down to the natural time scale of the electron, the attosecond. For this reason, attosecond science has increasingly focused on the possibilities for measuring and controlling correlated electron motion in complex many body systems such as polyatomic molecules as one of the key applications of this new science.

There are two broad motivations for extending the measurement of electron/hole dynamics in chemical systems to the attosecond time scale. The first is the study of electron correlation itself. Though electrons interact on an attosecond time scale, most measurements are made over much longer time scales, meaning that

evaluate high harmonic spectroscopy as a probe for studying charge migration dynamics in chemical systems by developing an integrated relationship between theory and experiment, as shown in what follows. The initial experimental campaigns are laboratory based but with the probes' maturation will translate onto a large-scale facility, like LCLS, a natural progression for the science.

Recent Progress

In our effort to understand and observe charge migration with strong laser fields, we have identified three main tasks on which we focus our early efforts. Illustrated in Figure 1, they correspond to (i) orientation and ionization of molecules, (ii) charge migration dynamics, and (iii) spectroscopic methods for measuring the migration. They loosely correspond to the three steps – ionization, propagation, recollision – of the recollision model [Schafer 1993, Corkum 1993], which is at the heart of high-harmonic generation (HHG). It also corresponds to the three building blocks of HHG spectral factorization in semiclassical models [Mauger 2016, Abanador 2017-a].

As demonstrated in what follows, all three nodes – Louisiana State University (LSU), the Ohio State University (OSU) and University of Virginia (UVa) – of the ATTO-CM network are closely involved in each task. In short, our key results are

1. Orientation and Ionization:
 - a. Demonstration of transient molecular alignment in measurement of single- and double-ionization of carbonyl sulfide (OCS), and comparison with time-dependent density functional theory (TDDFT) computations.
 - b. THz field enhancement for improved molecular orientation or enhancement of the laser-driven electron dynamics responsible for HHG and non-sequential ionization.
 - c. Identification of the role played by multi-channel ionization as a precursor to charge migration.
2. Charge migration:
 - a. TDDFT algorithm to identify and represent the principal modes of charge migration in a molecular cation.
 - b. Precise removal of background from experimental HHG phase measurements to reveal target and dynamics-specific signals.
3. Spectroscopy:
 - a. Angle-resolved high-harmonic spectroscopy (HHS) of aligned OCS molecules.
 - b. Experimental probe of the binding potential through which an electron travels during the first femtosecond after emission with a RABBITT+ ("rabbit plus") apparatus.

Orientation and Ionization

The first ATTO-CM task, ionization, is the precursor to charge migration. As an initial value problem, the electronic configuration in which the molecular cation is left following the removal of one, or several, electron(s) determines how its dynamics subsequently unfolds. The alignment/orientation of the molecules, which can be achieved by using optical and/or THz fields, is an important control knob for charge migration. Orientation of the molecules in space allows control over which ionization channels contribute to the electron-hole motion, and selection rules, in combination with the laser polarization, can then be used to selectively couple the cation states.

Measuring and computing ionization yields

In conjunction with experiments at UVa, LSU has made progress towards using TDDFT to simulate strong-field ionization of the OCS molecule, as shown in Figure 2. Comparison with experiment allows for validation of TDDFT algorithms for ionization across a wide range of laser intensities and polarizations. Crucially, these simulations are a first step towards reliably predicting the channels (molecular orbitals) involved in strong field ionization, and ultimately what the charge migration dynamics will be. The technique we use to calculate ionization yields is an extension of one we previously reported [Sissay 2016]. The TDDFT code uses atom-centered basis sets, calibrated complex absorbing potentials, and ionization potential-tuned, range-separated hybrid (RSH) functionals. This Gaussian orbital approach enables efficient use of these hybrid functionals, which have the correct asymptotic

Coulomb potential, accurate ionization potentials, and significantly reduced self-interaction and localization errors as compared to traditional density functionals.

Figure 2 shows the measured (left panel) and simulated (right panel) single- and double-ionization yields for unaligned OCS. Here, the single molecule yields were computed from the change in charge number resulting from a laser pulse with temporal parameters chosen to match the UVa experiment. Because of focal volume effects, it is not possible to directly compare the entire intensity scan of experimental yields to the single target theoretical predictions. It is possible, however, to compare the saturation intensities (I_{sat}) [Hankin 2001] and we found very good agreement for the single ionization signal, where both experiment and theory find $I_{\text{sat}} \sim 70 \text{ TW/cm}^2$. We also find fair agreement for double ionization – $I_{\text{sat}} \sim 230\text{-}250 \text{ TW/cm}^2$ for experiment vs. 180 TW/cm^2 for theory. The saturation intensities are labeled with vertical dashed lines in Figure 2. We find the agreement encouraging, especially for double ionization, given the intrinsic difficulty of defining and separating single and double ionization since only the total charge is well-defined in TDDFT.

On the other hand, we find that our TDDFT calculations slightly, but systematically, overestimate the yields as compared with experiment. This likely arises from two issues that are being tackled independently. First, although IP-tuned DFT functionals are an improvement over traditional DFT, subtle self-interaction errors remain. The LSU team is currently exploring the use of explicitly self-interaction-minimized functionals as well as single and double IP-tuned functionals to address this issue. Second, computing double ionization rates or yields from the TDDFT density can be quite challenging, as a given simulation in general includes both single and double ionization contributions. Here, LSU is developing functionals of the density for extracting the single- and double-ionization parts from the one body density.

Controlling the orientation of molecules in space: Angle-resolved ionization yields

The UVa team has made a series of measurements employing transient laser-alignment to extract angle-dependent strong-field ionization yields for linear and symmetric top molecules. Because the angular dependence of the strong-field ionization rate depends critically on the relative contributions of different molecular orbitals, comparisons of experimental and theoretical ionization anisotropies in angle-resolved yields can serve as important tests of the accuracy of the TDDFT calculations that the LSU team use to calculate charge-migration dynamics (see the corresponding section below).

Following Kumarappan, *et al.* [Kumarappan 2015] the UVa node has recorded the ionization yield as a function of the delay between two 800 nm laser pulses, a 70 fs non-ionizing alignment pulse and a 35-fs ionizing pulse. Using known molecular rotational constants, experimental ionization yield anisotropies are determined from fits to the delay-dependent yield (angularly symmetrized versions are used for symmetric tops). These can be directly compared to calculations. Figure 3 shows such a comparison, with single-ionization yields for OCS at three different peak intensities (left panels) as well as the (sequential) double-ionization yield (right). The experimental results at intermediate intensity are in excellent agreement with previous measurements in which the molecular angular distributions were directly measured rather than inferred from fits to theory [Hansen 2012]. UVa has obtained analogous results for CH_3Cl and is currently performing measurements in CH_3Br , for comparison.

Besides the agreement on saturation intensities mentioned above, the TDDFT angle-resolved single-ionization yields are generally in good agreement with the UVa experiments, as can be seen in Figure 3 (B-C), with an observed yield about 1.5 times faster in the direction perpendicular to the molecule than

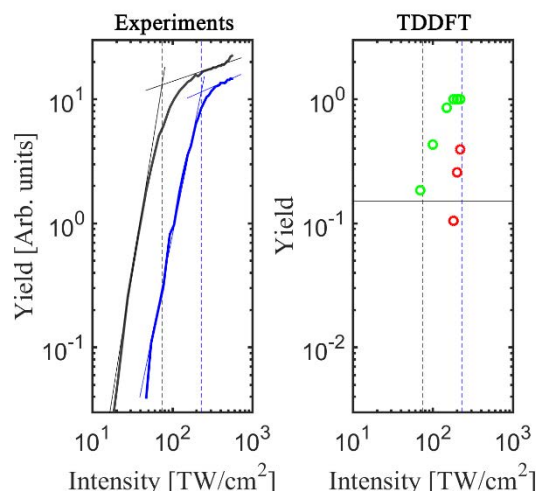


Figure 2: Single- and double-ionization yields of unaligned OCS, as a function of the laser intensity, measured at UVa (left panel) and computed with TDDFT by LSU (right). For comparison, we label (vertical dashed lines) the experimental saturation intensities for each data set, which empirically corresponds to approximately 15% yield in the associated computations (vertical continuous line) [Hankin 2001].

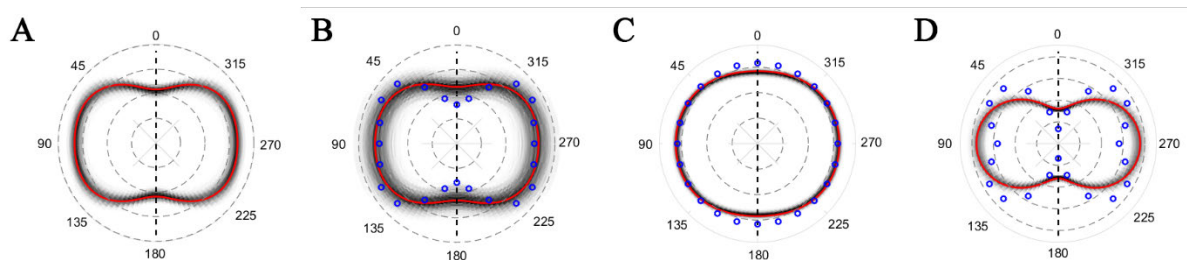


Figure 3: Comparison between experimentally determined angle-dependent yields (solid red curves) and their corresponding TDDFT computations (blue markers) for single- (A-C) and double-ionization (D) of OCS. The experimental uncertainty distributions are represented by the grey bands in each panel. The individual distributions are normalized to give the same angle-integrated yield. The ionizing intensities are: (A) 45 TW/cm^2 ($0.65 I_{\text{sat}}$), (B) 70 TW/cm^2 (I_{sat}), (C) and (D) 200 TW/cm^2 ($2.9 I_{\text{sat}}$). (A) is the result of a single data run with statistical uncertainties only. (B)-(D) are averages of multiple runs with the standard deviation of the individual determinations included in the uncertainty.

on-axis. The TDDFT time-resolved signal also provides additional information on the ionization process, *e.g.*, by showing that it predominantly occurs from the S end of the OCS target. Correctly capturing this angle/subcycle-dependence is crucial for constructing an electron-hole state for subsequent dynamics simulations. On the other hand, the theory has not been as successful in regard to double ionization. The differences in the experimental and theoretical results suggest that the theory may not yet be correctly determining the relative contributions from different molecular orbitals, perhaps due to inaccuracies in relative binding energies. As discussed above, *ab initio* computation of double ionization signal is a challenging task. We intend to use it as a benchmark for how theory could be improved.

A manuscript detailing the combined experimental and theoretical work on angle-dependent single and double ionization of OCS is in progress [Sándor 2017]. In the next phase of this work TDDFT calculations on single ionization for CH_3Cl and CH_3Br will be compared to measurements in these symmetric top systems. LSU and UVa have maintained close contact on this topic with recurrent Skype meetings, emails and exchange visits between each node (to LSU during fall 2016 and to UVa in spring 2017). As discussed in the spectroscopy section below, the OSU node has also shown their capacity to align molecular targets in space. The two experimental nodes have actively shared experience and training in alignment of selected targets via Skype meetings, emails and exchange visits to OSU during winter 2016/17 and to UVa in spring 2017.

Towards better orientation schemes: THz field-enhancement near nano-structured metals

Field-free head vs tail molecular orientation along a space-fixed axis is considerably more difficult to achieve in the laboratory than simple alignment, yet it may be necessary if we are to induce and interpret specific charge migration processes. While phase-controlled $1\omega+2\omega$ laser-based methods can successfully induce field-free orientation [Znakovskaya 2014], non-negligible ionization may preclude their use in more complex, lower IP molecules. As a non-ionizing alternative, strong THz fields can transiently orient molecules [Machholm 2001, Fleischer 2011, Kitano 2013, Egodapitiya 2014]. In addition, strong, quasi-static THz fields can alter intense-laser-driven electron dynamics, potentially influencing processes governed by electron recollisions. Both of these influences could prove valuable for probing and controlling ultrafast electron dynamics in molecules. The main obstacle to implementing these and other THz-based control methods is the lack of sufficient THz field strengths attainable in a typical table-top laboratory. To circumvent that obstacle, UVa has been exploring the use of nano- and micro-structured metals for single-cycle THz field enhancement. As with the RABBITT+ (see spectroscopy section below), this project was initiated with funding from Prof. Jones' individual PI grant. The relevant THz field enhancement work and its application to transient orientation and quasi-static field modification of laser-based electron rescattering has continued with support from this collaborative grant.

The UVa team's initial work focused on nano-tip geometries from which they were able to infer huge local THz field enhancements (as large as 3000x near tungsten nano-tips with radii of ~ 20 nm), resulting in peak THz fields of 1 GV/cm. A description of their results on THz field enhancement near, and electron field emission from, nano- and micro-tipped wires was recently published in Nature Communications [Li 2016]. Unfortunately, the volume of the enhanced field region in the nano-tip geometry is far too small to be useful for affecting the entire sample of gas in the laser focal volume that defines a strong-field or pump-probe experiment. Therefore, the UVa team have begun to explore alternative geometries that can amplify THz fields over a much larger volume, yet provide substantial field-enhancement factors.

Specifically, the UVa team has been studying THz field enhancement along metal razor edges. This geometry can provide field enhancements on the order of 10x throughout a cylindrical volume more closely matched to the focal volume of a laser, *i.e.* a few microns in diameter and millimeter lengths. They are currently attempting to quantify the local field enhancement in this geometry via the observation and characterization of THz field-induced second harmonic generation (alternatively described as THz+optical four-wave mixing) in the air immediately above a razor's edge. They find, not surprisingly, that when a 100 fs, 800 nm laser pulse is weakly focused along a razor's edge, 400 nm radiation is produced via surface second harmonic generation. However, they also observe a large (up to 10x) increase in the 400-nm yield when the 800 nm pulses pass over the edge in the presence of a strong THz field (see Figure 4). They are now working to determine if the increased second-harmonic generation (SHG) is due to THz enhanced surface-SHG, or to THz induced SHG in the air above the blade, or a combination of both. UVa's goal is to identify an experimental geometry through which they can exploit THz field enhancement to alter electron rescattering processes and/or to dramatically improve upon the degree of orientation available in the dense molecular targets needed for HHS measurements.

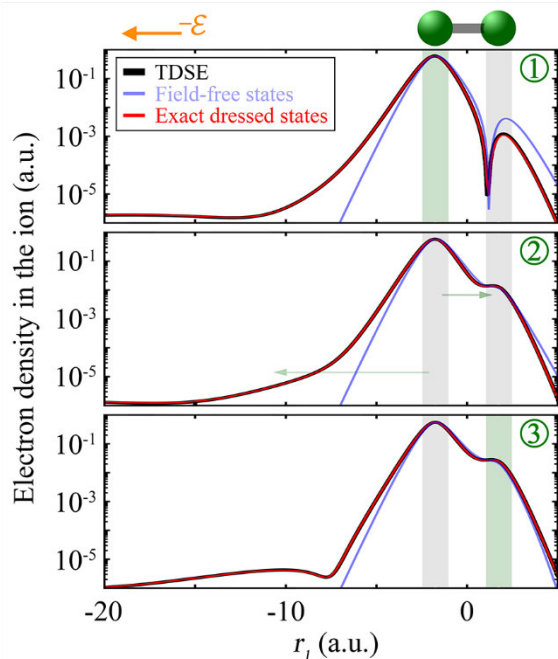


Figure 5: Charge migration dynamics following strong-field ionization of a first electron with a static field. Here we compare the results of full *ab-initio* TDSE with semiclassical representations of the cation electronic structure.

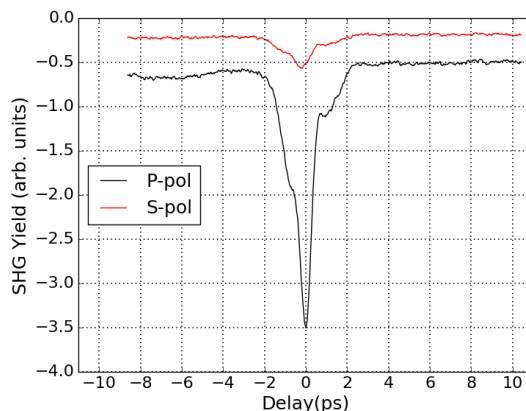


Figure 4: THz-enhanced 400 nm yield as a function of delay between a 100 fs, 800 nm laser pulse and a single-cycle THz pulse that are co-incident along the edge of a razor blade at grazing incidence. For P(S)-polarized light the laser field is perpendicular (parallel) to the THz field which is normal to the surface of the blade. Larger 400 nm yield is represented by more negative values.

Ionization as a trigger for charge migration

Ionization to multiple competing channels is one of the most straightforward ways to induce charge migration in a cation. The effect is illustrated in Figure 5, which shows the electron density in a model cation, a 1D two-electron molecule, for three different delays following ionization in a static field [Mauger 2017] (in preparation). One advantage of the simplicity of such reduced models is that they allow for *ab-initio* integration of the full time-dependent Schrödinger equation (TDSE), which can be used as a benchmark for more approximate models. In this way LSU has validated their extension of the semiclassical model of strong field ionization to account for the interplay between different ionization channels. From the

spectroscopic perspective, a signature of this ionization-induced charge migration is observed in the modulation of the double ionization signal, as can be seen in the figure, when one electron is far from the core ($|r_1| \ll 1$).

LSU is also investigating how to reconcile the nonlinear, one-body density-based formalism of TDDFT with the linear wave-function-based framework of the TDSE. Aside from issues with the choice of a particular functional, TDDFT and TDSE describe the same physics but represent it in different ways. TDDFT keeps a 3-dimensional representation of virtually independent particles irrespective of the number of electrons, with the drawback that observables that are not *explicit* functions of the one-body density can be challenging to recover. This is, for instance, the case for channel-resolved ionization or separating ionization orders (single, double, *etc.* see above), or disentangling the charge migration modes (see below). On the other hand, the TDSE keeps a linear (superposition principle) formulation where all observables are deduced with the appropriate projection, with the drawback that the total dimension grows with the number of degrees of freedom. In practice, this means in the TDSE formalism multi-electron systems are limited to (semi-) analytical approximations. The semiclassical framework for HHS we use is such an example: It is built upon the linearity of the TDSE but still requires molecular and ionization input parameters, which we intend to obtain through TDDFT, to accurately represent the laser-driven/probed dynamics.

Charge migration

Next, we focus on the task of following the charge migration dynamics illustrated in Figure 1. For that, we need to identify and separate the different modes that compose the electron dynamics in the molecular cation in the theoretical calculations. We also need to isolate signals relevant to the observation of charge migration in the experimental data by precisely determining and removing generic components due to propagation in the continuum.

Spectral decomposition tools for identifying charge migration

LSU has developed tools for identifying charge migration modes from within the full manifold of excitations of an ionized molecule, *i.e.*, distinguishing (interesting) charge migration from (uninteresting) localized excitations. In a nutshell, this requires identifying electron dynamics in a molecule that result in electron-hole motion across a significant length of the molecule. In molecules, these modes occur at the ~ 1 -2 fs time scale, which is consistent with the time scale for HHG in the near- to mid-infrared regime considered by the experimental nodes in the collaboration. This is in contrast to less relevant local excitations, which are typically higher frequency and involve “sloshing” of density around bonds. An illustration of each mode is displayed in Figure 6 (A-B).

To address this, LSU has developed a spectral decomposition method wherein the time-dependent electron-hole density $\rho_H(z, t)$ is first computed over a few periods of motion. Here, the initial state of the ionized molecule can come from a TDDFT simulation of strong field ionization, or some other scenario such as sudden core-hole formation following X-ray absorption. The resulting time-dependent electron-hole density is then Fourier transformed to space and frequency $\rho_H(z, \omega)$ to identify the various electron-hole modes of the system. Plotting this at a frequency of interest gives an electron-hole transition map showing the regions in the molecule associated with electron-hole migration of a particular time-scale. This is more illuminating than time-dependent plots, which show contributions due to all modes. Figure 6, for example, shows the spectral analysis for electron-hole migration in iodoacetylene immediately following ionization by a 1064 nm, 1.5×10^{14} W/cm² field polarized perpendicular to the molecular axis. The low energy mode

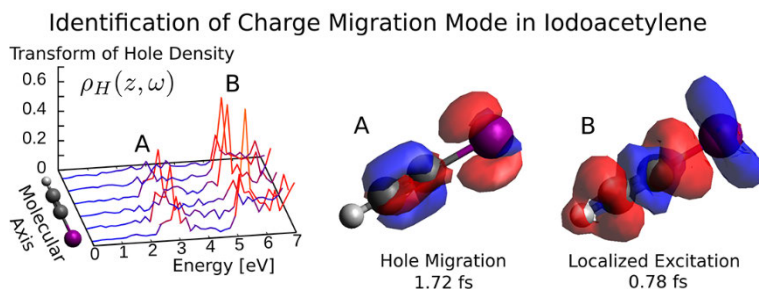


Figure 6: Identification of the charge migration mode in iodoacetylene via spectral decomposition of the electron-hole density. The low frequency mode (A) corresponds to a coherent motion of the electron-hole across the molecule, whereas the higher frequency mode (B) is a local excitation.

(2.4 eV) corresponds to an electron-hole migration across from the iodine to the C≡C bond (red→blue in mode A), whereas the higher energy mode (5.3 eV) is a local excitation (red, blue, red, blue in mode B). This electron-hole migration has essentially the same time-scale and character as that previously reported in the literature for this molecule [Kraus 2015]. In conjunction with ionization simulations, spectral analysis of the dynamics will enable us to predict candidate systems for charge migration to be probed by the experimental nodes of the ATTO-CM network. For instance, the result of a similar analysis is displayed in the Figure 1 for OCS, which has been used by both UVa (see above) and the OSU (below). A manuscript detailing this approach is currently in preparation.

Observing the charge migrating: Validation of TDDFT for attosecond dynamics

The algorithm described above for identifying and isolating charge migration modes is contingent upon TDDFT accurately reporting that dynamics. The accuracy of TDDFT for attosecond processes in molecules remains poorly understood, largely due to the adiabatic (local-in-time) approximation of the exchange-correlation functional. However, the LSU team recently validated the ability of TDDFT to capture valence electron dynamics immediately following sudden X-ray ionization of a core electron [Bruner 2017]. In this case, they essentially showed that adiabatic hybrid functionals gave accurate dynamics, at least for the case of a core-hole trigger. This is a key step towards TDDFT prediction of charge migration following tunnel ionization, and naturally follows from the ionization comparison with the UVa experiments discussed above. Core-electron-hole initial states are simpler to deal with than those produced by strong field ionization, as they can be constructed without knowledge of the molecular orbital populations. This, in turn, allows for a simple test of the accuracy of the theory without ambiguity arising from the choice of initial state.

Figure 7 (a) shows the computed electron-hole migration dynamics in nitrosobenzene following nitrogen K-edge ionization. The results show excellent agreement with previously reported fourth-order algebraic diagrammatic construction (ADC(4)) results (not shown) [Kuleff 2016]. Here, the rapid core-hole ionization leads to a valence electron-hole migration across the molecule in ~ 0.7 fs, which occurs faster than the Auger decay time. Moreover, by visualizing electron-hole motion using a time-dependent electron localization picture, the charge migration can be interpreted “chemically” as a superposition of Lewis dot structures. The migrating electron-hole manifests as an attosecond evolution of the double bonds in the benzene ring in a manner suggestive of the redistribution of bonds and lone pair electrons due to chemical resonance. Generalization to larger conjugated molecules, as well as compounds investigated by the experimental nodes of the ATTO-CM network (see, e.g., Figure 1), is ongoing.

Unveiling target-specific information in HHG spectra: Attochirp removal

In order to properly identify dynamic signals related to charge migration from high-harmonic spectroscopies, it is necessary to accurately characterize and remove the contributions of additional effects from the measurements. With the RABBITT (Reconstruction of Attosecond Beating By Interfering Two-photon Transitions) [Paul 2001] approach perhaps the most significant contribution is the “attochirp,” which results from the dispersion of the different electron trajectories. Since the different trajectories result in emission of XUV photons of different energies, the emission time is encoded in the phase of the outgoing harmonics, and extends to a significant fraction of the period of the driving field, on the order of femtoseconds. Accordingly, this is a major source of background when attempting to isolate attosecond-scale deviations due to the dynamics of interest. The theoretical treatment by Lewenstein [Lewenstein

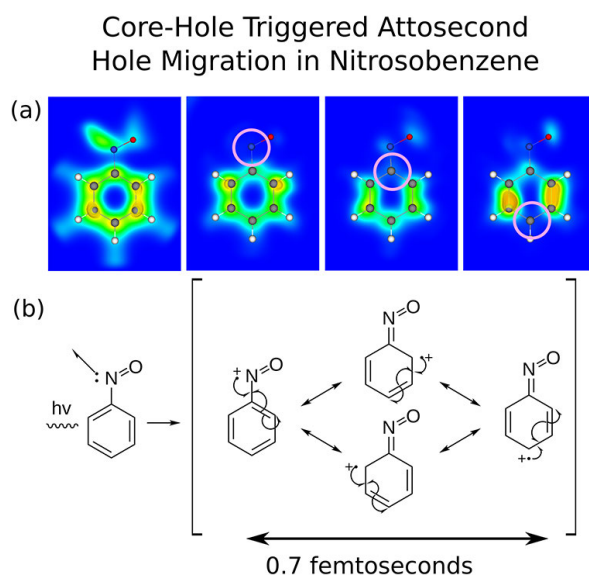


Figure 7: (a) Time-dependent electron localization function snapshots of valence electron-hole migration following ionization from the nitrogen 1s orbital. (b) The dynamics can be interpreted “chemically” as a superposition of Lewis dot resonance states [Bruner 2017].

1994], which relies on neglecting the electric potential of the ion, has historically been employed to estimate the attochirp. Its *experimental validation* has been scarce, and limited to simple atoms. Its applicability to molecular systems has not been previously investigated.

Using their RABBITT apparatus, the OSU node has performed the most complete tests of the SFA to date, and the first validation of the model in a molecular system. An example of an experimental intensity scan in CH_3Cl can be seen in Figure 8. Accurate characterization of the attochirp has multiple benefits: the removal of the femtosecond-scale group delay which can obscure smaller-scale dynamics, accurate measurement of the laser intensity (which comes from the only free parameter of the model's fit to the data), and extension of the atomic SFA model to small molecular systems. Measurements have been performed to validate the approach in CH_4 and CH_3Cl molecules of the CH_3X family (see below), which are of broad interest to the network (see, e.g., ionization studies by UVa and LSU discussed above). Cross-training between the two experimental nodes working with these targets has occurred during exchange visits to the OSU during winter 2016/17 and to UVa in spring 2017.

Validation of a common atomic approach for removing the attochirp is obtained by fitting a constrained set of calculations to multiple data sets with a single free parameter, the laser intensity. The development of the fitting algorithm is the result of a joint effort between the OSU and LSU, during an exchange visit to the OSU (winter 2016/17). An efficient version of the SFA attochirp code developed by LSU has been integrated into the OSU data processing routine and now allows for fully automated real-time analysis of their measurements. Besides a refined reconstruction of the experimental laser intensity, the precision of the fit is essential in removing as much of the attochirp as possible and fully revealing the signal specific to the target under investigation, as discussed in the following subsection.

High-harmonic spectroscopy in the CH_3X family: Molecular Cooper Minimum in Chloromethane

By comparing CH_3Cl to CH_4 , the OSU team was able to measure a group delay structure, which they

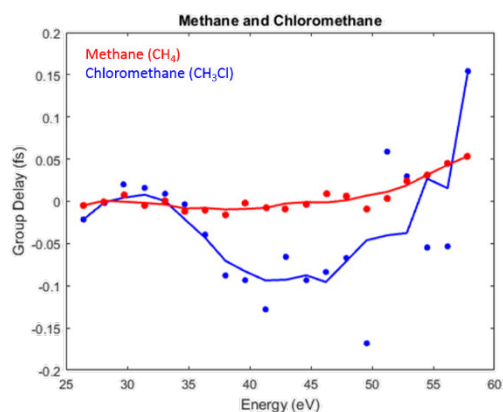


Figure 9: RABBITT measurement from the OSU of unaligned CH_4 (red) and CH_3Cl (blue), where the SFA attochirp has been removed (see text). A ~ 100 fs “dip” in the CH_3Cl data around 45 eV corresponds to a Cooper minimum, similar to the case of atomic argon.

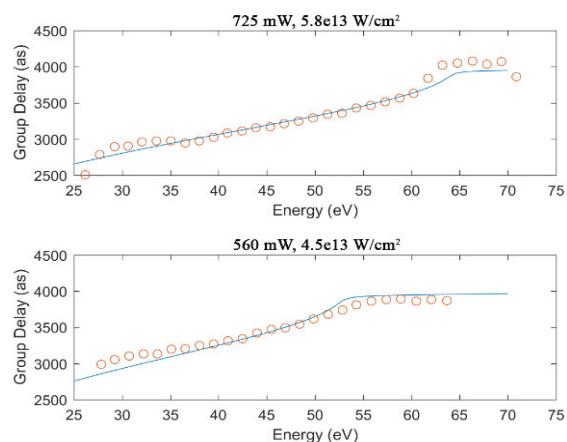


Figure 8: Illustration of the attochirp removal in RABBITT measurements of CH_3Cl for various intensities (see panel title) of a $1.7 \mu\text{m}$ laser. Red circles correspond to measured group delays and the continuous curve to the generic attochirp, as predicted by the Lewenstein model [Lewenstein 1994].

identify as interference in the continuum between outgoing electronic wave functions known as a Cooper minimum (CM) [Cooper 1962]. Figure 9 shows the measured flat phase (after removal of the SFA attochirp as described above) in CH_4 (red curve) as compared to CH_3Cl (blue curve) which has a pronounced dip around 45 eV. This dip, similar to that reported previously due to a CM in argon [Schoun 2014], corresponds to a group delay difference of ~ 100 fs over the CM. Because the highest occupied molecular orbital of CH_3Cl is predominantly of atomic chlorine character, the C-Cl bond serves to fill the chlorine p-orbital, mimicking the case of atomic argon. As such, it is expected that the response should qualitatively match that of argon. While Cooper minima have been observed before in molecules through high harmonic spectra, the group delay structure of a molecular Cooper minimum has never been previously reported.

With the extraction of the target-specific signals and their comparison for two members of the CH_3X family,

Figure 9 shows a clear perspective of the use of HHG as a powerful spectroscopic tool.

Spectroscopy

Last but not least, the spectroscopy component of the tasks illustrated in Figure 1 specifically focuses on the target- and electronic structure-specific signatures in experimentally measurable signals and their evolution on attosecond to femtosecond times. It naturally builds upon our abilities to model, analyze, and identify interesting charge migration dynamics discussed in the previous section.

Phase Characterization of Aligned Molecules

As discussed in the ionization section above, the spatial orientation of the molecular target with respect to the laser field is a control knob for charge migration dynamics. As such, it is also a parameter through which it can be analyzed. Therefore, one of the central tasks of the ATTO-CM collaboration is performing angle-resolved HHS on molecules. An illustration of this is shown in Figure 10 with aligned and anti-aligned RABBITT scans of OCS measured at OSU. Figure 10 (a) shows the response of the harmonic yield as the pump-probe delay is scanned through the rotational half-revival, corresponding to measurements at different angles between aligned and anti-aligned configurations of the OCS molecule, relative to the drive laser polarization. Figure 10 (b) shows the associated RABBITT group delay scans of harmonics generated in aligned (black) and anti-aligned (red) OCS. In the absence of a common reference, each set of data is measured up to an (unknown) constant and the displayed data have been arbitrarily normalized at 25 eV (near where we expect them to match). Practical avenues for defining such a reference within the current OSU experimental setup have been discussed between the ATTO-CM partners (during the exchange visit to UVA in spring 2017 and subsequent Skype meetings). Application of possible approaches, along with further expansion on the preliminary results shown in Fig. 10 (b), are ongoing. Irrespective of what the common reference is, Figure 10 (b) shows a clear difference between observed group delays for aligned and anti-aligned samples. This establishes angle-resolved RABBITT as a spectroscopic tool to probe the target electronic structure (note in the figure how the two alignment angles “see” different orbital structures).

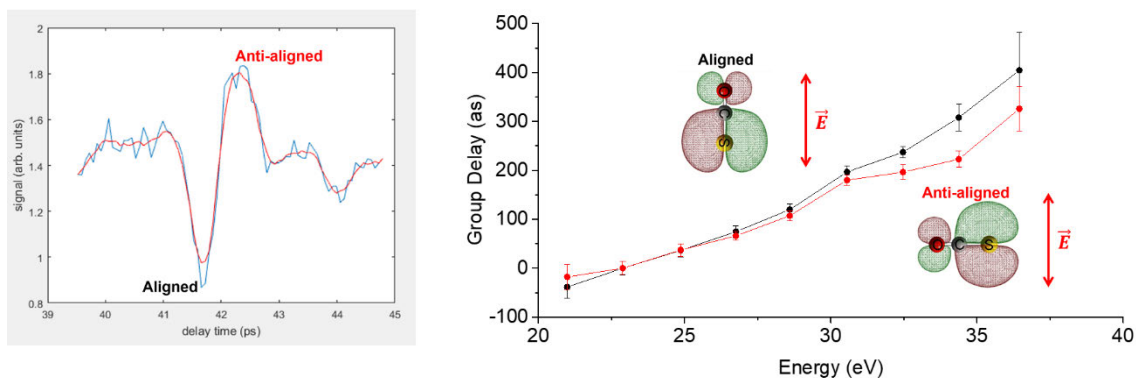


Figure 10: a) Variation of the HHG signal going through a half-period revival structure, i.e., scanning through different angles between aligned and anti-aligned orientation of the molecule. b) Associated RABBITT measurements of aligned and anti-aligned molecules. Both panels correspond to OCS.

Probing atomic potentials with near threshold attosecond photoelectrons

Building on several years collaboration, the UVA and OSU teams have been exploring the use of near threshold photo-electrons as time-resolved probes of the effective binding potential through which those electrons escape. The UVA participation in this project was initially supported by Prof. Jones' individual PI grant (DE-FG02-00ER15053). Because the work is relevant to the exploration of attosecond and femtosecond electron dynamics and strengthens the connection between the UVA and OSU groups, UVA's continued participation was supported by this collaborative grant during a one-year period when the original support was on a one-year no-cost extension and insufficient funds were available.

In the experiments performed at OSU, attosecond pulse trains are used to photoionize noble gas atoms near threshold in the presence of a moderately intense, infrared dressing laser. As in the standard RABBITT technique, the phase of interference modulations in photoelectron sidebands as a function of

the delay between the dressing laser and the attosecond pulse train is measured. Another dimension is added to the measurement by considering the information that can be extracted from the sideband amplitudes, in addition to the phase of the interference modulations. By comparing the amplitudes and phases of the low-energy sidebands for Ar, Ne, and He we can extract time-resolved information regarding the average depth and gradient of the He^+ and Ne^+ effective binding potentials experienced by the photoelectrons during the first 1 fs or so following their birth. The analysis of the measurements and the interpretation of the results were finalized over the past year. We find qualitative agreement between the RABBITT+ measurements and previous theoretical results from members of the LSU team [Mauritsson 2005]. In principle, a variant of these measurements might provide a time-resolved view of changes in an atomic/molecular potential due to an external stimulus. A manuscript describing this collaborative work was recently accepted for publication in Nature Physics [Kiesewetter 2017].

Spectroscopy of intermediate excited states

As mentioned in the previous subsection, while RABBITT typically focuses on relative phases within HHG spectra, additional relevant information can also be contained in the harmonic. With this perspective, LSU has investigated signatures of multi-electron dynamics in a one-dimensional, two-active-electron (TAE) model which we designate A_2 , by solving the full TDSE. We identify the role of rescattering by the first ionized electron in the HHG process by comparing the TAE model with commonly used single-active-electron (SAE) model. As seen in Figure 11, the HHG spectrum from the TAE model (red curve) has two noticeable cutoffs: (1) a primary cutoff that closely matches the SAE model (blue curve) and (2) a secondary cutoff due to the A_2^+ cation, extending beyond the SAE model. Compared to HHG initialized from the cation (green curve) without any recollision effects, we find the HHG yield in the secondary cutoff is enhanced by several orders of magnitude for the TAE model. This enhancement in the HHG can be explained by excitation in the cation resulting from energy exchange between the two electrons during recollision. Particularly at low intensities, effects related to non-sequential double ionization are expected to become important. We are currently studying different properties of the recollision-enhanced HHG such as its efficiency with respect to the driving wavelength. A manuscript detailing these findings is currently in preparation [Abanador 2017-b].

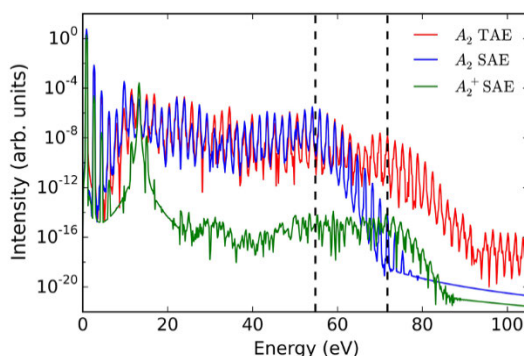


Figure 11: HHG spectra generated from the A_2 TAE (red) and SAE (blue) molecule and from its corresponding cation A_2^+ (green). Here the driving laser field has a peak intensity of $5 \times 10^{13} \text{ W/cm}^2$ and a wavelength of 1400 nm. The vertical dashed lines correspond to the primary and secondary cutoffs, which are extracted from SAE calculations for A_2 and A_2^+ , respectively.

Cross-training and interactions between the partners

In order to develop and maintain the symbiotic relationship between theory and experiment mentioned in the Project Scope and illustrated throughout the present abstract, the ATTO-CM partners have used a variety of communication channels:

- Monthly Skype meetings between all partners to discuss recent progress, results, setbacks, and future plans. Additional, and frequent, internode emails, phone and Skype communications also take place between smaller working groups that target specific tasks on an as-needed basis.
- An intranet website (with content access restricted to members of the ATTO-CM network) has been set up to facilitate sharing of information (wiki section), papers, information, and meeting notes of common interest. The site is also attached to a cloud storage site for sharing data between partners and is used as a common backup/archive.
- Extended visits between the partners: 1 week at LSU in fall 2016, 3 weeks at the OSU in the winter 2016/17, and 1 week at UVa in spring 2017. For each visit, all nodes were represented in an effort to maximize coordination and information sharing between them. These visits have been great opportunities for cross-training:

- Between the two experimental nodes, on each-other's setups, related to alignment/orientation studies (of interest to both the OSU and UVa), the RABBITT apparatus (at the OSU) and ionization studies (UVa).
- Of the experimental nodes on theoretical and numerical methods and capabilities from LSU.
- Of the theoretical node with the basics of the OSU and UVa experimental setups, the resolution of measurements and how raw data are processed to reveal meaningful physical information (for example, the integration of attochirp calculations into real-time data analysis).

These active exchanges have resulted in building a strong collaborative community among the PIs, students and postdocs. Results of the collaboration were showcased in numerous international conferences. These conferences also provided additional opportunities for in-person discussions/interactions when more than one node was present (DAMOP 2017, Erice Attosecond School).

Future Plans

Specifics for future plans have been laid out throughout the abstract, above. Here we focus on defining the main avenues we intend to pursue to advance our chances of observing charge migration with strong laser fields. First of all, we believe that the continued interactions and cross-training between the three nodes of the ATTO-CM network is a cornerstone to our success. We fully intend to continue our current interactions, *i.e.*, with regular communication (Skype, phone, emails) and exchange visits between the nodes. Building upon our Recent Progress, for each main task (Figure 1) we intend to focus our efforts as follows:

- Orientation and Ionization: Both UVa and the OSU aim to routinely achieve alignment of families of molecular targets identified as being of interest. UVa aims to initiate demonstration of experimental orientation and comparison of THz schemes with standard two-color impulsive alignment [De 2009, Znakovskaya 2014]. Compared to simple alignment, oriented samples will provide discrimination between target head vs. tail contributions to the signal. In conjunction with UVa measurements, LSU will continue their efforts to benchmark TDDFT calculations and develop algorithms to recover the cation channel-specific ionization information required in their semiclassical HHS model. Building on their expertise in ionization studies, UVa plans to initiate an effort to develop a sub-3fs UV source as an alternative to strong field ionization for triggering charge migration dynamics.
- Charge migration: LSU will continue their efforts refining their algorithms to identify, analyze, and separate charge migration modes in the electronic dynamics following ionization. They will use it to scan through families of molecular targets to guide experimental runs at OSU and UVa. This will double as an infrastructure for identifying generic chemical properties that mediate the charge migration (type of bounds, functional groups, etc.).
- Spectroscopy: LSU aims at obtaining and/or developing the tools to determine all the molecular parameters required for their semiclassical HHS model, and perform direct comparison with the OSU measurements (and possibly adapt them to UVa ionization investigations, upon relevance). The OSU aims at routinely achieve angle-resolved, target-specific (attochirp removal & well defined absolute reference, see above) HHS. In selected molecular families, they aim at sufficient signal resolution to quantitatively compare the different members of the family. In recorded signals, they aim at discriminating between static (due to a specific electronic configuration, eventually dressed by the laser) and dynamics (the actual charge migration we are interested in) contributions.

References

- [Cooper 1962] J. W. Cooper, "Photoionization from Outer Atomic Subshells. A Model Study," *Phys. Rev.* 128, 681 (1962).
- [Corkum 1993] P. B. Corkum, "Plasma perspective on strong field multiphoton ionization", *Phys. Rev. Lett.* 71, 1994 (1993).
- [De 2009] S. De et al., "Field-Free Orientation of CO Molecules by Femtosecond Two-Color Laser Fields," *Phys. Rev. Lett.* 103, 153002 (2009).
- [Egodapitiya 2014] K. Egodapitiya et al., "THz Induced Field-Free Orientation of Rotationally Excited Molecules," *Phys. Rev. Lett.* 112, 103002 (2014).

- [Fleischer 2011] S. Fleischer et al., "Molecular Orientation and Alignment by Intense Single-Cycle THz Pulses," *Phys. Rev. Lett.* 107, 163603 (2011).
- [Hankin 2001] S. M. Hankin et al., "Intense-field laser ionization rates in atoms and molecules," *Phys. Rev. A* 64, 013405 (2001).
- [Hansen 2012] J.L. Hansen et al., "Orientation-dependent ionization yields from strong-field ionization of fixed-in-space linear and asymmetric top molecules," *J. Phys. B* 45, 015101 (2012).
- [Kitano 2013] K. Kitano et al., "Orientation of jet-cooled polar molecules with an intense single-cycle THz pulse," *Phys. Rev. A* 88, 061405(R), (2013).
- [Kraus 2015] P. M. Kraus et al., "Measurement and laser control of attosecond charge migration in ionized iodoacetylene" *Science* 350, 790 (2015).
- [Kuleff 2016] A. I. Kuleff et al., "Core Ionization Initiates Subfemtosecond Charge Migration in the Valence Shell of Molecules," *Phys. Rev. Lett.* 117, 093002 (2016).
- [Kumarappan 2015] V. Kumarappan et al., "Fully angle-resolved strong-field ionization and dissociation of ethylene from rotational wavepacket dynamics," *Bulletin of the American Physical Society, DAMOP* 2015.
- [Lewenstein 1994] M. Lewenstein et al., "Theory of high-harmonic generation by low-frequency laser fields", *Phys. Rev. A* 49, 2117 (1994).
- [Machholm 2001] M. Machholm et al., "Field-Free Orientation of Molecules," *Phys. Rev. Lett.* 87, 193001 (2001).
- [Mauritsson 2005] J. Mauritsson et al., "Accessing properties of electron wave packets generated by attosecond pulse trains through time-dependent calculations," *Phys. Rev. A* 72, 013401 (2005).
- [Paul 2001] P.M. Paul et al., "Observation of a Train of Attosecond Pulses from High Harmonic Generation," *Science* 292, 1689 (2001).
- [Schafer 1993] K. J. Schafer et al., "Above threshold ionization beyond the high harmonic cutoff", *Phys. Rev. Lett.* 70, 1599 (1993).
- [Schoun 2014] S. B. Schoun et al., "Attosecond Pulse Shaping around a Cooper Minimum," *Phys. Rev. Lett.* 112, 153001 (2014).
- [Znakovskaya 2014] I. Znakovskaya et al., "Transition between Mechanisms of Laser-Induced Field-Free Molecular Orientation," *Phys. Rev. Lett.* 112, 113005 (2014).

Peer-Reviewed Publications Resulting from this Project (2015-2017)

- [Abanador 2017-a] P.M. Abanador et al., "Semiclassical modeling of high-order harmonic generation driven by an elliptically polarized laser field: the role of recolliding periodic orbits" *J. Phys. B* 50, 035601 (2017)
- [Bruner 2017] A. Bruner et al., "Attosecond Charge Migration with TDDFT: Accurate Dynamics from a Well-Defined Initial State" *J. Phys. Chem. Lett.* 8, 3991 (2017).
- [Geneaux 2017] R. Geneaux et al., "Radial index of Laguerre-Gaussian modes in high-order harmonic generation", *Phys. Rev. A* 95, 051801 (2017).
- [Kiesewetter 2017] D. Kiesewetter et al., "Probing Electronic Binding Potentials with Attosecond Photoelectron Wavepackets," *Nat. Phys.* (accepted for publication).
- [Li 2016] S. Li et al., "High-Energy Electron Emission from Metallic Nano-tips Driven by Intense Single-Cycle Terahertz Pulses," *Nat. Comm.* 7, 13405 (2016).
- [Mauger 2016] F. Mauger et al., "Semiclassical-wave-function perspective on high-harmonic generation" *Phys. Rev. A* 93, 043815 (2016)
- [Sissay 2016] A. Sissay et al., "Angle-dependent strong-field molecular ionization rates with tuned range-separated time-dependent density functional theory", *J. Chem. Phys.* 145, 094105 (2016).

Manuscripts in preparation

- [Abanador 2017-b] P.M. Abanador et al., "Wavelength and intensity dependence of recollision-enhanced multielectron effects in high-harmonic generation". (*cf.* Fig 11)
- [Mauger 2017] F. Mauger et al., "Signature of charge migration in modulation of double ionization". (*see* Fig. 5)
- [Sándor 2017] P. Sándor et al., "Angular-dependence of Strong-field Single and Double Ionization of OCS". (*see* Fig. 3)
- [Scarborough 2017] T. Scarborough et al., "Full characterization of a molecular Cooper minimum through high harmonic spectroscopy". (*see* Fig. 9)

Project Title: Strong Field Control in Complex Systems

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1. Project Scope:

The thrust of our AMOS-supported research was initially the problem of strong-field alignment in complex systems. Over the years, this research was generalized to strong field control, including alignment, three-dimensional alignment, torsional control and molecular focusing in moderately intense laser fields (by “moderately intense” I intend nonperturbative but below off-resonance ionization threshold). A second, related theme that was added to our AMOS-supported research was the physics, theory and potential applications of high harmonic generation from aligned molecules. This second thrust was motivated by the intense interest of the AMOS Program in attosecond science and rescattering electrons physics, and has been carried out in collaboration with AMOS experimentalists colleagues.

During the past year, we focused mostly on the problem of strong field control in complex systems. We completed all the research proposed in my last renewal application in this area and accomplished two related projects that were not planned at the time of submitting my proposal, as discussed below. In the area of HHG we focused on the development of improved numerical approach for calculation of the electronic dynamics which will be extensible to large molecules.

2. Recent Progress:

2.1 Laser-Controlled Torsions: Four-Dimensional Theory and the Validity of Reduced Dimensionality Models

A multitude of possible applications along with unique coherence, chirality, and symmetry properties makes the control of molecular torsion with moderately strong, nonresonant laser pulses a fascinating subject. A description of combined rotation and torsion requires at least four angular degrees of freedom, which is challenging for the majority of systems. Lower-dimensional models have been proposed but also questioned. In a recent publication, we develop a four-dimensional model for the coupled rotational-torsional motions of molecules consisting of two identical moieties. By comparing four-dimensional calculations with a two-dimensional model, we define conditions under which the lower-dimensional model is valid. In particular, we point to the crucial role of coordinate dependence of the polarizability tensor. Our results do not agree with those of previous four-dimensional calculations but support the conclusions of recent experiments. An article was published in Phys. Rev. Lett.

2.2 Alignment Thresholds of Molecules

In a recent letter we illustrate and explore the physical origin of a previously unexplored phenomenon in the adiabatic alignment dynamics of molecules, which is fundamentally

interesting and has an important practical implication. Namely, the intensity dependence of the degree of adiabatic alignment exhibits a threshold behavior, below which molecules are isotropically distributed rotationally and above which the alignment rapidly reaches a plateau. Furthermore, we show that both the intensity and the temperature dependencies of the alignment of all linear molecules exhibit universal curves and derive analytical forms to describe these dependencies. Finally, we illustrate that the alignment threshold occurs very generally at a lower intensity than the off-resonance ionization threshold, a numerical observation that is readily explained. This finding illustrates the generality of nonresonant alignment.

The threshold behavior is attributed to a tunneling mechanism that rapidly switches off at the threshold intensity, where tunneling between the potential wells corresponding to the two orientations of the aligned molecules becomes forbidden.

2.3 Laser-Driven, Surface-Mounted Unidirectional Rotor

Related to strong-field molecular alignment, both in underlying concepts and in theoretical considerations, is the problem of molecular rotors. Making a subtopic of the theme of molecular machines, the surface-mounted, unidirectional rotor is also a timely problem. In recent work we proposed a design for a class of molecular rotors fixed to a semiconductor surface, induced by a moderately intense, linearly polarized laser pulse. The rotor consists of an organic molecule possessing a polarizable headgroup that is attached via a linear component to the surface. The polarization direction in parallel to the surface plane is determined so as to maximize the torque experienced by the molecular headgroup and, hence, the duration of the ensuing rotation, while also controlling the sense of rotation. We find that the molecule continues to rotate for many rotational periods after the laser pulse turns off, before multiple scattering by the potential barrier results in dephasing. An article was published in *J. Phys. Chem. C*.

2.4 Dynamics from Noisy Data with Extreme Timing Uncertainty

Imperfect knowledge of the times at which snapshots of a system are recorded degrades our ability to recover dynamical information, and can scramble the sequence of events. In X-ray free-electron lasers, for example, the uncertainty—the so-called timing jitter—between the arrival of an optical trigger (pump) pulse and a probing X-ray pulse can exceed the length of the X-ray pulse by up to two orders of magnitude, marring the otherwise precise time-resolution capabilities of this class of instruments. In collaboration with AMOS colleagues Abbas Ourmazd and his group, we combined laser alignment with an analytical approach developed by the Ourmazd group to introduce an that can recover the history and dynamics of a system from a dense collection of noisy snapshots spanning a sufficiently large multiple of the timing uncertainty. The power of the algorithm was demonstrated by extracting the underlying dynamics on the few-femtosecond timescale from noisy experimental X-ray free-electron laser data recorded with 300-femtosecond timing uncertainty. Using a noisy dataset from a pump-probe experiment on the Coulomb explosion of nitrogen molecules, our analysis revealed vibrational wave-packets consisting of components with periods as short as 15 femtoseconds, as well as more rapid changes. This approach can potentially be applied whenever dynamical or historical information is tainted by timing uncertainty. An article was published in *Nature*

2.5 Alignment and Orientation of Semiconductor Nanorods with a Combination of Static and Laser Fields

Colloidal nanoparticles are the subject of extensive research, motivated by their utility in fabrication of a wide range of new materials and devices, from optoelectronics and photovoltaics to medicinal diagnostic and therapeutic tools. All the electric, magnetic and optical properties of these particles depend on their order in space. In a recent publication we present the results of molecular dynamics simulations of semiconductor nanorods aligning and orienting under the combined influence of static electric and laser fields. The transformation of the isotropic ensemble into an orientationally ordered assembly, is a slow (microseconds) process, but in sharp contrast to previously oriented systems yields high levels of both alignment and orientation at elevated temperatures (300 K) and rather low fields (1.4 GWcm^{-2} laser intensity and $2\text{--}4 \text{ V}\mu\text{m}^{-1}$ static field amplitude). The resulting long range orientational order could assist several of the application of the nanorods assembly.

3. Future Planes

3.1 Alignment and Orientation in an Ion Trap

Here I am motivated in part by the rapidly growing experimental interest in cold molecules and cold molecular collisions, in part by new physical effects expected in the low temperature limit and in part by the potential application of well prepared quantum states to sensor technology due to their high sensitivity to small environmental changes. Further, the possibility to measure the time-dependent signal in traps to long times (ns or even μs) suggests the possibility of combining theory with experiments to determine weak molecular interactions. My objective is to develop a model that will account for the interaction of the molecules with the laser and the trap fields, for the spin-orbit interaction and for the effect of vibrations. Upon completion, this model will serve as a predictive tool for experiments and will assist in designing experiments and choosing the molecule and the laser and trap parameters.

3.2 Extensions and Applications of Torsional Alignment

Two applications of torsional alignment will be interesting to explore. One extends alignment of a single angle to that of many torsional angles. In applications of torsional alignment, such as control of electron transport, energy transfer and dichroism, I expect enhancement in the multiple angles as compared to single torsional angle control. Preliminary calculations support this expectation but quantitative research needs to be done. A second application considers surface absorb molecules that have one or more torsion angles and are subjected to a laser pulse that is linearly polarized in the surface plane and restricts the molecules to the axially chiral configuration. Electrons that are photoejected from the surface and transmitted through the layer are spin selected and their spin can be flipped by changing the polarization direction and hence changing one enantiomer into the other. This work will be carried out in collaboration with an experimental group.

4. Selected Peer-Reviewed Publications Resulting from this Project (2015-2017)

T. Grohmann, M. Leibscher, T. Seideman, Laser-Controlled Torsions: Four-Dimensional Theory and the Validity of Reduced Dimensionality Models, *Physical Review Letters*. 118, 203201 (2017).

X.Y. You, S. Ramakrishna, T. Seideman, Plasmon-Mediated Absorption and Photocurrent Spectra in Sensitized Solar Cells, *ACS Photonics*. 4, 1178-1187 (2017).

J.E. Szekely, F.K. Amankona-Diawuo, T. Seideman, Laser-Driven, Surface-Mounted Unidirectional Rotor. *Journal of Physical Chemistry C*. 120, 21133-21137 (2016).

R. Fung, A. M. Hanna, O. Vendrell, S. Ramakrishna, T. Seideman, R. Santra, A. Ourmazd, Dynamics from noisy data with extreme timing uncertainty, *Nature*. 532, 471-475 (2016).

I.F. Tenney, M. Artamonov, T. Seideman, P.H. Bucksbaum, Collisional decoherence and rotational quasirevivals in asymmetric-top molecules, *Physical Review A*. 93, 013421 (2016).

B. A. Ashwell, S. Ramakrishna, T. Seideman, Strong field coherent control of molecular torsions-Analytical models, *Journal of Chemical Physics*. 143, 064307 (2015).

D.V. Zhdanov, T. Seideman, Wigner representation of the rotational dynamics of rigid tops, *Physical Review A*. 92, 012129 (2015).

M. Artamonov, T. Seideman, Time-Dependent, Optically Controlled Dielectric Function, *Journal of Physical Chemistry Letters*. 6, 320-325 (2015).

DYNAMICS OF FEW-BODY ATOMIC PROCESSES

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PROJECT SCOPE

The goals of this project are to understand, describe, control, and image processes involving energy transfers from intense electromagnetic radiation to matter as well as the time-dependent dynamics of interacting few-body, quantum systems. Investigations of current interest are in the areas of strong field (intense laser) physics, attosecond physics, high energy density physics, and multiphoton ionization processes. Nearly all proposed projects require large-scale numerical computations, involving, e.g., the direct solution of the full-dimensional time-dependent or time-independent Schrödinger equation for two-electron (or multi-electron) systems interacting with electromagnetic radiation. In some cases our studies are supportive of and/or have been stimulated by experimental work carried out by other investigators funded by the DOE AMOS physics program. Principal benefits and outcomes of this research are improved understanding of how to control atomic and molecular processes with electromagnetic radiation and how to transfer energy optimally from electromagnetic radiation to matter.

RECENT PROGRESS

A. Electron Vortices in Photoionization by Circularly-Polarized Attosecond Pulses

Single ionization of He by two oppositely circularly-polarized, time-delayed attosecond pulses was shown to produce photoelectron momentum distributions in the polarization plane having helical vortex structures sensitive to the time-delay between the pulses, their relative phase, and their handedness. The matter-wave vortex patterns we predicted have a counterpart in optics, in which similar vortex patterns have been produced by interference of particular kinds of laser beams. However, such vortices have never before been either observed or predicted by interference of electron matter waves. *We thus have here a dramatic example of wave-particle duality.* Results are obtained by both *ab initio* numerical solution of the two-electron time-dependent Schrödinger equation and by a lowest-order perturbation theory analysis. The energy, bandwidth, and temporal duration of attosecond pulses are ideal for observing these vortex patterns. Our results indicate the exquisite sensitivity of the spiral vortex patterns to both the properties of the two laser pulses and the time-delay between them, thus indicating (i) that this is a new means to control electron motion with laser pulses and (ii) that this process provides a new diagnostic tool for characterizing the laser pulses and for determining the delay between them. (See publication [P1] in the list of project publications below.)

B. Favorable target positions for intense laser acceleration of electrons in hydrogen-like, highly-charged ions

Classical relativistic Monte Carlo simulations of petawatt laser acceleration of electrons bound initially in hydrogen-like, highly-charged ions show that both the angles and energies of the laser-accelerated electrons depend on the initial ion positions with respect to the laser focus. Electrons bound in ions located after the laser focus generally acquire higher (\approx GeV) energies and are

ejected at smaller angles with respect to the laser beam. Our simulations assume a tightly-focused linearly-polarized laser pulse with intensity of $\approx 10^{22}$ W/cm². Up to fifth order corrections to the paraxial approximation of the laser field in the focal region are taken into account. In addition to the laser intensity, the Rayleigh length in the focal region is shown to play a significant role in maximizing the final energy of the accelerated electrons. Results are presented for both Ne⁹⁺ and Ar¹⁷⁺ target ions. (See publication [P2] in the list of project publications below.)

C. Multi-start Spiral Electron Vortices in Ionization by Circularly Polarized UV Pulses

Multi-start spiral vortex patterns have been predicted for the electron momentum distributions in the polarization plane following ionization of the He atom by two time-delayed circularly polarized ultrashort laser pulses. For two ultraviolet (UV) pulses having the same frequency (such that two photons are required for ionization), single-color two-photon interferometry with co-rotating or counter-rotating time-delayed pulses was found to lead respectively to zero-start or four-start spiral vortex patterns in the ionized electron momentum distributions in the polarization plane. In contrast, two-color one-photon plus two-photon interferometry with time-delayed co-rotating or counter-rotating UV pulses was found to lead respectively to one-start or three-start spiral vortex patterns. These predicted multi-start electron vortex patterns were found to be sensitive to the carrier frequencies, handedness, time delay, and relative phase of the two pulses. Our numerical predictions are obtained by solving the six-dimensional two-electron time-dependent Schrödinger equation (TDSE). They are explained analytically using perturbation theory (PT). Comparison of our TDSE and PT results for single-color two-photon processes probes the role played by the time-delay-dependent ionization cross channels in which one photon is absorbed from each pulse. These cross channels can be controlled by means of the parameters of the fields and the ionized electron detection geometries. (See publication [P3] the list of project publications below.)

D. Discontinuities in the electromagnetic fields of vortex beams in the complex source-sink model

Laser beams that carry orbital angular momentum (OAM) provide a novel means of investigation into laser-matter interactions. Multiple nonparaxial analytic representations have been developed to model tightly-focused beams having nonzero OAM. A leading model is the so-called *complex source-sink model* [1] for solving the scalar Helmholtz equation analytically. From that solution, termed the phasor, the laser electric and magnetic fields can be calculated. However, we discovered an analytical discontinuity in what was thought to be the discontinuity-free exact nonparaxial vortex beam phasor obtained within the complex source-sink model [P4]. This discontinuity appears for all odd values of the orbital angular momentum mode. Such discontinuities in the phasor lead to nonphysical discontinuities in the real electromagnetic field components. We identified the source of the discontinuities, and provided both analytic and graphical evidence of the discontinuous real electric fields for the first and third orbital angular momentum modes. We then presented a simple means of avoiding these discontinuities. (See publication [P4] in the list of project publications below.)

E. Kinematical Vortices in Double Photoionization of Helium by Attosecond Pulses

Two-armed helical vortex structures are predicted in the two-electron momentum distributions produced in double photoionization (DPI) of the He atom by a pair of time-delayed elliptically polarized attosecond pulses with opposite helicities. These predictions are based upon both a first-order perturbation theory analysis and numerical solutions of the two-electron, time-dependent

Schrödinger equation in six spatial dimensions. The helical vortex structures originate from Ramsey interference of a pair of ionized two-electron wave packets, each having a total angular momentum of unity, and appear in the six-fold differential DPI probability distribution for any energy partitioning between the two electrons. The vortex structures are exquisitely sensitive to the time delay between the two pulses, their relative phase, their ellipticity, and their handedness; moreover, they occur in a variety of electron detection geometries. However, the vortex structures only occur when the angular separation β between the electron momenta \mathbf{p}_1 and \mathbf{p}_2 is held fixed. The vortex structures can also be observed in the four-fold differential DPI probability distribution obtained by averaging the six-fold differential probability over the emission angles of one electron. Such kinematical vortices are a general phenomenon that may occur in any ionization process, initiated by two time-delayed short pulses with opposite ellipticities, for particular detection geometries. (*See publication [P5] in the list of project publications below.*)

F. Doubly-Excited State Effects on Two-Photon Double Ionization of Helium by Time-Delayed, Oppositely Circularly-Polarized Attosecond Pulses

We have studied two-photon double ionization (TPDI) of helium by a pair of time-delayed (non-overlapping), oppositely circularly-polarized attosecond pulses whose carrier frequencies are resonant with $^1P^o$ doubly-excited states. All of our TPDI results are obtained by numerical solution of the two-electron time-dependent Schrödinger equation for the six-dimensional case of circularly-polarized attosecond pulses, and they are analyzed using perturbation theory (PT). As compared with the corresponding non-resonant TPDI process, we find that the doubly-excited states change the character of vortex patterns in the two-electron momentum distributions for the case of back-to-back (BTB) detection of the two ionized electrons in the polarization plane. The doubly-excited states also completely change the structure of fixed-energy, two-electron angular distributions. Moreover, both the fixed-energy and energy-integrated *angular* distributions, as well as the two-electron *energy* distributions, exhibit a periodicity with time delay τ between the two attosecond pulses of about 69 as, *i.e.*, the beat period between the $(2s2p)^1P^o$ doubly-excited state and the He ground state. Using PT we derive an expression for an angle-integrated *energy* distribution that is sensitive to the slower beat period ~ 1.2 fs between different doubly-excited states as well as to the long timescale ~ 17 fs of autoionization lifetimes. (*See publication [P6] in the list of project publications below.*)

FUTURE PLANS

Our group is currently carrying out research on the following additional projects:

- We are investigating kinematical vortices in double photoionization of the H_2 molecule by a pair of time-delayed, oppositely elliptically polarized attosecond pulses for a variety of experimental configurations. Our initial calculations assume fixed internuclear separations. We are also investigating the possibility of controlling the two-electron angular distributions by means of the time delay between the two pulses.
- We are investigating the use of radially polarized, non-zero Laguerre-Gaussian (LG) radial mode laser pulses for vacuum acceleration of electrons. Currently, the most effective vacuum acceleration schemes for creating electron bunches involve a high power radially polarized Gaussian laser beam (the zero LG radial mode) incident on a diffuse gas target [2]. We calculate the fields for our simulations using the perturbative phasor of Bandres and Gutiérrez-Vega [3].

- We are investigating a number of extensions of our prior harmonic generation work [4, 5] with the aim of understanding the conditions under which a harmonic generation plateau can be produced in the multiphoton regime when doubly (or possibly singly) excited states are on resonance with the driving laser field. These extensions include study of the sensitivity to the initial state, the use of chirped driving laser fields, and the use of elliptically polarized driving laser fields.

REFERENCES

- [1] Z. Ulanowski and I.K. Ludlow, “Scalar field of nonparaxial Gaussian beams,” *Opt. Lett.* **25**, 1792 (2000).
- [2] C. Varin, V. Marceau, P. Hogan-Lamarre, T. Fennel, M. Piché, and T. Brabec, “MeV femtosecond electron pulses from direct-field acceleration in low density atomic gases,” *J. Phys. B* **49**, 024001 (2016).
- [3] M.A. Bandres and J. C. Gutiérrez-Vega, “Higher-order complex source for elegant Laguerre–Gaussian waves,” *Opt. Lett.* **29**, 2213 (2004).
- [4] J.M. Ngoko Djiokap and A.F. Starace, “Evidence of the 2s2p(1P) Doubly Excited State in the Harmonic Generation Spectrum of He,” *Phys. Rev. A* **84**, 013404 (2011).
- [5] J.M. Ngoko Djiokap and A.F. Starace, “Resonant Enhancement of the Harmonic Generation Spectrum of Beryllium,” *Phys. Rev. A* **88**, 053412 (2013).

PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2015 – 2017)

- [P1] J.M. Ngoko Djiokap, S.X. Hu, L.B. Madsen, N.L. Manakov, A.V. Meremianin, and A.F. Starace, “Electron Vortices in Photoionization by Circularly Polarized Attosecond Pulses,” *Phys. Rev. Lett.* **115**, 113004 (2015). *This work was featured on the cover of the 11 September 2015 issue of Physical Review Letters. It is also a Research Highlight in Nature Physics 11, 800 (October 2015) and on the DOE BES web page: <http://science.energy.gov/bes/highlights/2016/bes-2016-09-a/>.*
- [P2] L.-W. Pi, S.X. Hu, and A.F. Starace, “Favorable Target Positions for Intense Laser Acceleration of Electrons in Hydrogen-Like, Highly-Charged Ions,” *Phys. Plasmas* **22**, 093111 (2015).
- [P3] J.M. Ngoko Djiokap, A.V. Meremianin, N.L. Manakov, S.X. Hu, L.B. Madsen, and A.F. Starace, “Multistart Spiral Electron Vortices in Ionization by Circularly Polarized UV Pulses,” *Phys. Rev. A* **94**, 013408 (2016).
- [P4] A. Vikartofsky, L.-W. Pi, and A.F. Starace, “Discontinuities in the Electromagnetic Fields of Vortex Beams in the Complex Source-Sink Model,” *Phys. Rev. A* **95**, 053826 (2017).
- [P5] J.M. Ngoko Djiokap, A.V. Meremianin, N.L. Manakov, S.X. Hu, L.B. Madsen, and A.F. Starace, “Kinematical Vortices in Double Photoionization of Helium by Attosecond Pulses,” *Phys. Rev. A* **96**, 013405 (2017).
- [P6] J.M. Ngoko Djiokap and A.F. Starace, “Doubly-Excited State Effects on Two-Photon Double Ionization of Helium by Time-Delayed, Oppositely Circularly-Polarized Attosecond Pulses,” *J. Optics* (accepted; <https://doi.org/10.1088/2040-8986/aa8fc0>). *This is an invited contribution to a special issue on emerging attosecond technologies.*

FEMTOSECOND AND ATTOSECOND LASER-PULSE ENERGY TRANSFORMATION AND CONCENTRATION IN NANOSTRUCTURED SYSTEMS

DOE Grant No. DE-FG02-01ER15213

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1 Project Scope

The program is aimed at theoretical investigations of a wide range of phenomena induced by ultrafast laser-light excitation of nanostructured or nanosize systems, in particular, metal/semiconductor/dielectric nanocomposites and nanoclusters. Among the primary phenomena are femtosecond and attosecond processes of energy transformation, generation, transfer, and localization on the nanoscale and control of such phenomena.

2 Recent Progress and Publications

The recent progress is illustrated below by selected peer-reviewed articles that we consider most significant. All peer-reviewed publications resulting from this DOE Grant and acknowledging this DOE support during the period of 2015-2017 are: [1-12]. Among these publications, the following articles acknowledging this Grant's major support have been published: [1, 4, 6, 9-11]. The following articles have received, as acknowledged, supplementary support of this grant during the Grant: [2, 3, 5, 7, 8, 12].

2.1 Attosecond nanoscale near-field sampling [5]

The promise of ultrafast light-field-driven electronic nanocircuits has stimulated the development of the new fundamental research field of attosecond nanophysics. An essential prerequisite for advancing this new area is the ability to characterize optical near fields from light interaction with nanostructures, with sub-cycle resolution. In this article [5], we demonstrate attosecond near-field retrieval for a tapered gold nanowire. By comparison of the results to those obtained from noble gas experiments and the corresponding theory, the spectral response of the nanotaper near field arising from laser excitation can be extracted.

Photoemission from solids is one of the most fundamental and long-studied electron phenomena in nature. Related photon–electron interactions form the basis for modern optoelectronics, where light can trigger electron transfer, amplification and emission; vice versa, electron injection and excitation can result in the emission of light. Attosecond nanoscale near-field sampling (ANNS), proposed by us in 2007 has been shown to provide sub-cycle resolution of optical near-field dynamics in nanostructured materials. The ANNS relies on the emission of photoelectrons with high initial momentum by an attosecond extreme ultraviolet (XUV) pulse, and subsequent acceleration of the photoelectrons in the near fields. In this work, we perform ANNS measurements and develop the corresponding theory for a nanotaper at near-infrared (NIR) intensities well below the onset of non-linear effects. Using the gold nanotaper sample geometry, we show that through theoretical analysis of field homogeneity and streaking electron trajectories, a meaningful attosecond characterization of near fields can be performed in spite of the inherent challenges associated with the large emission area.

2.2 Graphene superlattices in strong circularly polarized fields: Chirality, Berry Phase, and attosecond dynamics [10]

Topological properties of quantum-mechanical Hilbert space have had pronounced influence on physics as a whole and condensed matter physics in particular. Nontrivial topological properties of graphene in the reciprocal \mathbf{k} -space are due to the presence of nonzero Berry, which is a geometric counterpart of a magnetic field localized at the Dirac points. In this work, we propose an approach to directly observe the Berry phase without a magnetic field. The idea is to use a superlattice superimposed on graphene to cause electron diffraction (Bragg reflection) in the reciprocal space. This diffraction from the superlattice creates a “which way” quantum-mechanical uncertainty causing interference of the electron wave with itself and making the Berry phase directly visible in discontinuities of the self-referenced electron interferogram, which can be experimentally observed using the time-resolved angle-resolved electron photoemission (TR-ARPES) method.

2.3 Interaction of crystalline topological insulator with an ultrashort laser pulse [11]

We theoretically study the interaction of crystalline topological insulator (CTIs), characterized by surface quadratic gapless bands, with an ultrashort (few-femtosecond) optical pulse. The electron dynamics in such an optical pulse is determined by a strong lattice-momentum dependence of the interband dipole coupling, which is anisotropic and singular at the degeneracy point. The interband mixing induced by the ultrashort pulse results in a finite conduction band population, the distribution of which in the reciprocal space is correlated with the profile of the interband dipole matrix elements and has a high contrast. The number of such high-contrast regions depends on the polarization direction of the optical pulse. The ultrashort pulse also causes an electrical current and a net charge transfer through the system in the direction of the maximum field. These findings open up routes to ultrafast optical-field control of the CTIs and petahertz-band optoelectronics.

2.4 Semimetallization of dielectrics in strong optical fields [9]

At the heart of ever growing demands for faster signal processing is ultrafast charge transport and control by electromagnetic fields in semiconductors. Intense optical fields have opened fascinating avenues for new phenomena and applications in solids. Because the period of optical fields is on the order of a femtosecond, the current switching and its control by an optical field may pave a way to petahertz optoelectronic devices. Lately, a reversible semimetallization in fused silica on a femtosecond time scale by using a few-cycle strong field ($\sim 1 \text{ V/\AA}$) is manifested. The strong Wannier-Stark localization and Zener-type tunneling were expected to drive this ultrafast semimetallization. Wider spread of this technology demands better understanding of whether the strong field behavior is universally similar for different dielectrics. In this publication [9], we develop theory of the universal semimetallization; experimentally, we employ a carrier-envelope-phase stabilized, few-cycle strong optical field to drive the semimetallization in sapphire, calcium fluoride and quartz and to compare this phenomenon and show its remarkable similarity between them. The similarity in response of these materials, despite the distinguishable differences in their physical properties, suggests the universality of the physical picture explained by the localization of Wannier-Stark states. Our results elucidate fundamental limit on optical field-induced processes in solids and may blaze a trail to PHz-rate optoelectronics.

2.5 Graphene in ultrafast and superstrong laser fields [1]

For graphene interacting with a few-fs intense optical pulse, we predict unique and rich behavior dramatically different from three-dimensional solids. Quantum electron dynamics is shown to be coherent but highly nonadiabatic and effectively irreversible due to strong dephasing. This dephasing is due to the absence of the bandgap – graphene is a semimetal. Electron distribution in reciprocal space exhibits hot spots at the Dirac points and oscillations whose period is determined by nonlocality of electron response and whose number is proportional to the field amplitude. The optical pulse causes net charge transfer in the plane of graphene in the direction of the instantaneous field maximum at relatively low fields and in

the opposite direction at high fields. This behavior of graphene is related to peculiarities of the Wannier-Stark states of electrons in strong fields. The phenomena described in this article [1] promise ultrafast optoelectronic applications with petahertz bandwidth.

2.6 Ultrafast field control of symmetry, reciprocity, and reversibility in buckled graphene-like materials [2]

In this article, we theoretically show that buckled two-dimensional graphene-like materials (silicene and germanene) subjected to a femtosecond strong optical pulse can be controlled by the optical field component normal to their plane. In such strong fields, these materials are predicted to exhibit nonreciprocal reflection, optical rectification, and generation of electric currents both parallel and normal to the in-plane field direction. Reversibility of the conduction band population is also field- and carrier-envelope phase controllable. There is a net charge transfer along the material plane that is also dependent on the normal field component. Thus a graphene-like buckled material behaves analogously to a field-effect transistor controlled and driven by the electric field of light with subcycle (femtosecond) speed.

3 Future Plans

We will develop the present success in the optics of ultrastrong and ultrafast fields on the nanoscale. We will extend the existing theory to other systems focusing on modern two-dimensional solids such as graphene, transitional metal dichalcogenides, boron nitride, and topological insulators. We will extend theory to describe photoelectron emission caused by the strong ultrashort pulses and probe attosecond XUV pulses in the two-dimensional materials. Especially, we will theoretically describe ultrafast angular-resolved photoelectron emission spectroscopy (TR-ARPES) from two-dimensional materials and topological insulators. We will pursue topological properties of these solids that can be revealed by TR-ARPES. A case of particular interest to study will be effects of the Bloch band topology, the Berry phase in particular. Finally, we will turn to theory of topological insulators in strong fields and effects of spin-polarized ARPES.

4 Peer-Reviewed Publications Resulting from this Project (2015-2017)

1. H. K. Kelardeh, V. Apalkov, and M. I. Stockman, *Graphene in Ultrafast and Superstrong Laser Fields*, Phys. Rev. B **91**, 0454391-8 (2015).
2. H. K. Kelardeh, V. Apalkov, and M. I. Stockman, *Ultrafast Field Control of Symmetry, Reciprocity, and Reversibility in Buckled Graphene-Like Materials*, Phys. Rev. B **92**, 045413-1-9 (2015).
3. M. I. Stockman, *Quantum Nanoplasmonics*, in *Photonics, Volume II: Scientific Foundations, Technology and Applications*, edited by D. L. Andrews (John Wiley & Sons, Inc., Hoboken, NJ, USA, , 2015), p. 85-132.
4. V. S. Yakovlev, M. I. Stockman, F. Krausz, and P. Baum, *Atomic-Scale Diffractive Imaging of Sub-Cycle Electron Dynamics in Condensed Matter*, Sci. Rep. **5**, 145811-1-13 (2015).
5. B. Förg, J. Schötz, F. Süßmann, M. Förster, M. Krüger, B. Ahn, W. Okell, K. Wintersperger, S. Zherebtsov, A. Guggenmos, V. Pervak, A. Kessel, S. Trushin, A. Azzeer, M. Stockman, D. E. Kim, F. Krausz, P. Hommelhoff, and M. Kling, *Attosecond Nanoscale near-Field Sampling*, Nat. Commun. **7**, 11717-1-7 (2016).
6. Y. Abate, D. Seidlitz, A. Fali, S. Gamage, V. E. Babicheva, V. S. Yakovlev, M. I. Stockman, R. Collazo, D. E. Alden, and N. Dietz, *Nanoscopy of Phase Separation in $In_xGa_{1-x}N$ Alloys*, ACS Appl. Mater. Inter. **8**, 23160–23166 (2016).
7. M. H. Javani and M. I. Stockman, *Real and Imaginary Properties of Epsilon-near-Zero Materials*, Phys. Rev. Lett. **117**, 107404-1-6 (2016).
8. H. K. Kelardeh, V. Apalkov, and M. I. Stockman, *Attosecond Strong-Field Interferometry in Graphene: Chirality, Singularity, and Berry Phase*, Phys. Rev. B **93**, 155434-1-7 (2016).

9. O. Kwon, T. Paasch-Colberg, V. Apalkov, B.-K. Kim, J.-J. Kim, M. I. Stockman, and D. E. Kim, *Semimetallization of Dielectrics in Strong Optical Fields*, *Sci. Rep.* **6**, 21272-1-9 (2016).
10. H. Koochaki Kelardeh, V. Apalkov, and M. I. Stockman, *Graphene Superlattices in Strong Circularly Polarized Fields: Chirality, Berry Phase, and Attosecond Dynamics*, *Phys. Rev. B* **96**, 075409-1-8 (2017).
11. S. A. Oliaei Motlagh, V. Apalkov, and M. I. Stockman, *Interaction of Crystalline Topological Insulator with an Ultrashort Laser Pulse*, *Phys. Rev. B* **95**, 085438-1-8 (2017).
12. J. Schötz, B. Förg, M. Förster, W. A. Okell, M. I. Stockman, F. Krausz, P. Hommelhoff, and M. F. Kling, *Reconstruction of Nanoscale near Fields by Attosecond Streaking*, *IEEE J. Sel. Top. Quant. Elec.* **23**, 8700111 (2017).

Laser-Produced Coherent X-Ray Sources

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Project Scope

A recently developed laser-based ultrashort-pulse-duration x-ray light is being used to investigate ultrafast photo-induced atomic and electronic processes. Two separate light pulses—one optical and one x-ray—are generated by a single high-peak-power laser system at the Extreme Light Laboratory of the University of Nebraska-Lincoln. Near absolute synchronization allows both pulses (10^{-14} s) to be overlapped in space, and in time, with micron resolution. The optical pulse can be focused to a high intensity, corresponding to high electromagnetic field strength and photon density. With atomic-scale temporal and spatial resolution, the x-ray pulse can probe the dynamical evolution of matter under highly non-equilibrium conditions. The research is relevant not only to the Chemical Sciences Division, but several other areas that are also of interest to the Department of Energy, including controlled thermonuclear fusion energy, high-energy-density physics, materials in extreme environments, and non-equilibrium processes. Moreover, since the experimental test facility is small enough to fit in a university laboratory, STEM experimentalists receive training in-house, filling the workforce pipeline in critical research areas.

Recent Progress

To obtain a 5-20-keV x-ray beam suitable for ultrafast diffraction experiment, a 1.5-eV laser pulse was Thomson scattered by 10-30-MeV electron pulse, which was generated by means of laser wakefield acceleration. Optimal conditions to generate high-flux x-ray beam were obtained by optimizing the scattering beam pulse duration. Lastly, the x-ray pulse was used for in a static diffraction experiment.

Laser-driven electron accelerator

Stable and low energy electron pulses were generated by focusing intense laser light onto gas (10% nitrogen and 90% helium) flowing from a 0.4-mm diameter nozzle. As shown in the electron spectrum of Figure 1, the electron beam had energy 10-30 MeV, and a charge of 30 pC/pulse. With 2-J scattering-laser-beam energy, 10^9 x-ray photons in the energy range of 5-20 keV can be generated, which is ideal for x-ray diffraction.

X-ray photon flux optimization

For diffraction, it is critical to have high flux x-ray to obtain sufficient signal-to-noise ratio. While the photon flux of the Thomson source can be increased by increasing the scattering beam intensity, it will eventually cause the x-ray source to operate at nonlinear regime, which needs to be considered when the normalized vector potential $a_0 \geq 1$ (corresponding to a laser intensity of 10^{18} W/cm² for an 800-nm laser). To optimize the x-ray flux the laser pulse duration and thereby the number of undulator periods was adjusted by tuning the grating separation of the scattering-beam compressor, which changed the second-order dispersion of the laser pulse and stretched it in

pulse duration. The on-axis x-ray spectral intensity was measured at 35 fs, 100 fs, 200 fs and 400 fs pulse lengths. The simulation and experimental study showed a scattering-laser-beam pulse duration of 300 fs is the optimal to maintain the narrow x-ray spectrum bandwidth and high x-ray flux per solid angle, as shown in Figure 2. This duration was shown to increase spectral intensity of the scattered x-rays by factor of 4, as compared to 35-fs.

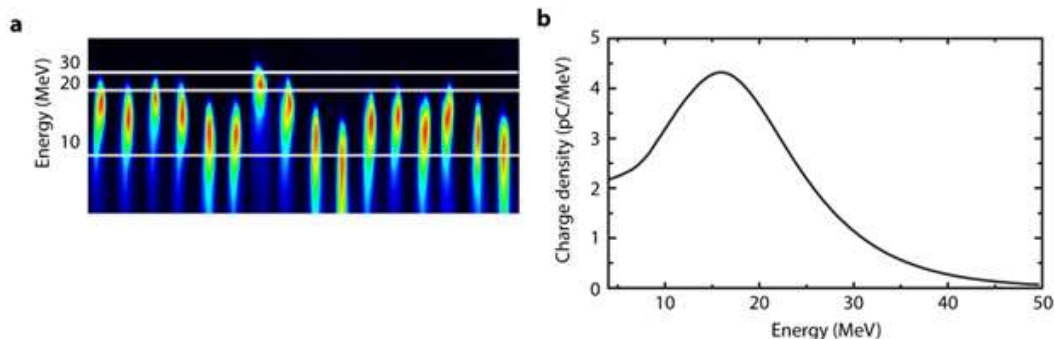


Figure 1. a) A panel of dispersed Lanex images of energy-dispersed electron beams in a series of 16 consecutive shots; b) Line-out spectrum of a typical spectrum of an electron beam. The beams are generated by a 0.4-mm long nozzle, mixed gas (10% nitrogen/90% helium), at 100 PSI backing pressure. The total measured charge is 30 ± 12 pC per shot.

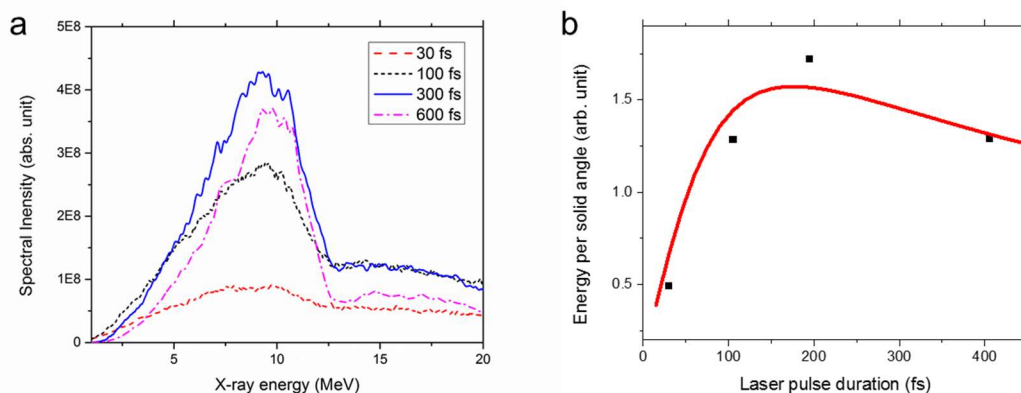


Figure 2. (a) Simulated on-axis x-ray spectral intensity at different laser pulse duration with the same laser energy and the same electron beam parameters. The x-ray spectral intensity is optimized around 200 fs-300 fs. (b) Measured on-axis x-ray energy per solid angle with laser pulse duration.

Static diffraction experiment

The optimized x-rays were used for single-crystal diffraction. The incident x-ray spectrum, measured by means of single-photon-counting, is shown in Figure 3a. A cylindrically bent Ge crystal in Laue transmission geometry was used as a target. Precise measurements of the crystal lattice spacing were performed, demonstrating 2.1-pm resolution with 87 averaged shots (see Figure 3b). A single-shot measurement was also demonstrated with an x-ray beam containing only $\sim 10^5$ photons in a spectral bandwidth of $\sim 50\%$ full-width-at-half-maximum (FWHM), see Figure 3c. Our approach allowed structural information to be obtained with an un-filtered x-ray spectrum. The results were obtained with 60-MeV electron beams and scattering laser beam energy of only 0.1 J.

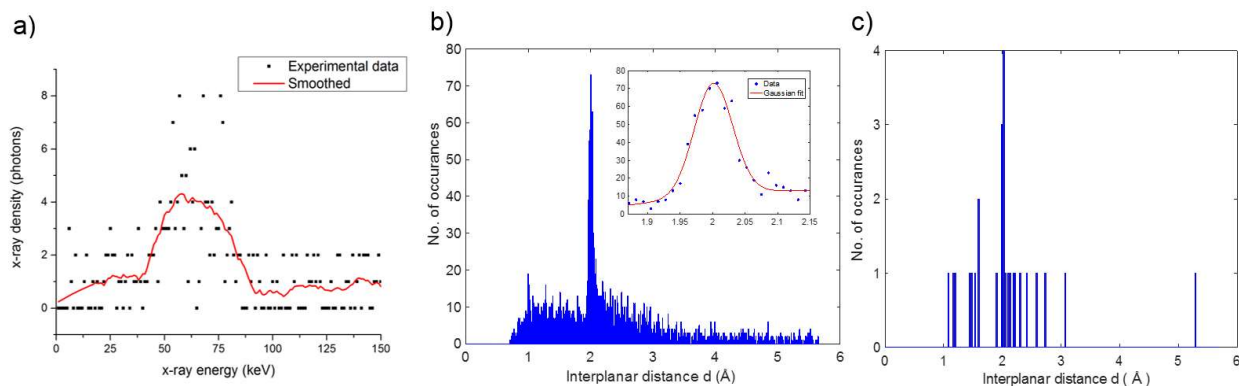


Figure 3. a) Low-energy X-ray spectrum, measured with a single-photon-counting technique. b) Measurement of bent Germanium crystal effective lattice constant, determined from the photon-energy resolved diffraction pattern. Multi-shot (87 accumulated X-ray shots) measurement, lattice constant resolution is 2.1 pm. c) single-shot measurement. The peaks on both b) and c) at $d = 2 \text{ \AA}$ correspond to the lattice spacing of the Ge (220) planes. Figs. b) and c) are from [2].

Future Plans

The above-described experiment constitutes the first step towards using our x-ray source for femtosecond time-resolved measurements of ultrafast atomic dynamics. In the next phase, we plan to lower the x-ray photon energy for static diffraction experiments using Al or Si. Over the longer-term, ultrafast time-resolved studies will be repeated that were previously performed with other types of x-ray sources (K-alpha, storage-ring synchrotron, and laser-wakefield-betatron [1]). One example is Bragg switching via ultrafast non-thermal melting, for which a solid crystalline surface is transformed into a disordered state following excitation with a femtosecond laser pulse. In this case, a crystal of indium antimonide (InSb), where melting will trigger solid-liquid phase transition, will be used for the sample. The transition and criticality due to loss of long-range order will both be measured. Crystal disorder, as a signature of the liquid phase, should manifest itself in a drop of diffracted x-ray signal. This process has been found to have a characteristic duration of 200 fs [1]. Once the technique is benchmarked against measurements with other sources, it will be used with the <10 fs duration x-ray pulses of our Thomson source to study even faster processes.

Peer-reviewed Publications (2015-2017)

1. W. Yan, C. Fruhling, G. Golovin, D. Haden, J. Luo, P. Zhang, B. Zhao, J. Zhang, C. Liu, M. Chen, S. Chen, S. Banerjee, and D. Umstadter, "High-order multiphoton Thomson scattering." *Nature Photonics* **11** 514-520 (2017). doi:10.1038/nphoton.2017.100
2. G. Golovin, S. Banerjee, C. Liu, S. Chen, J. Zhang, B. Zhao, P. Zhang, M. Veale, M. Wilson, P. Seller, and D. Umstadter, "Intrinsic beam emittance of laser-accelerated electrons measured by x-ray spectroscopic imaging," *Sci. Rep.* **6**, 24622 (2016). doi:10.1038/srep24622.
3. G. Golovin, S. Banerjee, S. Chen, N. Powers, C. Liu, W. Yan, J. Zhang, P. Zhang, B. Zhao, and D. Umstadter, "Control and optimization of a staged laser-wakefield accelerator," *Nuclear Instruments and Methods in Physics Research Section A* **830**, 375-380 (2016). doi:10.1016/j.nima.2016.06.022.

4. S. Chen, G. Golovin, C. Miller, D. Haden, S. Banerjee, P. Zhang, C. Liu, J. Zhang, B. Zhao, S. Clarke, S. Pozzi, and D. Umstadter, "Shielded radiography with a laser-driven MeV-energy X-ray source," *Nuclear Instruments and Methods in Physics Research Section B* **366**, 217-223 (2016). doi.org/10.1016/j.nimb.2015.11.007
5. G. Golovin, S. Banerjee, J. Zhang, S. Chen, C. Liu, B. Zhao, J. Mills, K. Brown, C. Petersen, and D. Umstadter, "Tomographic imaging of nonsymmetric multicomponent tailored supersonic flows from structured gas nozzles," *Appl. Opt.* **54**, 3491-3497 (2015). doi.org/10.1364/AO.54.003491
6. G. Golovin, S. Chen, N. Powers, C. Liu, S. Banerjee, J. Zhang, M. Zeng, Z. Sheng, and D. Umstadter, "Tunable monoenergetic electron beams from independently controllable laser-wakefield acceleration and injection," *Phys. Rev. STAB* **18**, 011301 (2015). doi:10.1103/PhysRevSTAB.18.011301.
7. S. Banerjee, S. Chen, N. Powers, D. Haden, C. Liu, G. Golovin, J. Zhang, B. Zhao, S. Clarke, and S. Pozzi, "Compact source of narrowband and tunable X-rays for radiography," *Nuclear Instruments and Methods in Physics Research Section B*: **350**, 106-111 (2015). doi.org/10.1016/j.nimb.2015.01.015
8. D. P. Umstadter, "All-laser-driven Thomson X-ray sources," *Contemporary Physics* **56**, 417-431 (2015). doi.org/10.1080/00107514.2015.1023519.

References

1. C. Rousse, S. Rischel, I. Fourmaux, S. Uschmann, G. Sebban, P. Grillon, E. Balcou, J. Förster, Geindre, and P. Audebert, "Non-thermal melting in semiconductors measured at femtosecond resolution," *Nature* **410**, 65-68 (2001).
2. R. Rakowski, G. Golovin, J. O'Neal, J. Zhang, P. Zhang, B. Zhao, M. Wilson, M. Veale, P. Seller, S. Chen, S. Banerjee, D. Umstadter, and M. Fuchs "Single-shot structural analysis by high-energy X-ray diffraction using an ultrashort all-optical source," *Scientific Reports* (submitted 2017).

Structural Molecular Dynamics Using Ultrafast Gas X-Ray Scattering

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I. Project Scope

Understanding the structures and chemical dynamics of molecules in their excited states is of great importance for basic energy science and myriad applications within and outside of Chemistry and Physics. This project develops two experimental tools and applies them to explore both the *nuclear dynamics*, i.e. the geometrical arrangement of atomic nuclei in molecules, and *electron dynamics*, i.e. the time evolution of electron probability density distributions during chemical reactions. The experimental approach focuses on ultrafast time resolved gas x-ray scattering, which is pursued at the LCLS light source at SLAC National Accelerator Laboratory. The x-ray scattering are supported by complementary time-resolved Rydberg fingerprint spectroscopy, which is conducted at Brown University. Both methods measure the structures of molecules in excited states with a time resolution of <100 fs. Because the experimental methods are complementary, their coordinated application to the same systems provides deeper insights into the molecular dynamics than each technique would give in isolation.

The experiments explore molecular phenomena associated with the nuclear and electron structural dynamics of molecules during reactions. This includes the motions through conical intersections, charge delocalization, the fracture of chemical bonds, vibrational motions and the propagation and spreading of wave packets. Model systems for those investigations include medium-sized organic systems: cyclohexadiene, trimethyl amine, N-methylmorpholine, quadricyclane, N,N-dimethylpiperazine, heterocyclic tetrazoles, and 1,2-dithiane. Those systems were deliberately chosen to broaden the investigations beyond standard prototypes. By focusing on structurally well-defined molecules, the project will advance our knowledge of molecules in excited electronic states and their chemical reaction dynamics. This will aid numerous applications and will also be valuable to the continued development of computational methods.

II. Recent Progress

This project has just started in August 2017. Consequently, none of the projects has reached the level of completion needed for a publication.

Current efforts are directed toward analyzing a data set obtained in a prior beam run at LCLS. In the experiment, the target molecules (N-methyl morpholine, NMM) are intersected by a laser pulse at 400 nm. The ensuing structural motion is probed by scattering the x-rays off the molecules and projecting the scattering pattern onto the CSPAD detector, figure 1.

The intensity of the laser pulse was sufficient to induce an efficient three-photon ionization. The molecular response has two components:

First, the ejection of an electron causes an overall reduction of the scattering intensity. Since only one out of 56 electrons is ejected from the molecule, the effect is small. Nevertheless, it should, in principle, be observable. But because we had no absolute calibration of the scattering signal, the pulse-to-pulse fluctuations in x-ray intensity overwhelmed this small change in absolute scattering intensity. Consequently, this experiment remained insensitive to the ionization.

Secondly, the ionization induces a structural dynamics process because the tertiary amine group of the ion is nearly planar. Starting from the pyramidal ground state structure, the excitation in the Franck-Condon region leads to a point on the potential energy surface that is steeply sloped. Consequently, vibrational motions ensue that oscillate around the equilibrium geometry until dephasing delocalizes the structure.^{1,2} This nuclear dynamics signal was observed with the x-ray scattering experiment.

Figure 2 shows the time-dependent response of the molecular system. Shown is the change in the scattering signal upon ionization, as a function of delay time and scattering vector. The change of the scattering signal is given as a percentage, i.e. $(\text{laser-on signal} - \text{laser-off signal})/(\text{laser-off signal}) \times 100$.

The analysis of the data for figure 2 has proven challenging. A large amount of data had to be corrected for large intensity fluctuations. In addition, we found that the detector distance calibration made at the time of the experiment was insufficient. We were able to devise a novel method of calibrating the detector distance that does not require the measurement of a pattern of a calibration sample. Based on this advance, we now have an accurate detector distance.

As can be seen, our experiment is sensitive to changes in the scattering signal well below 1%. We were able to extract this small change by normalizing the overall intensity in each time slice. This leads to a distortion of the time dependent intensity, but one that can be

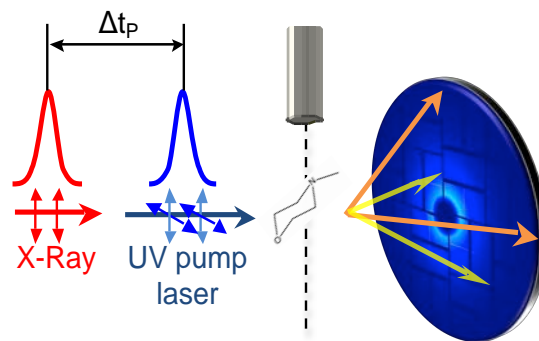


Figure 1: Experimental scheme: The molecules in the interaction region are intercepted by a linearly polarized UV laser (blue) and the x-ray pulse (red). Absorption of the UV pump pulse launches the molecular response. The x-ray probe is variably delayed (Δt_p) with respect to the UV pump pulse to image the time dependent dynamics. Scattering signals are captured by the CSPAD detector.

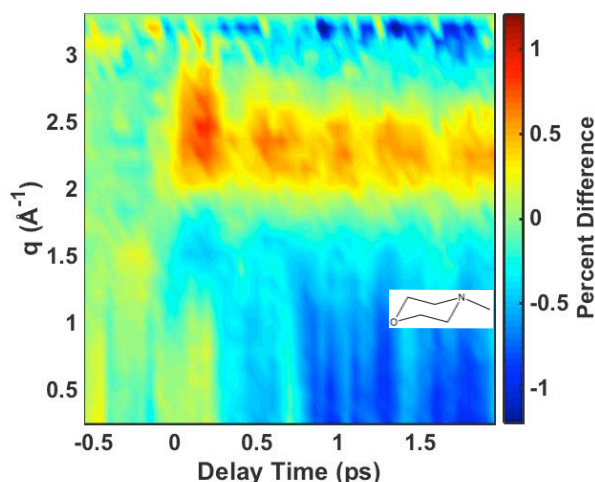


Figure 2: Time resolved percent difference x-ray diffraction pattern of N-methylmorpholine (NMM) after ionization.

reproduced by a simulation with computed data. Thus, we can extract changes in the scattering signal for nuclear motions well below 1%, even though we cannot extract (yet) the overall change arising from a loss of an electron due to ionization.

Excitingly, the time-dependent scattering signals reveal the oscillatory motions of the molecule upon ionization: the oscillations are clearly visible in the contour plot, figure 2.

III. Future Plans

Ongoing work continues to analyze the NMM data set and we anticipate publishing this soon. Going forward, we seek to develop a theoretical algorithm for extracting molecular dynamics from such patterns. While algorithms exist to obtain static molecular structures from scattering patterns, equivalent algorithms for dynamical motions remain elusive.

In October 2017 we will be at SLAC for beam time as part of run 15. Our aim for that run is to achieve an absolute calibration of the scattering signals. This is necessary for us to unmask the effect of electronic excitation, or ionization, which we could not see in our past data sets. An absolute calibration will be attempted by referencing each scattering pattern to a reference pattern (kapton). The reference pattern reveals the total photon flux of the x-ray pulse, and therefore should calibrate the scattering pattern. Our aim is to use this technical innovation to find the signature for electron dynamics processes, i.e. the transition between different electronic configurations in the molecule.

IV. References

“Coherence in Nonradiative Transitions: Internal Conversion in Rydberg-Excited N-Methyl and N-Ethyl Morpholine,” Yao Zhang, Hannes Jónsson, Peter M. Weber, *Physical Chemistry Chemical Physics*, **2017**, DOI: 10.1039/C7CP05244H.

Observation of Structural Wavepacket Motion: The Umbrella Mode in Rydberg-Excited N-Methyl Morpholine,” Yao Zhang, Sanghamitra Deb, Hannes Jónsson, Peter M. Weber, *J. Phys. Chem. Lett.* **2017**, 8, 3740 – 3744, DOI: 10.1021/acs.jpcclett.7b01274.

V. Peer-Reviewed Publications resulting from this Project (Project Start Date: 08/2017)

N/A

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Combining High Level *Ab Initio* Calculations with Laser Control of Molecular Dynamics

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1 Project Scope

We use intense, shaped, ultrafast laser pulses to follow and control molecular dynamics and high level *ab initio* calculations to interpret the dynamics and guide the control.

2 Recent Progress

Our scientific focus over the past year has been on coupled electron-nuclear dynamics and correlated electron dynamics in small organic molecules. Over the past year we have made a number of improvements to our UV/VUV apparatus (improved time resolution and implementation of velocity map imaging for ions). We have also made several new measurements using our UV/VUV pump-probe apparatus, and progress in our measurements of strong field molecular double ionization using coincidence velocity map imaging. We have also carried out a number of calculations in order to interpret the measurements and are working on non-adiabatic nuclear dynamics in polyatomic molecules.

We made three important measurements with the UV/VUV apparatus over the past year. One was of the relaxation of very highly excited pyrrole (excitation at 8eV, probing at 5eV). We wanted to address the question of how internal conversion competes with dissociation when there is a high density of states. Earlier experiments on pyrrole at lower excitation energy (5 eV) showed that dissociation dominated the decay dynamics. However, calculations that we carried out for radical cations with a similar high density of states showed that internal conversion dominated over excited state dissociation. Our measurements and calculations on pyrrole showed that internal conversion to the ground state dominated over excited state dissociation. We are currently following up on this work, aiming to see how this plays out for a number of other highly excited molecules. Furthermore, we would like to test our hypothesis based on calculation that the rate of internal conversion correlates with properties of the excited state that one can calculate at the FC location. This work was published in the Journal of Chemical Physics.

UV pump, VUV probe measurements on cyclohexadiene that we carried out revealed a substantial amount of below threshold ionization from the hot ground state following internal conversion from the photoexcited state. With the aid of electronic structure and FC factor calculations, we were able to interpret the results in terms of vibrationally assisted below threshold ionization, in which vibrational energy is converted to electronic energy for ionization. This is a relatively common process in diatomic molecules, but has not been widely observed in larger polyatomic systems, where it is more difficult to localize vibrational energy and convert it to electronic energy. This work was published in Physical Review A.

This observation of vibrationally assisted below threshold ionization motivated us to think more about the ground state dynamics after passing through a conical intersection. We hypothesize that the ionization occurs from the vibrationally “hot” ground state. Thus we are interested in understanding how the energy is distributed after the molecule passes through a CI. Most of the attention on non-adiabatic dynamics is focused on excited state decay and how fast the CI is reached in order to drive internal conversion to the ground state. However, less is known of the ensuing

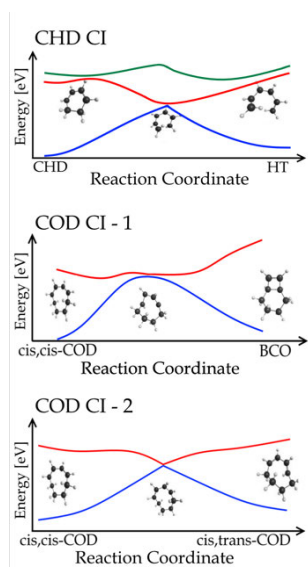


Figure 1: *Potential energy surfaces and relevant CIs for a) 1,3-cyclohexadiene b) cis,cis-1,3-cyclooctadiene that can lead to isomerization to cis-bicyclo[4,2,0]oct-7ene (BCO), and c) cis,cis-1,3-cyclooctadiene that can lead to isomerization to cis,trans-1,3-cyclooctadiene. Calculations were done at the CASSCF level, and the plots were obtained by linear interpolations between reactants-CI-products.*

ground state dynamics following internal conversion by S_1/S_0 CIs. Such dynamics are affected by the topography of the CI which will direct the momentum along the coordinates defining the branching plane. In order to address this point we are performing quantum dynamics calculation using the reaction surface (RS) formalism using a custom made propagation program. The RS formalism entails the definition of two generalized coordinates with the other coordinates treated via normal coordinates. This allows us to sample all the important configurations of cyclohexadiene while also providing a platform on which higher dimensions can be included systematically. In the experiments vibrationally assisted below threshold ionization was observed for cyclohexadiene (CHD) but not for cyclooctadiene (COD), even though conical intersections S_1/S_0 exist in both molecules (see Figure 1). The details of the dynamics are thus crucial for this phenomenon, and our aim is to clarify what may lead to vibrationally assisted below threshold ionization.

In addition to excited state dynamics we have been interested in controlling the motion of the excited state population through different channels. In a collaboration with Regina de Vivie-Riedle, an expert in optimal control theory, we examined whether shaped lasers can be used to control the excited state dynamics in nucleic acid bases. By using a reduced dimensionality surface of uracil and UV light in the form of shaped laser pulses, we showed that it is possible to influence the ultrafast relaxation process after photoexcitation. In our theoretical study, we performed wave packet dynamics of the excitation and relaxation process on a reduced-dimensional potential energy surface. By designing shaped laser pulses with optimal control theory, we were able to achieve two opposite control aims: The relaxation process can be accelerated, as well as delayed significantly through alteration of the excitation laser pulse. The optimized laser pulses are experimentally feasible. This work was highlighted on the cover of the Journal of the American Chemical Society.

Finally, we are currently working on a detailed comparison of strong and weak field probing of excited state dynamics. We consider both internal conversion and dissociation, probed by both weak field VUV ionization, and strong field near IR ionization. The measurements show interesting similarities and differences (see Figure 2).

For the double ionization work, we have recently implemented a Timepix camera, which has a time resolution of 1.6 ns. This allows us to measure electrons and ions with velocity map imaging resolution using a single camera, and without having to perform Abel inversion for the ion yields, since the full 3D momentum is encoded in the space and timing information for each ion hitting the detector. We are currently analyzing measurements of enhanced double ionization of cyclohexadiene

made with the Timepix camera.

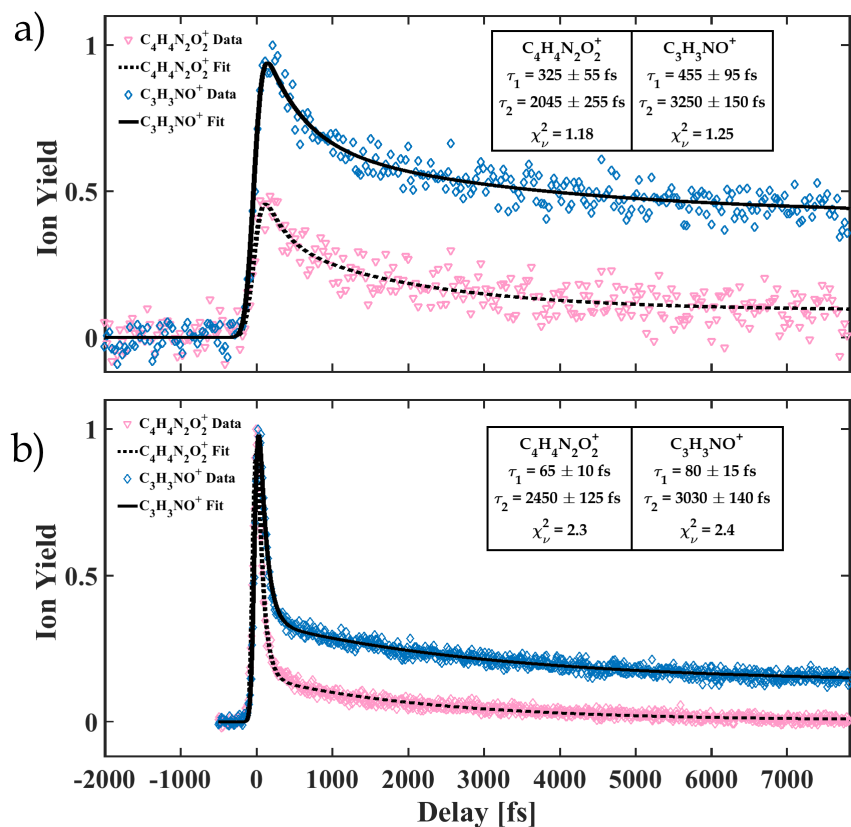


Figure 2: A comparison of weak and strong field probing of internal conversion in uracil. The top panel shows parent and fragment ion yields as well as fits for weak field ionization, while the bottom panel shows the parent and fragment ion yields as well as fits for strong field ionization probing. Note that the ps timescales for weak and strong field probing are comparable for both parent and fragment ion yields.

3 Future Plans

We have several goals for the immediate future:

1. We plan on carrying out UV/VUV experiments with VMI detection of ions and electrons.
2. We plan on interpreting our most recent quadruple coincidence measurements for the molecular double ionization work.
3. We plan on carrying out excited state dynamics calculations in conjugated systems in order to better understand the dynamics observed in the UV/VUV experiments. We will extend our theoretical capabilities to calculate time-resolved photoelectron spectra so that direct comparisons between theory and experiment can be accomplished.

4 Peer-Reviewed Publications Resulting from this Project (2015-2017)

- “Field-dressed orbitals in strong-field molecular ionization”, R. Siemering, O. Njoya, Thomas Weinacht, and Regina de Vivie-Riedle, *Physical Review A*, **92**, 042515, (2015)
- “Photoinduced Phenomena in Nucleic Acids”, Spiridoula Matsika, *Topics in Current Chemistry*, **355**, 209-243, (2015)
- “Photoelectron Spectrum and Dynamics of the Uracil Cation”, Mariana Assmann, Horst Köppel, and Spiridoula Matsika. *Journal of Physical Chemistry A*, **119**, 866, (2015)
- “Surface hopping investigation of the relaxation dynamics in radical cations. ”, Mariana Assmann, Thomas Weinacht, and Spiridoula Matsika. *Journal of Chemical Physics*, **144**, 034301, (2016)

- “Molecular double ionization using strong field few cycle laser pulses”, Arthur Zhao, Peter Sandor, Vincent Tagliamonti, Thomas Weinacht, and Spiridoula Matsika. *Journal of Physical Chemistry A*, **120**, 3233, (2016)
- “Vibrationally Assisted Below-Threshold Ionization”, Spencer Horton, Yusong Liu, Pratip Chakraborty, Spiridoula Matsika, Thomas Weinacht, *Physical Review A* **95**, 063413 (2017)
- “Coincidence velocity map imaging using a single detector” Arthur Zhao, Peter Sándor and Thomas Weinacht *Journal of Chemical Physics* **147**, 013922 (2017)
- “Ultrafast Internal Conversion of Highly Excited Pyrrole Studied with VUV/UV Pump Probe Spectroscopy” Spencer Horton, Yusong Liu, Pratip Chakraborty, Spiridoula Matsika, Thomas Weinacht *Journal of Chemical Physics*, **146**,064306 (2017)
- “Controlling photorelaxation in uracil with shaped laser pulses: A theoretical assessment”, Daniel Keefer, Sebastian Thallmair, Spiridoula Matsika, and Regina de Vivie-Riedle. *Journal of the American Chemical Society*, **139**, 5061, (2017)

**Atomic, Molecular, and Optical Sciences Research PI Meeting (AMOS)
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