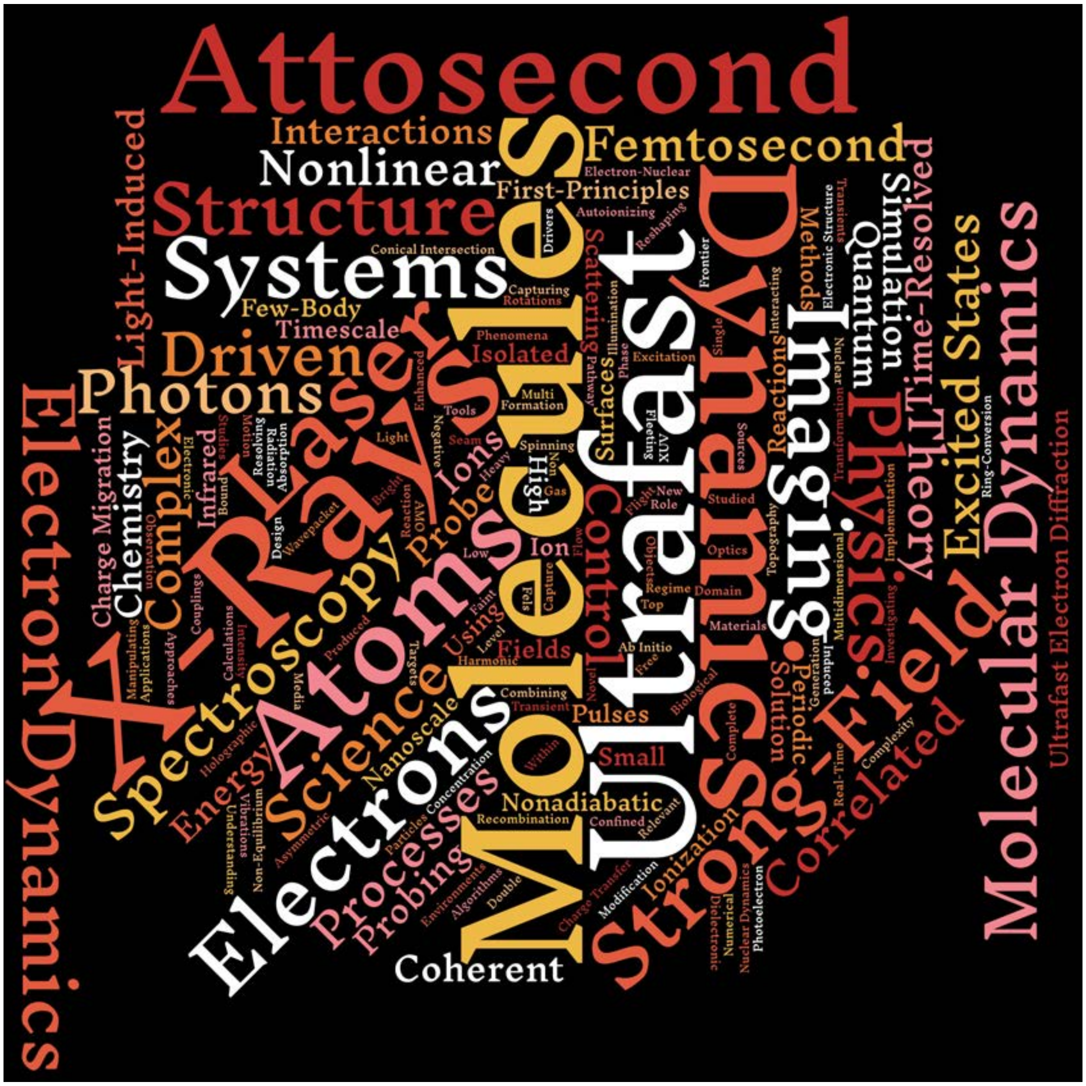
2019
Atomic, Molecular, and Optical Sciences Research PI Meeting



Gaithersburg Marriott Washingtonian Center
Gaithersburg, Maryland
October 28-30, 2019

U.S. DEPARTMENT OF ENERGY
Office of Science

Office of Basic Energy Sciences
Chemical Sciences, Geosciences &
Biosciences Division

Program and Abstracts

2019
Atomic, Molecular, and Optical Sciences Research PI Meeting

Gaithersburg Marriott Washingtonian Center
Gaithersburg, Maryland
October 28–30, 2019

Chemical Sciences, Geosciences, and Biosciences Division
Office of Basic Energy Sciences
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Cover Graphics: The input for the Wordclouds.com cover art is based on the titles of the abstracts for this year's meeting. The font is "Inknut Antiqua."

The research grants and contracts described in this document are supported by the U.S. DOE Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division.

FOREWORD

This volume summarizes the 39th 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 electronic 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 Gwen Johnson and Teresa Crocket in BES for their indispensable behind-the-scenes efforts in support of the BES/AMOS program.

Thomas B. Settersten
Jeffrey L. Krause
Chemical Sciences, Geosciences, and Biosciences Division
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AGENDA

2019 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 28–30, 2019

Monday, October 28

7:30 am	**** Breakfast ****
8:15 am	*BES/CSGB Update and Outlook* **Bruce C. Garrett**, CSGB Division Director
8:45 am	*Welcome and Introductory Remarks* **Thomas B. Settersten**, AMOS Program Manager
Session I	Chair: **Linda Young**, Argonne National Laboratory
9:00 am	*A Deviation from Studies of Autoionizing States Relevant to Dielectronic Recombination* **Thomas F. Gallagher**, University of Virginia
9:30 am	*Negative Ion Formation in Complex Heavy Systems* **Alfred Z. Msezane**, Clark Atlanta University
10:00 am	**** Break ****
10:30 am	*Real-Time Observation of Multi-Electron Processes in Atoms and Diatomic Molecules* **Guillaume M. Laurent**, Auburn University
11:00 am	*First-Principles Simulations of X-ray Probed Attosecond Dynamics* **Kenneth Lopata**, Louisiana State University
11:30 am	*Attosecond Atomic and Molecular Dynamics* **Stephen R. Leone**, Lawrence Berkeley National Laboratory
12:00 pm	**** Working Lunch **** Research Discussions

Monday, October 28 (continued)

Session II **Discussion Session: XFEL and UED Facilities for Ultrafast AMO Science**

1:30 – 3:00 pm Chair: **Artem Rudenko**, Kansas State University

LCLS-II X-ray Free-Electron Laser Facility at SLAC

1:30 pm Current Status and Perspectives
Robert W. Schoenlein, SLAC National Accelerator Laboratory

MeV Ultrafast Electron Diffraction Facility at SLAC

2:00 pm Current Status and Near-term Plans
Xijie Wang, SLAC National Accelerator Laboratory

2:10 pm Opportunities and Challenges for AMOS Experiments
Michael P. Minitti, SLAC National Accelerator Laboratory

Q&A and Open Facilities Discussion

2:30 pm - 3:00 pm

3:00 – 4:30 pm Collaboration Discussions

Session III Chair: **Edward Hohenstein**, SLAC National Accelerator Laboratory

4:30 pm *Structural Molecular Dynamics Using Ultrafast Gas X-Ray Scattering*
Peter M. Weber, Brown University

5:00 pm *Ultrafast Dynamics and Imaging at High X-ray Intensities*
Phay Ho, Argonne National Laboratory

5:30 pm *Non-Periodic Ultrafast X-ray Imaging*
Adi Natan, SLAC National Accelerator Laboratory

6:00 pm **** Working Dinner ****
Research Discussions

7:00 pm Continuation of Research Discussions (No Host, Lobby Lounge)

Tuesday, October 29

7:30 am	**** Breakfast ****
Session IV	Chair: **Jeffrey Moses**, Cornell University
8:30 am	*Molecular Dynamics Imaging from within at the Femto- and Atto-second Timescales Using FELs* **Nora Berrah**, University of Connecticut
9:00 am	*Studies of Atomic X-Ray and Inner-Shell transitions* **Stephen H. Southworth**, Argonne National Laboratory
9:30 am	*Solution-Phase Chemistry* **Kelly J. Gaffney**, SLAC Accelerator National Laboratory
10:00 am	**** Break ****
10:30 am	*Electronic and Nuclear Dynamics in Molecular Single and Double Ionization* **C. William McCurdy**, LBNL/University of California, Davis
11:00 am	*Coupled Electronic and Nuclear Dynamics of Molecules in Excited Electronic States* **Daniel S. Slaughter**, Lawrence Berkeley National Laboratory
11:30 am	*Low Energy Electron Interactions with Complex Targets* **Thomas M. Orlando**, Georgia Tech
12:00 pm	**** Working Lunch **** Research Discussions
Session V 1:30 – 2:15 pm	**Informational Session: Laser Facilities for Ultrafast AMO Science** Chair: **Daniel Rolles**, Kansas State University
	1:30 pm LaserNetUS **Kramer Akli**, U.S. Department of Energy
	1:45 pm NEXUS: National Extreme Ultrafast Science Facility at OSU **Louis F. DiMauro**, Ohio State University
	2:00 pm Q&A and Open Laser Facilities Discussion
2:15 – 4:30 pm	Collaboration Discussions

Tuesday, October 29 (continued)

Session VI Chair: **Luca Argenti**, University of Central Florida

4:30 pm *Attosecond Dynamics Driven by Ultrashort Laser Pulses*
Andreas Becker, University of Colorado

5:00 pm *Complexity and Correlated Motion of Electron in Atomic and Molecular Systems*
Steven T. Manson, Georgia State University

5:30 pm *Time-Domain Issues of Attosecond Pulses: Characterization, Control and Interpretation*
Chii-Dong Lin, Kansas State University

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

Wednesday, October 30

7:30 am **** Breakfast ****

Session VII Chair: **Amy Cordones-Hahn**, SLAC National Accelerator Laboratory

8:30 am *Light-Induced Modification and Control of Electronic Couplings*
Arvinder Sandhu, University of Arizona

9:00 am *Velocity Map Imaging of Ions and Electrons to Probe Excited State Molecular Dynamics and Strong Field Molecular Ionization*
Thomas C. Weinacht, Stony Brook University

9:30 am *Nonlinear X-ray Science*
David A. Reis, SLAC Accelerator National Laboratory

10:00 am *Hard X-Rays Generated by Means of High-Order Multiphoton Thomson Scattering*
Donald Umstadter, University of Nebraska

10:30 am *Closing Remarks*
Thomas B. Settersten, DOE BES
Adjourn

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Lawrence Berkeley National Laboratory

SLAC National Accelerator Laboratory

University Research Summaries (by PI)

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AMO Physics at Argonne National Laboratory

Gilles Doumy, Phay Ho, Anne Marie March, Stephen Southworth,
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1 Overview

The Argonne AMO physics program explores the frontiers of x-ray physics as enabled by accelerator-based light sources and, in so doing, lays the foundation for ultrafast x-ray applications in other scientific domains. We utilize the novel properties of accelerator-based coherent x-ray 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 in concert with ultrafast lasers, to create exotic and/or non-equilibrium states and to probe their rapidly evolving properties with atomic-scale spatial and temporal resolution. 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 complementary subtasks. The first subtask aims at a quantitative and predictive understanding of x-ray interactions with matter in the high-intensity limit. Here we explore new atomistic imaging approaches enabled by the most intense femtosecond x-ray pulses. We build upon our knowledge base of the response of atomic and small molecular systems to examine nanometer-sized samples and the resulting complex phenomena that impact single-shot imaging of single particles. Our computational code developments using the MIRA supercomputer uncover unusual phenomena associated with transient resonant excitation and provide guidance for optimal conditions for serial single shot coherent x-ray imaging of nanoscale samples.

In the second subtask we strive to understand and control the trajectory of ultrafast inner-shell excitations in molecular systems. We build upon our deep knowledge base of studying inner-shell phenomena in the energy domain and use ultrashort x-ray pulses from free-electron laser sources to explore new types of inner-shell spectroscopies in the time domain - e.g. x-ray pump/x-ray probe photoelectron spectroscopy to observe time-evolving chemical shifts and stimulated x-ray Raman spectroscopies to create localized electronic excitations which are then probed in a variety of ways to study the evolving charge densities. The tunable, intense attosecond pulses from XLEAP are a revolutionary tool to investigate electron dynamics with x-ray non-linear spectroscopies.

The third subtask focuses on understanding molecular dynamics in condensed phases at the atomic, molecular and electronic level. Here we use XFELs to access the femtosecond timescale and the APS for picosecond phenomena. Within this subtask we have developed uniquely sensitive high-repetition-rate methods to measure electronic and geometric changes of photo-excited molecules in solution in chemically relevant systems at the APS. Recent developments have improved the efficiency of x-ray emission spectroscopy more than 500-fold and the high statistics inherent with high-repetition-rate studies have allowed the implementation of “time-slicing” techniques which give a ~10-fold improvement in time resolution.

2 X-ray Physics at the Intensity Frontier

2.1 Fundamental processes for x-ray imaging applications

P. J. Ho, L. Young, S. H. Southworth, C. Knight[1], C. Bostedt[2], A. Rudenko[3], D. Rolles[3], S.-K. Son[4], R. Santra[4,19], J. Hajdu[5], F. Maja[5], T. Gorkhover[13], and other collaborators

Project Scope: The unprecedented intensity of XFELs enables exploration of a new frontier of light-matter interactions and the associated applications of imaging structure and chemical dynamics. We aim at a predictive understanding of the fundamental processes induced by intense x-ray pulses through a combined experimental and theoretical approach in systems of increasing complexity from atoms to molecules to clusters.

Recent Progress: Since the early vision for single-shot imaging experiments with XFELs [29], radiation induced damage has been an important topic. For atoms interacting with an intense XFEL pulse, early studies [31–35] have shown that sequential absorption [30] can be strongly enhanced through transient resonances. Recently, the interplay of resonant and relativistic effects was found to affect the charge state distributions from intense x-ray field ionization of heavy atom [9]. Beyond atoms, ultrafast charge transfer was also shown to give enhancement of ionization in molecular ionization [2]. For extended systems, the ionization dynamics are altered through the neighboring atoms [36] and any nanoscale sample in the x-ray focus is transformed into a highly excited state with a large fraction of delocalized electrons [37] and with strong electron - nuclear coupling [38].

Over the past years, our group has contributed to the development of novel experimental methods for ultrafast imaging [3, 4, 6, 8, 39], including two-color pump/probe imaging [38], coincident imaging and spectroscopy [37], and a holographic approach [5]. However, despite this progress, single-particle imaging experiments remain challenging [40]. To attain nanometer and potentially even sub-nanometer resolution, high quality diffraction images with signal out to large momentum transfer are needed. In linear scattering theory, away from resonances, the total scattered intensity scales with wavelength squared (λ^2) [41], often leading to the conclusion that single-shot imaging experiments should be performed at the longest wavelength supporting the desired resolution. Here, the so called water-window, referring to the range of photon energies between the carbon and oxygen K-edges, is often considered an ideal choice for imaging biological samples. In this spectral regime, water exhibits a high x-ray transparency and close to the absorption edge of oxygen high contrast images from biological specimens can be obtained at synchrotron sources. Also, it can be tempting to choose higher pulse energies over shorter pulse durations for single-particle imaging experiments. However, the effect of these pulse parameters under real imaging conditions has so far not been characterized in the water window or more generally near absorption edges where resonances play an important role at high x-ray intensities.

Last year, we investigated ultrafast diffractive imaging of sucrose ($C_{12}H_{22}O_{11}$) clusters, which are often used as benchmark organic samples. The scattering experiment was carried out at the AMO end station of LCLS in the photon energy range from 500 to 1500 eV and with an XFEL pulse duration of about 180 fs. From the recorded images, we found that there is an unexpected photon energy dependence of the scattering intensity. Far above absorption resonances, where the samples become increasingly transparent to the x-ray pulse, the linear model used previously [42–44] works satisfactorily. However, near an absorption edge at 530 eV, there is a loss of close to an order of magnitude in scattering intensity compared to the prediction from linear scattering theory.

To understand the scattering response of the sucrose clusters, we employed Monte-Carlo/Molecular-Dynamics (MC/MD) calculations [1, 45] on Mira, a BG/Q supercomputer at the Argonne Leadership Computing Facility. This method was built on the knowledge gained from earlier studies [31–35]. It incorporates all multiphoton ionization features of isolated atoms [30, 31, 34, 35], namely photoionization, Auger, fluorescence, elastic scattering and Compton scattering. To account for the effects of the cluster environment, electron collision dynamics as well as electron-ion recombination processes are included. In this hybrid MC/MD method, all these electronic processes are treated as quantum transitions, whereas the motion of the ionized electrons/ions/atoms are evaluated through classical molecular dynamics. To compute the scattering response of sugar nanoparticles with a size of 50 nm, we tracked 185,193 sucrose molecules in an intense XFEL pulse. Since each molecule has 182 electrons and 45 nuclei, the calculation for these big clusters requires tracking about 42 million particles.

The calculations for undamaged particles match the λ^2 dependence expected from linear scattering theory with exceptions around the oxygen K-edge and in the water window, where anomalous scattering processes lead to reduced form factors for the oxygen atom. In contrast, the calculations including the full electronic and nuclear dynamics exhibit a much flatter cross section over most of the photon energy range, and indicate that x-ray induced processes during a 180-fs pulse have a significant impact on the scattering cross section, even as high as 1 keV above an absorption edge, and cannot be neglected. The MC/MD results shows a suppression of the scattering cross section in the whole photon energy regime with a pronounced minimum at 530 eV, just below the oxygen K-edge, and is consistent with the experimental data. A manuscript has been submitted.

Future Plans: The sensitivity of the scattering response to the transient electronic structures near absorption edges suggest that both the pulse duration and photon energy can be exploited as control knobs for optimizing the scattering signal of single particle experiments. The broad bandwidth and sub-femtosecond capabilities of the XLEAP operation mode at LCLS will enable experimental investigation of the resonant and non-resonant imaging processes in a new regime - pulse duration below inner-shell decay timescales. Theoretically we will continue to develop and use our Monte-Carlo/Molecular Dynamics calculations for systems with heavier elements (for example, Xe) under realistic experimental pulse conditions.

2.2 X-ray imaging using higher-order correlations

P. J. Ho, L. Young, Y. Kumagai[6], C. Bostedt[2], C. Knight[1], and other collaborators

Project Scope: Coherent diffractive imaging (CDI) with XFEL pulses holds the promise to probe structure [7] and follow the dynamics of non-periodic entities with atomic resolution. However, this approach remains challenging due to the need to acquire a large number of images for reconstruction and the necessary pulse conditions for limiting sample damage during the pulse [45] are still not available. We aim to explore the potential of x-ray correlation methods as a high-resolution structural and dynamical probe by investigating the higher-order correlations associated with the fluorescence spectrum and speckle patterns from illuminated samples.

Recent Progress: Novel experimental spectroscopic and imaging techniques have been developed to exploit x-ray free-electron lasers (XFELs) for studying the structure and dynamics of non-periodic entities at atomic spatial resolution and femtosecond timescales. Recently, Classen and coworkers [46] proposed a fluorescence intensity correlation method for high-resolution imaging of single molecules with XFELs that is based on the Hanbury Brown and Twiss effect. This effect was discovered in 1956 when Hanbury Brown and Twiss observed interference effects in the measured intensity on two spatially separated detectors of light from Sirius, and from this could determine the star's angular size, as the effect can be interpreted by considering emission from an ensemble of spatially separated random/thermal sources. Here, by treating heavy atoms in molecules as random light emitters, the fluorescence intensity correlations are shown to be the Fourier transform

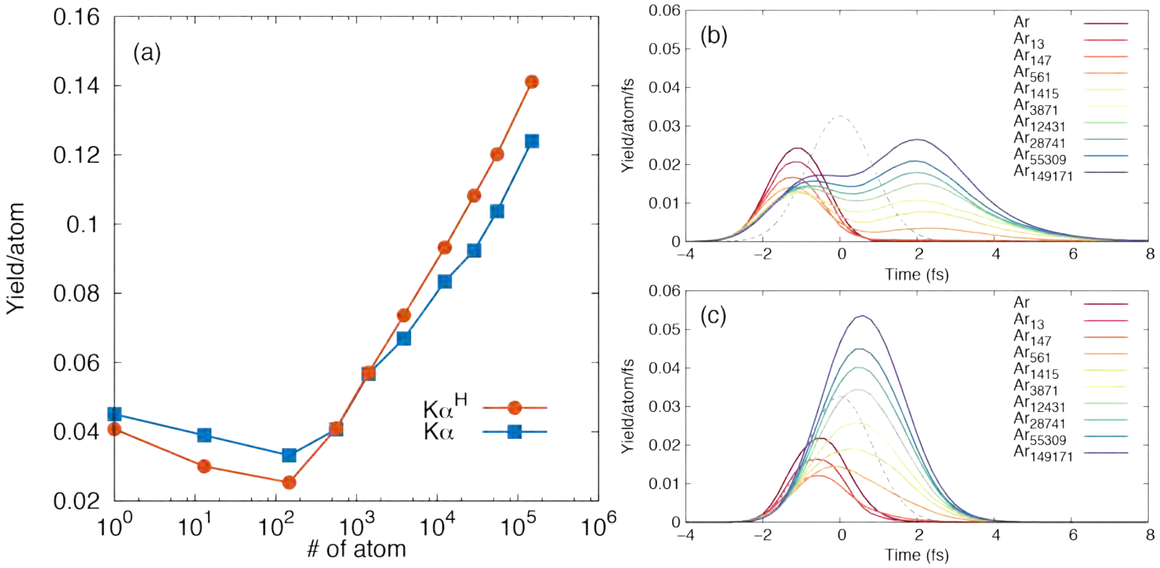

Figure 1: (a) Fluorescence yield as a function of the number of atoms. Temporal emission profile of (b) $K\alpha$ and (c) $K\alpha^h$ for Ar clusters with different number of atoms. Each system is exposed to a 5-keV, 2-fs and 3.5×10^{11} photons/μm^2. The dashed line in panel (b) and (c) shows the temporal x-ray profile.

of the spatial distribution of the fluorescence emitters in a sample. The EuXFEL and the upcoming LCLS-II, which can deliver intense few-fs pulses at high-repetition rate will facilitate this photon-hungry fluorescence intensity correlation measurement [48]. However, the fluorescence pathways and emission times, which are key to the visibility of the fluorescence intensity correlation function in extended systems under intense x-ray pulses are not yet understood.

To explore the applicability of this imaging approach, we theoretically investigated fluorescence processes of non-periodic systems from XFEL pulses over a range of fluences, including both the linear and non-linear x-ray regimes, with our MC/MD method [45]. Also, we compared the fluorescence dynamics as a function of system size, from Ar atom to clusters with close to 150-k Argon atoms. We found that the fluorescence dynamics in non-linear x-ray regime are very different from that in the weak x-ray field, where an intense x-ray pulse can interrupt the fluorescence dynamics by multi-photon absorption and create a dense electron environment within the sample on the femtosecond timescale. Already during the pulse, electron-ion recombination and massive electron rearrangement begin to transform the exposed cluster into a core-shell structure (neutral core and highly charged shell). These non-linear x-ray interactions coupled with the dynamically changing sample environment enable additional fluorescence pathways in clusters to reach the same fluorescence channels via electron-ion recombination processes. Our study reveals that the contribution of the recombination pathways is not negligible, even for a 2-nm system. Their contribution increases with system size and, for systems larger than 10 nm, they lead to more $K\alpha$ and $K\alpha^h$ events than those from the photoionization pathways. The presence of both the recombination pathways and the photoionization pathways gives rise to an enhanced $K\alpha$ and $K\alpha^h$ emission yield and extended emission time beyond the lifetime of the core-excited states. Our analysis suggests that in an intense x-ray pulse, $K\alpha^h$ emission line can be a good candidate for fluorescence imaging as it has a higher yield and relatively short emission time compared to the timescale of x-ray induced structural distortion. A manuscript reporting these results was written and submitted.

Future Plans: We plan to investigate the feasibility/potential of achieving both atomic and elemental resolution of in heterogeneous systems with fluorescence imaging. Due to the elemental specificity of the fluorescence process, the obtained fluorescence intensity correlation will be sensitive to the incident photon energy. By comparing the correlation obtained below and above an absorption edge, one might be able to extract the distribution of a particular element within a complex system. Multi-t, multi-q x-ray scattering correlations may also be used to study solvation dynamics at the APS.

2.3 X-ray transient absorption: from the weak- to strong-field regime

L. Young, K. Li[7], M. Gaarde[8], M. Labeye[9], P.J. Ho, G. Doumy, S.H. Southworth, A.M. March, M. Meyer [10], T. Pfeifer[9], Z.-H. Loh[11], J.-E. Rubensson [5] and other collaborators

Project Scope: We propose to study x-ray transient absorption in model gaseous systems as a function of intensity using broad bandwidth, ultrashort XFEL pulses. We focus on a quantitative understanding of deviations from a linear absorption model with increasing incident intensity. We anticipate being able to tailor the temporal and spectral properties of the transmitted pulse.

Recent Progress: Understanding fundamental x-ray/matter interactions at high intensity is a vibrant frontier enabled by the continued rapid development of x-ray free-electron lasers. Many early experiments involved understanding the interaction mechanisms [2, 30, 32] leading to x-ray damage resulting from stochastically varying self-amplified spontaneous emission pulses in the single atom/molecule regime. However, the propagation through thick resonant absorbing media, basic for studies in the solid state, solution phase and gases via transmission-based x-ray transient absorption, has been much less studied. Furthermore, XFELs now deliver nearly transform-limited pulses with sub-femtosecond duration at MHz repetition rates [49] over a wide range of x-ray energies thus universally enabling transient absorption studies near organic (C,N,O) and inorganic (transition metal and actinide) edges. The power density of XFEL pulses places one squarely in the x-ray intensity regime where effects such as stimulated Raman scattering [50, 51], amplified spontaneous emission, pulse compression, can occur [52]. These advances motivate us to reexamine the basics of resonant propagation of strong x-ray fields for a variety of applications.

During the past year, Labeye and Gaarde have developed a versatile code based on coupling the 3D MWE to a TDSE solution for a combination of few-level systems in both a neutral and singly-ionized species. The code includes coherent dipole coupling between relevant states in the neutral species as well as incoherent loss via Auger decay and photoionization. The relevant resultant ionized species are treated via a density matrix formulation. The code advances the relative predictive power over earlier implementations by providing both the spectral and temporal profiles and a 3D description. It has been benchmarked against earlier studies [51, 52]. A proposal to study transient absorption as a function of incident intensity has been submitted to the EuXFEL and unofficially granted beamtime.

Future Plans

With beamtime at the EuXFEL, we plan to address the following questions: In the weak-field regime, can SASE pulses be used to obtain single-shot absorption spectra, and, to perform x-ray pump-probe studies within a single pulse? In the strong-field regime, can propagation through dense resonant media be accurately modeled? The experimental effort will entail the design and implementation of instruments that measure the spectral content of the incident and transmitted x-ray pulse in collaboration with EuXFEL and Uppsala scientists.

3 Ultrafast X-ray Induced Phenomena

3.1 Time-resolved chemical shifts

G. Doumy, S.H. Southworth, D. Koulentianos, P. J. Ho, A.M. March, L. Young, L. Cheng[12], J. Cryan[13], and other collaborators

Project Scope: The possibility to use two short x-ray pulses with different photon energies [55–57] to first interact with the inner shell of one atomic site, and then probe a different site with the second pulse is opening new avenues of investigation of molecular dynamics following x-ray interaction, being potentially sensitive to both the electronic and nuclear dynamics. Like in our pioneering study on the prototypical CO, we use time-resolved x-ray photoemission spectroscopy as an instantaneous observable.

Recent Progress: The ability of synchrotrons to produce high average flux, high resolution soft x-ray radiation has been used for several decades to further the development of the ESCA technique (Electron Spectroscopy for Chemical Analysis) [58] and to study the possibility of site-selective photochemistry [59], by which selective excitation of a molecule could guide its dissociation paths. Powerful coincidence techniques have helped observe the outcome of site-selective ionization, as we used in our recent study on the molecule ethyl trifluoro acetate (known as the ESCA molecule for being a poster child of the sensitivity of the binding energy) [17]. As shown in Fig 2, little site-selectivity was observed, and additional insights were only provided by theory, suggesting that it was the character of the dicationic states obtained after Auger decay that was the dominant factor, and not a fast equilibration of internal energy as suggested before. The arrival of the upcoming LCLS-II, with its high repetition rate and short x-ray pulses, promises to be able to transplant this experiment into the time domain to try and follow the mechanism in real time.

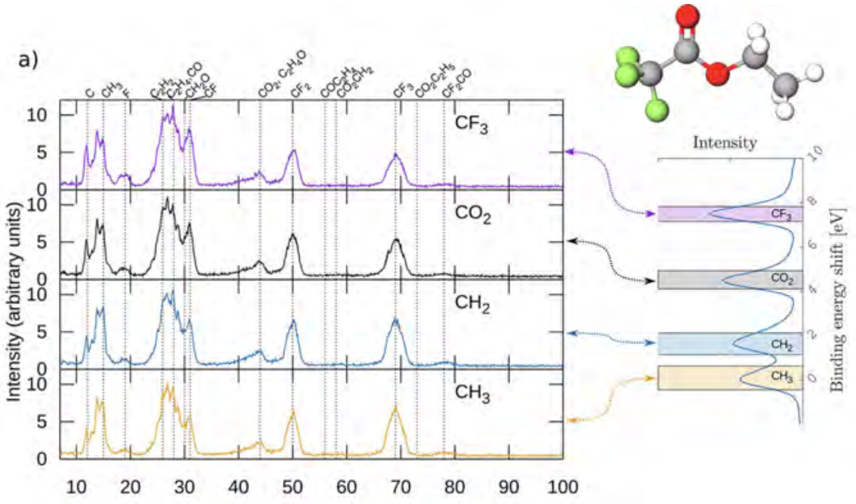

Figure 2: Search for site-selective dissociation in the ESCA molecule. The graphs on the left are shown the mass spectrometry measured in coincidence with specific Carbon ionization sites. Few differences are apparent, indicating that regardless of the ionization site, the same bonds are weakened, a sign of hole delocalization after Auger decay takes place.

In the meantime, as LCLS is going to restart operation at low repetition rate, we are proposing to continue building the necessary tools, both experimentally and theoretically, to fully understand the complex interplays following inner shell ionization of low-Z molecules. Starting with fluorinated hydrocarbons which exhibit large chemical shifts in the ground state [60], we want to try and follow the evolution of charge localization as a function of time, by measuring the evolution of the chemical shifts at selected molecular sites. We believe that the interpretation of these measurements will require highly accurate theoretical calculations, such as produced by our collaborator Lan Cheng using delta-coupled-cluster methods to treat the electron correlation [61]. He developed an extension to treat core-excited molecules, but while the calculations have been rather extensively proven to be accurate to better than 0.1 eV for the binding energies in the ground state, the lack of data for core-excited molecules is somewhat hampering development of systematic studies. We expect that this synergistic effort will be very profitable for both sides.

Future Plans: We are looking forward to LCLS return with advanced capabilities such as a much larger tunability for two-pulse/two-color techniques, as a preamble for the advent of high repetition rate operation. In addition to our studies using time-resolved x-ray photoemission spectroscopy, we are also exploring opportunities afforded by measuring the time-resolved x-ray absorption spectrum, for which Lan Cheng is also providing theoretical support.

3.2 Stimulated X-ray Raman Spectroscopy - Attosecond campaign at LCLS

G. Doumy, P. J. Ho, A.M. March, S.H. Southworth, L. Young, A. Al Haddad[2], C. Bostedt[2], J. Cryan[13], P. Walter[13], A. Marinelli[13] and other collaborators

Project Scope: The success of the XLEAP project at LCLS to produce intense, sub-femtosecond pulses in the soft x-ray regime [49] is opening new areas of investigation, including non-linear interaction between the x-ray fields and atoms and molecules [62]. The ability to study electronic processes before decay processes or nuclear motion take place, coupled with the site-selectivity afforded by x-ray interaction will open a new window on observing electronic motion and electronic coherences.

Recent Progress: In analogy with the optical domain, where stimulated Raman transitions can be driven by a femtosecond pulse to transfer populations to a vibrationally-excited state, the broad bandwidth of the soft x-ray attosecond pulses originating from XLEAP should be able to drive population transfer to valence electronic-excited states, while keeping the excitation localized owing to the localized nature of the inner-shell interactions at play [62]. Those localized excitations are expected to evolve via charge migration, and would represent a new way to study, in a more controlled way, how chemical reactivity arises from photoexcitation.

Before the shutdown of LCLS at the end of 2018, two pioneering experiments were attempted to probe the creation of the valence excited neutral molecules following stimulated, impulsive x-ray Raman processes. The first one looked for an excess in the production of ions from UV ionization in NO, and managed to identify such a signal with a non-linear intensity dependence. The second one was led by our group and attempted to not only detect the production of neutral excited states, but also characterize their electronic configuration by using time-resolved optical white light transmission as a probe in copper centered porphyrins, a much larger system. The very large optical cross section of the porphyrin ligands, as well as the well characterized optical absorption properties of singlet, triplet excited states, or ionic species meant that we should be able to perform such a measurement with a dilute gas target. While we were able to detect an x-ray induced transient optical signal, difficulties with the target source prevented from performing systematic studies necessary to clearly identify the process at play in the generation of that signal.

As LCLS is gearing towards a restart in the next year, it was recognized that the pursuit of efforts involving the use of intense attosecond pulses at XFELs would warrant a large community of both experimenters and theorists. A proposal for a LCLS-led scientific campaign for observing ultrafast electron motion using attosecond XFEL pulses was just put in place, with our group involved on the experimental side at this time. By using two attosecond x-ray pulses, the ultimate objective of the campaign would be to induce and measure coherent electronic motion in the inner or outer valence shells in molecules such as para-aminophenol, with the ability to use tunable x-ray energy to selectively probe different sites in the molecule. It is expected that this effort would properly launch the field of attosecond physics and chemistry at XFELs.

Future Plans: While LCLS, and then LCLS-II will provide the first attosecond pulses, first at low repetition rate, and then up to MHz, other XFELs are aiming to offer such capabilites to users, including the upcoming soft x-ray line at SWISSFEL, where very intense pulses may be possible.

3.3 Self-referenced measurement of electron dynamics

G. Doumy, A. Cavalieri[2], C. Bostedt[2], M. Meyer[10] and other collaborators

Project scope: Transposing the laser streaking methods from attophysics to XFEL studies has been an ongoing effort. The need for single shot characterization of intense but noisy pulses with jittering properties has created challenges, but also opened opportunities. One such opportunity allows to compensate for the temporal jitter between the optical laser and x-ray pulses, to recover a sub-femtosecond time resolution.

Recent Progress: Laser streaking is currently the only demonstrated way to characterize the x-ray pulse duration at an XFEL. Successful demonstrations have been made using both linear and circular polarization for the intense laser field, using wavelengths ranging from the IR to THz [18, 63–65]. However, these methods suffer from the unavoidable temporal jitter between the two independent sources. Shot-to-shot compensation is possible to a precision of about 20 fs in the best conditions, much larger than the potential sub-femtosecond resolution of the streaking technique. Several attempts have been made at the LCLS to develop a self-referenced measurement, where electrons promptly produced by photoemission provide a single shot reference for electrons produced by another process, e.g. Auger decay. Further analysis of early data from that collaboration has established a robust extraction method for the temporal profile of Auger electron emission in atomic Neon. A manuscript is in preparation.

Future Plans: All upcoming soft x-ray XFEL beamlines will include streaking capabilities. Diagnostics of the pulse properties, especially at high repetition rate, are very challenging, but laser streaking is one method with the potential to provide such information shot-to-shot.

3.4 Electron correlation in double K-shell photoionization of neon

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Project scope: The study of electron correlation in inner-shell photoionization has endured due to the challenges it presents to theoretical treatments of many-electron interactions and to the design of sensitive experiments. One such topic is double K-shell (KK) photoionization that has been extensively studied in helium. We have extended this topic to the case of neon in order to study the Z-dependence of the process and the effects of outer-shell electrons. Measurements of the double-to-single cross-section ratio (KK/K) made using synchrotron radiation explore electron

correlation [66,67] whereas measurements with intense XFEL pulses create KK holes by sequential absorption of two x rays [30]. The relatively simple 10-electron structure of neon makes it feasible and informative for exploring the mechanisms at work in the weak-field and strong-field cases.
Recent Progress: Double photoionization of helium is a process that necessarily involves electron correlation and illustrates key conceptual ideas [68–70]. The variation with photon energy of the double photoionization cross section is particularly interesting. The many-body perturbation theory treatment [69] identifies three first-order amplitudes in the electron-electron interaction that are referred to as ground-state correlation (GSC), shakeoff (SO), and two-step-one (TS1). The GSC amplitude accounts for angular and radial correlation between the two equivalent 1s electrons in the ground state. Upon ejection of the first electron, the SO amplitude accounts for ejection of the second electron due to orbital relaxation in response to the sudden change in screening. The TS1 amplitude describes a process in which a photo-excited electron undergoes a binary collision with the second electron and both are ejected. These mechanisms are invoked in a simpler treatment that describes double photoionization of helium as an incoherent sum of shakeoff (SO) and "knockout" (or TS1) contributions, with knockout calculated quasiclassically [70].

The concepts that underlie double photoionization of helium motivated theoretical studies of KK photoionization of helium-like ions and Z-scaling of the cross sections [71, 72]. Signatures of KK vacancies in heavier atoms have been observed from hypersatellites in x-ray emission spectra [73, 74], while hypersatellites in Auger electron spectra have been measured in neon [66, 67]. The KK/K cross-section ratios can be determined from the ratios of hypersatellite and diagram line intensities. However, other than helium, all of the experiments have been made on neutral atoms, in the presence of outer shell electrons, rather than helium-like ions. Using metal foils of Mg, Al, and Si, Hoszowska *et al.* measured KK/K ratios that are 50-70% larger than the ratios calculated for helium-like ions [74]. This suggests that KK/K ratios in neutral atoms are sensitive to electron correlations involving the outer-shell electrons. Motivated by this result and by the excellent setup for high-resolution inner-shell photoelectron and Auger electron spectroscopy at the SOLEIL synchrotron facility [75], we measured the Auger diagram and hypersatellite electron spectra of neon over the 2.3 - 8 keV x-ray energy range. The measurements complement the 2.3-keV measurement on the Auger electron spectrum of neon reported earlier that is rich with electron correlation effects [67]. The new measurements will be analyzed for electron correlation effects that vary with x-ray energy, in particular, the KK/K ratio.

Future Plans: The Auger electron spectra of neon recorded over 2.3 - 8 keV will be analyzed using peak fitting methods to determine relative intensities of final states from both K and KK inital hole states. From those measurements, the KK/K ratio will be determined as a function of x-ray energy. The measurements will be compared with theoretical calculations for both 10-electron and helium-like neon to determine the effects of outer-shell electrons. In addition, the role of electron correlation in the strong-field case has not been thoroughly studied. This suggests that an experimental and theoretical study of the high-resolution Auger and hypersatellite spectra of Ne produced by intense XFEL pulses would be informative.

3.5 Resonant inelastic x-ray scattering of actinide complexes

S. H. Southworth, G. Doumy, A. M. March, D. A. Walko,[17], R. E. Wilson,[18] and L. Cheng[12]

Project scope: The actinides comprise fifteen metallic elements with atomic numbers Z = 89 - 103. The chemistry and electronic properties of actinide compounds are rich in variety due to the Z dependence of the 5f and 6d valence orbital energies [76, 77]. The large nuclear charges result in strong relativistic effects acting on the atomic orbitals. Correlating the electronic and chemical properties of actinide compounds with their orbital structures is of both fundamental and practical interest. Theoretical calculations of their electronic structures and geometries require treatment of relativistic and many-electron interactions. Understanding their physical and chemical properties is relevant to their use in safe nuclear power, environmental remediation of legacy waste, and other applications.

Recent Progress: Studies of actinide samples require safety considerations of their radiological properties. X-ray spectroscopy is a viable technique since the compounds can be well contained within sample holders with x-ray transmissive windows. This enables x-ray-in/x-ray-out experiments using beamlines at the Advanced Photon Source. X-ray absorption by inner-shell electrons to unoccupied valence states produces resonant structure in the pre-edge region, i.e., several eV below the ionization threshold. The energies and intensities of the pre-edge structure can be compared with theory to gain information on valence electronic states. However, for higher-Z atoms, inner-shell level widths can be so large that the pre-edge structure is washed out in the total x-ray absorption cross section. To overcome this effect, high-resolution x-ray analyzers can be used to record partial fluorescence yields in which the inner-shell hole is transferred radiatively to outer shells with smaller level widths [78]. High-resolution x-ray beamlines combined with x-ray emission analyzers can be used to record "high-energy resolution fluorescence detection x-ray absorption spectra" (HERFD-XAS) and "resonant inelastic x-ray scattering" (RIXS) spectra [79, 80].

As a first experiment, we recorded RIXS data across the 17.166-keV L_3 ($2p_{3/2}$) edge of uranium in the compound $Cs_2UO_2Cl_4$. The electronic structure of the uranyl ion (UO_2^{2+}) is a prototypical system of interest for both experimental and theoretical studies [81–83]. The double-crystal monochromator at beamline 7ID was used with Si(311) crystals that produced an intense, tunable x-ray beam with an estimated bandwidth of ∼0.5 eV in the 17-18 keV range. For increased collection solid angle, a multi-crystal x-ray emission spectrometer was used with 12 Si(220) cylindrical crystals and a pixelated area detector in von Hamos geometry [20]. The incident x-ray energy was step-scanned from above to below the U L_3 edge while recording x-ray emission spectra. For increased resolution, the multi-crystal analyzer and detector were positioned to use higher-order reflections, up to Si(10 10 0), and Bragg angles in the 60° - 80° range. Three sets of RIXS data were recorded using U x-ray emission lines: $L\alpha_1$ ($2p_{3/2}$ - $3d_{5/2}$), $L\beta_2$ ($2p_{3/2}$ - $4d_{5/2}$), and $L\beta_5$ ($2p_{3/2}$ - $5d_{5/2}$).

Future Plans: The next step in this project is to reduce the data to generate RIXS maps from the three sets of x-ray emission spectra. The structure observed in the RIXS maps will be compared with previous experimental and theoretical studies. The relativistic equation-of-motion coupled-cluster calculations on uranyl reported recently in Ref. [83] will be extended to model the RIXS process. If the results on uranyl are informative, future experiments will be conducted on other actinide complexes.

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

4.1 Dynamics and coherence in strong-field ionized water

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Project Scope: Time-resolved x-ray spectroscopies in the water window provide a powerful and unique probe for understanding valence hole dynamics, electronic coherence and proton transfer in ionized liquid water. These elementary processes are of fundamental importance as the initiators of radiation damage in condensed matter systems [84, 85].

Recent Progress: Although understanding the birth and fate of an excess electron in liquid water created by ionization has been the subject of longstanding scientific inquiry [86], surprisingly its partner, the initially created cation H_2O^+, remains undetected due to its femtosecond lifetime and unclear spectroscopic signature in the UV/VIS region [87]. Our calculations demonstrate a clear signature for this and other relevant species (H_2O^+,OH, H_3O^+, H_2O) in the soft x-ray regime, thus providing a handle on electronic and chemical dynamics that extends to the earliest timescales. The calculations performed for gas phase species using with 6-311(2+,+)G(2df,p) basis with uncontracted core (oxygen) using fc-cvs-EOM-CCSD [89] show the valence core hole species (H_2O^+ and OH) have spectral feature that lie cleanly in the "water window" and are not subject to strong absorption by liquid water [90].

We used strong-field ionization in water to impulsively eject an electron along the field polarization axis to a radius of ≈ 35 Å. The ejected electron ultimately equilibrates in a spherical solvent cavity of ∼3 Å in an s-like ground state within ∼ 1 ps. How does this occur? Earlier studies of this process used an optical probe at 800 nm to monitor the hydrated electron and revealed surprising polarization oscillations on the tens-of-femtosecond timescale [88]. How are these hydrated electron polarization oscillations correlated with localized hole dynamics in the residual ion? Is the modulation of the polarization anisotropy due to charge density oscillations between oxygen centers, as hypothesized, or to something else? We studied the elementary dynamics of the valence hole following strong-field ionization of liquid water using transient absorption based spectroscopies at the SXR endstation at LCLS. A 2μm flat-sheet liquid jet system was developed and used for simultaneous time-resolved soft x-ray transmission, fluorescence and emission spectroscopy. In an optical-pump/x-ray probe configuration, we found signatures and followed the kinetics of the elusive H_2O^+ species and its subsequent reaction product the OH radical in the three detection channels. Moreover, modifications of the pre-edge structure, due to the injected electron were observed.

We completed analysis of the dynamics in the valence hole region, which track the H_2O^+ radical cation and OH radical. We observe three distinct time constants in the early-time dynamics of ionized liquid water: 46 ±10 fs, 0.18±0.02 ps, and 14.2±0.4 ps, tentatively assigned to the decay of the H_2O^+ radical cation via proton transfer, vibrational cooling of the hot OH radical produced from H_2O^+, and geminate recombination of OH with the hydrated electron byproduct, respectively. Theoretically we combine a quantum-mechanical (QM) description of a $(H_2O)_{12}^+$ cluster with a classical (MM) description of surrounding water molecules. The electronic structure is obtained at the Hartree-Fock level of theory employing Koopmans theorem to obtain singly-ionized states and using the 6-31G basis set as implemented in the CFEL software package XMOLECULE. On the ∼ 30-fs timescale the hole localization/non adiabatic dynamics are completed, whereas the proton transfer is predicted to occur on the∼ 60-fs timescale. The centroid of the x-ray absorption of the valence hole is found to be correlated with the O—O distance of the specific oxygen atom involved in the proton transfer to its nearest neighbor. This distance has been implicated in the earlier observation of oscillations in polarization anisotropies [88] in the hydrated electron. This work represents the first measurement of the elementary proton transfer timescale in water radiolysis and demonstrates the sensitivity of x-ray spectroscopy to structural dynamics near the ionization site. A manuscript describing these experimental and theoretical results is under review.

We also completed analysis of the quasi-static RIXS spectrum of the OH radical, obtained from the time-resolved dispersed fluorescence binned for delay times between 1-6 ps. The RIXS spectrum reveals the localized excitations, unlike the UV spectra which are dominated by charge transfer bands. The RIXS spectrum was also be compared to the x-ray emission spectrum of the hydroxide anion, OH^- [91]. The position of the energy loss peaks are very similar and the relative intensities of the elastic/inelastic (π/σ) transitions can be explained by polarization considerations. A manuscript is being prepared.

Future Plans: While observation of elementary proton transfer timescale in ionized liquid water is a considerable achievement, the time resolution available was insufficient to detect the previously observed polarization oscillations. We plan to improve the pump/probe time-stamping accuracy to $\sim$ 20 femtoseconds as should be possible with a co-located time-tool at the new ChemRIXS beamline by working with LCLS scientists. Similarly, high-statistics emission spectroscopy, and extended x-ray absorption fine structure measurements to further our ability to observe and understand elementary reactions in liquid water.

4.2 Tracking solution phase photoinduced reactions with sub-pulse duration temporal resolution: implementation of synchrotron time-slicing

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Project Scope: The MHz-repetition-rate, optical-pump/x-ray-probe endstation at beamline 7ID at the Advanced Photon Source (APS), built by our group over the past several years, enables tracking of photophysical and photochemical reactions in solutions using both x-ray absorption and x-ray emission spectroscopies [20, 22, 23, 25, 26, 92–98]. The range of timescales that can be probed is wide, spanning from picoseconds using a pump-probe method, out to the microsecond regime or longer utilizing a pump, probe, probe, probe ... scheme. The short timescale limit is typically assumed to be governed by the x-ray pulse duration, which is ~100 ps at the APS. We are exploring means to detect reaction intermediates that have lifetimes shorter than the x-ray pulse duration. Such sub-pulse-duration temporal resolution is important for bridging the gap between the femtosecond regime accessible at XFELs and the >100 ps regime considered the domain of synchrotrons, as well as for taking full advantage of the higher-brightness, but longer duration, x-ray pulses that will be provided by the upcoming upgrade of the APS.

Recent Progress: We have applied a "time-slicing" scheme to pump-probe x-ray absorption spectroscopy studies of the photo-induced ligand exchange reaction in aqueous ferrous hexacyanide [27]. In this scheme, a short duration pump pulse is temporally scanned across a longer probe pulse while measurements are collected at several timepoints within the probe temporal profile. With sufficient signal-to-noise ratio and accurate knowledge of the probe temporal profile, the set of measurements can be analyzed to extract signatures of short-lived photoreaction intermediates. The method has been utilized previously at synchrotrons to capture short-lived reaction intermediates using solution x-ray scattering [99–101].

We have taken full advantage of the high flux and stability of the x-rays at the APS to capture

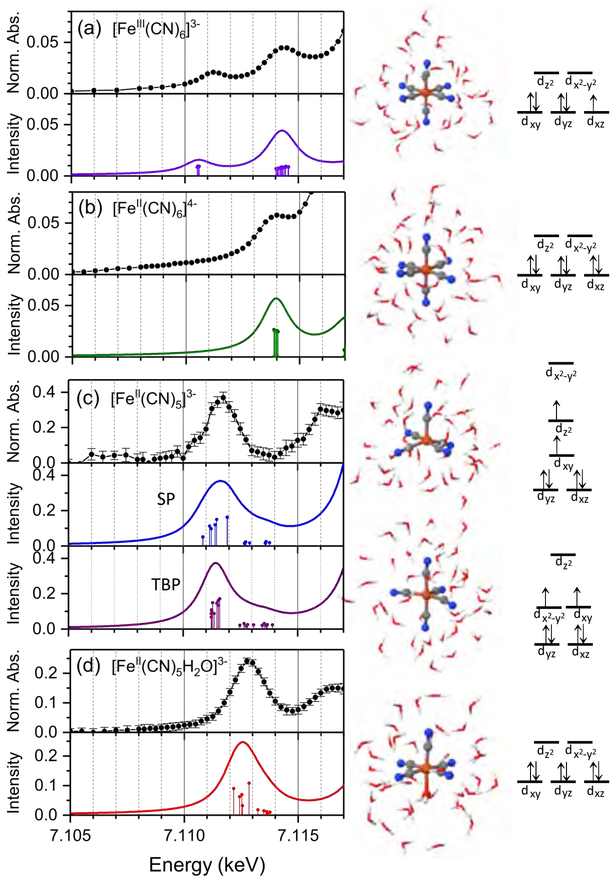

Figure 3: XAS spectral signatures of intermediates and products involved in the photoaquation reaction in aqueous $[\mathrm{Fe(CN)_6}]^{4-}$, including the 20 ps-lived $[\mathrm{Fe(CN)_5}]^{3-}$species [27].

high precision x-ray absorption spectra at the Fe K-edge that allowed us to extract the spectrum of the pentacoordinated intermediate species produced in the photoaquation reaction and determine its lifetime to be 19 (±5) ps. Combining our results with quantum mechanical, molecular mechanics (QM/MM) molecular dynamics (MD) simulations enabled elucidation of the ligand exchange mechanism. The release of the $\mathrm{CN^-}$ ligand from a triplet excited state occurs in ∼1.3 ps, leaving the $[\mathrm{Fe^{II}(CN)_5}]^{3-}$ pentacoordinated intermediate in a square pyramidal geometry. The dynamic water environment causes interconversion between this geometry and a trigonal bipyramidal geometry on a ∼3-4 ps timescale, with most of the time spent in the trigonal bipyramidal geometry and short intervals of ∼500 fs in square pyramidal. Steric effects prevent aquation in the trigonal bipyramidal geometry so aquation is only active in the square pyramidal geometry. These factors provide an explanation for the ∼20 ps lifetime of the pentacoordinated species.

Future Plans: The role of the solvent is quite important in this reaction and further analysis of the MD simulation results could help show the details of its influence. The model for the reaction assumes a triplet state for the initial precursor to dissociation and for the pentacoordinated intermediates, but this has not yet been experimentally verified. Measurement of the Kβ x-ray emission spectrum would be a definitive means of verifying this assumption. By utilizing our newly developed MHz pink beam capabilities (see Section 4.3), we will be able to apply the “time-slicing” technique to x-ray emission spectroscopy and verify the triplet state of the pentacoordinated intermediate. Additionally, the predicted fluxional pentacoordinated state from our dynamics simulations and the initial very fast dynamics after photoexcitation, including the change from singlet to triplet states, have not been explored experimentally and could be undertaken using ultrashort x-ray pulses available at XFELs.

4.3 Efficient time-resolved x-ray emission spectroscopy using pink beam at the APS

G. Doumy, M.-F. Tu, A. Al-Haddad[2], A. M. March, S. H. Southworth, Y. Kumagai[6], L. Young, C. Bostedt[2], D. Walko[17], A. Di Chiara[17], L. Assoufid[17]

Scope: We extended 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. As a result, time-resolved studies of the core-to-core emission lines are now possible for low-concentration or low-excitation systems, and the chemically sensitive valence-to-core emission lines become practical at synchrotrons.

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 first harmonic radiation from an undulator source (so-called pink beam) instead of monochromatic beam is a route to dramatically increase the XES signal. We have developed at Sector 7 of the APS a pink-beam microfocus capability at full repetition rate of the synchrotron [28]. A water-cooled harmonic rejection mirror, and water-cooled beryllium Compound Refractive Lenses (CRLs) are used to produce the small x-ray spot necessary for our pump/probe microprobe setup. The ability to collect the transient signals using laser repetition rates above 1 MHz while ensuring a fresh volume between laser excitations allows observing the fastest processes even in systems that present irreversible photoproducts.

The first demonstration was made on the prototypical spin-crossover iron complex $[\mathrm{Fe(bpy)_3}]^{2+}$, but in a recent beamtime where we incorporated our new multicrystal von Hamos spectrometer, we have successfully studied the photoaquation process in $[\mathrm{Fe(CN)_6}]^{4-}$ using Kβ in a 'time-sliced' configuration (see 4.2), as well as the energy transfer between the antenna ligand and the lanthanide center using XES instead of the previously demonstrated XAS [26] (see 4.4).

Future Plans: The ability to measure transients in the Kβ region so efficiently opens the possibility to use it as a feedback measurement when exploring the manipulation of the output of photochemical reactions using sculpted laser pulses. With the APS-U upgrade of the synchrotron, our pump/probe setup will be moved to a new spectroscopy beamline which will provide easy switching between monochromatic beam and pink beam using a multilayer monochromator, allowing for optimized pump-probe measurements of both XAS and XES in a single experimental beamtime.

4.4 Probing transient molecular dynamics in solution

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Scope: Our combined setup for high-repetition rate time-resolved x-ray absorption and x-ray emission spectroscopies is able to efficiently collect small transient signals, and the quick data acquisition allows for exploring several samples/conditions in a single beamtime. As such, it has attracted several collaborations, on problems related to molecular complexes used for photosensitizers or photocatalysts.

Recent Progress: Further improvement on our time-resolved x-ray spectroscopy setup at Sector 7 at the APS included the implementation of our own multi-crystal von Hamos XES spectrometer. Modeled on the spectrometer that had been tested earlier with collaborators from European XFEL [20], it enables two new kind of experiments on samples characterized by a small difference signal, either due to low concentration or low excitation. First, using monochromatic beam, we can now fully collect time-resolved RIXS maps, where the x-ray fluorescence signal as a function of incident photon energy is spectrally resolved. Second, coupled with our MHz pink beam capability (see section 4.3), time-resolved core-to-core x-ray emission spectroscopy, even the weaker Kβ line, can be captured fast enough to use the time-slicing technique to capture short-lived intermediates (see 4.2). We have also explored using high order crystal reflections such as Si(10 10 0) in order to capture emission lines from heavy elements, as described in section 3.5.

From our collaboration with groups from the European XFEL, the Hungarian Academy of Sciences and Michigan State University, the final results of the analysis of the properties of the light-induced excited state of a novel polypyridyl Iron complex have been published [25]. Dubbed $[Fe(dcpp)_2]^{2+}$ (where dcpp is 2,6-(dicarboxypyridyl)pyridine), the complex had been hypothesized to present an inversion between the triplet and quintet high spin state energetics, leading to an unusually short lifetime in the excited state. However, our combined x-ray absorption/emission spectroscopy study established decisively that the excited state is a quintet state, but with a highly anisotropic first coordination sphere around the metal, in sharp contrast with the near perfect octahedral structure of the ground state, and also with the results of high level DFT calculations.

With a group from the University of California Berkeley, we studied the mechanism for energy transfer in a class of Europium(III)-based photoluminescent complexes. These complexes aim at exploiting the long-lived emission in the visible/near-IR spectrum of trivalent lanthanide complexes by using a sensitizer ligand, which efficiently absorbs a photon and excites the lanthanide ion by energy transfer. The mechanism for this energy transfer is still debated, and it remains a mystery as to why some very similar complexes exhibit very different quantum efficiencies. Because optical transitions between 4f electrons is exceedingly weak, X-ray spectroscopies represent the only viable way to interrogate directly the rare-earth center, as opposed to the ligand. Last year, we performed time-resolved XAS at the Eu(III) L_3-edge following UV excitation, which provided the first direct experimental verification that Dexter electron exchange from the ligand triplet state is the dominant energy transfer mechanism in these photoluminescent systems [26]. In addition, using complementary optical studies following the ligand properties, we found that the variations in the sensitization efficiencies are determined almost entirely by differences in the ligand-centered intersystem crossing rates. Following this successful first experiment, we recently explored the sensitivity of x-ray emission spectroscopy to the electronic configuration in the lanthanide excited states that are populated after energy transfer. By measuring the 4d to 2p transitions, it should be possible to detect changes in the 4f electronic configuration through exchange interaction between 4f and 4d. Measurements were attempted using MHz pink beam and our new multicrystal spectrometer. A transient signal was detected, and comparison with calculations is needed to understand these changes.

Collaborative work continues with groups at the University of Kansas, which aims to better understand the behavior of a series of Mn-based CO_2 reduction catalysts with the form Mn(CO)3(bpy)Br, bpy = 2,2-bipyridyl. The Mn complex offers a promising alternative to the toxic and expensive rhenium complexes used for efficient CO2 reduction and other catalytic processes. Unfortunately, the Mn-based complex suffers from photodegradation under even mild ambient light, which imposes serious limitations for applications. Substitutions on the bpy ligand are used to tune the electronic structure of the complex in order to gain insight into the light-activated chemistry. TR-XAS measurements show a transient signal change consistent with the model involving first a ligand loss and then coordination of the solvent to the metal center before diffusion controlled bimolecular reaction occur on the nano to microsecond timescales. By changing the solvent it was demonstrated that solvent recoordination could be suppressed after ligand dissociation, resulting in alternative photoreactive pathways to investigate. A manuscript is being completed and a follow-up experiment in planned for this fall to precisely determine the excited state geometry.

Finally, with a group from University of Illinois, we studied the charge transfer properties of Lead Selenide quantum dots attached at the surface of Titanium dioxide nanoparticles, where the optical excitation occurs on the quantum dot with the expected process producing a charge injection on the TiO_2 nanoparticle. Using our high-repetition rate setup, time-resolved x-ray absorption measurements can be performed at several element edges (Pb, Se and Ti), which can provide insurance that the measurement is sensitive to electronic changes rather than simply heating of the nanosamples.

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 studies could happen at XFELS.

5 Affiliations of collaborators

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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 either "Strong-field and attosecond science" or "Correlated dynamics". 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, C. Blaga, B.D. Esry, V. Kumarappan, C.D. Lin, D. Rolles, A. Rudenko, and U. Thumm.

Strong-field and attosecond science: Attosecond science is motivated by the idea of observing electronic motion in atoms and molecules on its natural timescale. Important to this is characterizing the attosecond pulses themselves — a topic we have addressed theoretically with a new, improved scheme. We have also carried out a proof-of-principle demonstration of XUV-assisted high-harmonic generation at an FEL in a combined experiment-theory effort. Theory has proposed a way to shape attosecond pulses through high-harmonic generation from controllably aligned molecules, and development continues on a general framework for characterizing and predicting the dependence of strong-field processes on parameters of the laser without heavy computation. Strong-field ionization experiments were carried out on atoms and molecules from mid-infrared to X-ray regimes. These experiments include angle-resolved strong-field ionization studies of SO_2, and pump-probe studies of small polyatomic molecules, like CH_3I and other halomethanes.

Correlated dynamics: Coincidence measurements of strong-field induced C_2H_2 isomerization *without* ionization — but starting from multiple initial charge states both negative and positive — were performed, showing the sensitivity of the isomerization branching ratio to the initial state. The commonly used axial recoil approximation was put to the test for CO_2 following strong-field ionization. Pump-probe studies were performed to reveal the nuclear motion in molecular breakup triggered by NIR, UV, and XUV in the Lab and at FELs. We employed our native-frames technique to separate sequential breakup from concerted breakup in H_2O following single-photon double ionization, allowing us to identify the states involved.

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 C.W. McCurdy from Lawrence Berkeley National Laboratory have benefitted from working with 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, Aarhus, BNL, FLASH, Univ. of Frankfurt, ICFO Barcelona, Univ. of Jena, LBNL, LCLS, Max-Born Institute–Berlin, Max-Planck Institutes for Quantum Optics and Kernphysik, The Ohio State University, PULSE- SLAC, and others), and we actively seek new collaborations.

The laser facilities available to researchers at JRML include the high-repetition rate laser, PULSAR, and the high-power, tunable, long-wavelength laser, HITS, as our main systems. Both have received significant recent investment from the University and are operating near their original specifications again. In fact, due to the efforts of our newest member, C. Blaga, HITS is operating in some aspects better than the original specifications. While the old workhorse laser, KLS, is still yielding high-quality results, supplemental funding will allow us to replace it with a robust system with specifications lying between PULSAR and HITS. We will then transition KLS to a training and development laser.

Finally, there has been a change of leadership within JRML as our long-time Director, I. Ben-Itzhak, stepped down after devoting more than 12 years to the position, skillfully leading us through many challenges and changes. Taking over is the equally long-serving Associate Director for Research, B.D. Esry, with A. Rudenko filling his vacated position. While change in JRML is continuous, the group's dedication, spectrum of expertise, and long legacy of theoretical and experimental synergy promise that exciting physics will continue in JRML.

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

Itzik Ben-Itzhak, J. R. Macdonald Laboratory, Physics Department, Kansas State University, Manhattan, KS 66506; ibi@phys.ksu.edu

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.*[i]

Recent Progress: We focused our experimental work, employing 3D-momentum imaging techniques, on ion-beam and gas-phase targets, while continuing our collaborative research with others. A couple of examples are presented below.

Strong-field driven isomerization of C_2H_2 cations and anions

Bethany Jochim, Ben Berry, T. Severt, M. Zohrabi, P. Feizollah, K. J. Betsch, Kanaka Raju P., J. Rajput, E. Wells, K.D. Carnes, and I. Ben-Itzhak

Over the years, acetylene has served as a prototype system for examining isomerization processes [1,2]. Specifically, studies have focused on the conversion between its acetylene (HCCH) and vinylidene (H_2CC) isomers, an example of 1,2 hydrogen migration [3]. A wide array of experimental techniques have been applied to examine isomerization of C_2H_2 molecules. For example, photodetachment spectroscopy of C_2H_2 anions has probed vinylidene → acetylene isomerization dynamics (see, e.g., Ref. [4]). Alternatively, a far less "gentle" approach has been taken, breaking the molecule and extracting information from the measured fragments. The common signatures of isomerization in fragmentation studies are the measured $C^q + CH_2^{q'}$ and $CH^q + CH^{q'}$ final products for vinylidene and acetylene configurations, respectively (q and q' are the charge states of the final products) [5-9].

Using coincidence 3D momentum imaging, we investigate intense ultrafast laser-induced isomerization through two-body fragmentation of keV beams of various charge states of C_2H_2, including $C_2H_2^-$, $C_2H_2^+$, and $C_2H_2^{2+}$. Whereas most of the previous work on strong field isomerization and fragmentation of acetylene has necessarily involved ionization step(s) [5-9], by focusing on dissociation, we ensure that the dynamics ensue within a single molecular ion species, potentially simplifying interpretation [5,10]. Also, the use of ion-beam targets enables control of the initial configuration, which our measurements indicate strongly influences the final products associated with isomerization. Our targets allow studies of acetylene, vinylidene and *cis*/*trans* initial configurations. This is demonstrated in Fig. 1 for $C_2H_2^+$ undergoing efficient HCCH→H_2CC isomerization, where in contrast $C_2H_2^-$ isomerization in the opposite direction, i.e. H_2CC→ HCCH, hardly happens (see Pub. [17]).

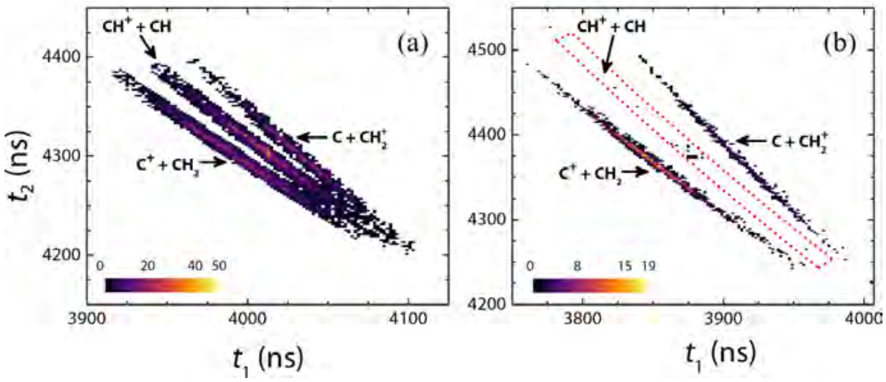

Figure 1. Coincidence time-of-flight (CTOF) fragmentation spectra of $C_2H_2^+$ generated from (a) C_2H_2 and (b) $C_2H_2^-$ after momentum conservation. The dashed red "box" in panel (b) indicates the expected position of the $CH^+ + CH$ channel, i.e., the channel associated with the HCCH final configuration (adapted from Pub. [17]).

Native frames: separating sequential from concerted three-body fragmentation in the single-photon double ionization of water and ammonia

T. Severt[1]*, W. Iskandar, K.A. Larsen, Z.L. Streeter, D. Reedy, B. Jochim,*
A. Gatton, E.G. Champenois, M.M. Brister, R. Strom, D. Reedy, B. Griffin, D. Call,
A.L. Landers, J.B. Williams, D.S. Slaughter, R.R. Lucchese, C.W. McCurdy, Th. Weber, and I. Ben-Itzhak

During the fragmentation of polyatomic molecules, two or more bonds may break in a concerted manner ("simultaneously") or sequentially (stepwise). Separating these competing processes has been a main goal toward improving our understanding of fragmentation dynamics. Recently, we proposed the native-frames method (see Pub. [8] and Ref. [11]) to analyze three-body breakup and accomplish the goals above. Our analysis method is based on the use of relative momenta, therefore following the fragmentation steps in their respective center-of-mass reference frames. When the intermediate molecular fragment rotates long enough in the fragmentation plane, we identify sequential fragmentation as a uniform angular distribution between the relative momenta. This allows us to reconstruct the distribution of sequential fragmentation events masked by competing breakup processes and separate the sequential and concerted breakup distributions in any plot created from the measured momenta.

As an example, we consider the double-ionization and fragmentation of H_2O into H^+ + H^+ + O + $2e^-$ using a single 57 eV photon. The protons and electrons are measured in coincidence, and the momentum of the neutral oxygen is evaluated using momentum conservation. We arbitrarily label the identical protons as red and blue, in order to identify the step in which each hydrogen is ejected in the sequential breakup. The signature of sequential fragmentation via an OH^+ intermediate breaking into H^+ + O is a uniform $N(\theta_{\mathrm{OH,H}})$ distribution for a second step kinetic-energy-release of $\mathrm{KER_{OH}} < 2.4$ eV. This is the expected $\mathrm{KER_{OH}}$ for predissociation of $\mathrm{OH^+}$ via the metastable $a^1\Delta$ and $b^1\Sigma^+$ states [12]. In Fig. 2(c), we show the $N(\theta_{\mathrm{OH,H}}, \mathrm{KER_{OH}})$ distribution for sequential fragmentation after reconstructing the distribution for $\theta_{\mathrm{OH,H}} < 90°$, where concerted breakup masks the sequential fragmentation. In addition, we plot the $N(\theta_{\mathrm{OH,H}}, \mathrm{KER_{OH}})$ distribution for sequential fragmentation via an OH^+ intermediate in Fig. 2(d), demonstrating that the breakup step each H^+ fragment follows can be distinguished by $\mathrm{KER_{OH}}$. The concerted breakup distribution shown in Fig. 2(b) is evaluated by subtracting panels (c) and (d) from all breakup events shown in Fig. 2(a).

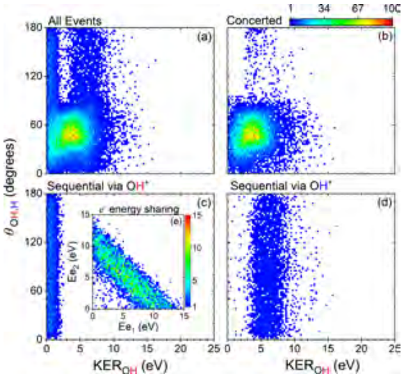

Figure 2. The $N(\theta_{\mathrm{OH,H}}, \mathrm{KER_{OH}})$ distribution for (a) all, (b) concerted, and sequential fragmentation via the (c) $\mathrm{OH^+}$ and (d) $\mathrm{OH^+}$ intermediate molecules. (e) The electron energy sharing for this sequential breakup.

We also show, in Fig. 2(e), the electron-energy sharing indicating that autoionization does not play a role in this sequential fragmentation process.

Furthermore, we experimentally track the sequential-fragmentation dynamics step-by-step and compare it directly to our[2] theoretical treatment of the molecular dynamics. This enables us to identify two pathways and the electronic states involved as demonstrated by the energy correlation map shown in Fig. 3(a) for the D_2O isotopologues. Specifically, we

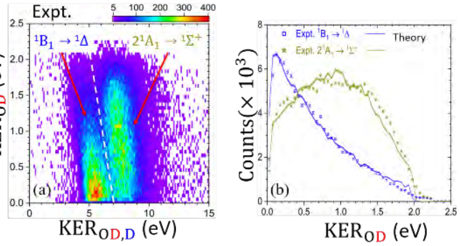

Figure 3. (a) The KER correlation map of the first and second fragmentation step of D_2O, and (b) the second fragmentation step KER.

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[1] *Travis* was invited to present this project at the VUVX19 conference, where he received the Student Award in Atomic, Molecular and Optical Science "*for his investigations of molecular breakup following the double ionization and his contributions to the development of the 'native frames' technique*"

[2] Theory by *Z.L. Streeter*, *R.R. Lucchese*, and *C.W. McCurdy*

show the dissociation of the 2^1A^1 and $^1B^1$ states of D_2O^{2+} into the $a^1\Delta$ and $b^1\Sigma^+$ states of OD^+, respectively, which later predissociates to the $D^+ + O(^3P)$ limit. Moreover, the measured and calculated KER in each of these pathways are in very good agreement as shown in Fig. 3(b).

In addition, we have employed the native frames analysis method to strong field driven fragmentation of other polyatomic molecules as part of our ongoing collaboration with *D. Rolles*, *A. Rudenko*, and *B.D. Esry*. Part of this effort is focused on extending the native-frames analysis method and determining its limitations.

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, bond-rearrangement, as well as hydrogen migration and elimination processes.

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Peer-Reviewed Publications Resulting from this Project (2017-2019)

19. "Adaptive strong-field control of vibrational population in NO^{2+}", O. Voznyuk, Bethany Jochim, M. Zohrabi, A. Broin, R. Averin, K.D. Carnes, I. Ben-Itzik, and E. Wells, J. Chem. Phys. – accepted.
18. "Strong-field induced bond rearrangement in triatomic molecules", S. Zhao, Bethany Jochim, Peyman Feizollah, Jyoti Rajput, F. Ziaee, Kanaka Raju P., B. Kaderiya, K. Borne, Y. Malakar, B. Berry, J. Harrington, D. Rolles, A. Rudenko, K.D. Carnes, E. Wells, I. Ben-Itzhak, and T. Severt, Phys. Rev. A **99**, 053412 (2019).
17. "Dependence on initial configuration of strong field-driven isomerization of C_2H_2 cations and anions", Bethany Jochim, Ben Berry, T. Severt, Peyman Feizollah, M. Zohrabi, Kanaka Raju P., E. Wells, K.D. Carnes, and I. Ben-Itzhak, J. Phys. Chem. Lett. **10**, 2320 (2019).
16. "Tracing intermolecular Coulombic decay of carbon-dioxide dimers and oxygen dimers after valence photo ionization", W. Iskandar, A.S. Gatton, B. Gaire, F.P. Sturm, K.A. Larsen, E.G. Champenois, N. Shivaram, A. Moradmand, J.B. Williams, B. Berry, T. Severt, I. Ben-Itzhak, D. Metz, H. Sann, M. Weller, M. Schöffler, T. Jahnke, R. Dörner, D. Slaughter, and Th. Weber, Phys. Rev. A **99**, 043414 (2019).
15. "Time-resolved imaging of bound and dissociating nuclear wave packets in strong-field ionized iodomethane", Y. Malakar, W.L. Pearson, M. Zohrabi, B. Kaderiya, Kananka Raju P., F. Ziaee, S. Xue, A.T. Le, I. Ben-Itzhak, D. Rolles, and A. Rudenko – Phys. Chem. Chem. Phys. **21**, 14090 (2019).
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[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 Molecular Excitation and Ionization with Midinfrared Laser Drivers: The Role of Molecular Vibrations

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Program Scope: *The scope of this new JRML project is to investigate and understand the role played by molecular resonances in strong field physics, with emphasis on excitation and ionization. The ionization step is the least understood ingredient in laser-induced electron diffraction (LIED), an emerging ultrafast molecular imaging technique we are aiming to develop into a robust and efficient probe to serve JRML's molecular dynamics studies.*

Recent Progress: During my first year at JRML, efforts were concentrated on recruiting the personnel for my research group, refurbishing and upgrading HITS, JRML's most powerful Ti:sapphire laser system, and on constructing a double-sided, multi-detector time of flight apparatus for our planned LIED-based strong field ionization studies.

(A) Development of an independently wavelength tunable, multi-pulse light source for molecular dynamics studies.

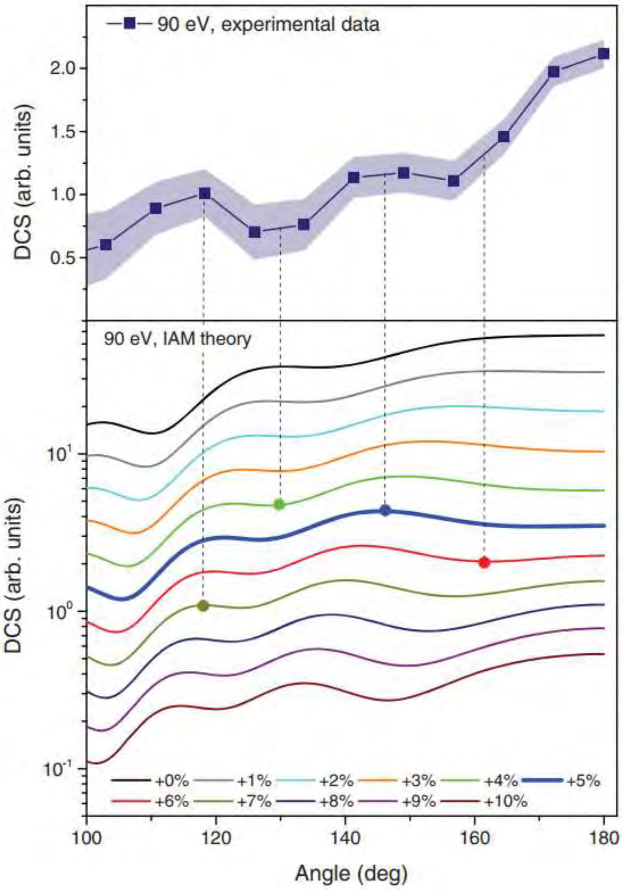
The High Intensity Tunable Source (HITS) is commercial laser system designed to provide broadband, tunable pulses for JRML experiments. Commissioned in 2014, HITS consists of a Ti:sapphire front-end (KMLabs, Red Dragon – 1 kHz, ~20 mJ, 25-30 fs) pumping an optical parametric amplifier (Light Conversion, HE-Topas Prime). After more than 30,000 hours of operation, by the end of the Summer 2018 the performance of the Ti:sapphire front-end has decreased by 40% due to the normal aging of its pump lasers, too low to allow us to reliably drive the tunable OPA. To address this, the laser entered a complete refurbishing phase in November 2018, a task completed with recommissioning the laser in early April 2019. The performance of the 1 kHz Ti:sapphire front-end after commissioning was 29.2 mJ pre-compression, 17.5 mJ post-compression (~60% compressor efficiency) and 27 fs pulse duration at output.

Although HITS has been a productive laser system since its 2014 installation, it was often plagued by operation difficulties and reliability issues that often led to optical damage of various components. The root cause of this problems was traced to the relatively short pulse duration of the chirped oscillator pulse throughout the amplifier stages (~100 ps), a solution chosen by the manufacturer to deliver sub 30 fs pulses. This ultimately led to a relatively large B-integral of the system and poor compressor efficiency through the use of low grove density holographic gratings (1,200 g/mm).

After its April 2019 commissioning, HITS entered an upgrade phase to address its weaknesses. Retaining the same pre-compressor optics, we increased the amount of dispersion imparted by the stretcher to lengthen the uncompressed beam to ~210 ps. With this solution, the B-integral has been halved and the damage threshold of optical materials increased by over 40% (in this regime the damage threshold scales as square root of the pulse duration [1]). The amplifier's performance has remained the same and the mode quality improved. Due to the now larger stretching factors, higher groove density (1,500 g/mm) compressor gratings were required [2]. As the higher groove density gratings are also more efficient, compression losses have been halved, the new compressor having an efficiency of 80%. Thus, under the same pumping conditions, the Ti:sapphire front-end now delivers >23 mJ pulses, a significant 33% post-commission performance boost. The shortest supported pulse duration is still limited by fourth order dispersion, as before, but due to the larger stretching factors the pulse duration has lengthened from 27 fs to 32 fs. We are currently working to shorten the pulse duration below 30 fs by compensating the forth order dispersion using only compressor grating alignments (no active compensation based on acousto-optic devices) [3].

(B) A time of flight spectrometer for multi keV photoelectron angular resolved spectroscopy.

Laser induced electron diffraction (LIED) has emerged in recent years as a promising tool for determining atomic positions inside molecules undergoing transformations like bond relaxation [4], bond breaking [5] and more recently, large macromolecular deformations in C_{60}[6]. The C_{60} result, presented graphically in Figure 1 in the form of an elastic electron-ion differential cross section, was a DOE-funded experimental collaboration between Ohio State [Prof. Louis DiMauro, DEGF02-04ER15614] and JRML under current grant [Prof. Matthias Kling, now at MPQ, Garching, Germany]. For a detailed presentation of the results of this experiment the reader is referred to the abstract of the OSU group presented in this document. Here, we note that the experimental data presented in Figure 1 was collected by the OSU group over 6 hours in a single detector, single-sided time-of-flight (TOF) apparatus where the high energy (~ 1 keV) photoelectron electron angular distribution was measured with an angular resolution of 2.1°, rotating the laser polarization in 4°steps.



experimental LIED data (upper panel) vs IAM calculation (lower panel) at 90 eV. Each line in the lower panel corresponds to a cage elongated along the laser polarization by the value indicated in the legend with respect to the field-free, spherical cage. The minima and maxima indicated in the figure are diffraction extremes, whose angular positions are determined by the size of the cage. The four circles indicate the elongations that best match the corresponding experimental values. From the highest angle to the lowest angle extrema, the elongations are 6%, 5%, 4%, and 7%. (see [6] for details)

To make LIED a robust and reliable ultrafast molecular dynamics probe, during the last year we began construction of a new TOF apparatus specifically designed for LIED studies, a project funded by my K-State startup. Using a double-sided design and a five detector per side, the new K-State TOF will attain a 10-fold increase in data collection rates compared to a regular single-sided TOF. Each side measures approximately 0.5 m and each detector will have a 2° collection angle, capable of recording up to 8-10 electrons per laser shot with an energy resolution ΔE/E = 2% up to 3 keV in a field-free configuration. With these specifications, using either the 1 kHz HITS or the 10 kHz PULSAR laser, the multi-detector TOF will record 5-100 million electrons per minute with a 10^7-10^8 dynamic range, a rate sufficient to probe the molecular structure. Alternative detections schemes based on velocity map imaging or TOF based on position sensitive detectors were investigated, but where found inadequate for LIED due to critical limitations (low electron energy detection limit, reduced dynamic range, low count rates, etc.).

Future Plans: For the first half of the next year, efforts will be focused to finalize the infrastructure buildup outlined in this document. The significantly improved output of HITS front-end will be split post-compression into 3 beams. Two beams will each drive an optical parametric amplifier to generate *independently tunable* pulses in the 180-4200 nm range for pump-probe experiments. The third beam (~1-2 mJ) will be used as a molecular alignment pulse or it will drive a second, third or fourth order harmonic generation stage that will serve as VIS-UV pump. The multi-TOF chamber is currently under construction in the mechanical shop and the electronics and the data acquisition system are under development. We estimate the new LIED-TOF to be commissioned in Winter 2019/2020. Upon the completion of our new laser sources, we will begin measuring the ionization rate of aligned small organic molecules driven by midinfrared laser pulses whose wavelength is at or near vibrational resonances (with the Kumarappan, Lin and Rolles groups) and start our pump-probe LIED studies in small molecules (same groups). Meanwhile, my group is part of an international collaboration with Ohio State University (Prof. Louis DiMauro), Max Planck Institute – Garching, Germany (Prof. Matthias Kling), IFCO-Barcelona, Spain (Prof. Jens Biegert) and Tohoku University, Japan (Profs. Kiyoshi Ueda, Hirohiko Kono, Kaoru Yamazaki), an effort not only dedicated to image with LIED deformations in fullerenes induced by intense, near-infrared pulses under impulsive Raman excitations, but also to demonstrate and disseminate the LIED technology and expertise developed at K-State for ultrafast molecular dynamics investigations.

Peer-Reviewed Publications Resulting from this Project in the Last Three Years (2017-2019):

None yet.

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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 carry out quantitative comparisons with experiment for these highly non-perturbative processes.

Extracting total- and net-photon-number pathways in theory and experiment

Recent progress

One of the challenges to understanding strong-field phenomena sufficiently to predict outcomes without detailed calculation or explicit experiment is the lack of a simple, general, systematic picture for these highly nonlinear processes. Our early success [R1,R2] in developing such a picture for carrier-envelope phase (CEP) effects showed us, though, that it was possible.

Our "general theory" [R1, R2] is based on an exact representation of the time-dependent Schrödinger equation (TDSE). The simple picture that it produced — the interference of *net*-photon-number pathways — describes all known CEP experiments, whether they involve electronic motion, nuclear motion, or both. The representation we identified takes advantage of the fact that the TDSE depends parametrically on the CEP by transforming the wave function to a conjugate space, immediately suggesting even broader possibilities for parametric expansions.

With this idea in mind, time-dependent perturbation theory (TDPT) can be recognized as another example of a parametric expansion. When applied to strong-field phenomena, one concludes that it identifies *total*-photon-number pathways. The distinction between net and total photon numbers is, of course, relevant when many photons are exchanged with the field — as happens in a strong field.

We have combined both of these parametric expansions, thus enabling all possible quantum mechanical pathways to be labeled by their total- and net-photon number in an exact, *ab initio* manner. Whether this decomposition provides greater insight remains to be explored, but our preliminary results are encouraging.

Figure 1 illustrates our decomposition for an energy spectrum that might result from ionization or dissociation from an initial state with energy E_i by a laser pulse with central frequency ω. The usual one-photon absorption pathway, producing the $E_i + \omega$ peak, is

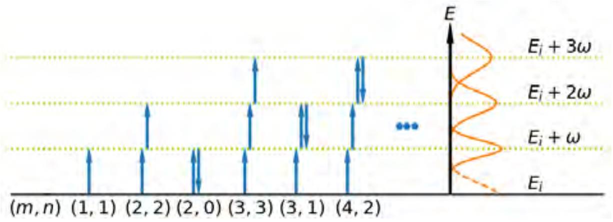

Figure 1: Enumeration of the lowest several total- and net-photon-number pathways for absorption from a state with energy E_i driven by a laser pulse with central frequency ω. The total photon number is m; and the net, n. The resulting energy spectrum is sketched on the right, showing peaks characteristic of above-threshold ionization or dissociation.

denoted $(m,n){=}(1,1)$ where m is the total photon number and n is the net. The net-photon number thus gives the final energy while the total represents how many photons were exchanged with the field during the process.

From the figure, the next contribution to the $E_i + \omega$ peak can only come from $(3,1)$ since energy conservation rules out $(2,1)$. Now, the $(2,2)$ and $(2,0)$ pathways might well have a contribution at energies near $E_i+\omega$ — but only because of the bandwidth of the laser pulse.

Similar arguments show that the next contribution to $E_i+\omega$ comes from $(5,1)$, then $(7,1)$, and so on. Sketching out arrows as in Fig. 1 also shows that these higher-order contributions are themselves composed of several pathways depending on the order of absorption and emission in intermediate states (as do the pathways in Fig. 1 if emission from E_i is allowed). These pathways could be extracted in an explicit perturbation-theory calculation but would not be gauge invariant and would not be accessible from experiment.

The observable spectrum is, of course, the square of the coherent sum of the $(1,1)$, $(3,1)$, $(5,1)$, and all higher amplitudes. Each higher order is thus building intensity dependence into the observable and accounting for things like AC Stark shifts and intensity broadening. We therefore believe that having the total-net-photon-number decomposition can provide useful insights, especially if it can be extracted directly from experimental measurements.

Mathematically, everything follows from the "parametric expansion" of the wave function — *i.e.*, expanding the parametric dependence of the wave function on a convenient basis set. In the present example,

$$|\Psi(t)\rangle = \sum_{m=0}^{\infty} \sum_{n=-\infty}^{\infty} \epsilon^m e^{in\varphi} |\psi_{mn}(t)\rangle. \qquad (1)$$

In this expression, ϵ is a field-strength parameter as in TDPT; and φ is the CEP. We note that the amplitudes $|\psi_{mn}(t)\rangle$ do not depend on the field strength or the CEP. With this expansion, all observables can be derived with the ϵ and φ dependence explicitly accounted for.

Figure 2 shows an application of the total-net decomposition to strong-field dissociation of non-rotating H_2^+. The TDSE for this system was solved including only the $1s\sigma_g$ and $2p\sigma_u$ electronic states in a Gaussian laser pulse. Explicitly, the figure shows the real part of the energy-projected amplitude $|\psi_{mn}(t)\rangle$ from which the kinetic energy release spectrum is calculated.

The figure focuses on the energy range of the one- and two-photon peaks ($n{=}1$ and 2 in the present notation), showing that many more than one or two photons, respectively, are actually exchanged with the field ($m > 2$). Since the system is initially in $v{=}6$ of $1s\sigma_g$, dipole selection rules dictate that only even photon numbers will contribute to the $1s\sigma_g$ amplitudes; similarly, only odd numbers will contribute to $2p\sigma_u$. We see, for instance, that the net-one-photon peak has significant

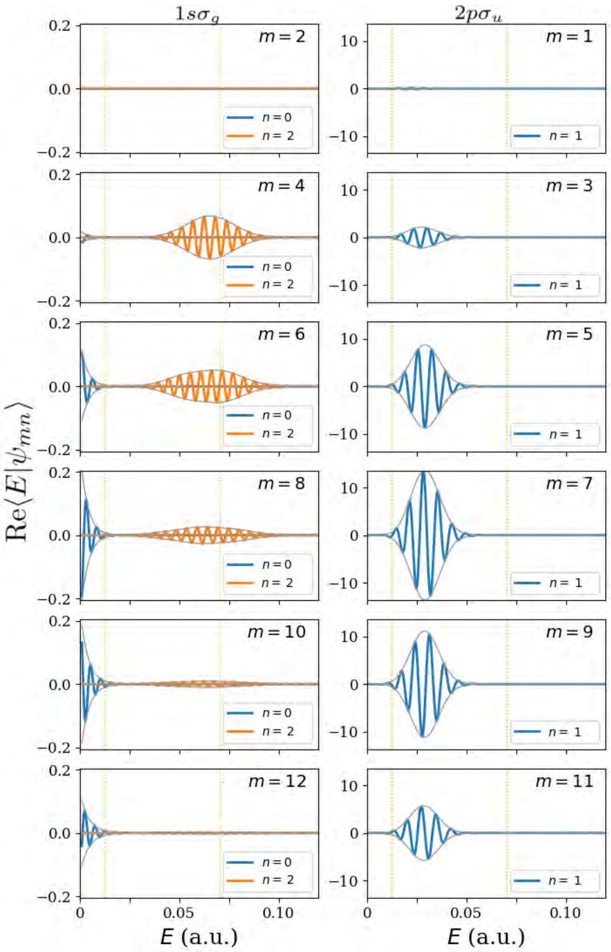

Figure 2: Energy-projected total-net-photon-number amplitude for strong-field dissociation of non-rotating H_2^+ in a 5-fs, 800-nm, $1{\times}10^{13}$-W/cm^2, Gaussian laser pulse. The net-one-photon peak (n=1) has contributions from at least 11-photon (m=11) processes, but effectively none from one-photon (m=1).

contribution from an 11-photon process. Also notable is the fact that there is almost zero contribution from single photon absorption in the net-one-photon peak.

Future plans

The full interpretative power of this representation remains to be explored. Our first steps will be to apply it to a range of examples to see its utility. We want to establish its potential benefits before investing further time and effort to develop these solutions since they are technically demanding. The understanding we gain may even allow us to identify what further qualitative predictions can be made simply based on the structure of the decomposition without any calculation.

Technology transfer

Recent Progress

My group has several collaborations with experimentalists in the J.R. Macdonald Lab not only on science, but also on transferring theoretical and computational technology to their groups. For instance, Pub. [P2] was, in part, the result of sharing our knowledge of few-body formalism and helping apply it to the analysis of experimental data. We have also made our strong-field diatomic dissociation code, including rotation [R3], available to I. Ben-Itzhak's group and have helped them run it to understand their experiment on NO^{2+}. More recently, we have begun to help V. Kumarappan's group improve the performance of their rigid-rotor TDSE code. Based on the discussions so far, we hope for a couple of orders of magnitude reduction in runtimes. If this turns out to be the case, then they will be able to more accurately treat the molecules they already consider as well as being able to effectively treat more complicated systems such as asymmetric tops.

Future Plans

We will continue these technology transfers as they benefit everyone. Our philosophy is to transfer "routine" calculations to the experimentalists as much as possible. This leaves my group free to develop new capabilities and gives the experimental students and postdocs valuable experience with these computational tools. With such experience, they can begin to go beyond calculations for experiments already done to exploratory calculations that focus and guide their experiments. Moreover, the close and frequent interactions within the JRML group guarantee more such opportunities in the future.

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Controlling rotations of asymmetric top molecules: methods and applications

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Program 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 photo-ion and photoelectron angular distributions, and to extract the complex dipole responsible for high-harmonic generation.

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. These include the analysis of momentum distributions of ions and electrons, and extracting the phase and amplitude of high order harmonics. Some examples are discussed below.

Photoelectron angular distributions from multiphoton ionization of molecules:

Molecular-frame photoelectron angular distributions (MFPADs) carry information that is obscured by laboratory-frame measurements. For non-dissociative processes like valence ionization to stable cationic states, pre-aligning the molecules is an attractive alternative to recoil-frame measurements. In the past year, we have focused on measuring photoelectron angular distributions from small molecules using the third harmonic of a Ti:sapphire laser. We impulsively align rotationally-cold molecules with a linearly polarized 785-nm pump pulse, and then ionized the molecules with a 261-nm (third harmonic) probe pulse also linearly polarized in the same direction. Photoelectron

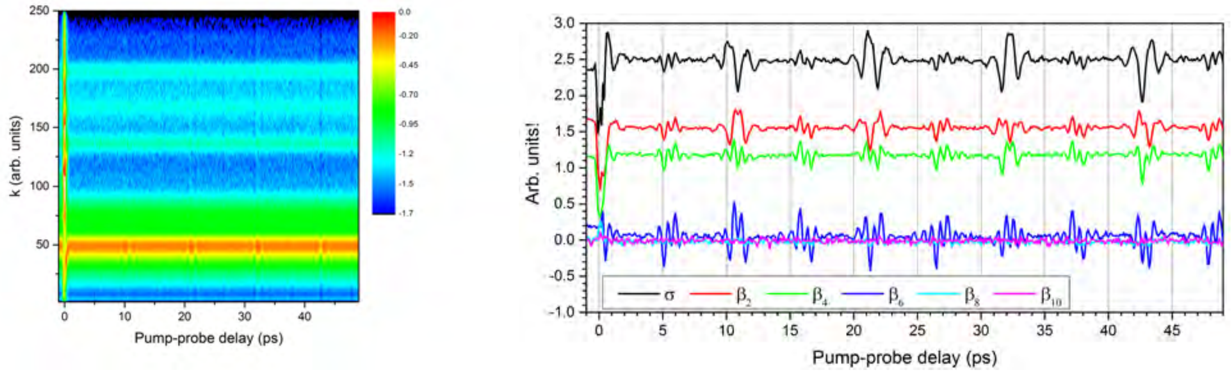

Figure 1: (Left) Delay dependence of the radial momentum component photoelectron momentum for three-photon ionization of CO_2 by 261-nm pulses. The color scale is logarithmic. the dominant channel at k=50 corresponds to 0.3 eV electrons. (Right) Yield and asymmetry parameters as a function of delay for the 0.3 eV channel. The yield is in arbitrary units.

angular distributions are then recorded with a VMI spectrometer. The parallel-polarization scheme allows us to maintain the axial symmetry of the momentum distribution, which allows us the use the pBasex algorithm to Abel invert the data. As the rotational wavepacket evolves, the ionizing pulse encounters a different angular distribution of molecular axes at each delay, and the laboratory-frame photoelectron angular distribution — a convolution of the molecular frame distribution and the molecular axis distribution — changes as well. Our goal is to extract molecular frame photoionization parameters from this data.

Figure 1 shows the delay dependence of the momentum distribution extracted from VMI spectra of photoelectrons produced from CO_2^+. The molecules where cooled to 3 K in a supersonic expansion, and aligned using a 190 fs pump pulse The dominant and lowest energy channel has 0.3 eV electrons corresponding to three-photon ionization to the $X^2\Pi_g$ ground state of the cation. By fitting the electon angular distribution from VMI images to a Legendre polynomial basis, we can also extract several laboratory frame asymmetry parameters. The delay dependence of each of these parameters is then fit using ORRCS. The data and fits are shown in Fig. 1. Measured asymmetry parameters for 4-photon ionization of nitrogen are shown in Fig. 2. For this photoionization channel we can reliably measure asymmetry parameters up to β_{10}. These measurements were made with $\langle \cos^2\theta \rangle > 0.8$; a high degree of alignment is necessary to see high-order rotational coherence.

We have carried out similar measurements on several molecules, including symmetric tops (iodomethane) and asymmetric tops (sulfur dioxide and ethylene). The next step is to develop an algorithm to extract complex photoionization matrix elements from the experimental data using knowledge of the rotational wavepacket. The fitting functions used in ORRCS (Figs. 1 and2 are time-dependent expectation values of the moments of the molecular axis distribution and the fit coefficients connect the lab-frame values of asymmetry parameters to the complex dipole matrix elements. For single-photon ionization of linear molecules, Marceau *et al.* [1] used ORRCS to determine the molecular axis distribution moments and a bootstrapping algorithm to determine complex photoionization matrix elements, but this method needs to be extended to address asymmetric tops and multiphoton ionization.

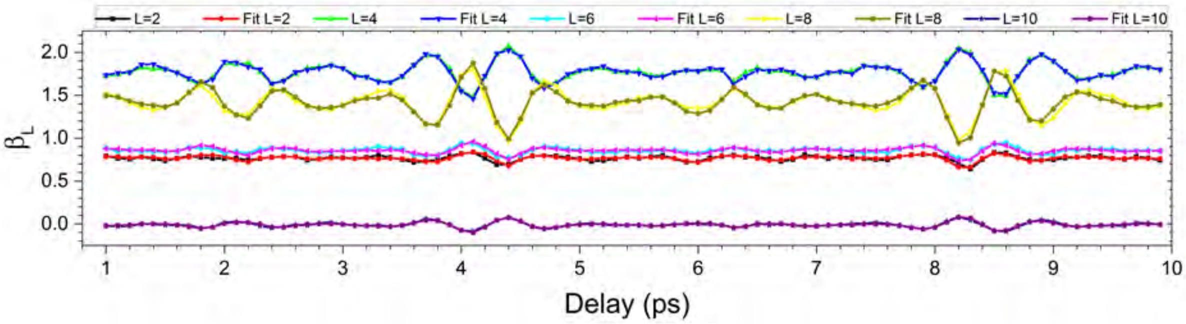

Figure 2: Delay-dependent asymmetry parameters obtained from 4-photon ionization (by a 261 nm probe) of N_2 to its ionic ground state following alignment by a an 785 nm pulse at zero delay. Also shown are the fits obtained using ORRCS. Data from before 1 ps delay are not used in the analysis to avoid pump-probe overlap.

Testing the axial recoil approximation:

By measuring the lab frame momentum distribution of ionic fragments and independently determining the molecular axis distribution using ORRCS allows us to test the axial recoil approximation. For the break up of CO_2 into CO^+ and O^+ by 785 nm pulses, we found that the asymptotic momenta do not correspond to the molecular axis distribution (Lam *et al.*, in prep.). It is likely that the molecules undergo significant reorientation in the 35 fs, 10^{15} W/cm^2 probe pulses before double ionization and fragmentation—in fact, reorientation in the leading edge of such intense pulses at 800 nm is likely to be unavoidable. To reduce the effect of this reorientation, we have measured fragmentation by the third harmonic. This data is is being analyzed to look for the breakdown of the axial recoil approximation.

Future plans

In collaboration with Brett Esry, we are working to improve our rotational TDSE code to handle asymmetric top dynamics more efficiently. We expect that this will not only speed up the data analysis for ORRCS, it will also allow us to address a wider set of molecules and experiments. For instance, we plan to extend our measurements to chiral molecules to investigate photoelectron circular dichroism, which is expected to be significantly enhanced in measurements from aligned molecules. As the first experiments in this direction, we have measured photoelectron angular distributions from camphor. We have built an HHG source for photoionization and are preparing to couple it to the VMI spectrometer so we can study single-photon ionization of asymmetric top molecules using ORRCS. The HHG spectrometer is also being used with a OPA to investigate molecular frame harmonic generation in the 1200–1500 nm range. We will soon expand this wavelength range with a higher-power OPA. We were able to extract the phase and amplitude of harmonic dipole as a function of two Euler angles for an asymmetric top for a few harmonics (Makhija *et al.*, EPJ Web Conf. 205, 02005 (2019)), and with the OPA we expect to be able to extend these measurements to a wider range of photon energies.

Peer-Reviewed Publications Resulting from this Project (2017-2019):

[P1] 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).

[P2] Ren, X., Summers, A. M., Kanaka Raju, P., Vajdi, A., Makhija, V., Fehrenbach, C. W., Kling, N. G., Betsch, K. J., Wang, Z., Kling, M. F., Carnes, K. D., Ben-Itzhak, I., Trallero-Herrero, C. and Kumarappan, V., "Single-shot carrier-envelope-phase tagging using an f-2f interferometer and a phase meter: a comparison", Journal of Optics, 19, 124017 (2017).

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Strong field rescattering physics and attosecond physics

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Program Scope:

We investigated the interaction of ultrafast intense lasers and attosecond pulses with atoms and molecules. Two most notable accomplishments in the past year are: (1) the success of finding an efficient and accurate method of retrieving the phase of broadband soft-X-ray isolated attosecond pulses; (2) by fine-tuning the alignment, harmonic spectra from CO_2 can be efficiently controlled to generate shaped attosecond pulses. Efforts toward providing theoretical support for experiments within the JRML in the coming year are also addressed.

1. A PROBP-AC method for retrieving broadband single attosecond pulses in the water-window region

Recent progress

In 2017, using 1850 nm mid-infrared lasers, three experimental groups [R1-R3] reported high-order harmonics in the water-window region. Using the streaking technique, two groups [R1,R2] reported that they have generated isolated attosecond pulses (IAP) with pulse duration of 53 as and 43 as, respectively, while another group [R3] was only able to claim that their pulse is shorter than 225 as. The conventional method of retrieving the pulse duration of an IAP is to determine its spectral phase since the amplitude of the IAP in the energy domain is easily retrieved from the electron energy spectra by photoionizing a rare gas atom by an IAP pulse alone. If the spectral bandwidth is of the order of 10 eV or less, the so-called FROG-CRAB method may be used to retrieve the pulse. When the bandwidth extends to about 100 eV and above, the condition of narrow bandwidth used in the FROG-CRAB method is not valid. We removed this limitation by developing the so-called PROBP (**P**hase **R**etrieval **o**f **B**roadband **P**ulse) [R4] method for such pulses. It turns out that PROBP, as well as the VTGPA method [R5], would suffer from slow convergence and cannot be applied to bandwidth beyond 200 eV if the pulse has nonnegligible chirp. We thus set to finding a new retrieval method for calibrating ultra-broadband pulses in the last two years.

For an attosecond pulse, its temporal duration is shortest [called transform limited (TL)] when the spectral phase is constant or is linearly dependent with energy over the bandwidth. Clearly this is nearly impossible over a bandwidth of hundreds of electron volts. To determine the phase of a soft-X-ray (SXR) attosecond pulse in the water-window region, the SXR is used to ionize a rare gas atom in the presence of a time-delayed mid-infrared (MIR) laser that was used to generate the SXR pulses. The photoelectron spectra vs the time-delay between the two pulses, called spectrogram or streaking trace, is then analyzed using algorithms such as FROG-CRAB, VTGPA, PROBP, to retrieve the spectral phase of the SXR. Since the MIR field usually is not known either, the retrieval method is aimed at getting both the SXR and the MIR fields, where the spectrogram is simulated using the strong field approximation (SFA). To reach "convergence", one sets a criterion that the difference between the theory-generated spectrogram and the one from the experiment is less than a merit. This procedure works well for narrow-band pulses, but we found that such a criterion does not work for broadband pulses.

Within the last year, we have developed an updated version of the PROBP method. From the streaking spectra, we first calculate the auto-correlation (AC), S (τ_1, τ_2), of the spectral trace, at two delay times, τ_1 and τ_2. We found that the ACs, unlike the streaking trace, are smooth functions that show clear dependence on the spectral phase of the SXR. We further retrieve the spectral phase from the AC directly, instead of from the spectrogram. This new method retrieve the spectral phase from a smaller data set, which also speeds up the convergence. We called this new method PROBP-AC. We first tested this method against FROG-CRAB and PROBP for IAPs that have bandwidths of less than 100 eV. We found that the new method indeed converges faster and more accurate. The results were published in [A3].

In the last year, we have been able to obtain the streaking data from the three experimental groups. Using our PROBP-AC method we were able to show that the pulse durations of 43 as [R2] and 53 as [R1] are too short. Rather, both pulses were determinedd to be about 61 as. In addition, the pulses in the time domain show significant sub-peaks away from the central peak. For such broadband attosecond pulses, pulse duration alone cannot be used to describe an IAP. Instead, both the spectral amplitude and phase should be fully characterized. A report of this study has been submitted for publication.

Future plans

Experimentally, getting good streaking spectra is still a great challenge and it takes a long time. So far all the analysis of streaking spectra is limited to electrons at ‘zero” degree along the polarization axis of both fields. Thus electrons emitted along other directions were not used. To increase the counts it is desirable to use streaking spectra covering a much larger angular range. Furthermore, instead of using a large number of time delay steps and covering the whole pulse duration of the IR (MIR), we intend to study how to retrieve streaking spectra with “minimum” amount data that are enough for accurate phase retrieval. We will be modifying our PROBP-AC method in the coming year to accomplish this goal.

2. Shaping attosecond pulses by harmonic generation from CO_2 by fine tuning the alignment of molecules

Recent Progress

Harmonic generation from aligned CO_2 molecules has been well studied since 2005 using 800 nm intense lasers, for molecules that are aligned or non-aligned. Typically the harmonic spectra would show a minimum at a certain photon energy. In 2011, Vozzi et al [R6] reported HHG spectra of CO_2 with laser wavelength from 1450 to 1700 nm. They found a very deep minimum at about 60 eV and its position is independent of laser intensity and wavelength. Subsequently in 2013, Rupenyan et al [R7] reported similar studies for wavelength up to about 1450 nm. They also observed a sharp minimum in the harmonic spectra, but its position is at 47 eV. In both experiments, the molecules are aligned with $\langle\cos^2\theta\rangle = 0.6$. The significant discrepancy between these two experiments has never been resolved.

In our group, over the years we have developed a Quantitative Re-Scattering model (QRS) for calculating the HHG spectra for atoms and molecules. This model has been tested widely on many experiments and many molecules in prior grant periods. In last year, we decided to take a look at the origin of the discrepancy between the two experiments. Since the position of the minimum in both experiments is independent of laser wavelength and intensity, according to the QRS theory, we speculated and confirmed that these harmonics originated from the valence orbital only.

To calculate HHG spectra from aligned molecules, according to the QRS, one needs accurate fixed-in-space photo-recombination dipole amplitude and phase. Since molecules are only partially aligned, the harmonics from the ensemble of molecules should be added up coherently to obtain an averaged single molecule harmonic yield. To compare with experimental results we also have to account for the propagation of the harmonics in the gas medium using focusing parameters used in the experiment. From our simulation, we were able to reproduce the minimum at 47 eV for $<\cos^2\theta> =0.6$, in good agreement with Rupenyan et al. To obtain the minimum position at 60 eV reported in Vozzi et al, from our simulation, the degree of alignment would have to be $<\cos^2\theta> =0.40$, instead of $< \cos^2\theta> =0.6$ reported in Vozzi et al.

In our simulation, we also found that near $<\cos^2\theta> =0.40$, the position of the minimum is very sensitive to the degree of alignment in CO_2, even when the value of $<\cos^2\theta>$ is changed by as small as 0.02. Note that at $<\cos^2\theta> =0.40$, the molecules are only slightly aligned. In fact, if the molecules are isotropic ($<\cos^2\theta> =0.33$), there is no minimum in the HHG spectra. Thus we have witnessed extremely sensitive dependence of the HHG spectra on the degree of alignment in CO_2 that has never been reported before.

As a result of this theoretical study, we eventually were able to resolve the discrepancy between the two experiments. In Vozzi et al, their alignment laser is focused and has 10 times the peak intensity than the one used in Rupenya et al. The $<\cos^2\theta>$ of 0.6 was the value at the focus point. In the interaction region of the gas jet, the intensity is smaller and $<\cos^2\theta>$ should be closer to 0.40. In Rupenya et al, the aligning laser is much weaker and is uniformly distributed, with $<\cos^2\theta>=0.6$. After accounting for this nonuniform intensity distribution in the gas cell we were able to reproduce the result of Vozzi et al. Thus the alignment distributions of molecules are different in the two experiments, which is the source of the discrepancy of the two HHG spectra.

A much more significant result from this theoretical study is that one can use the strong alignment dependence to control the harmonic spectra (and the phase) to create shaped attosecond pulses. In particular, each single burst in the harmonic pulse train can be made to split into two bursts through the change of degree of alignment. This method can be used to shape attosecond pulses with the desired profiles at the generation level. One notes that there is no efficient way for post shaping attosecond pulses after they are generated due to the efficient absorption of such lights in the medium.

Future plans

The strong alignment dependence of HHG is the result of the property of CO_2 that its photo-recombination transition dipole has sharp minimum that depends strongly on the angle between the molecular and polarization axes. Such strong dependence has never been explored in conventional photoionization experiments with synchrotron lights, but can be readily explored using HHG from aligned molecules. As a consequence of this study, in the future we will be aiming at (1) finding algorithms to retrieve fixed-in-space photoionization transition dipole and phase; (2) identifying possible interesting experiments that can be investigated with shaped attosecond pulses.

3. Other projects

In the last year we continue to have collaborations on nonsequential double ionization of helium [A4], and on the retrieval of atomic bond lengths based on the LIED (laser induced electron diffraction) experiments of Jens Biegert's group [A1,A2] in Bacelona. On the LIED front, new development in JRML has driven us to look for a newer and more efficient retrieval method of interatomic bond lengths and/or angles directly from the laser-induced high-energy photoelectron spectra. In the coming year we will test the method based on theory-generated data, including data of molecules that are undergoing dynamic evolution with changing geometries. We will also begin to explore the possibilty of studying molecular breakup for triatomic molecules using realistic potential surfaces.

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R4. P. D. Keathley et al. New J. Phys. 18, 073009 (2016).

R5. Xi Zhao et al., Phys. Rev. A95, 033418 (2017).

R6. C. Vozzi et al., Nat. Phys. 7, 822 (2011).

R7. A. Rupernyan et al., Phys. Rev. A87, 033409 (2013).

Partial Peer-Review Publications (2018-2019)

A1. “Imaging an isolated water molecule using a single electron wave packet”, Xinyao Liu, Kasra Amini, Tobias Steinle, A. Sanchez, M. Shaikh, B. Belsa, J. Steinmetzer, Anh-Thu Le, R. Moshammer, T. Pfeifer, J. Ullrich, R. Moszynski, C.D. Lin, S. Gräfe, Jens Biegert, **J. Chem. Phys**. **151**, 024306 (2019).

A2. “Imaging the Renner–Teller effect using laser-induced electron diffraction”, K. Amini, M Sclafani, T. Steinle, Anh-Thu Le, A. Sanchez, C. Müller, J. Steinmetzer, Lun Yue, J Ramón M. Saavedra, M. Hemmer, M. Lewenstein, R. Moshammer, T. Pfeifer, M. G Pullen, J. Ullrich, B. Wolter, R. Moszynski, F J García de Abajo, CD Lin, S. Gräfe, Jens Biegert, **PNAS, 116**, 8173 (2019).

A3. "Method for spectral phase retrieval of single attosecond pulses utilizing the autocorrelation of photoelectron streaking spectra, "Wei-Wei Yu, Xi Zhao, Hui Wei, Su-Ju Wang, C. D. Lin”, **Phys. Rev. A 99**, 033403 (2019).

A4. "Pulse-duration dependence of the double-to-single ionization ratio of Ne by intense 780-nm and 800-nm laser fields: Comparison of simulations with experiments", Zhangjin Chen, Lina Zhang, Yali Wang, Oleg Zatsarinny, Klaus Bartschat, Toru Morishita, C. D. Lin, **Phys. Rev. A 99**, 043408 (2019).

A5. Xi Zhao, Hui Wei, Wei-Wei Yu, and C. D. Lin, “Reconstruction of the complex angle-dependent photoionization transition dipole from a laser-dressed streaking experiment**”**, **Phys. Rev. A** 98, 053404 (2018).

A6. L He, P Lan, AT Le, B Wang, B Wang, X Zhu, P Lu, CD Lin, “Real-time observation of molecular spinning with angular high-harmonic spectroscopy”, **Phys. Lett. Lett**. 121, 163201 (2018).

A7. Tobias Kroh, et al., “Enhanced high-harmonic generation up to the soft X-ray region driven by mid-infrared pulses mixed with their third harmonic”, **Optics Express** 26, 16955 (2018).

A8. C D Lin, Anh-Thu Le, Cheng Jin and Hui Wei, “Elements of the quantitative rescattering Theory”, **J. Phys. B51**, 104001 (2018).

A9. Shan Xue, Hongchuan Du, Bitao Hu, C. D. Lin, and Anh-Thu Le, “ Following coherent multichannel nuclear wave packets in pump-probe studies of O_2 with ultrashort laser pulses, “ **Phys. Rev.** A97, 043409 (2018)

A10. Zhangjin Chen, X. Li, O. Zatsarinny, K. Bartschat, “Ratios of double to single ionization of He and Ne by strong 400-nm laser pulses using the quantitative rescattering theory”, **Phys. Rev**. A97, 013425 (2018).

Imaging Ultrafast Electronic and Nuclear Dynamics in Polyatomic Molecules

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***Program 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 and free-electron lasers, complemented by experiments with 3rd generation synchrotrons. The aim of the experiments is to test the suitability of different wavelengths and techniques for probing molecular dynamics, and to study exemplary ultrafast reactions in gas-phase molecules with the goal of clarifying their reaction mechanisms and pathways.*

Recent Progress: As in previous years, my research primarily consisted of projects that linked experiments with our laboratory laser sources at the J.R. Macdonald Lab (JRML) with larger-scale efforts at the free-electron lasers LCLS, FLASH, and the European XFEL and the ALS synchrotron radiation facility. We continued studying the strong-field ionization and the dissociation dynamics of halogenated hydrocarbons upon photoexcitation in the ultraviolet (UV), and started first pump-probe experiments on more complex photo-induced isomerization reactions such as ring-opening of cyclic hydrocarbons, e.g. cyclohexadiene. To extend the range of available wavelengths for photoexcitation into the deep UV, we recently commissioned a fourth harmonic (200 nm) generation setup and are currently performing first experiments with it.

Due to the shutdown of LCLS for the upgrade to LCLS II, our FEL activities in the last year mainly concentrated on FLASH and, in particular, the European XFEL, where my group and I participated in the commissioning and first user experiments at the end-station for "small quantum systems" (SQS). Nevertheless, I was also actively involved in the planning for LCLS II, e.g. through my participation in the TMO instrument advisory panel.

(i) Photodissociation and isomerization dynamics probed by femtosecond pump-probe experiments, *K. Borne, F. Ziaee, B. Kaderiya, T. Severt, Kanaka Raju P., I. Ben-Itzhak, A. Rudenko, D. Rolles, B. Erk[1], M. Burt[2], M. Brouard[2], A. Rouzee[3], R. Forbes[3] et al.; [1]DESY, Hamburg, Germany; [2]Oxford University, UK; [3]Max-Born-Institut, Berlin, Germany; PULSE, Stanford, CA.*

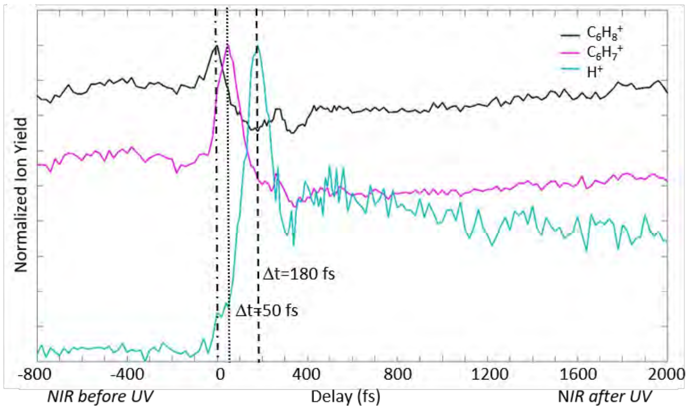

***Figure 1:** (a) Time-resolved fragment ion yields after strong-field ionization of UV-excited cyclohexadiene recorded with our COLTRIMS coincidence setup at JRML.*

Using NIR-NIR, UV-NIR, and UV-XUV pump-probe experiments performed at JRML and at the FLASH free-electron laser, we have continued to study the UV-induced photodissociation and NIR-strong-field ionization of the (di-)halomethanes CH_3I, CH_2IBr, CH_2I_2, and CH_2ICl by means of different electron-ion and ion-ion coincidence and covariance techniques [8, 10, 21, 22, 27]. In particular, our efforts to shorten our UV-pulse duration at JRML to sub-40-fs have allowed detailed insights into the dissociation and ionization dynamics in the first hundred fs, where potential energy surfaces are very steep, and the fate of the molecule is decided as the excited-state wave packet crosses through conical intersections. In parallel to these investigations, which are currently in the final stages of being written up for publication, we also started to extend our pump-probe studies to more complex photo-induced isomerization reactions such as ring-opening of cyclic hydrocarbons, e.g. cyclohexadiene (see Fig. 1). All of these studies greatly benefit from non-time-resolved electron-ion coincidence experiments and high-resolution electron spectroscopy measurements that we performed with synchrotron radiation [7, 12, 13, 26].

(ii) High harmonic generation in mixed XUV and NIR fields at a free-electron laser, *J. Troβ, S. Pathak, A. Summers, D. Rompotis[1], B. Erk[2], R. Boll[1], V. Kumarappan, A.-T. Le, C.-D. Lin, Cheng Jin[3], C. Trallero[4], and D. Rolles, et al.; [1]European XFEL, Schenefeld, Germany; [2]DESY, Hamburg, Germany; [3]Nanjing University of Science and Technology, China; [4]University of Connecticut.*

Despite considerable overlap between the communities involved in high-order harmonic generation (HHG) and free-electron laser (FEL) science and despite the potential for increased experimental flexibility and capabilities if both technologies were combined, no experiments have been reported to date that have combined HHG and FELs. We have recently performed an experiment investigating the generation of high-order harmonics by a femtosecond near-infrared (NIR) laser pulse in the presence of an extreme ultraviolet (XUV) field provided by a free-electron laser, a process referred to as XUV-assisted high-order harmonic generation. Our experimental findings show that the XUV field can lead to a small enhancement in the harmonic yield when the XUV and NIR pulses overlap in time, while a strong decrease of the HHG yield and a red shift of the HHG spectrum is observed when the XUV precedes the NIR pulse (see Fig. 2). The latter observations are in qualitative agreement with model calculations that consider the effect of a decreased number of neutral emitters but are at odds with the predicted effect of the correspondingly increased ionization fraction on the phase matching. Our study demonstrates the technical feasibility of XUV-assisted HHG experiments at free-electron lasers, which provides new

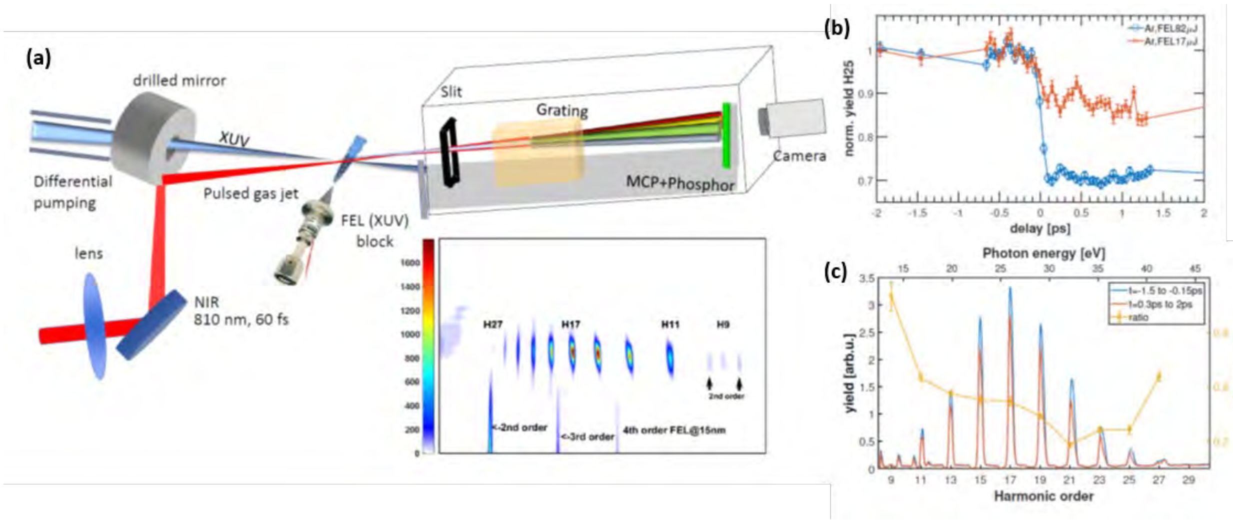

Figure 2: *(a) Sketch of the experimental setup for our XUV-assisted HHG experiment at FLASH. A typical HHG spectrum generated during the experiment is shown in the inset. (b) Yield of the 25th harmonic of the NIR drive laser produced in Ar gas as a function of delay between NIR and FEL pulses and for two different FEL pulse energies. At positive delays, the FEL pulse, which has a photon energy of 82.6 eV, precedes the NIR pulse, causing a drop in the harmonic yield produced in the experiment. (c) Averaged HHG spectrum for the NIR pulse arriving between 1.5 and 0.15 ps before the XUV pulse (blue), and between 0.3 and 2 ps after the XUV pulse (red). The yellow data points show the ratio of the integrated yield of each harmonic order for the two spectra shown in red and blue. (Troβ et al., submitted).*

avenues to investigate correlation-driven electron dynamics as well as novel ways to study and control propagation effects and phase matching in HHG.

Future Plans: We will use our new deep-UV-NIR pump-probe and coincidence capabilities at JRML (and continue to use our NIR-NIR and UV-NIR pump-probe setups) to study the wavelength dependence of photodissociation and photoisomerization dynamics in various hydrocarbon molecules. The deep-UV region is much less studied than the more easily accessible near-UV region around 266 nm and typically exhibits quite different dynamics due to excitation into higher-lying excited states. At LCLS, we will be actively involved in the recommissioning and first experiments at the new TMO instrument, which will start in Spring 2020 and extend through the rest of the year. We will also participate in several user experiments at the European XFEL and have submitted new proposals for the next beamtime cycle. In particular the experiments using the new COLTRIMS end-station at EuXFEL provide an important testbed for the planned high-repetition-rate coincidence experiments at LCLS II.

Peer-Reviewed Publications Resulting from this Project in the Last Three Years (2017-2019):

1. N. Berrah, …, D. Rolles, …, R. Santra, *Femtosecond-resolved observation of the fragmentation of buckminsterfullerene following X-ray multiphoton ionization*, Nature Physics, in press (2018).
2. D. J. Wilson, A. M. Summers, S. Zigo, B. Davis, S.-J. Robatjazi, J. Powell, D. Rolles, A. Rudenko, C. A. Trallero-Herrero, *An intense, few-cycle source in the long-wave infrared*, Scientific Reports **9**, 6002 (2019).
3. L. Mercadier, …, A. Rudenko, D. Rolles, J. R. Crespo Lopez-Urrutia, and N. Rohringer, *Evidence of Extreme Ultraviolet Superfluorescence in Xenon*, Phys. Rev. Lett. **123**, 023201 (2019).
4. S. Zhao, B. Jochim, P. Feizollah, J. Rajput, F. Ziaee, Kanaka Raju P., B. Kaderiya, K. Borne, Y. Malakar, B. Berry, J. Harrington, D. Rolles, A. Rudenko, K.D. Carnes, E. Wells, I. Ben-Itzhak, and T. Severt, *Strong-field-induced bond rearrangement in triatomic molecules*, Phys. Rev. A **99**, 053412 (2019).
5. K. Toyota, …, N. Berrah, …, D. Rolles, A. Rudenko, R. Santra, *xcalib: a focal spot calibrator for intense X-ray free-electron laser pulses based on the charge state distributions of light atoms*, J. Synch. Rad. **26**, 1017-1030 (2019).
6. A. V. Golovin, …, D. Rolles, *The effect of elliptical polarization in MSXα calculations of the molecular-frame photoelectron angular distributions of CO C(1s) ionization*, Eur. Phys. J. D **73**, 131 (2019).
7. U. Ablikim, …, S. Augustin, S. Pathak, …, N. Berrah, and D. Rolles, *A Coincidence Velocity Map Imaging Spectrometer for Ions and High-Energy Electrons to Study Inner-Shell Photoionization of Gas-Phase Molecules*, Rev. Sci. Instr. **90**, 055103 (2019).
8. Y. Malakar, …, B. Kaderiya, Kanaka Raju P., F. Ziaee, S. Xue, A.T. Le, I. Ben-Itzhak, D. Rolles, and A. Rudenko, *Time-resolved imaging of bound and dissociating nuclear wave packets in strong-field ionized iodomethane*, Phys. Chem. Chem. Phys. **21**, 14090-14102 (2019).
9. N. Ekanayake, M…, T. Severt, P. Feizollah, B. Jochim, B. Kaderiya, Kanaka Raju P., F. Ziaee, K. Borne, K.D. Carnes, D. Rolles, A. Rudenko, I. Ben-Itzhak, B.G. Levine, J.E. Jackson, and M. Dantus, *H_2 roaming chemistry and the formation of H_3^+ from alcohols in strong laser fields*, Nature Communications 9, 5186 (2018).
10. F. Allum, …, A. Rudenko, …, F. Ziaee, M. Brouard, T. Marchenko, D. Rolles, *Coulomb explosion imaging of CH_3I and CH_2ClI photodissociation dynamics*, J. Chem. Phys. **149**, 204313 (2018).
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12. R. Forbes, ..., D. Rolles, ..., J. G. Underwood, D.M.P. Holland, *Photoionization of the iodine 3d, 4s, and 4p orbitals in methyl iodide*, J. Chem. Phys. **149**, 144302 (2018).

13. R. Forbes, ..., D. Rolles, ..., J. G. Underwood, D.M.P. Holland, *Auger electron angular distributions following excitation or ionization of the I 3d level in methyl iodide*, J. Chem. Phys., J. Chem. Phys. **149**, 094304 (2018).
14. M. Sauppe, …, D. Rolles, ..., T. Möller, D. Rupp, *XUV double-pulses with femtosecond to 650 picoseconds separation from a multilayer mirror based split-and-delay unit at FLASH*, J. Synchr. Rad. **25**, 1517-1528 (2018).
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Imaging Light-Induced Dynamics of Small Quantum Systems: From Infrared to Hard X-ray Domain

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Program Scope: The main goals of this research are 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 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. In particular, it focuses at (i) understanding multiple ionization processes in atoms and molecules; (ii) time-domain studies of light-induced ultrafast electronic and nuclear dynamics in molecules and (iii) developing new strong-field and X-ray imaging schemes.

Recent Progress:

1. Experiments at XFELs: interplay between resonant effects, charge rearrangement and nuclear dynamics in multiphoton X-ray ionization of molecules (in collaboration with D. Rolles, R. Boll (European XFEL), T. Jahnke (Univ. of Frankfurt) and R. Santra (CFEL theory division, Hamburg)

Because of the LCLS shutdown in 2019, our main effort in XFEL-based research during this time focused on finishing the analysis of the earlier LCLS campaigns, and on performing experiments at other XFEL facilities worldwide, such as FLASH, SACLA and especially at the newly-commissioned European XFEL. Following our recent LCLS studies of the wavelength dependence of resonantly-enhanced x-ray multiphoton ionization (REXMI) of atoms [R1,P16] and of charge rearrangement enhanced ionization of molecules (CREXIM) [P1] in the *hard* x-ray domain, we performed a series of measurements aimed at investigating the interplay of these effects in *soft* x-ray ionization and fragmentation of iodine-containing molecules at ultrahigh intensities. As illustrated in Fig. 1, which displays the charge state distributions (CSDs) of iodine ions from CH_3I molecules measured for three different photon energies at the EuXFEL, at 1.2 keV and 1.5 keV the CSDs exhibits local maxima characteristic for REXMI. In contrast, at 2 keV, where resonant effects are expected to be negligible [R2], the CSD is rather flat. Interestingly, for two lower photon energies, where the signatures of REXMI are observed, the highest iodine charge states observed resemble those measured for atomic xenon, indicating that the overall ionization of CH_3I molecule is significantly enhanced compared to isolated xenon atoms, because of the charge carried by the carbon and hydrogen fragments. This enhancement, which is most likely a manifestation of the recently discovered CREXIM mechanism [P1], is much less pronounced at 2 keV, where the charge states reached for atomic xenon are

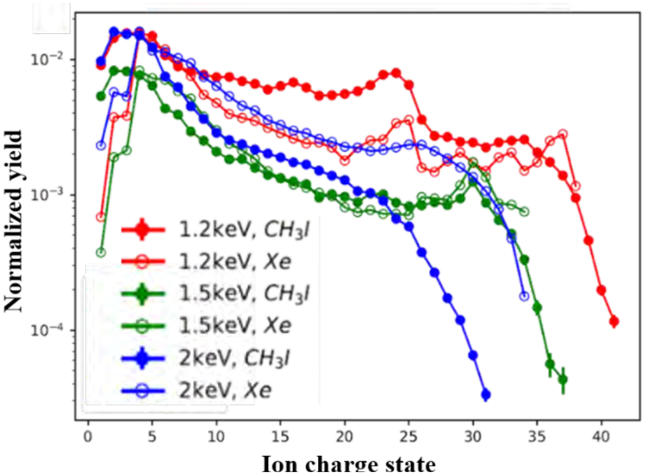

Figure 1: *Charge state distribution for iodine ions (solid symbols) from CH_3I in comparison to xenon ions (open symbols) measured at the same experimental conditions (15-20 fs pulse duration, ~ 1 mJ pulse energy on target).*

higher than for iodine from CH_3I. A more quantitative understanding of the wavelength-dependent CSDs is expected once the XMOLECULE toolkit [R3], which was successfully applied to describe CH_3I ionization by ultraintense 8.3 keV LCLS pulses [P1], can be upgraded to include resonant effects.

Besides measuring the ion CSDs, our recent experiments on CH_3I as well as larger iodine-containing molecules at the SQS end station of the EuXFEL yielded detailed information about kinetic energies, momentum and angular distributions and angular correlations of created ionic fragments. Preliminary data analysis suggests that such coincident ion momentum imaging, enabled by the increased repetition rate of this facility and a dedicated "reaction microscope" spectrometer, might serve a sensitive probe of the instantaneous molecular geometry. This technique is particularly promising for the upcoming LCLS-II with its MHz repetition rate.

2. State-selective analysis of XUV-induced molecular dynamics (in collaboration with D. Rolles, U. Thumm and I. Ben-Itzhak)

Ultrashort XUV pulses produced by high-harmonics generation can be efficiently used to excite electronic and nuclear wave packets in highly excited or ionic molecular states, and to probe them in the time domain. One of the key challenges here is identifying particular states contributing to the dynamics. We have recently taken a two-fold approach to address this issue. First, we developed a narrow-band, single-harmonic XUV source with ~100 fs pulse duration, which allows for state-selective excitation [R4,P15]. Second, we employ coincident photoelectron-photoion imaging with a newly-developed double-sided VMI spectrometer for state-specific analysis for processes driven by broadband, ~25 fs XUV pulses, as illustrated in Fig. 2. We apply these complementary tools to study the dynamics of the photoionized O_2 and CO_2 molecules. For O_2, we have performed the initial experiments with a single-harmonic source, restricting the initial excitation to just two ionic states [P15]. The follow-up orientation-resolved data analysis aimed at verifying theoretical predictions on

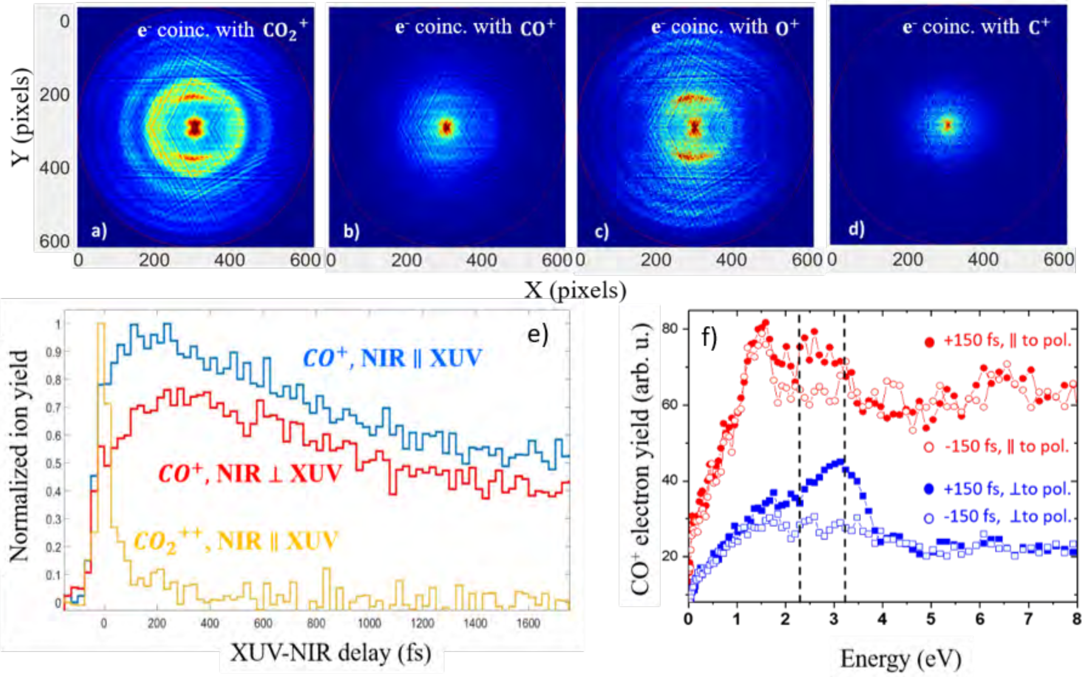

Figure 2: ***(a-d)*** *The raw VMI images of the photoelectrons resulting from ionization and fragmentation of* CO_2 *molecules by 25 fs XUV pump and NIR probe pulses detected in coincidence with different ionic fragments at 150 fs delay. Both pulses are linearly polarized along the vertical direction.* ***e)*** *The delay-dependent yield of the* CO^+ *and* CO_2^{++} *ions.* ***f)*** *Photoelectron spectra coincident with the* CO^+ *ions measured at two different XUV-NIR delays. Vertical dashed lines show the positions expected for the contributions from the* $A^2\,\Pi_u$ *(right), and* $B^2\,\sum_u^+$ *(left) ionized by the 13th harmonic.*

the importance of rotational excitation is currently underway. For CO$_2$, we focus on understanding the role of different cationic states in the observed delay-dependent dynamics of ionic fragments (see Fig. 2e). By analyzing coincident electron spectra (Fig. 2f), we conclude that the slow decrease of the CO$^+$ fragments observed in Fig 2e is defined by the rotational dynamics of the superposition of the $A^2\ \Pi_u$, and $B^2 \sum_u^+$ states. Because of their different symmetry, the ionization to these two states yield different dependence on the molecular orientation ("geometric alignment"), which makes the data in Fig. 2e rather insensitive to the NIR laser polarization, in contrast to earlier results [R5], where only the $B^2 \sum_u^+$ state was playing an important role. As shown in Fig. 2f, by selecting the photoelectrons of a certain energy emitted in a particular direction, we can analyze the delay-dependent signals dominated by a specific electronic state.

Future Plans: We plan to continue research activities in both areas outlined above. The efforts in the experiments using intense, ultrafast x-rays will focus on understanding the response of larger polyatomic systems, on the analysis of many-particle Coulomb explosion data from EuXFEL and on developing schemes for multi-particle ion-electron coincidence schemes for high repetition-rate LCLS-II. For studies of XUV-induced dynamics, we will focus on the photoion-photoelectron coincidence experiments aimed at characterizing the created ro-vibrational wave packets, in close interaction with theory. We will also continue our effort to map the evolution of transient molecular configuration in photochemical reactions [P2,P8,P17,P18,P23], focusing on further developing few-body coincident ion momentum imaging as a probe technique. Besides its direct purpose, this work will be also important for developing experimental schemes and data analysis approaches for LCLS-II with its MHz repetition rate, where the multi-coincidence detection of the reaction products is expected to open up a variety of new techniques for imaging ultrafast dynamics.

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Structure and light-induced dynamics of atoms, ions, and molecules

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A. Controlling and imaging the nuclear dynamics in small molecules

Project scope: To develop conceptual, analytical, and numerical tools to (i) predict the effects of intense short pulses of light in the IR to soft X-ray frequency range on the bound and free electronic and nuclear dynamics in small molecules, (ii) image laser-controlled nuclear and electronic molecular dynamics, and (iii) extend our investigation on dimers to examine the coupling between nuclear degrees of freedom in trimers.

Recent progress: Molecular ionization in short intense IR, VUV, and XUV pulses typically excites ro-vibrational nuclear wave packets that propagate coherently in several electronic states of the residual molecular ions. Near the ion's intrinsic (i.e. external-field-free) and light-induced avoided crossings (conical intersections) nuclear probability amplitude adiabatically follows or diabatically crosses field-dressed Born-Oppenheimer potential curves (surfaces). This excited bound and dissociative nuclear wave-packet motion is being scrutinized in pump-probe experiments and theoretical modeling at JRML [R1-R9,A1].

Ro-vibration dynamics of laser-excited O_2^+ (in collaboration with A. Rudenko and V. Kumarappan). Following up on our previous modeling of dissociative ionization (DI) of oxygen [R2,R3], nitrogen [R9], carbon-oxide [R9], and noble-gas [R2,R10] dimers based on the propagation of nuclear wave packets in one nuclear degree of freedom, the internuclear distance R, we significantly extended the scope of our investigations (i) addressing the coupling between nuclear degrees of freedom and (ii) increasing the number of included Born-Oppenheimer (BO) channels. Addressing open questions [R3-R5] in the interpretation of in-house IR- [R9] and EUV- [R5] pump -- IR-probe experiments, we started to examine the light-induced ro-vibrational nuclear dynamics in O_2^+. Our interest in the DI of O_2 is driven by (i) recent evidence for the participation of the weakly populated O_2^+ ($b\ ^4\Pi_g^-$) state in the dissociation dynamics [R4] and (ii) the possible stabilization of O_2^+ against dissociation due to population trapping in excited electronic states and light-induced potential wells [R2,R11-R14]. We are further encouraged by (iii) the tracking of transient light-induced bond hardening remaining a subject of speculation, even though theoretical investigations of H_2, O_2, and noble-gas dimers [R2,R14] predict noticeable light-induced-state populations.

Investigating the effects of coherent ro-vibrational excitation [R6-R8] on the dissociation dynamics of O_2^+, we assume the rapid ionization of unaligned O_2 molecules, i.e., random alignment angles θ between the molecular axis and linear laser polarization direction, launching a ro-vibrational nuclear wave packet $\psi(R, \theta, 0)$ in the $O_2^+(a\ ^4\Pi_u)$ state [R5]. We calculated potential curves and dipole couplings using the quantum-chemistry code GAMESS [R1] and numerically propagate $\psi(R, \theta, t)$ through a 50 fs delayed IR probe pulse to follow its evolution subject to IR-field-induced dipole couplings between the $a\ ^4\Pi_u$, $b\ ^4\Pi_g^-$, and dissociative $f\ ^4\Pi_g$ states of O_2^+. We propagate $\psi(R, \theta, t)$ long enough to ascertain that identical converged KER spectra are obtained by either (i) Fourier transformation in R or (ii) "virtual-detector" analysis [R2,R15,R16]. To reveal rotational excitation effects in O_2^+, we compare results from our 2D ro-vibrational propagation (in R and θ) with 1D propagation calculations (in R) at fixed molecular orientations θ [R17]. In the 1D calculations, θ is introduced as a parameter in the projection of the laser electric field E(t) on the molecular axis, E(t) cos θ. Figure 1 shows calculated fragment angular distributions P(θ) for two laser peak intensities and 10 to 50 fs IR-pulse lengths. For initially almost aligned molecules (small θ), our 2D results predict enhanced O_2^+ dissociation, due to rotational excitation promoting alignment. One might expect this dynamical O_2^+ alignment to depend on the pulse duration (pulse energy), since longer pulses more likely excite higher rotational states needed to form a narrow angular distribution. Indeed, the angular distributions calculated allowing for rotational excitation in Fig. 1 become more narrowly aligned near θ=0 for increasing pulse lengths. For 6x10^{14} W/cm^2 laser peak intensity and pulse lengths larger than 20 fs, Fig. 1 also displays modulations in the angular distributions due to ro-vibrational excitation at laser-induced (avoided) crossings between cationic Born-Oppenheimer states [R18,R19]. We tentatively assign these oscillations to the nodal structure of the dominant rotationally excited states.

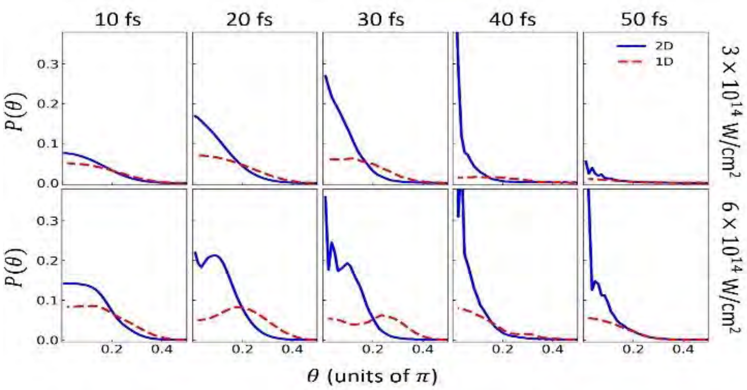

Fig. 1. Effects of coherent ro-vibrational excitation on fragment angular distributions. O^+ angular distribution P(θ) after DI of O_2 in 3x10^{14} W/cm^2 (upper panels) and 6x10^{14} W/cm^2 (lower panels) 800 nm Gaussian pulses with lengths between 10 fs and 50 fs. Red dashed and blue solid lines show P(θ) without (1D) and allowing for (2D) rotational excitation.

Interestingly, the total, angle-integrated, dissociation yields P_{tot} do not monotonously increase with the pulse length (pulse energy) and thus raise questions with regard to possible population trapping into either light-induced (bond hardening) or intrinsic (structural) potential wells. To better display this stabilization effect, Fig. 2 shows angle-integrated dissociation probabilities of Fig. 1. One might anticipate that increasing the pulse duration promotes transfer to the dissociative O_2^+ ($f\ ^4\Pi_g$) state, increasing P_{tot}. However, as seen in Fig. 2, P_{tot} begins to decrease for laser pulses durations above 20 fs. This trend is observed in 1D and 2D calculations, and the decrease of P_{tot} persists in rotating molecules.

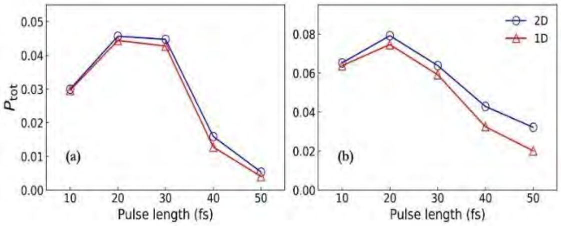

Fig. 2. Stabilization against dissociation. Total dissociation probabilities as functions of the pulse length for the laser parameters of Fig. 1, **(a)** 3x10^{14} W/cm^2 and **(b)** 6x10^{14} W/cm^2. Red triangles and blue circles show results without (1D) and allowing for (2D) rotational excitation.

To further examine (i) rotational-excitation effects on P(θ) (Fig. 1) and (ii) stabilization against dissociation (Fig. 2), we scrutinize the coherent nuclear wave-packet evolution in the $a\ ^4\Pi_u$, $b\ ^4\Pi_g^-$, and $f\ ^4\Pi_g$ states of O_2^+ in the time and complementary quantum-beat (energy) domains [R2,R3,R20]. Figure 3 shows vibrational quantum-beat (QB) spectra for the dynamics of an initial Franck-Condon nuclear wave packet in the O_2^+ ($a\ ^4\Pi_u$) state, driven by a flat-top probe pulse with 50 fs ramp-up time for a delay range of 10 ps (middle and right panels), vis-à-vis the field-free Franck-Condon wave–packet motion in the O_2^+ ($a\ ^4\Pi_u$) state (left panel). Below 30 THz, the middle panel shows (Δv=1) QBs between adjacent bound vibration states of the O_2^+ ($a\ ^4\Pi_u$) potential well and fainter "intruder lines" from overtones (Δv>1). These frequencies are strongly shifted compared to the frequency differences of the field-free Born-Oppenheimer states. The beat frequencies in the field-dressed $f\ ^4\Pi_g$ (right panel) and $a\ ^4\Pi_u$ states (middle panel) coincide. Excitation to the repulsive $f\ ^4\Pi_g$ state thus occurs without significant dispersion of the nuclear wave packet. The weak signal strength in the $f\ ^4\Pi_g$ spectrum (right panel) indicates that the excited portion of the wave packet is transiently trapped in the light-dressed $f\ ^4\Pi_g$ state. This population trapping is consistent with the suppressed dissociation shown in Figs. 1 and 2. Indeed, our calculations show that the final population transferred to the field-dressed $f\ ^4\Pi_g$ potential curve decreases for pulse lengths above 30 fs, akin to IR-pulse induced bound-hardening and molecular stabilization, predicted for H_2^+ in time-independent Floquet and wave-packet-propagation calculations [R11].

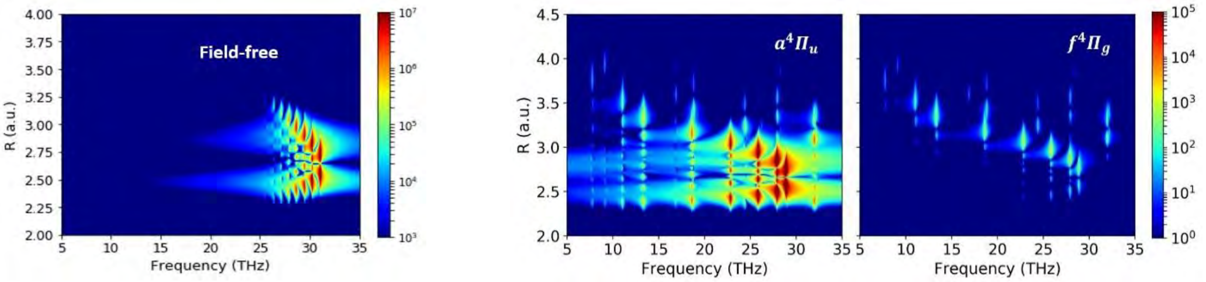

Fig. 3. Coupled nuclear motion in two electronic states. **Left:** Vibrational QB spectrum for the field-free nuclear wave–packet motion in the O_2^+ (a $^4\Pi_u$) state. **Middle and right**: Field-coupled nuclear-wave-packet motion in the field-dressed a $^4\Pi_u$ and f $^4\Pi_g$ states of O_2^+ in an 800 nm, 10^{14} W/cm^2 continuous probe pulse with a 50 fs $\sin^2$ ramp. The dynamics is initialized in the O_2^+ (a $^4\Pi_u$) state by rapid ionization of O_2.

Future plans: We plan to (i) expose the underlying mechanisms of field-induced molecular orientation and stabilization effects in pump-probe-delay-dependent KER and ro-vibrational QB spectra, (ii) proceed to finite initial rotational temperatures of the molecular gas by incoherent sampling over Maxwell-Boltzmann-distributed initial rotational states, and (iii) phenomenologically include laser-alignment of the neutral parent molecules. After (iv) applications to N_2 and CO, we intend to (v) examine light-induced DI in triatomic molecules, to start with CO_2, applying GAMESS [R1] to obtain potential energy surfaces and dipole-coupling strengths. In particular, we will reveal and quantify dynamical ro-vibrational couplings between normal (stretching and bending) modes [R21], as functions of the external-field parameters and molecular orientation, in pump-probe-delay-dependent KER spectra and multi-dimensional QB spectra.

B. Probing electronic correlation in He with IR and XUV pulses

Project scope: To reveal and understand signatures of electronic correlation during the excitation and ionization of two-electron systems in pump-probe combinations of ultrashort XUV and laser pulses.

Recent progress: We have optimized our finite-element (FE) discrete-variable-representation code for solving in full dimensionality the TDSE for two-electron atoms exposed to linearly polarized laser pulses [R22-R24,A2]. Major code improvements and extensions include (i) the implementation of a more efficient matrix-exponentiation algorithm, (ii) optimized memory allocation, (iii) machine-specific parallel processing options, (iv) an added restart option (for premature run termination), (v) adjustable non-equidistant rectangular radial (in r_1 and r_2) grids, (vi) added shake-up (single) ionization channels, and (vii) revised angular-momentum-coupling for ionization in elliptically polarized fields. Figure 4 benchmarks these improvements for single-photon double ionization of He. For this test we included 23 partial waves. We used a (57 a.u.)^2 radial grid with 50 FEs on each side, 4 Gaussian quadrature points in each element, and 0.01 a.u. propagation time steps. We calculated XUV shake-up ionization cross sections for He.

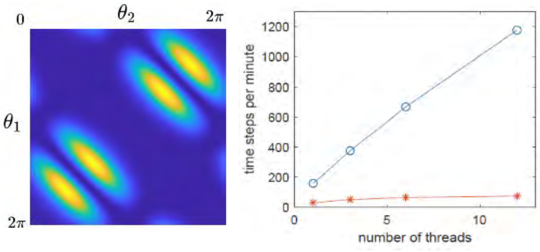

Fig. 3. Benchmarking recent code optimizations for coplanar double ionization of He in 1 fs, 10^{12} W/cm^2, 90 eV photon energy pulses. **Left:** Joint angular distribution [R24] at equal energy sharing. **Right:** Compared to our previous implementation [R23] (red stars), the optimized and extended code (blue circles) is 16x faster on a local workstation with a 28 core hyper-threaded Intel Xeon E5-2697 v3 processor and 128 Gb of RAM.

Future plans: We started to calculate, *ab initio*, streaked and interferometric direct and shake-up ionization of He. We will (i) scrutinize our results against recent shake-up streaking experiments [R25] and (ii) characterize the induced dynamical dipole in He^{+*}.

Peer-reviewed publications acknowledging DOE support (2017-2019)

[1] E. Saydanzad, J. Li, and U. Thumm, *Spatiotemporal imaging plasmonic fields near metallic nanoparticles beyond the diffraction limit*, Phys. Rev. A **98,** 063422 (2018).

[2] J. Li, E. Saydanzad, and U. Thumm, *Imaging plasmonic fields near Au nanospheres with spatiotemporal resolution*, Phys. Rev. Lett. **120**, 223903 (2018).

[3] M. J. Ambrosio and U. Thumm, *Energy-resolved attosecond interferometric photoemission from Ag (111) and Au (111) surfaces*, Phys. Rev. A **97**, 043431 (2018).

[4] M. J. Ambrosio and U. Thumm, *Electronic structure effects in spatiotemporally resolved photoemission interferograms of copper surfaces*, Phys. Rev. A. **96**, 051403(R) (2017).

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

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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 program consists of a variety of closely coupled experimental-theory efforts, united by the overarching goal to provide deep insight into the physics and chemistry of the fundamental interactions that drive key chemical processes in simple molecules, complex molecular systems and molecules in complex environments. Major areas of emphasis include inner-shell excitation, photo-ionization, multiple-ionization and dissociation dynamics of small molecules as well as time-resolved studies of energy- and charge-transport dynamics involving molecules in the gas phase, in the condensed phase, and at interfaces. Experiments apply a broad span of existing and emerging tools based on a combination of laboratory-scale extreme ultraviolet light sources in the femtosecond and attosecond regime, X-ray free electron lasers, synchrotron radiation, and low-energy electron beams with state-of-the-art experimental techniques including transient X-ray absorption and photoemission spectroscopy, XUV nonlinear and four-wave mixing spectroscopy, electron and ion momentum imaging, coincidence techniques, as well as ultrafast X-ray scattering and coherent diffractive imaging. 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 key roles in the dynamics of the systems under investigation. The close coupling between experiment and theory as well as the complementary nature of the different activities within a single program provide a framework to tackle problems across a broad range of timescales, system sizes and, in particular, complexity, that are otherwise intractable.

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 studies in which experiment and theory are tightly integrated.

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

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

Attosecond Dynamics

The attosecond dynamics subgroup utilizes attosecond extreme ultraviolet (XUV) pulses produced by high harmonic generation (HHG) to investigate ultrafast electronic dynamics and electronic-nuclear motion directly in the time domain. Delayed few-cycle near-infrared (NIR) pulses probe the evolution of an XUV-induced coherent superposition of ground and excited states. Spectral dispersion after the pump-probe interaction ensures that exceptional time and energy resolution are obtained without violating the time-energy Fourier relationship. In attosecond transient absorption spectroscopy (ATAS), perturbation of the absorption lineshape as a function of pulse delay results in complex, time-dependent spectra that encode excited-state dynamics. These spectra, however, are often complicated by multiple, overlapping NIR-induced spectral effects (Li, *et al*. **2015** *J. Phys. B* 48, 125601). Noncollinear attosecond wave-mixing spectroscopies recently developed in this program capitalize on wavevector phase-matching conditions to isolate signals originating from multiple higher-order processes. These delay-dependent wave-mixing signals have been successfully employed to measure electronic and, if allowed, vibrational wavepacket dynamics in long-lived Rydberg states of atoms (Cao *et al.* **2016** *Phys. Rev. A*. 94, 053846) and diatomic molecules (Cao *et al.* **2018** *Phys. Rev. A* 97, 023401). In N_2, coherent control on a double-well potential dark state allowed for structural characterization of the poorly studied valence-like outer well (Warrick *et al.* **2018** *Faraday Discuss.* 212, 157-174). A joint experimental-theoretical effort with Mette Gaarde and Kenneth Schafer at Louisiana State University examined the dynamics of the nonlinear signal generation process itself, revealing few-femtosecond delays associated with the accumulation of an AC Stark phase grating (Fidler *et al.* **2019** *Nat. Comm.*, 10, 1384). These techniques provided a route toward the successful development of an XUV multidimensional spectroscopy (Marroux *et al.* **2018** *Science Advances*, 4, 9, eaau3783), analogous to those utilized in the optical and infrared regimes.

Attosecond Transient Absorption and XUV Wave Mixing Studies *(Leone, Neumark)*

Recent Progress: Current work focuses on extending these techniques toward more complex molecular species and dynamics occurring on shorter timescales. ATAS has proven effective in measuring few-femtosecond core-excited state lifetimes in simple atomic systems (Hütten *et al*. **2018** *Nat. Comm.*, 9, 719). Recent experiments performed here investigate $4d^{-1}6p$ core-excited states at the iodine $N_{4,5}$ pre-edge of ICl and demonstrate the power of ATAS measurements on molecular species in which orbital alignment relative to the internuclear axis becomes relevant. As shown in the transient spectrum in Fig. 1-1a, ligand field splitting separates Rydberg transitions with different core-hole alignments relative to the molecular axis. At moderate NIR intensities, the observed transient signal can be attributed primarily to the non-resonant Stark effect, as the resonant dark state necessary for NIR-coupling is located outside the NIR bandwidth. Examination of these states as a function of delay reveals that core-hole lifetimes depend strongly on the alignment of the core vacancy (Fig. 1-1b-c). Core-hole states aligned parallel to the I-Cl bond are observed to decay with lifetimes of 3.5 ± 0.4 fs and 4.3 ± 0.4 fs (black lines), while those aligned perpendicular to the internuclear axis exhibit significantly longer lifetimes of 7.5 ± 0.8 fs and 8.8 ± 0.8 fs (red lines). The short timescales of these decays ensures negligible influence of nuclear motion on the results. *Ab initio* calculations using the Fano-algebraic diagrammatic construction (ADC)-Stieltjes method performed by collaborator Alexander Kuleff at the University of Heidelberg indicate that greater participation of non-local decay channels involving the adjacent chlorine atom enhances the decay rates for core-hole states aligned along the molecular axis. These experiments are the first to measure orbital alignment-dependent core-excited state lifetimes and suggest an interesting new avenue of research exploring the relationship between core-hole lifetime and molecular structure.

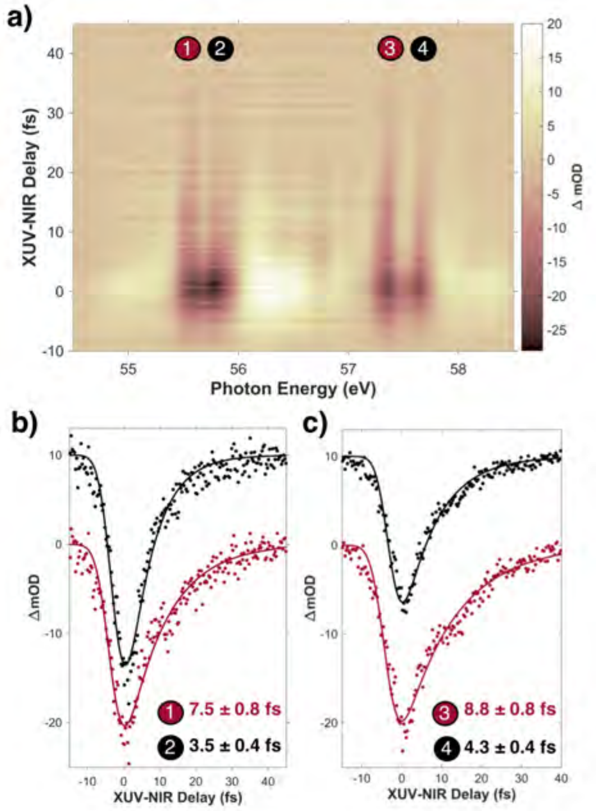


Fig. 1-1: Iodine $4d^{-1}6p$ state lifetimes depend on the alignment of the core hole relative to the molecular axis. (a) ATAS of the iodine 4d $N_{4,5}$ pre-edge absorption spectrum of ICl. The numbered labels designate the following states: 1. $4d\delta_{5/2}6p$, 2. $4d(\pi_{3/2};\sigma_{1/2})6p$, 3. $4d\delta_{3/2}6p$, and 4. $4d\pi_{1/2}6p$. Red (black) labels indicate the core hole is perpendicular to (along) the I-Cl bond. Comparisons of states (b) 1 and 2 as well as (c) 3 and 4 reveal that core holes aligned with the molecular axis exhibit reproducibly shorter lifetimes than those aligned perpendicular to the molecular axis.

Complementary efforts aim to apply XUV wave-mixing spectroscopies to the study of dynamics on ultrafast timescales. In atomic krypton, biexponential fits of wave-mixing signals arising from the manifold of $(^2P_{1/2})nd/s$ autoionizing states yield lifetimes consistent with literature lineshape measurements of the short-lived $(^2P_{1/2})nd$ states (Fidler *et al.* **2019** *J. Chem. Phys.*, accepted). Recent work in collaboration with Arvinder Sandhu at the University of Arizona extends these wave mixing techniques to lifetime measurements in molecular systems. In O_2, the broadband XUV pulse generates a coherent superposition of Rydberg states converging to the ionic c $^4\Sigma_u^-$ state between 20.8 – 24.5 eV. The potential energy surfaces of these electronic states primarily support two vibrational levels (v = 0, 1). Although both vibrational levels can decay via autoionization, the v = 1 state lifetimes are shortened due to significant contributions from dissociative decay mechanisms. While there have been some time-resolved experiments on the higher-lying Rydberg states, the lifetimes of the rapidly decaying v = 0, 1 levels of the 3s state have not been accessible experimentally. Using two noncollinear, time-coincident NIR pulses to probe the XUV-induced coherence, transient absorption and wave-mixing signals from the 3s states are generated simultaneously. A fit of the wave-mixing signal emitting at the 3s (v = 0) state produces an excited state lifetime of 9.9 ± 0.2 fs, which is consistent with the factor of two longer polarization decay of 19.1 ± 0.5 fs measured by transient absorption. This preliminary measurement represents the first molecular excited state lifetime extracted by an XUV wave-mixing technique with attosecond pulses. Experiments are ongoing to determine the v = 1 excited state lifetime and to quantify the contributions of autoionization and dissociation to excited state decays as a function of vibrational level and effective principal quantum number.

Future Plans: Enabled by the purchase of a new higher energy Ti:sapphire ultrafast laser system, future work will focus on extending XUV wave-mixing spectroscopies to the study of core-hole dynamics at greater photon energies. Initial experiments with the new apparatus will build on the ATAS core-hole lifetime measurements described above and generate wave-mixing signals from the $4d^{-1}6p$ core-excited states of iodine-containing species. An example of an initial target system is CH_3I. The ample additional NIR pulse energy will permit the generation of 400 nm pulses in a nonlinear crystal while simultaneously improving XUV photon flux from 800 nm-driven harmonics at the iodine $N_{4,5}$ edge. Dark-state mediated coupling processes made possible by the 400 nm pulse will provide the resonance enhancement necessary to observe wave-mixing signals from core-excited states and measure core-hole lifetimes without complications from other NIR-induced spectral effects. These wave-mixing signals will then be employed to characterize more fully the non-local decay mechanisms in core-excited molecules. By varying the delay between a dissociative 266 nm actinic pulse and the XUV pulse, four-wave mixing signals that arise after the introduction of the 400 nm probe pulses will provide measurements of core-hole lifetimes as a function of I-CH_3 bond length. This work will elucidate the distance dependence of non-local decay mechanisms and operate as a benchmark for theoretical models.

When coupled to an optical parametric amplifier (OPA), the new laser system will permit wave-mixing experiments at the absorption edges of other atomic species, including the critically important carbon K-edge. The multidimensional wave-mixing techniques already implemented at lower XUV photon energies will provide detailed time- and energy-resolved information on ultrafast processes occurring in chemically significant organic molecules. The development of wave-mixing spectroscopies will ultimately lend insight into the electronic dynamics that form the foundations of chemical reactions, but remain inaccessible by other techniques.

Ultrafast Excited State Dynamics Probed by Multidimensional Momentum Imaging

Angle-resolved atomic and molecular photoionization measurements are sensitive to dynamics, mechanisms, selection rules, electron correlation and entanglement. In particular, Molecular Frame Photoelectron Angular Distributions (MFPADs), i.e. the body-fixed frame electron emission patterns in molecules, interrogate the molecule from within and shed light on fundamental properties such as symmetry, structure, energy transfer between electrons and nuclei as well as vibrational dynamics such as bending and stretching of the molecular backbone. The cold-target recoil ion momentum spectroscopy (COLTRIMS) method is among the most powerful approaches to investigate kinematics and dynamics of molecular systems by detecting the 3D momenta of electrons and recoil ions in coincidence. The method gives access to the square of the final state wave function in momentum space and is hence ideally suited to study many-body interactions of model systems in great detail. Studies focus on fundamentally important systems that are within reach of both complete experimental characterization and accurate theoretical treatment and interpretation, enabling tight coupling of the experimental and the theoretical thrusts, which directly complement, inspire and inform each other.

Fingerprints of Core-Hole Localization in the Inner-Shell Ionization of Carbon Tetrachloride (CCl_4) *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: We used COLTRIMS at the Advanced Light Source (ALS) to study chlorine L-shell photoionization of CCl_4 with subsequent Auger decay resulting in the fragmentation $CCl_3^+ + Cl^+ + e_A + e_p$. The shape of the kinetic energy release (KER) distribution is similar to that due to fluorine K-shell ionization of CF_4 (C.W. McCurdy *et al.* **2017** *Phys. Rev. A* 95, 011401(R)). Both are dominated by high energies and exhibit a bimodal KER distribution. Similar to our previous findings at the fluorine K-edge of CF_4, the measurements indicate a fingerprint of core-hole localization in the Cl 2p inner-shell ionization of the CCl_4 molecule as indicated by the pronounced forward/backward (left/right) asymmetry of the recoil-frame photoelectron angular distribution (RFPAD) shown in Fig. 1-2. Here, ionization of each of the four Cl atoms may contain multiple orbital contributions from the p_x, p_y and p_z orbitals. Rich structures are observed in the RFPADs for light polarization orthogonal to the recoil axis (Fig. 1-2). Less complex patterns are observed when the polarization is aligned along the recoil axis. This is contrary to the trend in CF_4, where F K-shell RFPADs exhibit the most

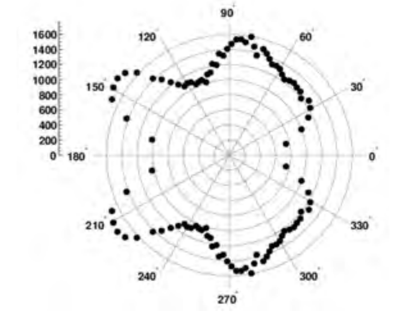


Fig. 1-2: RFPADs for the Cl^++CCl^{3+} channel of the PDI of CCl_4 (3.5 eV < KER < 7 eV), relative to the Cl^+ direction at 0° to the right. Shown for a photoelectron energy of 5.14 eV (originating from the Cl ($2p_{3/2}$) level) using 212 eV photons, polarization orthogonal (+/- 20°) to the recoil axis.

complex structures when the polarization is aligned along the recoil axis. It appears that spin-orbit coupling has little impact on the RFPADs, which are very similar for ionization from the Cl $2p_{3/2}$ and the Cl $2p_{1/2}$ orbitals as long as the photoelectrons have the same kinetic energy. The experimental results strongly suggest that core-hole localization is observed in inner-shell ionization of both CF_4 and CCl_4. Its detailed manifestation in the RFPADs, however, noticeably differs for the two systems and requires further analysis through *ab initio* theory. This analysis will be performed in collaboration with the LBNL AMOS theory team to establish the fundamental physics underlying the core-hole localization mechanism (Gaire *et al*., manuscript in preparation, *Phys. Rev. R*).

Symmetry Breaking in the Body-Fixed Electron Emission Patterns of H_2^+ and D_2^+ due to Electron-Retroaction in Photodissociation Close to Threshold *(Weber, Slaughter)*

Recent Progress: We have performed a detailed investigation of symmetry breaking in the MFPADs of singly ionized H_2 and D_2 molecules near the dissociation threshold (Heck *et al*., submitted to *Phys. Rev. R* (August 2019)). We find that the Coulomb field of the ejected electron couples the electron and nuclear dynamics via retroaction, i.e. a post-ionization interaction, in which the electric field of the emitted electron influences the dissociation process of the parent molecular cation. The highly differential MFPADs and associated photoelectron asymmetry parameters are exquisitely sensitive to coupled electronic-nuclear dynamics. The experimentally observed asymmetry and dynamics as a function of the photoelectron kinetic energy, the dissociation KER, and the mass of the nuclei can be well described classically except for photoelectron energies very close (<100 meV) to the dissociative photoionization threshold, where a more sophisticated treatment appears to be required. In this low-energy regime, depicted in Fig. 1-3, the photoelectron velocity is about 10 times faster than the nuclei in the dissociation process, but the asymmetry parameter δ, which quantifies the relative yield of electrons emitted in the direction of the charged nuclear fragment, shows a noticeable deviation from the classical trend, which predicts a factor of 1.5 to 2 higher asymmetries. This may be a fingerprint of strong electron-nuclei interplay that cannot be described by classical retroaction. Instead, it requires more advanced modeling, beyond the Born-Oppenheimer approximation, to capture the instantaneous interaction between all particles during the ionization step. The data serve as a sensitive testbed for future benchmark computational treatments of near-threshold photoionization.

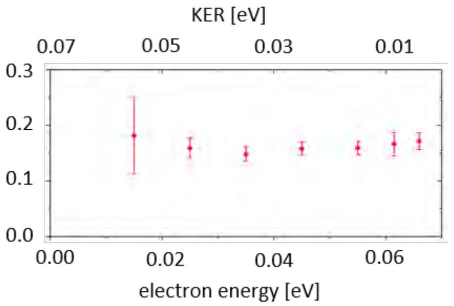


Fig. 1-3: Photoelectron asymmetry parameter delta for the dissociation of H_2^+ with 18.16 eV photons plotted as a function of the electron kinetic energy and the corresponding H^++H fragment KER.

Single-Photon Double-Ionization of Small Polyatomic Molecules: Nuclear Dynamics and Electron Correlation Effects *(Weber, Slaughter, Lucchese, McCurdy, Rescigno)*

Recent Progress: We recently conducted preliminary investigations on the single-photon double-ionization (PDI) of H_2O (Reedy *et al.* **2018** *Phys. Rev. A* 98, 053430) and NH_3 (Larsen *et al.,* manuscript in preparation for submission to *Phys. Rev. R*) molecules, with the goal to achieve the first kinematically complete analysis of the dissociative PDI of polyatomic molecules. These challenging experiments enable the simultaneous probing of electron-electron correlation and electron-nuclei interactions in unprecedented detail. In a first step, we focus on the nuclear dynamics of 2-body and 3-body dissociation. We have identified eight active states, out of nine accessible states (see Subtask 3 for more detail), in the PDI of H_2O and four in NH_3 and extract dissociation angles as well as branching ratios. Moreover, we can distinguish between prompt and indirect ionization mechanisms and focus on the latter processes in the second step. With the newly-developed native frames analysis method introduced by our collaborators from the Kansas State University (I. Ben-Itzhak), and in cooperation with the LBNL

AMOS theory team, we separate and model the evolution of concerted and sequential fragmentation contributions on individual potential energy surfaces. By plotting the energy difference of the expelled protons as a function of their relative emission angle (see example in Fig. 1-4), we identify specific momentum contributions in each degree of freedom of the dication intermediate state and determine how they correlate to the final state momenta in dissociation. We are presently tracing these dynamics back all the way to the Wigner distribution of the initial ground state of the neutral molecule.

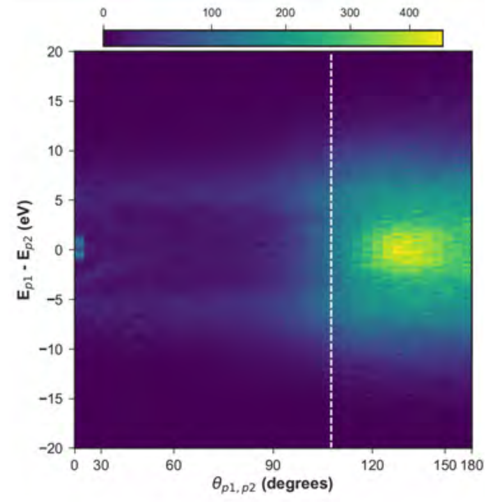


Fig. 1-4: Energy difference of two ejected protons as a function of their relative ejection angle for the PDI of NH_3 at a photon energy of 61.54 eV.

Future Plans: We will analyze the two emitted electrons in coincidence with the nuclei for the three-body breakup in the PDI of D_2O to capture the complete break-up dynamics in full dimensionality. In order to break down the 15-dimensional momentum space, we are generating 2D body-fixed frame electron emission patterns from polar and azimuthal angles for various molecular frame coordinate systems available from the triatomic breakup. So far, we find that the electrons are mostly emitted along the polarization vector. There is also a strong tendency for the oxygen recoil axis to be orientated along the polarization vector. We are in the process of comparing this oxygen reference axis to the axis that bisects the bond angle of the deuterons; these axes differ in cases of unequal kinetic energy sharing between the deuterons. The result of this comparison will enable us to clearly define the electronic dynamics in the appropriate molecular frame, which yields the richest and most sensitive electron emission patterns with respect to the nuclear arrangement. This will form the basis for a molecular movie of the photoionization reaction in this triatomic molecule. The studies will be extended from D_2O to NH_3 and CH_4, in order to understand the dynamics in planar, asymmetric top, and tetrahedral geometries, respectively. Experiments will be carried out in close collaboration with the LBNL AMOS theory team. The investigations will serve as precursors to study dissociation processes of even more complex molecular structures such as CH_3OH in the future. For this target with its many reaction pathways, we expect direct fragmentation as well as delayed Auger processes for different channels, e.g. CH_3^++OH^+ vs CH_3O^++H^+, which should strongly influence the body-fixed frame electron emission patterns.

Angle-Resolved Non-Resonant Two-Photon Single Ionization of Ar using 9.3 eV Photons Produced via Intense High-Harmonic Generation *(Weber, Slaughter, Lucchese, McCurdy, Rescigno)*

Recent Progress: Non-resonant two-photon valence ionization of multi-electron atoms is very sensitive to electron correlation in both the initial and final states. It encodes information on the fundamental interactions and photoionization dynamics of the target. A particularly sensitive observable is the photoelectron angular distribution (PAD), which can provide a detailed view of the mechanisms underlying the photoionization process. The PAD is generated from a coherent superposition of a set of final continuum states, and its sensitivity arises from its dependence on the amplitudes and phases of the different angular momentum (partial wave) components of this coherent sum, which interfere. Predictions of the PAD and its anisotropy parameters β_2 and β_4 for two-photon absorption in Ar atoms were made almost 30 years ago (Pan and Starace **1991**, *Phys. Rev. A* 44, 324–329). The development of high-intensity femtosecond high-order harmonic generation in our laboratory has now enabled the first experimental study of this non-resonant process. Driving HHG in krypton with a frequency-doubled high-energy 400 nm pulse, we produce ~100 nJ pulses of 9.3 eV photons. Using a 3-D momentum imaging spectrometer, we detect photoelectrons and ions produced in the non-resonant two-photon single ionization of Ar in coincidence (see Fig. 1-5). Photoionization from the 3p orbital populates final states with ^{1}S and ^{1}D total symmetry that interfere, resulting in measured PADs peaking perpendicular to the VUV polarization of the two photons. The measured β-parameters ($\beta_2 = -0.95$, $\beta_4 = 0.2$) differ significantly from the correlated velocity predictions ($\beta_2 = -0.55$, $\beta_4 = -0.1$). The results will be compared with new time-dependent *ab initio* calculations from the LBNL AMOS theory team.

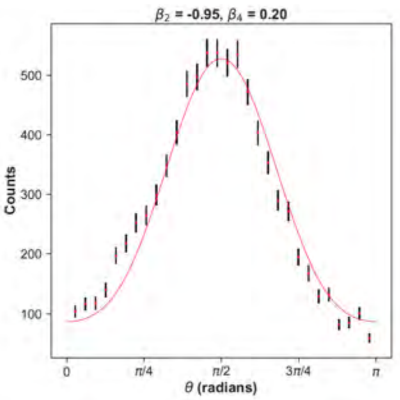


Fig. 1-5: Angle-resolved photo-ionization cross section for 2-photon ionization of Ar at 9.3 eV with Legendre polynomial fit.

Future Plans: We will compare the 9.3+9.3eV two-photon non-resonant experimental results with new measurements of resonant two-color 15.5+3.1eV ionization of Ar. This will enable an investigation of the contributions of real and virtual intermediate states in two-photon ionization to the symmetry and angular momentum of the same final state. The two-color experiment is less straightforward due to the possible introduction of three-photon processes such as 15.5+2×1.55eV. Additional IR-rejecting mirrors will be implemented in the beamline to address these challenges. In the next step, we will extend these investigations towards the non-dissociative ionization of small diatomic molecules (O_2 and N_2). First tests also show dissociation from ion + anion pair production (O^+ and O^-) via resonant 9.3+9.3eV two-photon absorption, which could involve interference between two electronically excited states ($B^3\Sigma_u$ and $a^3\Pi_u$). Together, these projects will lay the foundations to study body-fixed frame electron emission patterns in dissociative VUV+VUV ionization processes of singly ionized molecules such as CO and CH_4 via resonantly excited electronic states and non-adiabatic transitions.

Body-Fixed Frame Photoelectron Imaging of a Molecular Break-up Using Sequential Core-Ionization at an X-ray Free-Electron Laser *(Weber)*

Recent Progress: Body-fixed frame photoelectron imaging was recently envisioned as a powerful technique for time-resolved imaging of molecular dynamics with atomic resolution using X-ray free electron lasers. The method exploits photoelectron waves emitted from well-localized core orbitals to illuminate the molecular structure from within after the absorption of one or more ultrashort X-ray pulses. In a large international collaboration including several PIs from the DOE-BES-AMOS program, the first successful implementation of this technique was achieved using a COLTRIMS reaction microscope at the European XFEL. Two core-holes with subsequent Auger decays result in a Coulomb explosion of the O_2^{4+} ion. Two recoiling fragment ions and two photoelectrons are detected in coincidence. During the first 20 femtoseconds of the dissociation process of the molecule, the body-fixed frame second photoelectron emission patterns from two-photon sequential K-shell ionization of O_2 ($h\nu = 670$ eV) image the increase of the internuclear distance. The second photoelectron may be emitted before or after the first Auger decay, therefore, the MF2ndPAD carries information on both the nuclear motion as well as the electronic relaxation channels throughout the dissociative ionization reaction. The work demonstrates that body-fixed frame photoelectron imaging is a viable route for analyzing molecular dynamics, while employing high repetition rate XFELs. Even without direct access to real-time information, the evolution of the dissociation process can be followed via scanning the kinetic energy release of the Coulomb explosion (Kastrike *et al.*, submitted to *Nature* (Aug. 2019)). Remarkably, this is possible despite the multistep ionization process triggered by the XFEL and reveals a first body-fixed frame molecular movie of a dissociating molecule after two core-hole ionization events (two snapshots are depicted in Fig. 1-6). The experiment paves the way towards time-resolved pump-probe

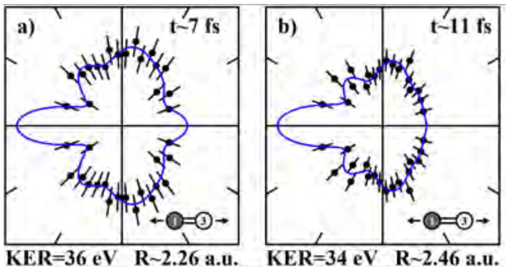


Fig. 1-6: MFPADs of the second photoelectron (~127 eV) of the quadruple ionization of O_2 with XFEL radiation for two KERs as noted below the polar plots. The blue line is a fit using Legendre-polynomials up to l = 9. The internuclear distances R and the absorption time t of the second photon have been obtained using a simple Coulomb explosion model. The triply charged oxygen ion is ejected to the right, as indicated in the insets.

photoelectron diffraction imaging at high-repetition rate XFELs. Moreover, these first prototypical COLTRIMS experiments at an X-ray FEL guide the design of gas jet target and momentum imaging detection schemes for the planned DREAM endstation at LCLS-II.

Future Directions: COLTRIMS experiments at the European XFEL will be extended towards pump–probe measurements. The goal of the proposed project is to monitor the concerted electronic and nuclear dynamics in acetone, leading to dissociation in a so-called Norrish type I reaction scheme. In this process, a photon is absorbed by an electron of the C=O double bond. However, instead of breaking this bond, the energy is transferred to one of the C-C bonds of the methyl-groups via an intersystem crossing from the $^{1}n\pi^{*}$ surface to the $^{3}n\pi^{*}$ surface. Quantum dynamics simulations predict a conformational change of the molecular structure towards a pyramidalization, eventually leading to fragmentation into methyl and acetyl radicals. Previous studies indicated an extremely fast fragmentation within ~100 fs (Zhong *et al.* **1999** *J. Chem. Phys.* 110, 192). On the other hand, newer predictions comprise an ultrafast structural relaxation in the $^{1}n\pi^{*}$ state followed by subsequent intersystem crossing on timescales of several 10-100 ps and fragmentation in the triplet state (Rusteika *et al*. **2008** *Chem. Phys. Lett.* 461, 193 and Hüter *et al*. **2016** *J. Chem. Phys.* 145, 214312). A direct time-resolved measurement is needed to unravel this puzzle. This can help to benchmark and improve quantum chemical calculations on this simplest aliphatic ketone, which serves to predict more accurate models for larger molecules. To accomplish this, we intend to combine element-specific and time-resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy with orientation and structural information based on Coulomb explosion imaging with the COLTRIMS instrument. In this scheme, exciting the molecule by UV pulses produced by the 4th harmonic (100 μJ, 257 nm) of a Yb laser will facilitate a new O1s-to-valence resonance at 526 eV. Exploiting these resonantly excited core-hole states as tracers of the UV-induced valence-excited states, a COLTRIMS experiment will excite and ionize valence-excited molecules, while monitoring the coincident electron-ion energy and angular distributions.

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

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

Probing Ultrafast C–Br Bond Fission in the UV Photochemistry of Bromoform with Femtosecond Core-to-Valence Transient Absorption Spectroscopy *(Gessner, Leone, Neumark)*

Laboratory-based ultrafast transient XUV/X-ray absorption (TXA) spectroscopy is applied to probe unimolecular reaction dynamics from the perspectives of well-defined reporter atoms. Experiments are complemented by high-level *ab initio* calculations of both coupled electronic-nuclear dynamics as well as their spectroscopic fingerprints accessible *via* inner-shell transitions.

Recent Progress: The replacement of the primary Ti:Sapphire based femtosecond laser system of this effort together with a series of experimental improvements has enabled the recording of high-quality XUV transient absorption spectra from single-photon excited molecules. UV pump – XUV probe femtosecond transient absorption spectroscopy is used to study the photodissociation dynamics of bromoform ($CHBr_3$) after excitation with 268 nm. Core-to-valence transitions probe changes in valence electronic structure from the perspective of the Br atoms, while ultrafast time resolution enables the tracing of atomic motion, providing a sensitive method to unravel chemical mechanisms. The transient XUV spectra track, in particular, the population and evolution of singly occupied molecular orbitals (SOMO) created by UV-induced HOMO-LUMO excitation throughout the C–Br bond fission, eventually leading to the formation of radical Br and $CHBr_2$ products. The experiments are interpreted with the aid of first-principles calculations performed by the Prendergast group. They include both excited-state molecular dynamics (MD) simulations to capture the coupled electronic-nuclear dynamics on excited state electronic surfaces as well as time-dependent density functional theory (TDDFT) based predictions of the corresponding XUV spectral fingerprints for transient atomic arrangements. Measured and calculated Br 3d-to-valence transient absorption spectra are shown in Fig. 2-1. C–Br fission follows an approximately C_S symmetrical reaction pathway, leading to a continuous change of electronic orbital characters and atomic arrangements. Changes in the corresponding transient XUV absorption spectra are dominated by two timescales of 40 fs and 85 fs, reflecting the different characteristic motions of the light C and H atoms and the heavy Br atoms, respectively. A previously proposed ultrafast "roaming" isomerization pathway that includes the transient formation of iso-$CHBr_3$ on sub-100 fs timescales is not reproduced. The MD simulations hint that transient isomers may form on multi-100 fs timescales, albeit with a much smaller likelihood than direct $CHBr_2$ – Br scission. This work has been accepted for publication in Structural Dynamics.

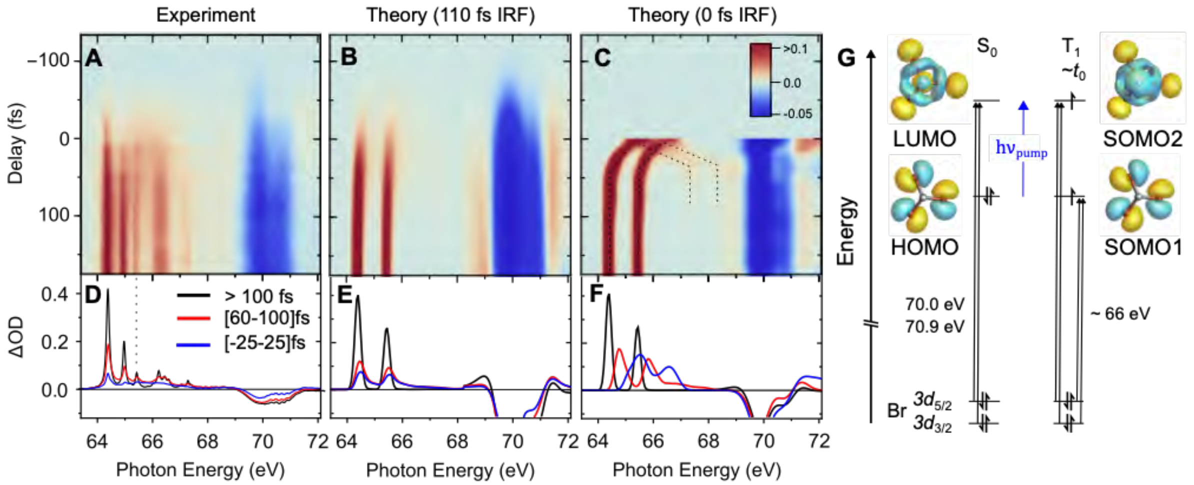


Fig. 2-1: (A) Measured and (B,C) TDDFT-derived Br 3d-to-valence transient absorption as a function of XUV energy (horizontal) and pump-probe time delay (vertical). Negative-going signal (blue) near 70 eV corresponds to decreased absorption due to depletion of the parent molecule concentration by the pump pulse. Positive-going signal (red) corresponds to emerging absorption features due to UV photoexcitation and subsequent dissociation. The theoretical spectra in (B) have been broadened spectrally and temporally to match the experimental resolution. (C) Theoretical transient absorption without temporal broadening, dotted lines emphasize the bifurcation of a spectral feature due to the emergence of distinguishable intra- and inter-atomic transitions. Integration of (A), (B) and (C) over pump-probe time delays specified in the legend in (D) results in the spectra in panels (D), (E) and (F). (G) Illustration of energy levels and orbitals involved in UV-pump/XUV-probe transient absorption experiment.

Future Plans: By combining the new laser system with a high-power optical parametric amplifier (OPA), generation of high-harmonics up to 300 eV will be enabled, extending the reach of ultrafast TXA studies to the inner-shell absorption edges of sulfur and carbon atoms. The broad high-harmonics bandwidth will enable the changes in valence chemical environments to be monitored simultaneously from the perspectives of multiple atoms within the same molecule. For instance, chemical substitution affects the fate of photoexcited thiophenes. While ring-opening dominates in the unsubstituted molecule, substitution can enable efficient intersystem crossing (ISC) and dissipation of energy into internal vibrational modes. TXA at multiple edges will view the evolution of chemical bonds from the atoms on "each side" of the bond.

Dynamics of Excited Electronic States Probed by Ultrafast Transient Polarization Spectroscopy - Photoexcited Liquid Nitrobenzene *(Slaughter, Weber)*

The aim of this project is to develop nonlinear spectroscopic techniques to retrieve information about the motion of electrons and nuclei in complex molecules and molecular systems, with high sensitivity and femtosecond time-resolution. Ultrafast Transient Polarization Spectroscopy (UTPS) employs a four-wave mixing scheme to probe the 3rd-order nonlinear response of excited electronic states in molecules by exploiting the optical Kerr effect in the time domain. The technique produces a signal that is free of background from linear processes, such as absorption, or other nonlinear processes, such as sum-frequency generation. The measurement results from a nonionizing, nonresonant interaction with the sample and the signal is sensitive to electronic structure and the correlated motion of electrons and holes. When UTPS is applied near absorption edges with XUV or X-ray photons, it is expected to be sensitive to the chemical environment and to access atomic site-specific information within a molecule.

Recent Progress: The experiments employ an ultrashort laser excitation (pump) pulse, followed by delayed drive and probe laser pulses (each 40 fs in duration at the target sample) to monitor the excited state dynamics in liquid nitrobenzene. A pair of crossed polarizers on the probe beam enables the measurement of the transient birefringence initiated with the drive pulse, by detection of the polarization signal along the probe direction. This signal provides a relative measurement of specific elements, $\chi^{(3)}_{\mathrm{eff},}$ of the 3rd-order optical susceptibility, $\chi^{(3)}$. A lock-in amplifier, referenced to the modulated pump pulse train, allows the measured $\chi^{(3)}_{\mathrm{eff}}$ of the excited system to be isolated from the ground electronic state. $\chi^{(3)}_{\mathrm{eff}}$ is sensitive to molecular geometries and electronic coherences and, by monitoring $\chi^{(3)}_{\mathrm{eff}}$ over the time delays between all three pulses, the UTPS experiment extracts unique information on the molecular dynamics of excited electronic states. One major advantage of UTPS is that it is virtually background-free, enabling up to 3 orders of magnitude (Wieman and Hänsch, **1976** *Phys. Rev. Lett.* 36, 1170-1173) higher sensitivity than the signal intensity changes in transient absorption spectroscopy experiments.

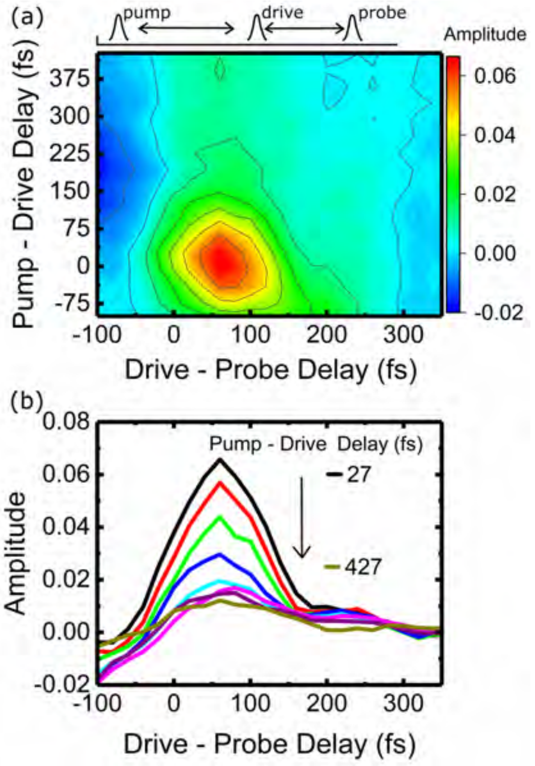


Fig. 2-2: a) Measured 3rd-order nonlinear optical response (amplitude) of liquid nitrobenzene for time delays between NIR drive and probe pulses (horizontal) and a NIR excitation (pump) pulse (vertical). The instrument response function has a full-width at half-maximum of 69 fs. b) Horizontal slices extracted from the 2-dimensional data in a), showing the evolution of the 3rd-order nonlinear optical response with drive-probe delay, for select pump–drive pulse delays.

In collaboration with Niranjan Shivaram (Purdue University), recent UTPS measurements performed on photoexcited liquid nitrobenzene have revealed a distinct 3rd order nonlinear response of the system following multiphoton excitation with a 40 fs NIR pulse

(Fig. 2-2). The results show structures in $\chi^{(3)}_{\mathrm{eff}}$, resolved on few-fs timescales following multi-photon NIR excitation, revealing new observations on a system that has been extensively studied by other ultrafast experimental methods, but nonetheless remains poorly understood. In their time-resolved photoelectron spectroscopy study, Shalk *et al.* (**2018** *Chem. Phys. Lett.* 691, 379-387) recently measured a decay time of 500 fs following 200 nm photoexcitation of nitrobenzene, suggesting the decay pathway to the ground electronic state occurs via a conical intersection between the excited $\pi\pi^*$ state to the $n\pi^*$ state that is localized on the NO_2 functional group. We measure a comparable decay time in $\chi^{(3)}_{\mathrm{eff}}$, following a NIR multiphoton excitation (pump) pulse. This trend appears in Fig. 2-2a as a decay of the main feature near 80 fs drive-probe delay with increasing pump-drive delay. Note that the pump, drive and probe pulses are all derived from a single laser pulse; therefore, we expect to find additional information on electronic coherence in the liquid nitrobenzene sample in the drive-probe delay, where the measured $\chi^{(3)}_{\mathrm{eff}}$ appears to exhibit dephasing times on the order of ~250 fs (Fig. 2-2b). The present results demonstrate the high sensitivity of UTPS to changes in $\chi^{(3)}$, and to electronic and nuclear dynamics on excited electronic states.

Future Plans: Preliminary electronic structure calculations are underway to determine the evolution of $\chi^{(3)}$ in a simplified model system and to gain a more detailed physical interpretation of the observed dynamics. More advanced theory support has recently been enabled through a newly established collaboration with Liang Tan (Molecular Foundry, LBNL). This new theory-experiment collaboration will produce the first tools to connect UTPS measurements to electronic structure models and predictions of excited state coherent dynamics. Future experimental tools under development include flowing liquid or gas samples in a windowless cell, enabling a future UTPS setup to be deployed to the LBNL 1 kHz ultrafast XUV beamline. Higher photoexcitation energies will enable direct access to higher-lying excited electronic states, where multi-electron correlation becomes increasingly important. Extension of the drive and probe pulses to XUV and soft X-ray photon energies is expected to achieve atomic site-specificity by tuning the photon energy near inner-valence and core absorption edges.

Monitoring Photoinduced Charge Carrier Dynamics in Au Nanoparticle-sensitized TiO_2 and N_3 Dye-sensitized ZnO with Time-resolved X-ray Photoelectron Spectroscopy *(Gessner)*

In this effort, time-resolved X-ray photoelectron spectroscopy techniques are deployed at synchrotrons and X-ray free-electron lasers (XFELs) to study the flow of charge and energy in photoexcited interfacial systems.

Recent Progress: The combination of plasmonic metal nanoparticles (NPs) and photo-catalytically active semiconductor (SC) materials provides a promising route toward improved solar energy conversion schemes based on tunable, large bandwidth light absorption, efficient interfacial charge carrier separation, and high photocatalytic activity. The predominant model for plasmon-enabled charge-separation is based on ultrafast surface plasmon damping and dephasing, resulting in the population of hot electrons that are able to undergo transfer from the NP donor to the semiconductor acceptor. A considerable number of time-resolved studies in the visible and IR regimes have been reported, which are mainly sensitive to the free electron charge densities in the SC acceptor. Very little information, however, is available about time-dependent charge- and energy-distributions from the viewpoint of the plasmonic NPs and about the transient interfacial band structure. Picosecond time-resolved X-ray photoelectron spectroscopy has been applied to investigate the photoinduced charge transfer dynamics at the AuNP–TiO_2 interface. The technique provides access to local charge distributions selectively from the perspectives of the electron donor and acceptor, complementing previous time-resolved studies in the optical regime. Clear differences between the photoresponses of the Au 4f and Ti 2p photolines are observed (Fig. 2-3). The Au 4f lines exhibit a distinct shift to higher binding energies while the Ti 2p lines are unaffected by the interfacial charge transfer. The extent and dynamic evolution of the Au 4f shift provide direct, quantitative information about the injection efficiency and electron back transfer rate, respectively, both of which have significant impact on the performance of the interface. Interestingly, the study indicates a significantly lower electron injection yield than reported in previous studies. The missing TiO_2 response is consistent with a limited electron diffusion length in the substrate that also follows from the fast electron-hole recombination observed in this and previous studies.

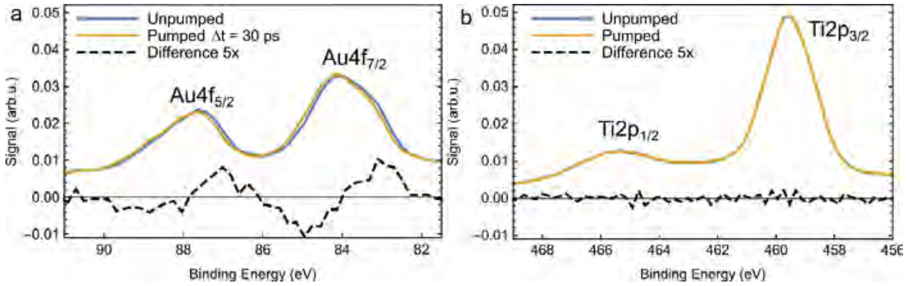


Fig. 2-3: Plasmon-enabled charge-transfer at Au nanoparticle - TiO_2 interface studied by TRXPS. a) The Au4f peaks exhibit a clear photoinduced shift between the ground state (blue) and the excited state (orange) spectra. The black dashed line is the differences between the spectra. b) In comparison, the Ti2p doublet measured under identical conditions on the same sample does not display any photoresponse. The extent and dynamics of the Au4f line shift provides direct access to injection efficiencies and electron-hole recombination rates.

A related study investigates charge injection from N_3 dye molecules into a nanoporous ZnO substrate. In this case, however, both the N_3 electron donor as well as the SC substrate exhibit notable photoresponses. Fig. 2-4 shows the temporal evolution of the Zn 3d (blue) and C 1s/Ru 3d (red) line shifts associated with the SC substrate and the dye, respectively, after excitation with 532 nm. Circles represent the measured line shifts, solid lines are the result of a fit procedure based on a system of coupled rate equations. The underlying model includes electron transfer, delocalization, and electron-hole recombination. This modeling approach yields a ~290 ps injection time from the surface region into the ZnO conduction band (CB), in agreement with previous time-resolved terahertz and optical absorption spectroscopy studies. The timescale is clearly visible in Fig. 2-4a as a delayed onset of the ZnO response, in particular, after scaling the Zn 3d fit to the same maximum as the C 1s/Ru 3d fit (gray line) and comparing it to the C 1s/Ru 3d signal (red). The time-tagging approach of the TRXPS technique developed in this activity enables the simultaneous recording of the picosecond scale injection dynamics seen in Fig. 2-4a, as well as the relaxation and recombination dynamics proceeding on timescales up to ~microseconds shown in Fig. 2-4b. A quantitative model of the observed trends is currently being developed to elucidate the underlying physics of charge injection, delocalization, and recombination across the dye-SC interface.

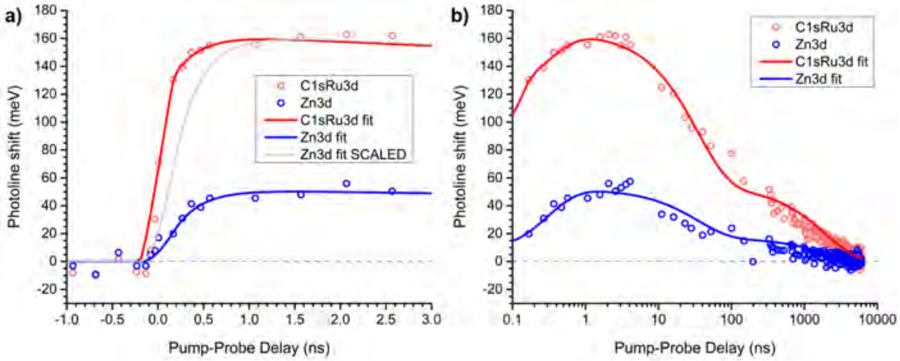


Fig. 2-4: Shift between excited and ground state spectra of the C1s/Ru3d (red circles) and Zn3d (blue circles) photolines. Solid lines are fits of the data to a coupled rate equation model. a) Photoresponses up to 3 ns pump-probe delay using a linear delay scale and b) from 100 ps to ~7 µs using a logarithmic delay scale.

Future Plans: Building on the expertise gained through the picosecond time-resolved experiments on “clean” molecule-SC and NP-SC interfaces, two major areas for future advances are envisioned, one aiming at higher temporal resolution, the second at the inclusion of chemical environments. Experiments at the FLASH free-electron laser in Hamburg will extend the reach of TRXPS studies into the femtosecond domain. To this end, we have established an international collaboration with groups at

CFEL, European XFEL, FLASH, and the University of Freiberg, which has been awarded FLASH beamtime in November 2019. Using the picosecond TRXPS setup at the ALS, the impact of chemical environments on interfacial charge transfer dynamics will be probed by exposing the SC surfaces and interfaces to controlled levels of background gases, such as water vapor. Given that the stationary energy landscapes of interfaces are known to be strongly affected by molecular coverage, similarly strong effects are expected in their dynamic properties. The TRXPS setup at BL11 of the ALS is equipped with an ambient-pressure capable electron analyzer and, thus, ideally suited to explore these effects, which are crucial to our understanding of photoinduced dynamics in operating photoelectrochemical interfaces.

Towards Time-resolved X-ray Absorption Measurements of Photoinduced Dynamics in Complex Interfacial Systems (*Gessner*)

This effort concentrates on the development of time-resolved X-ray absorption techniques to probe photoinduced interfacial energy- and charge-transfer dynamics.

Recent Progress: A systematic picosecond time-resolved transient X-ray absorption (TXA) study involving two different pump wavelengths and a variety of pump fluences has been performed on cupric oxide (CuO). Motivators for this study are the determination of the relative impact of electronic and nuclear dynamics on time-domain inner-shell TXA data of transition metal oxides as well as a quantitative understanding of heat transport phenomena that inevitably accompany any pump-probe experiment and will require a lot of attention, in particular, at future high-repetition rate XFELs such as LCLS II. The experiment is enabled by a mobile TXA setup recently developed in our group (Neppl *et al.* **2016** *Faraday Discuss.*, 194, 659-682). It is deployed at ALS beamline 8.0.1 and based on a time-stamping technique that facilitates efficient use of the 500 MHz ALS bunch train. The pump pulse repetition rate of 127 kHz is comparable to the current 100 kHz design target for the first stage of the Linac Coherent Light Source upgrade. Figure 2-5a shows the O1s near-edge X-ray absorption spectrum (NEXAFS) in the range of the Cu e_g resonance (gray, left ordinate) together with spectral changes induced by a 10 ps long, 532 nm pump pulse (colored, right ordinate). Comparison to steady-state temperature-dependent NEXAFS spectra (not shown) indicates that the spectral dynamics at delays $\Delta t \geq 150$ ps are entirely dominated by lattice heating effects. Careful calibration of the spectral changes facilitates quantitative modelling of the depth-dependent initial energy deposition profile by the pump pulse as well as the spatiotemporal evolution of the depth-dependent temperature profile with 10s of picoseconds temporal sensitivity and 10s of nanometer spatial selectivity (Fig. 2-5b,c). Detailed

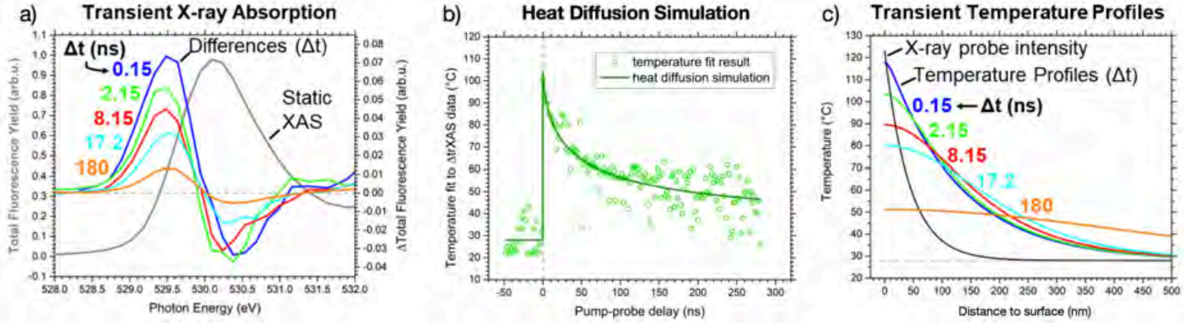


Fig. 2-5: a) TXA spectra of CuO in the range of the O1s-Cu e_g resonance following excitation with 532 nm. The gray curve is the static O1s absorption profile (left ordinate), colored lines indicate photoinduced spectral changes at a variety of pump-probe time delays Δt as indicated (right ordinate). b) Using steady-state XAS spectra recorded at a variety of temperatures (not shown), the TXA spectra are calibrated on an absolute temperature scale (green circles) and their dynamic trend is well captured by a one-dimensional heat diffusion model (solid green line). c) The measurements give access to absolute transient temperature profiles with 10s of picoseconds temporal sensitivity and 10s of nanometer spatial selectivity. Precise modeling of these dynamics and their impact on X-ray spectra will become particularly important for studies at high-repetition rate XFEL light sources (Mahl *et al.*, *Faraday Discuss.,* **2019** 216, 414-433).

understanding of these dynamics and their impact on time-resolved X-ray spectroscopic data will enable both better mitigation of thermally induced artifacts as well as potential applications of ultrafast, well-controlled heat deposition, for example, for the study of thermally induced reactions using temperature-jump X-ray spectroscopy.

Future Plans: TXA studies will be extended to other types of samples relevant for interfacial energy- and charge-transfer applications, such as fullerenes and nanoparticles, and potential routes toward laboratory-based TXA studies based on high-harmonics sources will be explored. Preliminary efforts in these directions are underway.

Ultrafast Dynamics in Atomic and Molecular Clusters *(Gessner, Neumark)*

This effort employs HHG-driven photoelectron imaging to study ultrafast relaxation dynamics in electronically excited pure and doped helium nanodroplets. Laboratory-based studies are complemented by XFEL-based experimental campaigns using a variety of electron and ion spectroscopies as well as X-ray coherent diffractive imaging to probe fundamental dynamics of the superfluid droplets in both electronic ground and excited states as well as atomic and molecular clusters.

Recent Progress: Following our successful studies of relaxation dynamics after droplet excitation in the 3p/4p band around 23.7 eV, efforts are underway to implement an excitation scheme with direct access to the 2p electronic band below the adiabatic ionization potential (≈23 eV) and study energy transfer from neutral, excited droplet states to atomic and molecular dopants. The new laser system in the AMOS Chemical Dynamics laboratory has a central wavelength of 804 nm, which is ideally suited to reach the 2p band at 21.6 eV with a combination of second harmonic generation to 402 nm, followed by 7th harmonic generation of this frequency-doubled driver. Preliminary experiments with He atoms confirm the red shift in high harmonic generation as shown in Fig. 2-6. Figure 2-6a shows atomic He energy levels reached by the 15th harmonic of the previous (1s4p, 23.7 eV) and new (1s3p, 23.1 eV) laser system. The corresponding XUV-pump/IR-probe photoelectron spectra shown in Fig. 2-6b confirm the anticipated scaling of the excitation scheme. Application of the new scheme to excite helium droplets in the dominant 2p band as sketched in Fig. 2-6c is imminent.

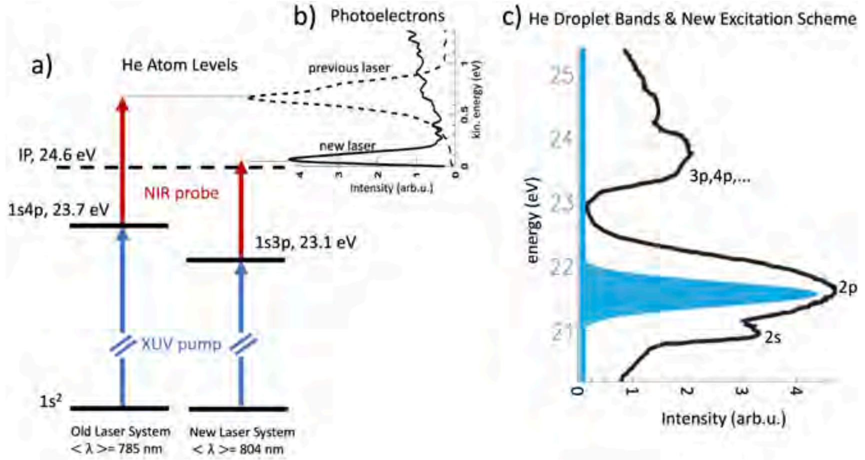


Fig. 2-6: Test of HHG energy shift between previous and new femtosecond laser system. a) Energy levels in atomic He. b) Photoelectron spectra recorded with a 15th harmonic XUV-pump/NIR-probe scheme as indicated in a) using the previous 785 nm (dashed) and the new 804 nm (solid) fundamental. The spectra confirm the intended red-shift of the HH spectrum, which will be exploited in the next step to resonantly excite helium droplets into the 2p resonance using a two-stage 2nd harmonic/7th harmonic HHG scheme, as illustrated in c).

A closely related experiment on pure, excited helium droplets using the FERMI FEL has been the subject of a large collaborative effort led by the Stienkemeier and Mudrich groups. The results directly confirm an efficient intra-band relaxation channel in the 2p band that was previously deduced indirectly from a cascaded relaxation process observed in our lab after excitation in the 3p/4p band. The FERMI experiment allows a more complete characterization of the relaxation pathways and products. The work is currently under revision with Nature Communications.

We continue the very productive collaboration with the Vilesov group to study dynamics of superfluid droplets in the electronic ground state by ultrafast coherent diffractive imaging. A manuscript describing the first experimental characterization of angular momentum composition by both vortex lattices and capillary waves in free, fast rotating superfluid droplets has just been submitted to Physical Review Letters. Our group also played an active role in an exploratory beamtime on the proton-buffered explosion of methane clusters in intense X-ray fields under the lead of the Rupp group at the SQS Instrument of the European XFEL.

Future Plans: Doped helium nanodroplets are an excellent system for studying solvent-solute interactions due to their relatively simple electronic structure that is still traceable with high-level first-principles calculations (see corresponding advances and future plans in the Head-Gordon group described in Subtask 3). With the new capability to target the lower absorption feature described above, experiments with noble gas dopants are underway to better understand the energy-transfer mechanism between electronically excited droplet and dopant species. This will enable further experiments to explore energy- and charge-transfer with more complex dopant species such as molecules and molecular clusters. Using the high-harmonic generated femtosecond XUV pulse to electronically excite the droplet and a UV probe pulse to modulate the photoelectron signal produced from the energy transfer to a dopant, the energy-transfer yield can be monitored as a function of pump-probe time delay, elucidating the relative importance of possible energy-transfer mechanisms such as Penning ionization or Interatomic Coulombic Decay (ICD). We will also continue to pursue spectroscopy and imaging campaigns on atomic and molecular clusters using X-FEL light source facilities.

Experimental and Theoretical Investigations of Dynamics in Transient Anions Formed by Electron Attachment *(McCurdy, Rescigno, Lucchese, Weber, Slaughter)*

Resonant electron attachment to a molecule can efficiently drive ultrafast dissociation, exhibiting a strong coupling between electronic and nuclear motion. Capturing the resultant nonadiabatic dynamics such as conical intersections (D.S. Slaughter *et al.* **2016** *J. Phys. B* 49, 222001) or electron transfer (Rescigno *et al.* **2016** *Phys. Rev. A* 93, 052704) between electronic states of the transient anion requires highly differential experimental measurements and reliable electron scattering calculations.

Bond-Selective Dissociation Dynamics in Electron Attachment to Formic Acid

Recent Progress: Formic acid (HCOOH), being the simplest organic acid, is a useful model system for developing a fundamental understanding of electron-driven chemistry in organic molecules. With Joshua Williams (U. Nevada, Reno), Ali Moradmand and Cynthia Trevisan (Cal. State Maritime), we have performed detailed experimental and theoretical investigations of Feshbach anion resonances of formic acid in the 5-9 eV range of electron attachment energies. Experimental results are shown in Fig. 2-7a, highlighting the site-selective dissociation that breaks C-H and O-H bonds in the lower energy A' resonance centered at 7.2 eV, but only the O-H bond at the higher energy A'' resonance (the shoulder at 8.5 eV in the lower panel of Fig. 2-7a). C-H break produces an H^- angular distribution (black diamonds in Fig. 2-7b) in agreement with the theoretical (black curve) angular dependence calculated from the molecular-frame electron attachment amplitude. This suggests prompt dissociation of the lower A' resonance along the C-H coordinate. In contrast, the O-H break measurements for the same resonance is more isotropic (red circles in Fig. 2-7b) than the axial recoil calculation (red curve in Fig. 2-7b), suggesting rotation of the O-H recoil axis during the dissociation.

Future Plans: Electronic structure and electron scattering calculations by the theory team (see Subtask 3) for the upper A'' resonance are currently underway. With the complete set of measured and calculated angular distributions, we will access the molecular frame of the dissociating formic acid anion for both resonances, to perform a detailed investigation of the dynamics of dissociative electron attachment for this fundamentally-important organic molecule. For the lower resonance, we recently resolved signatures of two final electronic states produced by O-H (and O-D) break in the kinetic energies of the H^- (D^-)

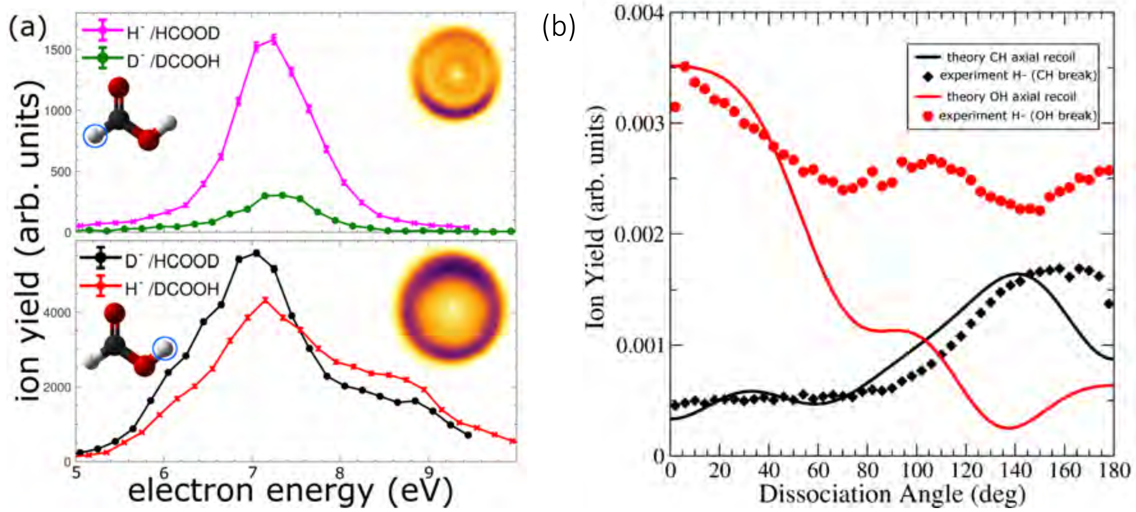


Fig. 2-7: (a) D⁻ and H⁻ yields and D⁻ momentum images (insets) for dissociative electron attachment to formic acid isotopologues DCOOH and HCOOD. The incident electron energy dependence shows two resonances break the O-H bond in formic acid, while only the lower resonance breaks the C-H bond. The incident electron momentum is upwards in the momentum images. (b) Lower A' resonance by 7.25 eV electron attachment. Experimental (symbols) and calculated (line) angular distributions for the H⁻ recoil by CH break (black diamonds) or OH break (red circles), relative to the incident electron direction (0°).

fragments. These bimodal kinetic energy distributions may reveal dynamics leading to low-lying excited electronic states and coupled electronic and nuclear dynamics of the formyl oxyl radical HCOO· as it evolves from the geometry of formic acid. This will be explored in further detail, and the tools developed here will be applied in near-future investigations to other, more complex organic molecules such as formamide and nitromethane.

Subtask 3: First-principles Theory of Dynamics and Electronic Structure

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

Overset Grid Based Complex Kohn Method for Electron-Polyatomic Molecule and Ion Scattering

(Lucchese, McCurdy)

Recent Progress: The original complex Kohn variational method for treating electron-molecule collisions and photoionization developed by the LBNL theorists is the basis of calculations of amplitudes for both ionization (including ultrafast) and dissociative electron attachment. It is being replaced by a new computational implementation that describes the scattered (or ionized) electrons on "overset grids" that combine local spherical grids centered on each atom, with one centered at the middle of the molecule and reaching to the asymptotic region that overlaps all the smaller grids. This method avoids several limitations of the original "basis set" Kohn approach and is also more accurate. We have implemented and tested the method on single-channel static-exchange calculations on small molecules. The initial version of this method was described in Greenman *et al.* (**2017** *Phys. Rev. A* 96, 052706). More recently, we have accomplished the critical step of extending of the new grid-based method to molecular photoionization. Because the new overset grid implementation depends on the construction of a Krylov series, $\Phi_n = (G_0 V)^n \Phi_0$, involving multiple operations of the free-particle Green's function, G_0, on the incoming wave Φ_0, a new matching scheme had to be developed and tested to make this critical step. Figure 3-1 shows applications to CF_4 and SF_6 from a manuscript in preparation.

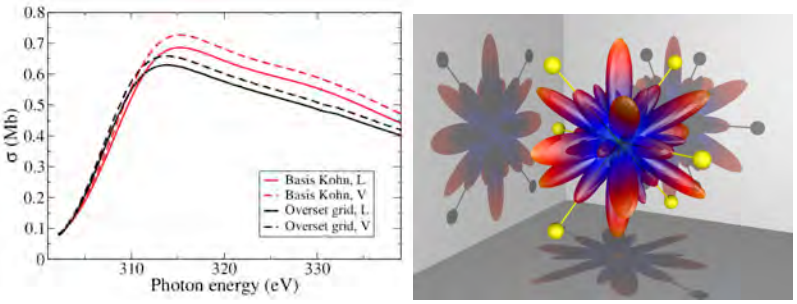


Fig. 3-1: Left: comparison of Carbon 1s photoionization cross section in CF$_4$ from the more accurate grid-based complex Kohn method with the original complex Kohn method using Gaussian and Bessel basis functions. Right: Body frame angular distribution for ionization of SF$_6$ averaged over polarization direction at a shape resonance 50 eV above threshold.

Future Plans: The overset grid implementation that we have developed thus far depended on polynomial masking functions intended to reduce linear dependence of the discrete variable representation in the various overlapping grids. We are developing and testing a new formulation with global orthogonalization that will eliminate the masking functions and allow us to use much smaller angular grids, making the method much faster. Having increased the efficiency of the overset grid method we will complete a general multi-channel implementation of the overset grid method for polyatomic molecules that will replace our current core computational capability for electronic collisions and photoionization of polyatomics. The planned theoretical and computational developments are producing 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 at LBNL and elsewhere on dissociative electron attachment and molecular photoionization.

Double Photionization of Water by One Photon *(McCurdy, Lucchese, Rescigno)*

Recent Progress: We are continuing a major effort to calculate and observe the angular dependence in the body frame of one-photon double photoionization of water. This will be the first such observation and *ab initio* calculation of this process for a polyatomic molecule. We unraveled the dissociation dynamics of the nine states of the water dication produced by removing two electrons from the highest three occupied orbitals of neutral water. Of those nine states, eight yielded three-body breakup by the process $\mathrm{H_2O} + h\nu \longrightarrow \mathrm{H_2O^{++}} + 2e^- \longrightarrow \mathrm{O} + 2\mathrm{H}^+ + 2e^-$. Those calculations appeared in two publications in 2018 that focused on this three-body dissociation. In those combined experimental and theoretical studies we speculated that a diffuse background in the kinetic energy release for the two protons versus the angle between them was due to a two-step process, $H_2O + h\nu \longrightarrow OH^+ + H^+ + 2e^- \longrightarrow O + 2H^+ + 2e^-$, in which states of the OH$^+$ cation are produced that are then predissociated by spin orbit coupling to another state. We have now simulated that two-step process completely and identified the two dynamical pathways responsible for it, as indicated in Fig. 3-2. The original

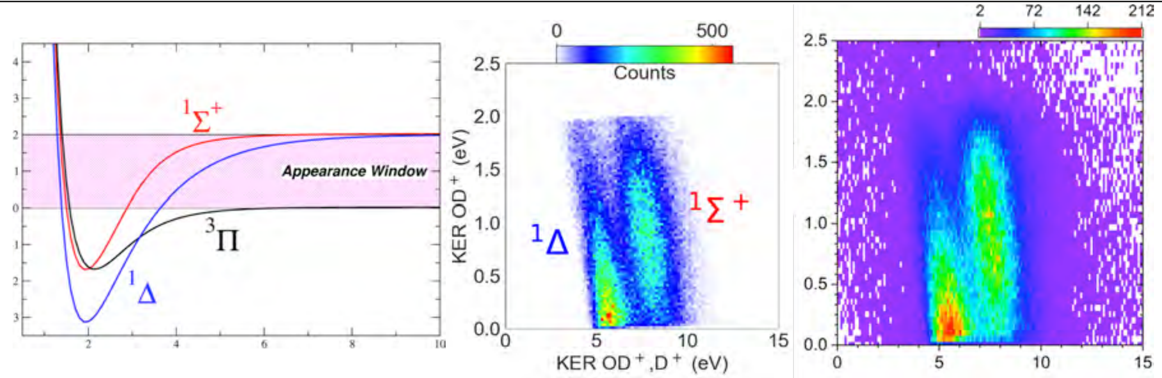


Fig. 3-2: Comparison of theoretical dynamics with native frames analysis of experimental COLTRIMS data for the sequential breakup of H$_2$O^{++} following double ionization. Left: Potential curves of the states of OH$^+$ produced from two excited states of H$_2$O^{++}, and the triplet state that predissociates them. Middle: Classical trajectory results plotted in the "native frame" as the kinetic energy of the slow proton versus that of the fast one. Right: Results of experimental native frames analysis.

experimental data has been reanalyzed by the Kansas State group led by Itzik Ben-Itzhak using the "native frames" method, which can detect the presence of sequential processes in a COLTRIMS experiment. The comparison in Fig. 3-2 of theory and experiment in this close collaboration identifies perfectly which processes are being revealed by this analysis of the experimental data, and these new results were presented at DAMOP 2019.

Future Plans: We will calculate the triple-differential cross section (TDCS) for double photoionization of water by one photon using our finite element discrete variable representation coupled with exterior complex scaling in time independent calculations that treat two active electrons, freezing the rest in Hartree-Fock orbitals. We solve the driven Schrödinger equation, $(E_0 + \hbar\omega - H)\Psi sc = \mu\Phi_0$, in which the right hand side is the dipole operator times the initial state, in a single-center expansion and extract the TDCS from Ψsc as we have done in our previous work on double photoionization of H_2. These large supercomputer calculations are in process, and we are making multiple improvements to the computational algorithms we previously applied to double photoionization of H_2 to make it possible to solve this challenging problem. New coincidence data has been taken at the ALS from which the TDCS will be extracted, and these comparisons will be the first of their kind on a polyatomic molecule. This work is being done in collaboration with Prof. Frank Yip (California State University, Maritime), who has participated in the visiting faculty program (VFP) at LBNL in recent summers.

Dissociative Attachment of Electrons to Formic Acid *(Rescigno, McCurdy, Lucchese)*

Recent Progress: To interpret the LBNL experiments on dissociative attachment to formic acid, we have carried out complex Kohn variational calculations of the electron scattering cross sections as well as extensive bound-state electronic structure calculations on the resonance states (metastable anion states) of formic acid and the neutral parent states of those resonance states together with Prof. Cynthia Trevisan of Cal State Maritime, who has participated in the Berkeley Lab Undergraduate Faculty Fellowship (BLUFF) program in recent summers. The experimental portion of this project is described in Subtask 2. Two resonances are observed. The lower energy resonance leads to the anion $[HCOOH]^-$ dissociating to produce H^- from both the CH and OH bonds, while the higher energy resonance leads only to H^- from the OH bond. The goals of these calculations are to (1) identify which resonances lead to these products, by calculating cuts of the potential surface to follow the resonance state into the bound anion product arrangements, and (2) to calculate angular distributions to compare with experiment in each case. The scattering calculations require 9 coupled channels with about 100 configurations describing each target state. Of three resonances we found, the lowest leads directly to H^- from CH and OH, the second highest is not dissociative and the highest produces only H^- from the OH bond. Thus, we think we have identified the two resonances as a $^2A'$ and a $^2A''$ anion state with electrons attached to

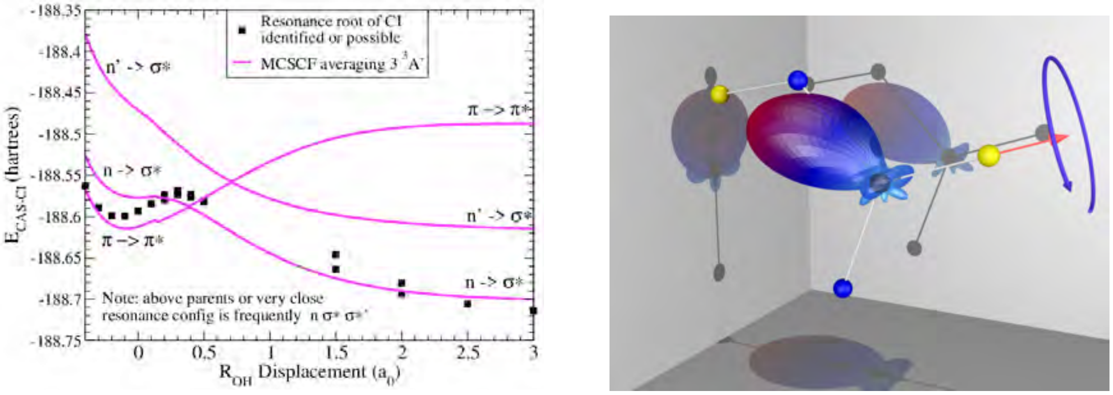


Fig. 3-3: Left: Potential curves for OH dissociation of the $^3A'$ states of HCOOH showing their conical intersections together with the resonance anion state of the lowest energy resonance correlating to $^2B_2$ state of HCOO and H^-. Right: Entrance amplitude for this resonance with an indication of averaging around the CH recoil axis to produce one of the curves in Fig. 2-7b.

the $2^3A'$ and $2^3A''$ excited states of neutral HCOOH, which are sigma or pi nonbonding to sigma antibonding transitions. We discovered that the $2^3A'$ state has a conical intersection for both dissociation pathways, so that the character of the resonance changes during dissociation. The scattering calculations produce an "entrance amplitude" for an electron to attach for various incident directions from which the angular dependence is calculated. Fig. 3-3 shows the entrance amplitude underlying Fig. 2-7b as well as one of the sets of potential curves from the electronic structure calculations.

Future Plans: Now that the resonances have been identified, we will refine and converge both the electronic structure and scattering calculations to verify these results and publish a joint theoretical and experimental study that finally unravels the dynamics of this interesting and complicated case of dissociative attachment.

One-Photon Double Photoionization as a Probe of Initial State Correlation *(McCurdy, Lucchese, Rescigno)*

Recent Progress: We completed the analysis of calculations of one-photon double ionization of He, H^- and H_2 in a systematic study in which the initial state is built up by the addition of uniquely defined terms in its expansion in natural orbitals that diagonalize the one-electron density matrix, while treating final state correlation essentially exactly for each different resulting approximation to the initial state. We thereby tested the frequent assertion in the literature that one-photon double ionization is exquisitely sensitive to correlation both in the initial electronic state of the neutral molecule and in the final doubly ionized state describing the departure of the electrons. The surprising result we found, and that appeared in our publication on this subject in 2019 (Bello *et al.* **2019** *Phys. Rev. A* 99, 013403), is that double photoionization by one photon is dramatically more sensitive to the initial state correlation of electrons in bonds than it is to non-bonding electrons. The Hartree-Fock approximation to the initial state is a sufficient basis upon which to predict the angular distributions of two electrons ejected from He. However, in H_2, for polarization parallel to the molecular axis, the computed angular dependence only begins to resemble the true result when 15 terms in the natural orbital expansion are included, with coefficients as small as 5×10^{-3}. Double photoionization is in fact a sensitive probe of correlation in molecular bonds.

Future Plans: This project is complete, but we will apply the same analysis to our calculations of the angular dependence of the double photoionization of water, comparing lone-pair ionization with ionization from the OH bonds.

Core-Hole Localization in CCl_4 *(Rescigno, McCurdy, Lucchese)*

Future Plans: We are in the process of calculating the MFPADs for ionization of the 2p orbital of Cl in CCl_4 for comparison with COLTRIMS experiments that have been performed at the ALS. The LBNL experiments found that ionization from the 2p orbital, but not from the 2s orbital, results in fragmentation to the two-body $CCl_3^+ + Cl^+$ channel following Auger decay, allowing COLTRIMS measurements in the recoil frame. The question is whether those distributions will carry the signature of core hole localization that we saw in our study of F K-edge ionization in CF_4 (McCurdy *et al.* **2017** *Phys. Rev. A* 95, 011401(R)). Our preliminary close-coupling calculations using the complex Kohn method may be qualitatively correct, but they show signs of not being converged with respect to the Gaussian and Coulomb function basis set in our original implementation. Now that we have the grid-based Kohn capability, we will perform single channel calculations with both methods to test the convergence of our basis-set Kohn results and, if the MFPADs from both methods agree, we will use the existing close-coupling approach to finish this joint theoretical and experimental study. The goal is to see if a Cl-2p hole, which can be distributed over three spatially inequivalent orbitals on each of the four equivalent Cl atoms, obscures any observable hole localization effects in the MFPAD.

Molecular Frame Photoelectron Angular Distributions in Two-Photon XUV+IR Experiments *(Lucchese, McCurdy)*

Future Plans: MFPADs are proportional to the absolute squares of the molecular frame transition amplitudes (MFTAs). The energy derivatives of the phases of the MFTAs can be related to the group delay of a wave packet generated by a short light pulse of ionizing light. The group delays can be used to probe the dynamics of the photoemission process and are particularly sensitive to resonances in such a process. In molecular systems, as shown in Fig. 3-4 for ionization of NO, these delays are functions of the photoelectron emission direction in the molecular frame. One experimental method to measure such phase derivatives is XUV+IR ionization, where the XUV light is produced by HHG and the IR light has the same frequency as was used in the generation of the HHG. In such experiments, one can measure the variation of the sideband intensity as a function of the relative phases of the IR and HHG light due to the presence of two interfering paths, XUV$_{2n-1}$+IR and XUV$_{2n+1}$-IR, leading to the same sideband at XUV$_{2n}$. The phase of the oscillations in the sideband intensity relative to the phase of the IR light can then give an estimate of the energy derivative of the transition amplitude phase. We have derived the expression for the full MFPAD for the two-photon process. Expanding the MFPAD intensities in real-valued coefficients times Legendre polynomials and trigonometric functions of the angles describing the photoelectron emission direction and field orientation in the molecular frame, we find that each term has its own sideband phase shift. For experimental measurements that are not as differential as a full MFPAD, e.g. photoemission direction is not detected and/or light polarization direction is not determined, the measured sideband phase is a different combination of the sideband phases of the various terms in the MFPAD expansion. We will combine computed XUV single-photon ionization amplitudes with an asymptotic approximation for the IR interaction with the photoelectron to compute the sideband intensities (Baykusheva and Wörner, **2017** *J. Chem. Phys.* 146, 124306). This approach will allow us to model current XUV+IR dissociative ionization experiments on NO, which are being performed by D. Dowek at Université Paris-Saclay, where both the photoemission direction and the field direction in the molecular frame are determined through coincidence spectroscopy. Additionally, we will be able to determine the extent to which the underlying one-photon ionization phase is modified by the phase contributions of the continuum-continuum interaction and, as a consequence, the possibility for such experiments to measure the group delay as a function of emission direction in the corresponding one-electron XUV ionization process.

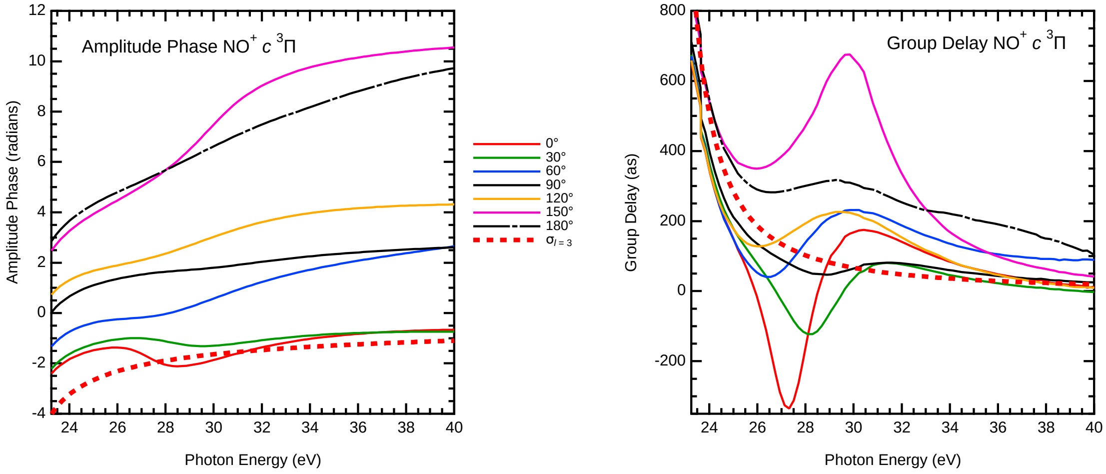
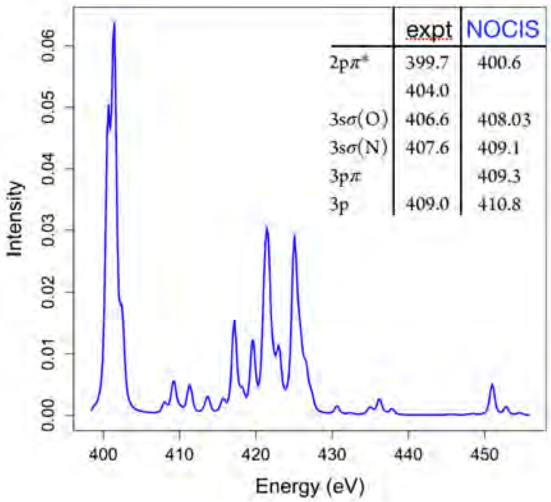


Fig. 3-4: Computed MFTA phases and group delays for photoemission from NO with light parallel to the molecular axis in the region of the $k\sigma^*$ shape resonance. The phase and group delay for pure l = 3 Coulomb scattering is also indicated.

Direct Targeting of Core-Excited States via Non-orthogonal Single Excitation CI *(Head-Gordon)*

Recent Progress: The creation of a core hole either due to excitation or ionization leads to dramatic orbital relaxation effects such as contraction of the valence shell towards the core. While it is common to capture such effects through brute force approaches, a potentially more natural and economical framework is offered by non-orthogonal CI (NOCI) treatment. For this purpose, we have recently defined and implemented the non-orthogonal configuration interaction singles (NOCIS) method for calculating core-excited states of closed-shell molecules (Oosterbaan *et al*. **2018** *J. Chem. Phys.* 149, 044116). NOCIS is a black-box variant of NOCI (that in itself makes NOCIS a very rare variant of NOCI), which uses *A* different core-ionized determinants for a molecule with *A* atoms of a given element to form single substitutions. The use of core-ionized determinants permits natural inclusion of orbital relaxation effects. In addition, NOCIS has a number of other desirable properties, NOCIS is variational, spin-pure, and size-consistent. As test cases, we benchmarked NOCIS for K-edge core-excitations (for C, N, O, F) in a set of small molecules, where roughly an 8-fold reduction in RMS error over standard CIS was achieved. This performance is competitive with DFT-based methods using short-range-corrected functionals that are adapted for computing core spectra. We have recently (Oosterbaan *et al.* **2019** *J. Chem. Theory Comput.* 15, 2966-2973) extended the NOCIS theory to doublet radicals, yielding promising results with accuracy comparable to those obtained for closed shell ground states. The extension of the theory proved to be non-trivial, because it was essential to include an additional *A* different reference determinants for a molecule with *A* atoms of a given element, corresponding to promotions from the core K-shell of interest to the half-occupied valence orbital. An example of the quality of the resulting predictions for K-edge spectra is shown in Fig. 3-5 for the NO radical: the corresponding CIS calculation shows a deviation of 6.9 eV for the lowest excitation, while NOCIS is within 0.9 eV.



	expt	NOCIS
$2p\pi^*$	399.7	400.6
	404.0	
$3s\sigma(O)$	406.6	408.03
$3s\sigma(N)$	407.6	409.1
$3p\pi$		409.3
3p	409.0	410.8

Fig. 3-5: *Ab initio* calculations of the K-edge spectra of the NO radical using the newly developed NOCIS method (blue trace, Gaussian broadening of 0.25 eV and a Lorentzian broadening of 0.2 eV) for radicals, and comparison of peak centers vs experiment showing very encouraging accuracy.

Future Plans: The initial implementation of the NOCIS method is not computationally efficient enough to permit application to medium or large molecules – we are actively developing a new implementation that can lift this limitation. As part of this effort, we are also exploring the potential for simplifying NOCIS to single-atom contributions. Such simplifications could make the development of dynamical electron correlation corrections more tractable (NOCIS includes only essential electron correlations). In the medium term, we also intend to include spin-orbit coupling to enable the treatment of the L-edge in third row elements. Additionally, as a higher accuracy alternative, we intend to explore the applicability of coupled cluster theory targeted at core excited states. This will be an unconventional approach that can potentially capture orbital relaxation and all main correlation effects, while still being applicable to medium-sized molecules.

Calculations of Core Excitation Spectra in Dimethyl Disulfide (DMDS) *(Head-Gordon)*

Recent Progress: Experimental time-resolved studies of the 267nm photodissociation of dimethyl disulfide (DMDS), CH_3SSCH_3, were performed in the groups of Gessner and Leone at LBNL. The time-development of core excitation spectra is a fingerprint for the photoproducts, provided the peaks can be assigned. For this purpose, we performed calculations of core excitations in CH_3SSCH_3 (DMDS) and its potential photoproducts: CH_3S, CH_3, and CH_3SS. These calculations used the extended second order algebraic diagrammatic construction (ADC-2X), with core-valence separation, as well as the RASPT2 approach, and covered the C K-edge and S L-edge core excitation spectra. To show the level of agreement obtained between theory and experiment (Schnorr *et al.* **2019** *J. Phys. Chem. Lett.* 10, 1382), as well as the manner in which the calculations permit assignment of the photoproducts, the observed and calculated S L-edge spectra are displayed in Fig. 3-6. The computational results play an important role in assigning CH_3S as the main photoproduct.

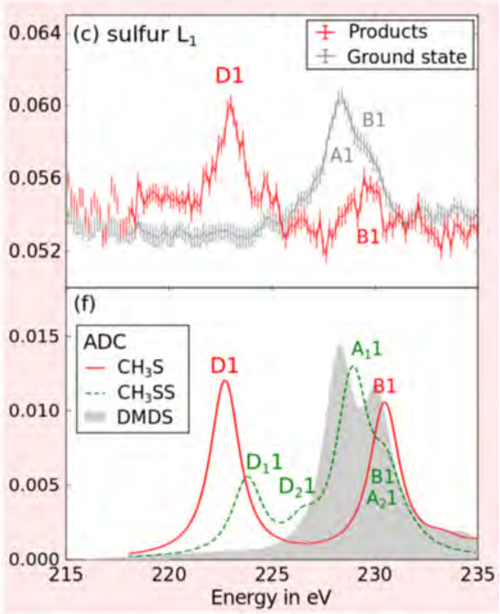


Fig. 3-6: Calculations (lower panel) and experiments (upper panel) on DMDS (grey) and its photoproducts (CH3S in red, and additional calculations for CH3SS in green). The good agreement between theory and experiment for DMDS itself provides validation of the computational ADC method. Thus validated, the ADC calculations for the photofragments clearly support CH_3S as the predominant photoproduct.

Second Order Correction to Non-orthogonal CI (NOCI-MP2) *(Head-Gordon)*

Recent Progress: As discussed above, NOCI methods are a powerful way to capture essential correlation effects within a very compact reference wavefunction. Nonetheless, as exemplified by the NOCIS case, one still wants a framework for including weak or dynamic electron correlation effects to correct a NOCI reference. This is a non-trivial problem because each NOCI determinant has its own orbitals, and there is hence no well-defined separation between occupied and virtual orbitals in the NOCI wavefunction. One promising framework to address this problem is NOCI-MP2, but there has been no efficient computer implementation available. To address this need, we developed (Yost *et al.* **2018** *J. Chem. Theory Comput.* 14) one based on reworking the NOCI-MP2 equations with the resolution of the identity (RI) approximation so that NOCI-MP2 has the same memory requirements and computational scaling as single reference RI-MP2. The working equations are extended to include single substitutions as required when the reference determinants do not satisfy the Hartree-Fock equations.

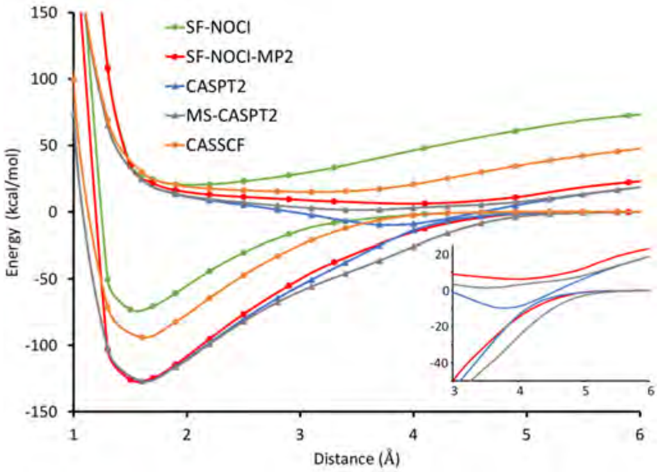


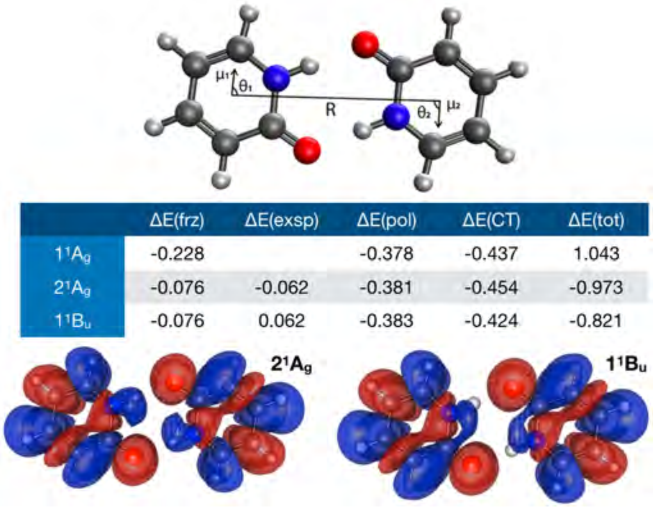
Fig. 3-7: Preliminary results for application of NOCI-MP2 to the avoided crossing in the LiF molecule. The SF-NOCI reference, while qualitatively correct, places the avoided crossing more than 1.5Å closer in than higher level methods (CASSCF exhibits similar behavior). A pilot version of the SF-NOCI-MP2 method produces results that are in good agreement with multi-state CASPT2 (MS-CASPT2) reference values.

Our current activity is aiming at a new formulation of NOCI-MP2 that can correct a spin-flip NOCI (SF-NOCI) reference calculation. SF-NOCI is a near black-box method for treating a manifold of strongly correlated electrons, including all spin states. The principal issue to be addressed is how to perform the open shell perturbation theory. The existing NOCI-MP2 theory (using unrestricted determinants) must be modified to ensure that spin-multiplet degeneracies that are present in SF-NOCI are preserved in NOCI-MP2. Straightforward application of the existing theory does not satisfy this condition. We are in the process of finishing this work, and Fig. 3-7 shows preliminary results for the avoided crossing in LiF showing that the pilot SF-NOCI-MP2 method performs very well for this benchmark problem.

Future Plans: The NOCI-MP2 framework appears very promising for efficiently and accurately treating dynamic correlation in excited states of molecules and molecular clusters. We intend to complete the implementation of SF-NOCI-MP2 and explore applications to medium-sized species with strong correlations, and also core excitations.

Computational Analysis of Excimers and Exciplexes *(Head-Gordon)*

Recent Progress: Much attention has been paid to developing and applying new computational methods for excited states of clusters over recent years. However, analysis of the corresponding calculations to unravel the physical driving forces behind differences in excited state binding versus the ground state is still often a matter of indirect inference. Qualitatively, effects such as charge resonance and excitonic resonance, modulated by state-specific permanent and induced electrostatics, Pauli repulsions, dispersion and charge transfer drive binding in excited complexes, but there is a lack of computational tools to quantify their respective contributions. To address this need, we have developed two versions of a new energy decomposition analysis (EDA) scheme for understanding intermolecular interactions in delocalized exciplexes (Ge *et al.* **2018** *J. Chem. Phys.* 148, 064105) and excimers (Ge *et al,* **2018** *J. Chem. Theory Comput.* 14, 5156). These new methods support treatment of excited states by either TDDFT, or configuration interaction singles (CIS). Three intermediate variational trial energies are introduced that define frozen, excitonic coupling, and polarized states, in addition to the final states and the isolated fragments. Excited state binding is thereby separated into frozen (frz), excitonic splitting (exsp), polarization (pol) and charge transfer (CT) contributions. An example of the application of this excited state EDA to the lowest 2 singlet excited states (as well as the ground state) of the 2-pyridone dimer is shown in Fig. 3-8. The analysis clearly shows the excitonic origin of the splitting between the first two excited states of this dimer, as well as the origin of the slight weakening of the double hydrogen bonding in its lowest two excited states. This weakening is also evident in the loss of electron density in the hydrogen bond in the excited states, as shown by the difference densities for these states vs the ground state. This suite of analysis tools should be useful for understanding a range of other complexes in their low-lying excited states, including clusters of experimental interest in the program.



	ΔE(frz)	ΔE(exsp)	ΔE(pol)	ΔE(CT)	ΔE(tot)
1^1A_g	-0.228		-0.378	-0.437	1.043
2^1A_g	-0.076	-0.062	-0.381	-0.454	-0.973
1^1B_u	-0.076	0.062	-0.383	-0.424	-0.821

Fig. 3-8: Application of the new energy decomposition analysis (EDA) to the two lowest excited states (2^1A_g and 1^1B_u) of the 2-pyridone dimer, as well as the ground state (1^1A_g). All energies are in eV, and calculations are performed via TDDFT with the wB97X-D density functional. The excimeric origin of the splitting between the two excited states is clearly identified from the excitonic splitting (exsp) term, modulated by charge transfer (CT). Difference densities vs the ground state (bottom panel) show weakening of the hydrogen bonds in the excited states.

Future Plans: We are interested in applications of this approach to understand the effect of clustering and environment on problems such as dopants in helium clusters, and excited states of other complexes that are of interest in the program. It may be possible to combine aspects of the ALMO-CIS method with the NOCI method to effectively treat charge-transfer excited state problems in clusters.

Time-Dependent Methods for Strong and Ultrafast Molecule-Field Interactions *(Head-Gordon, McCurdy)*

Future Plans: McCurdy and Head-Gordon have a new student who is beginning to work on time-dependent approaches to describing strong molecule-field interactions, as relevant to much of attosecond science. The major goal is to use a time-dependent form of the full non-linear coupled cluster wavefunction (truncated at e.g. doubles), while avoiding the commonly used linearization associated with the equation-of-motion approach. This also opens up interesting questions regarding the appropriate form of orbitals to employ, particularly regarding the role of symmetry-breaking to describe some strong correlation effects that are field-induced. Another goal is to use this explicit solution of the time-dependent Schrödinger equation to describe absorption and population transfer from multiple attosecond pulses with a coupled-cluster treatment of correlated electron dynamics.

Peer-Reviewed Publications Resulting from this Program 2017-2019

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PULSE Ultrafast Chemical Science

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Project Scope:

The PULSE Ultrafast Chemical Science program develops 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 and its associated electron beams, and in the future, even petawatt-class lasers. Our overarching goal is to establish research at SLAC that makes optimal use of these unique tools for fundamental discoveries and new insights in ultrafast chemical science.

A few highlights of discoveries and insights from recent research illustrate this point. For example, recent work led by James Cryan within our ATO task has shown for the first time molecular electrons moving in attosecond time scales under the influence of x rays. These remarkable observations were enabled by x-ray attosecond pulses made by the XLEAP team at LCLS and PULSE, together with our development of x-ray "ghost" imaging and attosecond streak cameras. These capabilities may help solve a wide range of problems in energy science, photocatalysis, and molecular photochemistry. Other ultrafast x-ray laser studies carried out by Kelly Gaffney in the SPC task on the mechanism of metal-to-ligand charge transfer excited state relaxation, could impact designs for earth-abundant photosensitizers and photocatalysts.

Recent related work led by Thomas Wolf and his EIM task utilizes the high degree of control of LCLS x-rays to capture excited-states as they are created during photochemistry. Finally, we mention some important new work that complements the discovery-science capabilities of LCLS by providing compact extreme ultraviolet light sources based on generation of high-harmonics in many materials, including ordinary glass. This work relies on the discoveries made by Shambhu Ghimire during his Early Career program.

Many more examples of the impact of our work are covered in the individual task abstracts that follow this overview. The two distinguishing advantages of this highly collaborative ultrafast chemical science program are the on-site presence of unique ultrafast x-ray and electron facilities, and our connection to Stanford University. These help to keep us competitive on an international level.

Recent Progress:

Our Ultrafast Chemical Science programs, along with highlights of recent research and future, are described fully in the abstracts for those subtasks, which follow this overview. Here we concentrate on cross-cutting themes, and overall management.

Management Structure: This Ultrafast Chemical Science program, directed by Professor Phil Bucksbaum. is in the Chemical Sciences Division directed by Kelly Gaffney, within the SLAC Energy Sciences Directorate, directed by Tony Heinz.

The intellectual vitality of our Ultrafast Chemical Science program is assisted greatly by its membership in a parallel Stanford University organizational unit, the Stanford PULSE Institute, directed by David Reis.

The PIs and co-PIs who receive their research support from this program are:

Professor Philip Bucksbaum, AMO Physics, the FWP director;
Professor David Reis, Nonlinear x-ray science, deputy director;
Professor Kelly Gaffney, Physical Chemistry;
Professor Tony Heinz, Optical Physics
Professor Todd Martinez, Theoretical Physical Chemistry;
Research Scientist Dr. Thomas Wolf, Physical Chemistry;
Research Scientist Dr. Adi Natan, AMO Physics;
Research Scientist Dr. Amy Cordones-Hahn, Chemistry;
Research Scientist Dr. James Cryan, AMO Physics;
Research Scientist Dr. Shambhu Ghimire; Nonlinear x-ray optics;

The program is organized into nine subtasks:

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, Cryan)
6. NLX:	Nonlinear X-Ray Science (Reis)
7. EDN:	Electron Dynamics on the Nanoscale (Heinz)
8. EIM:	Excitations in Molecules (Wolf)
9. HHG:	High Harmonics in Optical Media (Ghimire)

Awards Prizes, and other Honors*:* There are four noteworthy honors this year: **Tony Heinz** was named a 2019 Web of Science Group Citation Laureate. These are researchers whose work is deemed to be 'of Nobel class as demonstrated by analysis carried out by the Institute for Scientific Information (ISI). His citation reads, “For pioneering research on optical and electronic properties of two-dimensional nanomaterials. We recognize Heinz for contributions to understanding classes of nanoscale materials including carbon nanotubes, graphene, and two-dimensional semiconductors such as molybdenum disulfide.” **Todd Martinez** was elected to the National Academy of Sciences in 2019. **David Reis** was named an OSA Fellow. Finally, **Phil Bucksbaum** received the 2020 American Physical Society Norman F. Ramsey Prize in Atomic, Molecular and Optical Physics, cited “For pioneering explorations of ultrafast strong field physics from the optical to the X-ray regime.”. Bucksbaum will also be the President of the APS in 2020.

Personnel changes: Shambhu Ghimire will finish his DOE Early Career Award in 2019, and he has applied to start the new HHG subtask in the PULSE UCS program. Tais Gorkhover is a current DOE Early Career recipient in the AMOS program, and several groups in this program are working closely with her, particularly to co-develop new capabilities in ultrafast x-rays at FELs.

PULSE Ultrafast Chemical Science Major themes: Ultrafast science has emerged as one of the primary arenas for scientific progress across all areas of BES, and it has also now been established as a primary mission focus for SLAC.[1] PULSE has been advancing this area for

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[1] http://www-group.slac.stanford.edu/oa/strategic.htm

more than a decade and so we are in a good position to claim leadership in selected broad areas of the field. Our primary aim this year has been to focus on new research enabled by the improvements to the x-ray and electron sources at LCLS-II, which will allow us to explore the "electron frontier" for the AMOS program:

- Sub-femtosecond frame rates for femtosecond movies will capture the motion of electrons within molecules, using some methods that have not been possible without the improved characteristic of the LCLS-II linac and x-ray laser.
- Ultrafast methods with Angstrom resolution to record chemistry at the level of the intramolecular bonds.
- multiphoton x-ray interactions to explore the new capabilities of x-ray nonlinear spectroscopy.

These tasks are well-embedded in the themes of the BESAC 2017 report *Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science* (a.k.a. *Ultrafast Roundtable Report*), [2] and also line up with the BESAC 2015 report, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science,*[3] especially the section on *Imaging Matter across Scales*, and *Harnessing Coherence in Light and Matter.* The tasks are also in line with the 2004 report *Directing Matter and Energy: Five Challenges for Science and the Imagination* (a.k.a. *Grand Challenges Report*)[4] where our work is particularly relevant for the *Energy and Information on the Nanoscale* and *Control at the Level of Electrons* challenges. The eight subtask abstracts will discuss these themes further, but we like to cast them in three phrases that capture the essence of the opportunities. These are:

- Imaging on the nanoscale in space and the femtoscale in time.
- The architecture of light conversion chemistry.
- Harnessing coherence on the eV scale in time, space, and field strength.

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 10,000 square feet to research laboratories and a computer room for this FWP.

Collaborations: In addition to strong links to LCLS, 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 other BES-AMOS groups at the University of Michigan, the Ohio State University, the University of Connecticut, Louisiana State University, and Northwestern University.

Knowledge transfer to LCLS: The transfer of knowledge to and from LCLS is extremely fluid and critical to our success. Much of our research creates benefits for LCLS 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 work closely with instrument development teams at LCLS for the development of the next-generation LCLS-II instruments.
- We have assisted in the development of laser and timing tools currently at LCLS.

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[2] https://science.energy.gov/~/media/bes/pdf/reports/2018/Ultrafast_x-ray_science_rpt.pdf

[3] https://science.energy.gov/bes/efrc/research/transformative-opportunities/

[4] https://science.energy.gov/~/media/bes/pdf/reports/files/Directing_Matter_and_Energy_rpt.pdf

- Some of our postdocs and students have transferred to permanent staff positions at LCLS.
- We connect LCLS to the Stanford PULSE Institute, since all of our staff are members of PULSE, PULSE assists LCLS in student and postdoctoral recruitment and mentorship.
- PULSE conducts an annual Ultrafast X-ray Summer School to train students and postdocs about LCLS science opportunities.

UTS: Ultrafast Theory and Simulation (Todd J. Martínez, PI), SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA, 94025, toddmtz@slac.stanford.edu

Program 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 are also extending these approaches to predict and interpret diffraction signals from ultrafast electron and X-ray experiments. Primary application areas include 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

Ultrafast Electron Diffraction of Cyclohexadiene Ring-Opening: We have initiated numerous collaborations with the ultrafast electron diffraction team centered at SLAC. Two recent cases involved femtosecond electron diffraction of photoexcited cyclohexadiene (CHD) and pyrazine. AIMS modeling of CHD ring-opening dynamics (Wolf, et al. Nature Chem. 2019) gave rise to pair distribution functions in excellent agreement with measurements (as shown in Figure 1). This demonstrates both the accuracy of AIMS descriptions of excited state nonadiabatic dynamics and also the power of a straightforward probe such as diffraction (avoiding the many complexities that can arise when trying to map theoretical results onto complex spectroscopic probes). We are currently applying AIMS to pyrazine and modeling the electron diffraction signal beyond the independent atom model (which we used for CHD). In principle, it may be possible to see not only the nuclear distortions, but also the changes in the electron density during the dynamics. Our work (Parrish, et al. J. Chem. Theo. Comp. 2019) showed how to efficiently model the diffraction signal from ab initio electron densities and we are using this for pyrazine.

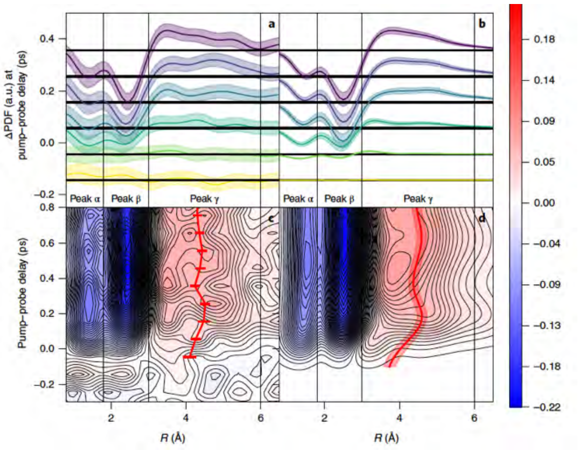

Figure 1. Comparison of experimental (left) and simulated (right) ultrafast electron diffraction signals after photoexcitation of cyclohexadiene (full extracted difference pair distribution function below and lineouts at specific time delays in the panels above). The increase in density for bond lengths longer than 3 Angstrom is a clear signature of ring-opening.

Effect of Carrier Envelope Phase (CEP) on Nonadiabatic Molecular Dynamics. We have investigated the role of CEP on excited state dynamics and shown that this can be used to modulate the absorption probability of sulfine (Mignolet, et al. J. Phys. Chem. Lett. 2019). We showed earlier that sulfine exhibits a very interesting photochemistry, forming up to ten different photoproducts. In our latest work, we investigated the possibility that the photoproduct branching ratio might be altered by the CEP. This would provide an exciting demonstration of reaction control by pulse phase. These simulations were made possible by our previous development of XFAIMS – the AIMS method incorporating an external field explicitly. We found that the absorption probability was strongly influenced by the CEP for sulfine molecules that were aligned with the laser polarization (see Figure 2). We also pointed out that a simple monitor for the absorption probability is the formation of oxathiirane. These simulations have been performed in advance of experiments, but suggest that sulfine is a prime candidate for molecule to be studied in order to further establish the role of CEP in ultrafast photoexcitation.

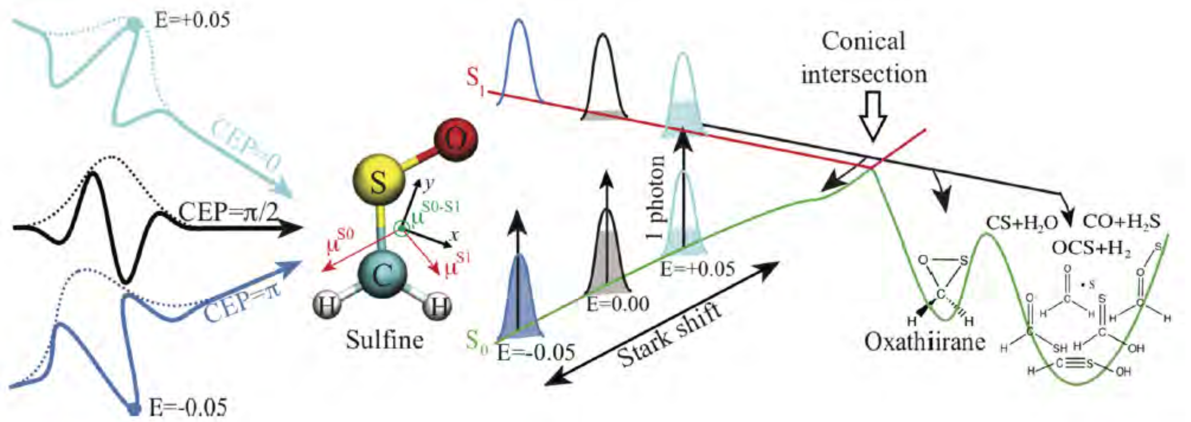

Figure 2. Schematic of CEP-controlled photochemistry in sulfine. The influence of the CEP on the absorption probability arises because of the Stark shift of the excitation energy induced by the strong field. Detection of oxathiirane can serve as an indicator of the amount of absorption (which is predicted to depend on the CEP for sulfine molecules aligned with the field).

Future Plans

Over the next year, we will develop a stochastic variant of the AIMS method which is appropriate for dense manifolds of electronic states. We will continue our simulations of pyrazine dynamics and connections with ultrafast electron diffraction experiments. We are also simulating electron diffraction experiments for a number of molecules where experimental data is not yet available and we expect these studies to clarify whether electron diffraction is likely to be successful in the context of larger molecules where the pair distribution function can be quite congested. We are very excited at the prospect of new UED experiments on liquid jets. We are developing the theoretical tools for calculations of excited state dynamics in solution in order to connect with these liquid jet UED experiments.

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ATO: Attosecond Science

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Jordan O'Neal, Anna Wang

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.

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, 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:

Attosecond Soft X-ray Pulses from an XFEL: (Duris 2019) In FY2019 we demonstrated the generation of isolated GW-scale soft X-ray (SXR) attosecond pulses with an X-ray free-electron laser (XFEL). This unique combination of high intensity, high photon energy, and short pulse duration enables the investigation of electron dynamics with X-ray non-linear spectroscopy. The shortest pulse achievable with an XFEL is limited by the available amplification bandwidth, which is typically ≤ 0.1%. For photon energies below 1 keV, this means pulse durations of 1-2 fs. The bandwidth limitation of the XFEL was overcome by compressing the electron beam with a high-power infrared pulse, a technique termed enhanced self-amplified spontaneous emission (ESASE) [1]. This FEL development was done though an on-going collaboration lead by Agostino Marinelli.

In order to diagnose the shot-to-shot variation of the X-ray pulse duration, we adapted the angular streaking (or atto-clock) method developed by Hartmann *et al.* [2]. A circularly polarized, 1.3 μm, infrared (IR) laser field is temporally and spatially overlapped with the X-ray pulse and the combined interaction of the fields produces photoelectrons where the temporal properties of the X-ray pulse are mapped onto the photoelectron momentum distribution [3]. The photoelectron momentum distribution is recorded using our specially designed velocity map imaging spectrometer [4].

Developing Methods for Attosecond Transient Absorption Spectroscopy at XFELs: (Driver2019) A widely used method for measuring ultrafast dynamics is X-ray transient absorption spectroscopy (TAS). One potential experimental challenge implementing this technique with attosecond SXR pulses from XFELs is the large bandwidth of an attosecond pulse. The natural implementation of TAS at an XFEL is to scan the central photon energy of a relatively narrow bandwidth (<1 eV) self-amplified spontaneous emission (SASE) pulse across the spectral region of interest and measure the absorption at each central photon energy by recording e.g. the total yield of photoproducts following resonant excitation [5]. The resolution of such measurements is set by the bandwidth of the incident XFEL pulse, and as such the broad bandwidth required to support attosecond pulses (>5 eV) pushes the resolution of these measurements below that required to resolve informative absorption features. The standard implementation of attosecond TAS for table-top sources (measuring the spectrum transmitted through a sample referenced to a different pulse) is greatly complicated by the natural fluctuations of SASE operation. Our group has developed an implementation for attosecond TAS at XFELs which is based on the statistical foundations of ghost imaging. We make full use of the natural fluctuations of ESASE pulses by correlating changes in the measured shot-to-shot spectrum with the single-shot yield of resonantly produced photoproducts. Making use of the alternating direction method of multipliers (ADMM), from this measurement we can reconstruct absorption features of width well below the bandwidth of the interrogating attosecond pulse.

Methods to create electronic coherences in molecules: The attosecond SXR pulses developed in collaboration with the SLAC accelerator directorate are intense enough to drive nonlinearities in molecular systems. A simple nonlinear technique for probing electronic motion, impulsive stimulated X-ray Raman scattering~(ISXRS), involves a single impulsive interaction to produce a coherent superposition of electronic states. We have demonstrated the ability of attosecond SXR pulses to produce valance excited states in the prototypical molecular system nitric oxide~(NO) using a time-delayed UV pulse to probe the valence excited states. The impulsive excitation is resonantly enhanced by the oxygen $1s\text{->}2p\pi^*$ resonance, and we observe an excitation fraction nearly 3% following the interaction with the attosecond X-ray pulse.

Electron Correlation in Attosecond Photoemission: (Kamalov2019) In addition to developing methods for studying ultrafast electron dynamics with XFELs we employ table-top, HHG-based attosecond pulse sources to study the photoemission process in the time domain. We combine attosecond interference measurements with calculations of photoionization matrix elements to demonstrate how multi-electron dynamics affect photoionization time delays in carbon dioxide. Attosecond photoionization has been primarily interpreted within the single-particle approximation, even for multi-electron systems. However, in molecular CO_2, electron correlation is observed to affect the time delays through two mechanisms: autoionization of molecular Rydberg states and accelerated escape from a continuum shape resonance.

Future Plans:

Photoemission Delays at Soft X-ray wavelengths: The angular streaking technique, which we developed for diagnosing attosecond SXR XFEL pulses, can be used to study the process of attosecond ionization of *K*-shell electrons. We have measured the photoionization delay between different *K*-shell continua: The N $(1s)^{-1}$ and O $(1s)^{-1}$ continuum in nitric oxide (NO). This data is currently under analysis, we will use the same reconstruction algorithm we developed for X-ray pulse characterization to reconstruct both the nitrogen and oxygen photoelectron wavepackets. The nitrogen 1*s* electrons can act as a reference wavepacket to understand the gross features induced by the phase of the ionizing x-ray pulse. Near 547 eV, lies the $2p\pi^*$ shape resonance in NO, we will reconstruct the low energy EWP from the oxygen 1*s* ionization as we scan over the resonance to observe any temporal reshaping of the wavepacket as it tunnels through the potential barrier.

In addition to the shape resonance phenomenon, the ionization of an inner shell electron will leave the system in a highly excited molecular state. The core-excited states of light atomic nuclei typically decay thru Auger emission, which produces high-energy electrons that carry excess energy away from the system. In addition to the low energy photoelectrons generated by the X-ray pulses, we collect the subsequent Auger electrons and are working to time-resolve the Auger emission process.

Angle-resolved Photoemission Delays: One particularly important aspect of the molecular photoemission process is the orientation of the molecular axis relative to both the ionizing laser polarization, and the electron emission angle. Our previous CO_2 measurements made use of an unaligned target, and an angle-integrating detector. We have developed impulsive alignment techniques, to align molecular targets for molecular frame (MF) photoemission experiments. MF photoionization delays show many interesting features, which are washed out in the angle-integrated measurement. In the next year we will repeat our CO_2 measurement with an aligned target.

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SPC: Solution Phase Chemistry (Kelly Gaffney (PI), Amy Cordones-Hahn (PI)), SLAC National Accelerator Laboratory, 2575 Sand Hill Rd., Menlo Park, CA, 94025
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Project Scope

Harnessing the strong optical absorption and photocatalytic activity of inorganic complexes depends on our ability to control fundamental physical and chemical phenomena associated with the non-adiabatic dynamics of electronic excited states. Internal conversion and intersystem crossing events governed by non-adiabatic interactions between electronic states critically influence the electronic excited state chemistry. Conventional wisdom predicts dynamics to occur with a hierarchy of time scales – vibrational energy redistribution followed first by internal conversion, and then by intersystem crossing. Contrary to conventional wisdom, ultrafast time-domain studies have shown that spin-state transitions can compete with spin-conserving electronic state transitions and both types of electronic-state transitions can occur on the time scale of vibrational energy redistribution.

There is a clear need for a new conceptual framework that can supplant the conventional wisdom for understanding electronic excited-state dynamics. The incisive observation of the electronic excited state dynamics is an essential step towards this objective. To achieve this experimental objective, the Solution Phase Chemistry (SPC) sub-task focuses on the application of ultrafast x-ray methods to the study of electronic excited state dynamics of inorganic molecules in complex chemical environments. More specifically, we endeavor to:

- Identify how excited state electron and spin density distributions control non-radiative relaxation with time resolved measurements, simple ligand exchange reactions, and simulation.
- Determine the importance of site-specific interactions between solvent and solute in electronic excited-state relaxation dynamics with ultrafast time-resolved measurements and molecular simulation.

Achieving these scientific objectives also requires development of ultrafast x-ray methods. Our previous research has emphasized the development of 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. We currently focus on methods that will be transformed by LCLS-II, in particular soft x-ray Resonant Inelastic X-ray Scattering (RIXS) as a probe of metal-ligand covalency in electronic excited states, and the extension of ultrafast electron diffraction (UED) to solution phase dynamics.

Recent Progress

***Mechanistic understanding of electronic relaxation dynamics in 3d coordination complexes* (Kjaer 2017; Lemke 2017; Liang 2017; Mara 2017; Zhang 2017; Biasin 2018; Kjaer 2018; Kjaer 2019):** The strength of the interaction between charge transfer and metal-centered excited states controls the rate and mechanism for electronic excited state relaxation dynamics in 3d transition metal complexes. To gain a mechanistic understanding of these processes, our approach is to disentangle the nuclear and electronic structure dynamics of MLCT excited states in iron coordination complexes using simultaneous WAXS and Fe K-edge XES (Kjaer 2019).

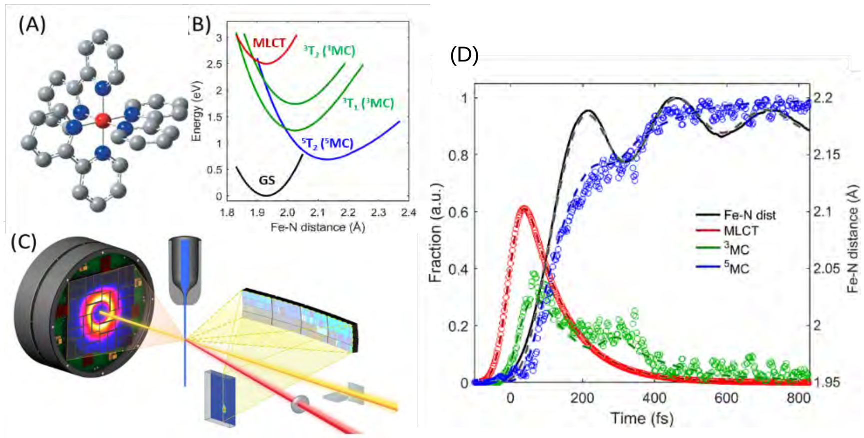

Fig. 1: The $[Fe(bpy)_3]^{2+}$ complex under investigation, Fe (red), N (blue), C (grey), H not shown (A), its most important ground and excited state potential energies as a function of Fe-N bond length (B) from Sousa *et al.* and the experimental setup (C). The MLCT, ^{3}MC, and ^{5}MC excited state populations extracted from the XES data and the average Fe-N bond length (solid black line). Note the transfer of ^{5}MC population back to the ^{3}MC state at the inner turning point on the ^{5}MC potential.

We have focused this effort on the archetypical photo-induced spin crossover complex iron tris-2,2'-bipyridine ($[Fe(bpy)_3]^{2+}$. By separating the measurement of nuclear and electronic dynamics, we have been able to identify the mean Fe-ligand bond length where transitions between metal-centered triplet and quintet states occur (Kjaer 2019). A summary on the results of this investigation can be found in Fig. 1. This detailed experimental characterization provides a benchmark for determining the impact of synthetic modifications on the relaxation mechanisms of other transition metal complexes, as well as a benchmark for the development of quantum chemical dynamics methods for transition metal complexes.

The ultrafast relaxation from charge transfer to metal-centered electronic excited states common to 3d transition metal complexes is an impediment to their utilization as cost effective replacements for 4d and 5d derived photo-redox catalysts. Suppressing spin crossover requires destabilizing high (^{5}MC) and intermediate (^{3}MC) spin metal-centered excited states relative to the optically allowed charge transfer excited states. We have made progress towards this objective by focusing on joint ultrafast optical and x-ray studies of charge transfer excited state relaxation in a series of mixed ligand complexes $[Fe(L)_{3-N}(CN)_{2N}]^{2-3N}$, where L is a series of polypridyl ligands. The interplay between chemical synthesis and ultrafast measurements has enabled us to investigate the impact of metal-ligand covalency, ligand field strength and symmetry, and solvation on the rate and mechanism of internal conversion and intersystem crossing in iron transition metal complexes (Kjaer 2017; Zhang 2017; Kjaer 2018) These studies have increased MLCT lifetimes by a factor of 400, compared to $[Fe(bpy)_3]^{2+}$.

Future Plans

***Controlling MLCT excited state lifetimes in 3d coordination complexes* (Kjaer 2017; Zhang 2017; Kjaer 2018; Koroidov 2018):** New systems aimed at suppressing spin crossover relaxation in Fe-based materials will be explored through ultrafast optical absorption, WAXS, and XES measurements. We will approach this goal using targeted ligand design to stabilize the MLCT or destabilize MC excited states. Modified polypyridyl ligands with low energy MLCT states have demonstrated significantly longer MLCT lifetimes, as described above. Future work will focus on how those ligand modifications influence not only the dynamics, but also the mechanism, of excited state relaxation. We will also identify if MLCT excitation to bipyridyl ligands with added solvation sites can induce strong H-bonding (or possibly PCET in optimal pH conditions) in the excited state, and its effect on relaxation dynamics. New carbene ligand constructs have been shown to destabilize MC excited states and similarly demonstrated significant enhancements of MLCT lifetime. Future work will focus on identifying the interplay of the ^{3}MLCT and ^{3}MC excited states and the role of strong metal-ligand covalency in the excited state relaxation mechanism.

In addition, we will extend these studies to identify the role of excited state relaxation on photochemical outcome for a series of Ni-centered complexes with dithiolene-inspired ligands. These complexes are known to evolve hydrogen, both electrocatalytically and by photoexcitation (direct and photosensitized), however their proposed mechanisms vary significantly with ligand design and their excited state 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 photochemical proton coupled electron transfer (PCET) reaction mechanisms. 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 a proton during the PCET reaction.

Preparing for science enabled by LCLS-II and UED **(Kunnus 2016; Titus 2017; Wolf 2017; Cordones 2018; Jay 2018; Koralek 2018; Norell 2018; Haldrup 2019; Kong 2019):** The SPC sub-task emphasizes the development and application of unique research infrastructure at SLAC to the objectives described above. For LCLS-II, we are collaborating with LCLS in the development of the chemRIXS endstation for solution phase ultrafast RIXS. We propose using ultrafast RIXS to investigate electronic excited state PCET and electronic excited state dynamics of 3d transition metal complexes. For PCET reactions, we will leverage the ability of x-ray spectroscopy to provide an atom specific fingerprint of the H or proton site, while the studies of transition metal complexes will focus on the interplay between the electron density distribution and excited state relaxation dynamics.

We have also established a strong collaboration with LCLS to extend UED to solution phase systems. This has involved the design of a vacuum chamber for solution phase UED measurements and the performance of the first ultrafast UED measurements in solution. Central to both solution phase UED and chemRIXS is the robust delivery of sub-micron thick flat liquid jets in vacuum (Koralek 2018). In collaboration with LCLS we are focusing on establishing optimal conditions for stable jet performance and how it depends on solvent and solution concentration.

Peer-Reviewed Publications Resulting from this Project (FY2017-FY2019)

Biasin, E., T. B. van Driel, G. Levi, et al. (2018). Anisotropy enhanced X-ray scattering from solvated transition metal complexes. *J. Synchrotron Radiat.* **25**: 306.

Cordones, A. A., J. H. Lee, K. Hong, et al. (2018). Transient metal-centered states mediate isomerization of a photochromic rutheniumsulfoxide complex. *Nature Comm.* **9**.

Haldrup, K., G. Levi, E. Biasin, et al. (2019). Ultrafast X-Ray Scattering Measurements of Coherent Structural Dynamics on the Ground-State Potential Energy Surface of a Diplatinum Molecule. *Phys. Rev. Lett.* **122**: 063001.

Jay, R. M., J. Norell, S. Eckert, et al. (2018). Disentangling Transient Charge Density and Metal-Ligand Covalency in Photoexcited Ferricyanide with Femtosecond Resonant Inelastic Soft X-ray Scattering. *J. Phys. Chem. Lett.* **9**: 3538.

Kjaer, K. S., K. Kunnus, T. C. B. Harlang, et al. (2018). Solvent control of charge transfer excited state relaxation pathways in $[Fe(2,2'\text{-bipyridine})(CN)_4]^{2-}$. *Phys. Chem. Chem. Phys.* **20**: 4238.

Kjaer, K. S., T. B. Van Driel, T. C. B. Harlang, et al. (2019). Finding intersections between electronic excited state potential energy surfaces with simultaneous ultrafast X-ray scattering and spectroscopy. *Chem. Sci.* **10**: 5749.

Kjaer, K. S., Z. Wenkai, R. Alonso-Mori, et al. (2017). Ligand manipulation of charge transfer excited state relaxation and spin crossover in $[Fe(2,2'\text{-bipyridine})_2(CN)_2]$. *Struct. Dyna.* **4**: 044030

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Koralek, J. D., J. B. Kim, P. Bruza, et al. (2018). Generation and characterization of ultrathin free-flowing liquid sheets. *Nature Comm.* **9**.

Koroidov, S., K. Hong, K. S. Kjaer, et al. (2018). Probing the Electron Accepting Orbitals of Ni-Centered Hydrogen Evolution Catalysts with Noninnocent Ligands by Ni L-Edge and S K-Edge X-ray Absorption. *Inorg. Chem.* **57**: 13167.

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

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 Kβ 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.

Norell, J., R. M. Jay, M. Hantschmann, et al. (2018). Fingerprints of electronic, spin and structural dynamics from resonant inelastic soft X-ray scattering in transient photo-chemical species. *Phys. Chem. Chem. Phys.* **20**: 7243.

Titus, C. J., M. L. Baker, S. J. Lee, et al. (2017). L-edge spectroscopy of dilute, radiation-sensitive systems using a transition-edge-sensor array. *J. Chem. Phys.* **147**.

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Zhang, W., 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 Ultrafast X-ray Imaging

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Project Scope

The NPI program studies the nature of time-resolved short wavelength scattering on photoexcited molecular systems. We develop methods to measure, analyze and understand how to image dynamics in molecular systems of increased complexity and in complex environments in the sub-angstrom and femtosecond scales. We strive to help LCLS develop effective science protocols for x-ray diffractive scattering experiments, to demonstrate important new capabilities as soon as they become feasible at LCLS and leverage development of new modalities and detection schemes.

Recent Progress

We have studied the limits to observe harmonic and dissociation motion from a model system molecule using ultrafast X-ray scattering. By measuring the amplitude, and frequency of harmonic motion about an equilibrium position, and comparing experimental results taken at LCLS to classical and quantum models that demonstrate a fundamental limitation on the ability to observe motion. We demonstrated limits on the spatial and temporal resolution through the maximal momentum transfer vector Q and delay timing resolution or delay sampling frequency ω, deriving analytical limits. We have then characterized dissociative motion in a diatomic molecule following laser-induced excitations, resolving several dissociative electronic states. Time-resolved x-ray scattering from these states can be difficult to isolate because they generally overlap in the angle-resolved x-ray scattering pattern. We demonstrated how temporal Fourier transform can isolate the dissociative motion from individual states. This delay frequency-resolved x-ray scattering (FRXS) signal separates bound from dissociative motion. This is because bound motion, which is mostly manifested by constant vibrational frequencies appears as stationary peaks in the frequency domain, while dissociative motion appears as straight lines along $\omega_k = v_k Q$, with slopes v_k as the effective dissociation velocities. We derive this relation and use FRXS to extract state-specific dynamics from experimental scattering patterns from molecular iodine. We use this method to also resolve

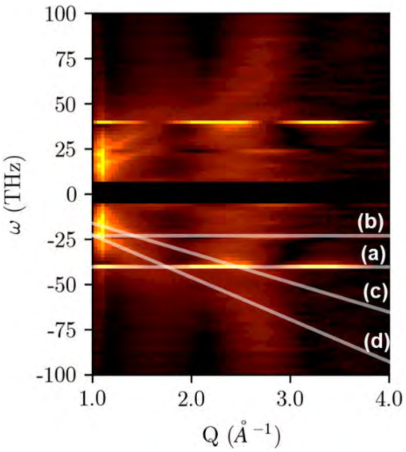

Fig 1 The power spectrum of angle integrated FRXS revealing (a) impulsive Raman and (b) spontaneous hyper-Raman scattering, as well as (c,d) dissociation.

dissociation via one- and two-photon absorption as well as vibrational wave packets. Moreover, we show how the time onset of dissociation as well as secondary processes such as impulsive Raman scattering, and spontaneous hyper Raman scattering can be resolved (Fig 1).

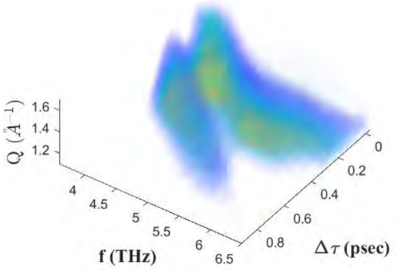

Fig 2 Wavelet power spectrum of angle integrated scattering signal uncovers temporal delays and acceleration details of two dissociation channels in I_2 without transforming to real space.

In addition, we are developing a wavelet-based analysis approach to time resolved scattering data that will make optimal use of the resolutions in temporal delay and momentum transfer collected in experiments in order to resolve in time and momentum weak signals below what is currently attainable using traditional methods. This method is a generalization to the previous FRXS method and combines the information about the time when processes happen, the dynamics for non-periodic and complex motions such as temporal accelerations, while allowing to extract dynamics from temporal Fourier space (Fig 2).

We have collaborated with ATO to establish attosecond X-ray pulse characterization using angular streaking. Initial experiments in the soft x-ray regime demonstrated this approach even in capturing more than a single attosecond x-ray pulse, and a manuscript about these results was recently accepted to Nature Photonics. This method will facilitate future hard x-rays scattering experiment in the attosecond regime to establish the x-ray probe properties as well as relative phase between two attosecond x-ray pulses in a single shot. Such information will open the way to develop new imaging modalities where the relative phase of the two x-ray pulses can be used for reconstruction of electronic motion of excited systems.

Future Plans

We have submitted a campaign proposal collaborating with the SPC and EIM subtasks to use high energy (18-25keV) ultrafast wide angle x-ray scattering, in conjunction with QM/MM simulations, to disentangle ultrafast solute and solvation dynamics and understand how intra- and intermolecular structural dynamics control photochemical and photocatalytic reactions. In particular, how electronic excited states change the interaction between the solvent and photo-catalytically active metal sites. In addition, to directly image the shape of nuclear wavepackets and the way intramolecular vibrational energy redistribution and relaxation to the solvent takes place, without bias toward the Franck-Condon active modes or the constraints of normal mode analysis. Details regarding the dynamic changes in shape and width of the excited wave-packets generally

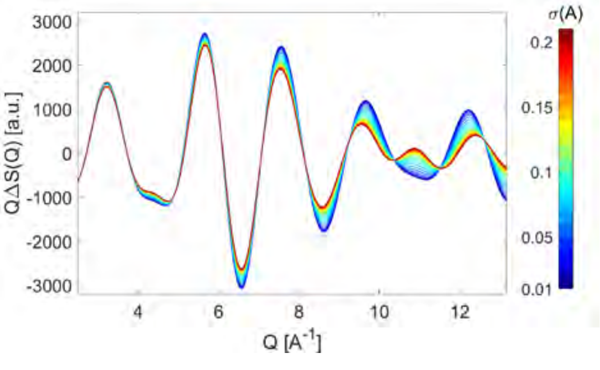

Fig 3 Wavepacket widths effect on calculated difference scattering signal of PtPOP molecules is significant at Q >10 $\AA^{-1}$. Different colors correspond to Gaussian wavepackets of increasing widths σ(Å) centered at 2.97 Å and 2.77 Å, relating to the ground and excited states Pt-Pt bond lengths.

elude direct probing with current scattering methods, as the $Q < 5$ Å^{-1} part of the signal is most often linear in the structural change of interest. This is not the case for larger momentum transfer. Fig 3 shows the calculated sensitivity of the scattering signal at high-Q to the width of the Pt-Pt bond stretch wavepacket extracted from a recent computational study. The difference for increasing wavepacket widths is prominent above >10 Å^{-1} demonstrating the ability to model the width and not only the position of these wavepackets. We plan to use optical control of electronic excited states to generate high energy, non-equilibrium distributions with sufficient fidelity that the redistribution and dissipation of energy can be followed experimentally to probe the optically controlled nuclear dynamics of IrDimen and PtPOP and to demonstrate how the high Q-range and anisotropic scattering signal can be used to directly measure the shape of wavepackets of excited molecules in a complex environments.

We are developing energy resolved scattering modality to open a path to resolve both inelastic and elastic parts of the scattering process, and consequently, to disentangle the contribution of electronic coherent motions, or coherences from charge density populations. This is because inelastic scattering is a process where scattering induced transitions between excited states in the electronic wavepacket and is dominated by electronic coherences. We can therefore correlate this signal with information about the different electronic excitations and its contributions at different energies. For non-periodic time-resolved scattering of ensembles of molecules, unlike ordered systems, each molecule scatters both elastically and inelastically regardless of its initial state. As a result, scattering from a single molecule can induce transitions to any electronic state, where the strongest contributions are usually between states that the excited electronic wave packet contains. We have made progress in design and calculation for a studded crystal analyzer apparatus that will allow to image high-energy scattered x-rays (>18 keV) resolving in energy for relevant UV\optical transitions at <5 eV.

We are also developing a high-order time-resolved approach to ghost imaging (GI) and ghost diffraction (GD) techniques. In 2018 we have recruited A. Schori, who is one of the pioneers on the implementation of GI and GD methods in the X-ray regime. High order GI and GD rely on creation of several reference beams which will enhance the visibility and resolution of the object under study, while reducing the induced radiation damage. This approach can be extremely important for studying non-periodic mesoscopic samples in the 10-50 Å range, and offer a bridge between the AMO and the biochemistry worlds. We are testing approaches using multilayer crystals to create the multi beam source, and plan to demonstrate the schemes first on simple static objects with synchrotron radiation before moving to time resolved FEL experiments.

Peer-Reviewed Publications Resulting from this Project (2017-2019):

- J. M. Glownia, A. Natan, J. P. Cryan, R. Hartsock, M. Kozina, M. P. Minitti, S. Nelson, J. Robinson, T. Sato, T. van Driel, G. Welch, C. Weninger, D. Zhu, and P. H. Bucksbaum, **Glownia et-al Reply**, Phys. Rev. Lett 119, 069301 (2017).
- L. J. Zipp, A. Natan, and P. H. Bucksbaum **Imaging the Breakdown of Molecular Frame Dynamics through Rotational Uncoupling**, Physical Review A **95** (6), 061403(R) (2017).
- 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 ππ*/nπ* internal conversion in organic chromophores via K-edge resonant absorption,** Nature Comm., 8, 29 (2017).
- M. R. Ware, J. M. Glownia, A. Natan, J. P. Cryan, and P. H. Bucksbaum, **On the limits of observing motion in time-resolved x-ray scattering** Philos. Trans. Royal Soc. A, 377(2154), 20170477 (2019)
- M. R. Ware, J. M. Glownia, N. Al-Sayyad, J. T. O'Neal, and P. H. Bucksbaum, **Characterizing dissociative motion in time-resolved x-ray scattering from gas-phase diatomic molecules**, Physical Review A 100, 033413 (2019)
- S. Li, R. Coffee, Z. Guo, A. Natan, K. Hegazy, J. O'Neal, T. Osipov, D. Ray, D. Rich, M Owens III, P. Walter, A. Kamalov, E. G. Champenois, A. Marinelli, and J. P. Cryan, **A Co-axial Velocity Map Imaging Spectrometer for Electrons,** AIP Advances, 8(11), 115308 (2018).
- G. Porat, G. Alon, S. Rozen, O. Pedatzur, M. Kruger, D. Azoury, A. Natan, G. Orenstein, B. D. Bruner, M. J. J. Vrakking and N. Dudovich, **Attosecond time-resolved photoelectron holography**, Nat. Communications 9 (1), 2805 (2018).
- S. Li, Z. Guo, R. N. Coffee, K. Hegazy, Z. Huang, A. Natan, T. Osipov, D. Ray, A. Marinelli, and J. P. Cryan, **Characterizing isolated attosecond pulses with angular streaking**, Opt. Express 26 (4), 4531-4547 (2018).
- J. Duris, S. Li, T. Driver, E. G. Champenois, J. MacArthur, A. A. Lutman, Z. Zhang, P. Rosenberger, R. Coffee, G. Coslovich, J. M. Glownia, G. Hartmann, W. Helml, A. Kamalov, J. Knurr, J. Krzywinski, M.-F. Lin, M. Nantel, Adi Natan, J. O'Neal, N. Shivaram, P. Walter, A. Wang, T. Wolf, J. Z. Xu, M. F. Kling, P. H. Bucksbaum, A. Zholents, Z. Huang, J. P. Cryan, A. Marinelli, **Tunable Isolated Attosecond X-ray Pulses with Gigawatt Peak Power from a Free-Electron Laser**, Nat. Photonics, *accepted* (2019).

SFA: Strong Field AMO Physics

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Participants: *Phil Bucksbaum, Ruaridh Forbes, Nick Werby, Ian Gabalski, Adi Natan, Matt Ware, James Cryan, David Reis*

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. 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 will be particularly relevant at x-ray FELs, since they are a source of some of the strongest electromagnetic fields available, up to kilovolts per Angstrom. It also has close connections to attosecond science, since strong fields induce rapid evolution of small quantum systems.

Personnel: This year Matt Ware graduated and has joined the PULSE Institute group of Taisia Gorkhover, and continues to collaborate with our task. A new postdoc, Ruaridh Forbes, and new graduate student, Nick Werby, joined this group this year. Another new graduate student, Ian Gabalski, will join this fall. We also actively collaborate with leaders of other tasks in the FWP: Adi Natan, James Cryan, and David Reis.

Recent Progress

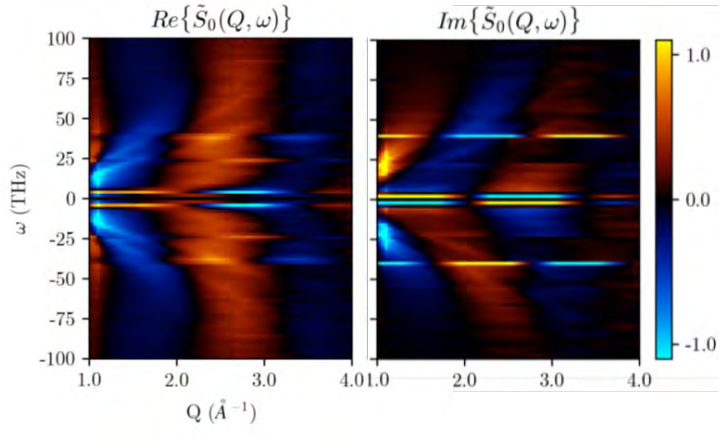

Fig. 1. Real and imaginary parts of the complex Fourier transform of $S_0(Q,\tau)$. Simulated Raman and Hyper-Raman processes are the horizontal bands; Sloped lines show both the speed and time-shift associated with different dissociation channels.

Here we highlight ongoing work in our SFA task with significant new progress in two areas. First, analysis of hard x-ray LCLS diffraction data from molecules *under the influence of strong fields* now identifies new observables that are made possible with ultrafast x-ray scattering. Second, we also have new VMI data on electron rescattering from tunnel-ionized molecules in the ATI regime, which shows electronic structure with high momentum and time resolution. Recent results that are collaborations with other tasks will be reported in those abstracts, including strong-field attosecond response of molecules probed by soft x-ray attosecond pulses, reported by the ATO task; and further work on hard x-ray scattering, reported in the NPI task.

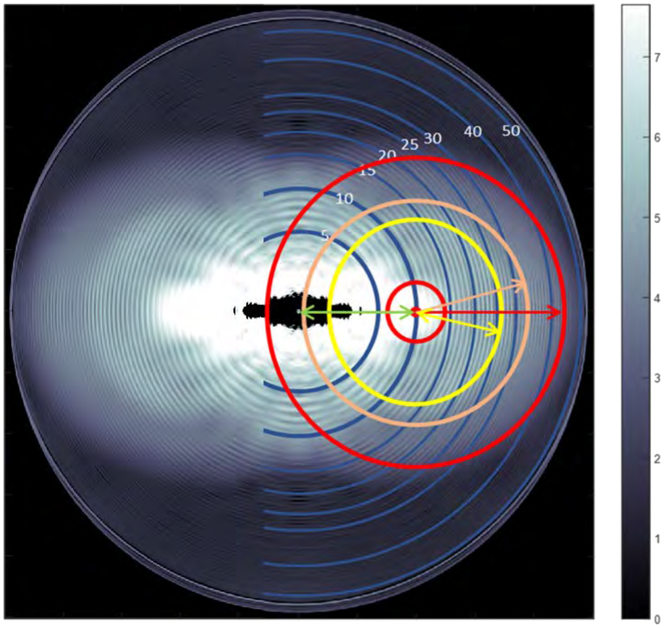

Fig.2: VMI image from strong-field ionization in N2. Here we focus on the rescattered electrons, viewed with a logarithmic grey scale:

- ●ATI peaks (numbered);
- ● A_0, the classical limit of ATI, $E_0=2U_p$ = 13.9eV (9th ATI peak)
- ● 1.24 A_0, scatt max, E_{scat}=21.4 eV;
- ● 0.74 A_0 ring, E_{scat}=7.6 eV,
- ● 0.95 A_0 dark ring, E_{scat}=12.5 eV

Strong-field processes in molecules viewed with hard x-ray diffraction: Strong fields typically excite multiple processes in molecules, which overlap each other in coherent diffraction data sets $S(Q,\tau)$. Ordinary methods such as Legendre decomposition are often unable to detect a weak channel such as nonlinear spontaneous Raman scattering or a weak dissociation channel when it is embedded in a far stronger channel such as excitation to a bound wave packet, or stimulated Raman excitation. We have found that the Fourier transformed data set $\tilde{S}(Q,\omega)$ can isolate the dynamics from individual channels, effectively acting as a “sparse” basis. This frequency-resolved x-ray scattering (FRXS) signal segregates bound states by vibrational frequencies ω_i, which appear as modulations at that frequency. The signal variation in Q and its spectral phase provide directly the position, amplitude and phase of the spatial oscillation. Still more, we have been able to show that *non-periodic* motion, such as dissociation, also forms definite sparse patterns in $\tilde{S}(Q,\omega)$. Scattering from ballistic dissociation fragments, for example, falls on straight lines that pass through $\omega = Q = 0$ and with slope $v = \omega/Q$ representing the speed of fragment separation. Furthermore, the *phase* of these features is directly related to the time shift of the separating fragments caused by the inter atomic forces. These results have been reported in two papers this year, and one more in preparation.

Strong-field rescattering. It is well known that strong-field ionized electrons may be driven back to the molecule by the oscillating laser field. A small fraction of them recombine, creating valuable sources of coherent radiation (high harmonics, attosecond pulse trains, VUV frequency combs, and isolated attosecond pulses). A far larger fraction scatter from the parent molecule, and these should be excellent probes of the strong-field process itself. Molecular diffraction of these returning electrons has already been used as a structural probe, but we will use them to study the transient *electronic* structure for strong-field or attosecond physics and chemistry. Transient phenomena and electron-electron configuration interactions are reflected in rescattering features. Some of the useful properties of high harmonic radiation, such as the attosecond chirp, ought to be exhibited by these electrons as well. We've updated our velocity-map imaging capability to start to explore this. The figure shows a recent strong-field ionization experiment on N2.

Future Work:

Strong-field excitation leads to laser-induced non-Born Oppenheimer effects because of the strong coupling between electronic sates in the presence of an external field. To study this using the tools of hard x-ray diffraction will require shorter laser exciation pulses and also shorter wavelengths than currently available in the XPP or CXI diffraction end stations at LCLS. Therefore we have begun a collaboration with the group of Peter Weber to implement 200 nm and sub-30 fs pump capabilities at the CXI end station. Our goal is to make this available for Run 18 in 2020.

Our future work on coherent diffraction will focus on a series of proposals for LCLS that makes use of the 200nm pump pulses. SFA has taken the lead on a Run 18 LCLS proposal aimed at using the harder x-ray capabilities at LCLS-II to resolve excitation channels in true 3-dimensional polyatomic molecules. We will study intermodal interactions of polyatomic molecules involving bends, stretches, dissociation, and roaming re-association using photoexcitation by femtosecond pulses of ultraviolet laser radiation and probing with LCLS hard x rays. Our target molecules are CS2 and CH2BrI. This work also involves collaboration with theory groups for modeling and simulation, such as the simulation of the dissociation pathways of CS2 displayed in Fig. 3.

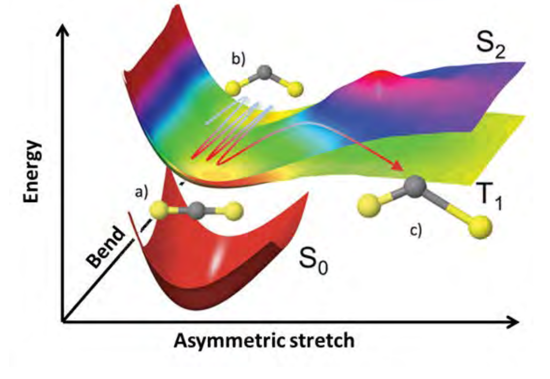

Fig. 3. Dissociation pathway in CS2 following excitation at 200nm.

Our electron rescattering experiments will develop along the lines described above to utilize rescattering to explore transient structure in molecules in the presence of strong laser fields. We have spoken to Robert Lucchese about a collaboration to model the transient electron specta that we are collecting in the lab. In addition we will add field shaping and impulsive alignment capabilities to the VMI apparatus.

Finally, we are active members of the attosecond campaign led by our ATO task and by Ago Marinelli of LCLS. Our primary goal is to explore the attosecond regime of strong-field laser-molecule interactions.

Peer-Reviewed Publications Resulting from this Project (2017-2019) [1–10]

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NLX: Nonlinear X-ray Science

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Project Scope:

In the NLX *program, we are focused on the nonlinear optics of short-wavelength, ultrafast 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.

Progress Report

Non-sequential two-photon interactions at x-ray wavelengths became possible with the advent of the LCLS free-electron laser. Much of the focus in this program has been the exploration of fundamental nonlinear x-ray interactions and their use for measurements of chemical and materials dynamics. However, we have also historically studied fundamentals of strong-field high-harmonics generation (HHG) in solids. This work continues through collaborations with other subtasks and will be described elsewhere.

Our emphasis in NLX is primarily on nonlinear optics in the hard x-ray regime, where the interaction of multiple photons is expected to give simultaneous and near instantaneous atomic-scale structural and spectroscopic information. Far from resonance, the linear x-ray matter interaction can be well approximated by the scattering off a collection of free-electrons. Thus, x-ray nonlinearities are nominally expected to be extremely weak compared to what is typical in the optical regime, especially off resonant. Such experiments are largely linear in the x-ray intensity but nonetheless require the extreme brightness and short pulses of the X-ray FEL, and will benefit from the high rep-rate of LCLS-II and II-HE, although we've already explored some of the most basic nonlinear optical processes under AMOS funding on LCLS and SACLA.

For example, we've found that models that treat the solid as a collection of free-electrons are successful at describing both the x-ray second-harmonic generation and within some limits (optically modulated) x-ray susceptibility in x-ray–optical sum frequency generation. We are utilizing this to try and understand the solid-state HHG process from an atomic-scale perspective. With our collaborators Daria Gorelova and Robin Santra we have recently reported a study of x-ray optical mixing using a Floquet formalism that allows one to calculate the scattering strength, and determine the regime under which it can be considered as scattering from the instantaneous charges and current densities. We recently performed first experiments looking for higher order-wave mixing on GaAs were performed at SACLA in collaboration with Matthias Fuchs at Nebraska. This first experiment allowed us to test the complex x-ray optical setup and characterize backgrounds.

As we have reported previously, we have found that in nonlinear two-photon Compton scattering, the free-electron model breaks down spectacularly. 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 seemed consistent with a novel nonlinear scattering mechanism involving bound-state electrons, despite an X-ray energy of approximately two orders of magnitude above the 1*s* binding energy. Nonetheless, in collaboration with Dietrich Krebs and Robin Santra, we've found that single electron, single atom processes involving two incoming and a single outcoming photon cannot explain our results, and are in fact largely consistent with the impulse approximation and the theory of free-electron scattering in a strong laser-field.

Finally, we have been able to set a limit on the cross-section for two-photon excitation of the nuclear resonance in ^{57}Fe, both in the half-resonant and two-color 1s bridge scenario. We are currently working on a manuscript with the Palffy group in Heidelberg. In the process of searching for the nuclear excitation, we've observed a relatively large single-photon resonantly enhanced two-photon scattering into a higher energy photon, that is independent of isotope and thus presumed to be purely electronic in nature. The effective cross-section appears to be orders of magnitude (>5) higher than in Be, such that we can excite it at much lower intensities. We have recently resolved the emitted photon spectra with sufficient resolution to identify several different, but presumably related processes, including the excitation of a double-core hole followed by the correlated single-photon two electron filling and what appears to be hyper-Raman from a core-excited state.

Future Plans:

Significant effort is ongoing to analyze the results of recent beamtimes at LCLS and SACLA. We have been awarded additional beamtime to study nonlinear x-ray optical mixing, and will write up results on the resonant two-photon scattering and two-photon Mossbauer limit. Future measurements are aimed at a better understanding of novel x-ray matter interactions and development of novel spectroscopies based theory.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

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Electron Dynamics on the Nanoscale

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Project Scope

This component of the SLAC research program examines the nature and dynamics of electron motion and electronically excited states in nanostructures. The research currently focuses on electrons in atomically thin two-dimensional (2D) layers of van-der-Waals crystals and heterostructures, using transition metal dichalcogenide semiconductors as model systems. The investigations make use of complementary spectroscopic techniques to probe radiative and non-radiative relaxation pathways after photoexcitation, including the role of Coulomb interactions and vibrational coupling as manifest in exciton formation, exciton-exciton and exciton-carrier interactions, intervalley scattering, and exciton radiative decay. The role of the external environment in modifying the electronic states and their dynamics is also a focus of attention, as are heterostructures composed of atomically thin 2D van der Waals layers combined with other 2D layers. 2D van der Waals layers, with their lack of chemical reactivity, can be combined in a wide variety of structures simply by mechanical assembly to provide a set of customizable systems in which to investigate underlying principles of excited-state dynamics.

Recent Progress

A focus of research in this program has been the elucidation of the nature and dynamics of excited states in atomically thin transition metal dichalcogenide layers in the class of MX_2 (M = Mo, W and X = S, Se, Te). These systems provide models for the behavior of electrons in two-dimensional (2D) semiconducting van-der-Waals layers, which are prototypes for laterally delocalized electronic states with strong vertical localization. The systems have attracted great interest because of their strong and anomalous excitonic interactions, their strong spin-orbit interactions, as well as the possibility of accessing the valley degree of freedom through their valley circular dichroism and of constructing diverse heterostructures from multiple layers.

Recent efforts have examined the influence of the environment of a given monolayer on electronic excited states and their dynamics. Here we briefly summarize two advances. One involves the role of a second layer in the crystallographic bilayer in altering exciton dynamics; the second involves studying the significant influence of the dielectric screening of the environment induced by stacked external layers on the excited states of a monolayer. Additional activities within this project, including contributions to ultrafast excited-states dynamics of dissociating molecules probed by ultrafast electron diffraction and electronic dynamics in bulk semiconductors, are not explicitly presented.

Dielectric disorder in 2D materials

Recently there has been rapid progress in understanding the nature and dynamics of electronic excitations in 2D semiconductors, particularly for the prototypical direct-gap monolayers in the transition metal dichalcogenide (TMDC) family and their heterostructures. These have included the identification of many-body excitonic states, such as trions and biexcitons, as well as observation of spin-forbidden triplet-like states. In addition to advances arising from extensive theoretical research, a key factor on the experimental side has been the ability to observe narrower spectral features, reaching widths at low temperatures defined by radiative broadening. Our previous research within this program has examined both lifetime broadening and dephasing-induced broadening of excitonic transitions associated with phonon scattering processes. In our recent research, we have examined factors behind *inhomogeneous* broadening of excitonic states in TMDC monolayers and, in particular, the mechanism through which encapsulation of TMDC layers by layered van-der-Waals material hexagonal boron nitride (h-BN) induces a dramatic reduction in exciton spectra linewidths. The physical basis behind the widely noted experimental observation that h-BN encapsulation can lead to a sharp decrease in inhomogeneous broadening had not been established prior to this work.

We addressed this issue through systematic studies of the spectral features of the WS_2 and WSe_2 monolayers in different external environments, with emphasis on a comparison between the width of the ground-state A exciton and excited Rydberg states of the exciton. The studies [1], through a combination of these experimental findings and theoretical analysis, identified a dominant role for inhomogeneity of the surrounding dielectric environment in defining the inhomogeneous broadening of the excitonic states. The research involved a collaboration with researchers at NIMS in Japan who supplied high-quality hBN crystals and theorists at Columbia and Chalmers Universities, as well as former group member A. Chernikov and his colleagues at the University of Regensburg, Germany.

The strong influence of the surrounding environment on the spectroscopic signatures of excitons in these 2D materials can be readily seen in Fig. 1 (left). Here we compare the ground (n = 1) and first excited (n = 2) exciton states of a WS_2 monolayer supported by a conventional oxide layer on Si and encapsulated in hBN.. There is a strong decrease in the linewidth of the n =1 exciton, but a still greater decrease in the linewidth of the n =2 exciton in the encapsulated environment. Since our previous research has demonstrated directly the role of the dielectric environment in inducing spectral shifts through modification of Coulomb interactions in the layer, a natural explanation for this pronounced effect lies in the role of dielectric inhomogeneity or disorder in creating line broadening. We further explored this hypothesis by examining correlations of n = 1 and n = 2 exciton linewidths in a wide range of samples. We consistently observed that the inhomogeneous broadening seen in the n = 1 exciton was observed to be amplified in the n = 2 features Fig 1 (center). This observed behavior was found to be entirely consistent with theory predictions of line broadening induced by environmental dielectric inhomogeneity Fig 1 (right).

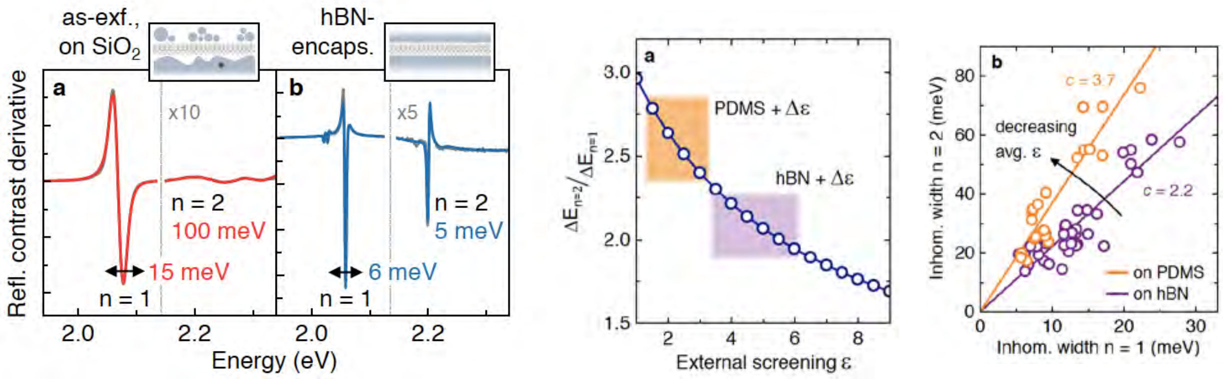

Fig. 1. Experimental and modeling results examining the role of the disorder of the dielectric environment on spectral broadening of excitonic transitions in semiconducting TMDC monolayers. (left) A comparison of the spectral signatures of the *n* = 1 and *n* = 2 A exciton absorption in monolayer WS_2 at low temperature, presented after differentiation with respect to energy. For the case of the hBN encapsulated monolayer, much narrower lines are seen, particularly for the excited exciton state than for the usual case of a monolayer on an oxide surface. (center) Statistical comparison of linewidths for the *n* = 1 and *n* = 2 A excitons in different environments, showing consistently greater broadening of the *n* = 2 state. (right) Theoretical predictions for the relative influence of dielectric disorder on the broadening of the more tightly bound (and more environmentally decoupled) *n* = 1 exciton and the less bound (and more environmentally sensitive) *n* = 2 exciton.

Interlayer exciton states in MoS_2/WSe_2 heterostructures

Combinations of 2D semiconductors in the TMDC family can give rise to new optically excited states in which the electron and hole are separated in the two layers. We have recently identified such interlayer exciton states in the MoS_2/WSe_2 heterostructure and found thereby the first example of such states lying well in the infrared spectral range. The states were identified by a number of signatures – from their emergence only in the combined system of the heterostructure (Fig. 2) to their sensitivity to crystallographic orientation (not shown). A key signature of these interlayer, charge-separated states is their strong spectral tuning with the application of an external electric field through their large linear Stark shift. In our configuration, we have achieved a tuning range in the emission energy of the interlayer exciton of nearly 200 meV in a gated structure. In addition to the usefulness of the Stark shift for determining the excited-state dipole moment of the interlayer exciton, these heterostructure systems hold promise for convenient tunable sources and absorbers of light for various applications. This work has been carried out in collaboration with researchers at Columbia University and NIMS, Japan, who assisted with sample preparation, and with researchers at the University of Erlangen, Germany, who modeled the interlayer excitonic states using electronic structure calculations.

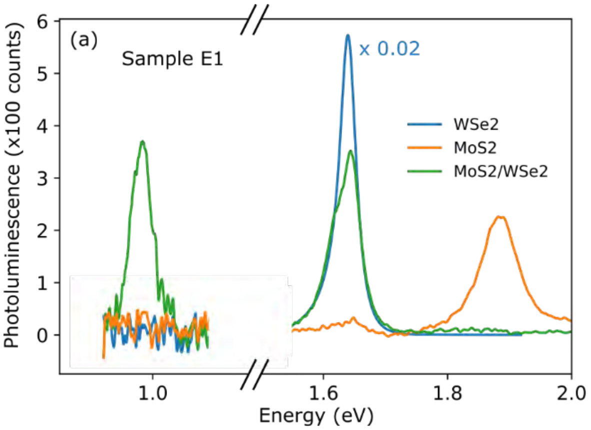

Fig. 2. Emission spectra for a heterostructure comprised of a monolayer of MS_2 stacked vertically on a monolayer of WSe_2. The heterostructure shows a strong emission feature around 1.0 eV. In the separated monolayers, we see no emission in this spectral range. In the visible part of the spectrum, we observe the expected characteristic exciton emission features of each monolayer, as shown. For the heterostructure, the emission of these excitons is strongly suppressed. This reduction of the emission reflects the rapid (sub-picosecond) charge separation process, which leads to the formation of the interlayer exciton, with its spectrally shifted emission around 1.0 eV.

Future Plans

A focus of future research will be to examine electron dynamics associated with the phenomena described about: spatially modulated potentials arising from dielectric disorder and charge transfer processes at various tailored vertical heterostructures. In particular, issues of how charge transfer processes depend on the alignment of energy levels and crystallographic orientation of the systems are of particular interest. Extension of optical studies to probe charge transfer with transitions from core-levels are also planned to provide an atomic-level view of charge transfer dynamics.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

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3. C. Jin, E. Y. Ma, O. Karni, E. C. Regan, F. Wang, and T. F. Heinz, "Ultrafast dynamics in van der Waals heterostructures," *Nature Nanotech.* **13**, 994–1003 (2018).
4. A. Raja, M. Selig, G. Berghäuser, J. Yu, H. M. Hill, A. F. Rigosi, L. E. Brus, A. Knorr, T. F. Heinz, E. Malic, and A. Chernikov, "Enhancement of exciton-phonon scattering from monolayer to bilayer WS_2," *Nano Lett.* (2018).
5. J. K. Kim. X. Shi, M. J. Jeong, J. Park, H. S. Han, S. H. Kim, Y. Guo, T. F. Heinz, S. Fan, C.-L. Lee, J. H. Park, and X. Zheng, "Enhancing Mo:$BiVO_4$ Solar Water Splitting with Patterned Au Nanospheres by Plasmon-Induced Energy Transfer," *Adv. Eng. Mater*. **8**, 1701765 (2018).
6. G. Wang, A. Chernikov, M. M. Glazov, T. F. Heinz, X. Marie, T. Amand, and B. Urbaszek, "Colloquium: Excitons in atomically thin transition metal dichalcogenides," *Rev. Mod. Phys*. **90**, 021001 (2018).
7. J. Yang, X. Zhu, T. J. A. Wolf, Z. Li, J. P. F. Nunes, R. Coffee, J. P. Cryan, M. Gühr, K. Hegazy, T. F. Heinz, K. Jobe, R. Li, X, Shen, T. Veccione, S. Weathersby, K. J. Wilkin, C. Yoneda, Q. Zheng, T. J. Martinez, M. Centurion, and X. Wang "Imaging CF_3I conical intersection and photodissociation dynamics with ultrafast electron diffraction," *Science* **361**, 64-67 (2018).
8. 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).
9. 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).
10. 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).
11. 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).

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 undertaken studies on the photoinduced structural dynamics of the molecules α-phellandrene and nitrobenzene at SLAC's Mega-electron-volt ultrafast electron diffraction (UED) facility. Our investigation of the ultrafast photochemical ring-opening of α-phellandrene builds up on our recently published study on the analog ring-opening reaction in 1,3-cyclohexadiene. Compared to 1,3 cyclohexadiene, α-phellandrene exhibits an isopropyl substituent at one of the carbon atoms at the site of the ring-opening reaction (marked with "1" and "2" in Fig. 1). The substitution has a two-fold effect on the ring-opening dynamics: a) It lifts the symmetry of the six-membered ring system. This leads to the existence of two possible ground state conformers in the gas phase with the isopropyl group either approximately in the ring plane or perpendicular to the ring plane. Preliminary *ab-initio* wavepacket simulations performed by the PULSE UTS subtask (PI Todd Martinez) suggest that ring-opening dynamics started from the two ground state conformers differ at least by their timescales. This can be rationalized by the fact that in the case of the isopropyl group being in

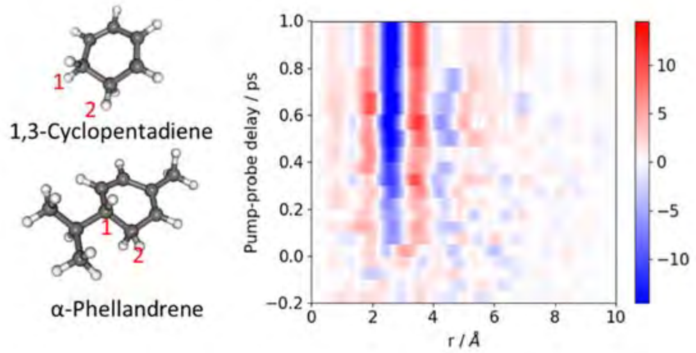

Figure 1: Structure of 1,3-cyclohexadiene and α-phellandrene (left) and preliminary time-resolved difference pair distribution functions from our ultrafast electron diffraction study of α-phellandrene (right)

the ring plane, the ring-opening motion of carbon atom 1 (see Fig. 1) can proceed to a certain degree around the isopropyl group. If the isopropyl group is pointing in perpendicular direction to the ring plane, the ring-opening motion drives the carbon directly into the isopropyl group. The second effect of the isopropyl group on the ring-opening dynamics is a localization of the nuclear wavepacket motion to carbon 2 of the ring-opening site (see Fig. 1). This is clearly evident from the photoproducts which show isomerization analog to 1,3 cyclohexadiene on the side of carbon 2 but not on the carbon 1 side.

Furthermore, we have studied the photoinduced structural dynamics of nitrobenzene. Nitrobenzene is known to undergo photoinduced dissociation reactions in the gas phase. Three different reaction channels have been identified in the literature leading to abstraction of NO_2, NO or O fragments. Additionally, there is evidence that a triplet state might be accessed. According to our preliminary analysis of the UED data, the molecule does not undergo substantial structural changes on the femtosecond and picosecond timescale, but gets vibrationally “hot”. Any photofragmentation reaction, thus, must take place thermally on considerably longer timescales. Comparison with ab-initio simulations from the PULSE UTS subtask suggest that we are observing rather the vibrationally hot singlet ground state than the triplet state. We are currently investigating, if the differences in the signatures from the hot singlet and triplet states are due to release of different amounts of kinetic energy into the nuclear degrees of freedom or due to differences in the singlet and triplet potential energy surfaces.

Additionally, we performed in collaboration with the PULSE SPC subtask (PIs Kelly Gaffney and Amy Cordones-Hahn) and SLAC’s UED facility the first UED studies in liquid samples. Preliminary results from ultrafast heating of bulk water suggest that UED gives unprecedented access to hydrogen bonding dynamics. Furthermore, we studied ultrafast structural dynamics of solutes in water, specifically I_3^-. These studies are complicated by the strong background from bulk solvent scattering. Nevertheless, our preliminary analysis shows that we can resolve the photoinduced dissociation dynamics of I_3^- in time.

Moreover, we have simulated the signatures from bond dissociation in time-resolved x-ray photoelectron spectra (XPS) in collaboration with Zheng Li and Ludger Inhester from CFEL, Hamburg. As a prototypical example we used the UV-induced C-I bond photodissociation of CH_3I. We find clear signatures of the electron density changes during the bond dissociation, which allow us to map the temporal evolution of the XPS signal onto the atomic distance axis. During the dissociation, an XPS shake-up satellite band changes in energy and becomes the dominant contribution to the XPS spectrum, whereas the originally dominating band becomes a weak contribution. The point in space and time, which marks the loss of bonding interaction between carbon and iodine can be directly connected to the intensity change of the two XPS bands.

Future Plans

We plan to continue our studies of ultrafast structural dynamics in molecules in the gas phase.

We will perform an additional study of an isomer of α-phellandrene, α-terpinene, which differs in the substitution sites of the cyclohexadiene ring. Additionally, we plan to investigate excited state dynamics of organic ketones with time-resolved soft x-ray spectroscopy and x-ray diffraction. Furthermore, we will continue our time-resolved photoelectron spectroscopy studies of nucleobases.

Peer-Reviewed Publications Resulting from this Project (2017-2019):

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

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Scope of the program

A new field of research has emerged quickly following the experimental discovery of high-order harmonic generation (HHG) in bulk crystals subjected to intense mid-infrared laser fields [Ghimire2010]. This is in part because high-harmonics provide a new window to view intense laser-solid interactions at atomic (both space and time) level and they promise stable attosecond pules in compact setups. Recent developments in the field [Vampa2015, You2017a] indicated that it might be possible to probe the atomic and electronic structure of bulk crystals using harmonics in an all-optical setting. However, many of these applications require a clear understanding of the underlying mechanism. In the condensed phase, the field-driven electron is never far from the atomic cores, so the usual strong-field approximation is no longer a good approximation. Consequently, the three-step re-collision model [Corkum1993] becomes questionable in describing the HHG process and other strong-field phenomena in dense optical media. The main fundamental questions we are addressing in this program are: (i) how the HHG mechanism in solids compares to the gas phase cousins, (ii) what is the recipe to develop HHG into an atomic-scale probe of generating medium, (iii) how does the time-domain profiles of harmonics look like and would that information be useful to determine the relative contribution from multiple HHG channels, and (iv) what is the fundamental role of periodicity of the crystal?

Progress Budget Period (7/16/2018 – 7/15/2019)

Our paper titled, "*Interferometry of dipole phase in high-harmonics from solids*" is published in *Nature Photonics*. An editor-suggested graphic had also appeared on the home page of the journal.

In this work, we employed a robust homodyne interferometric approach to measure the laser-induced dipole phase of high-order harmonics from crystals. A schematic of the setup is shown in figure 1a) and b). We split the laser beam into two beams using a birefringent optics-based interferometer and focus them collinearly onto the sample. The laser focus spots on the sample are far apart such that the laser beams do not interfere, but in the far-field high-harmonic beams could overlap both spatially and temporarily. This overlap produces fringes in the high harmonic spectrum, as shown in figure 1 c) and d), measured using transmission and reflection geometry respectively. Fringes have good visibility when two laser beams have equal intensities. Then, by adjusting waveplates in the interferometer we change relative peak intensities on two laser spots and track the fringe positions in each harmonic. We find substantial phase shifts (about -350 *as*) in the transmission geometry (as seen in e) compared to smaller shifts (about +190 *as*) in the reflection geometry (as seen in f), for a 50 percent change in laser intensity.

We reproduced our experimental results in simulations by considering a strongly driven two-level system, whose energy separation corresponds to the band-gap in the source material. In simulations, we can separate adiabatic and diabatic contributions, which are analogical to intra-band current and inter-band polarization respectively. We find that the diabatic component closely reproduces the results from reflection geometry. We understand the large and reversed directional shifts in transmission geometry by considering the influence of the nonlinear index of refraction to the pump laser field. Therefore, our analysis shows that the reflection geometry closely represents the microscopic picture. Once we separate propagation effects, we also perform comparative measurements between two different optical media, MgO and SiO_2. We find the phase shifts in SiO_2 are much smaller as shown in figure 1 g). Our results indicate clearly that the dipole phase in harmonics from solids depends strongly on the source material. This is in stark contrast to the case in the gas phase, where the dipole phase is largely independent of the target atom.

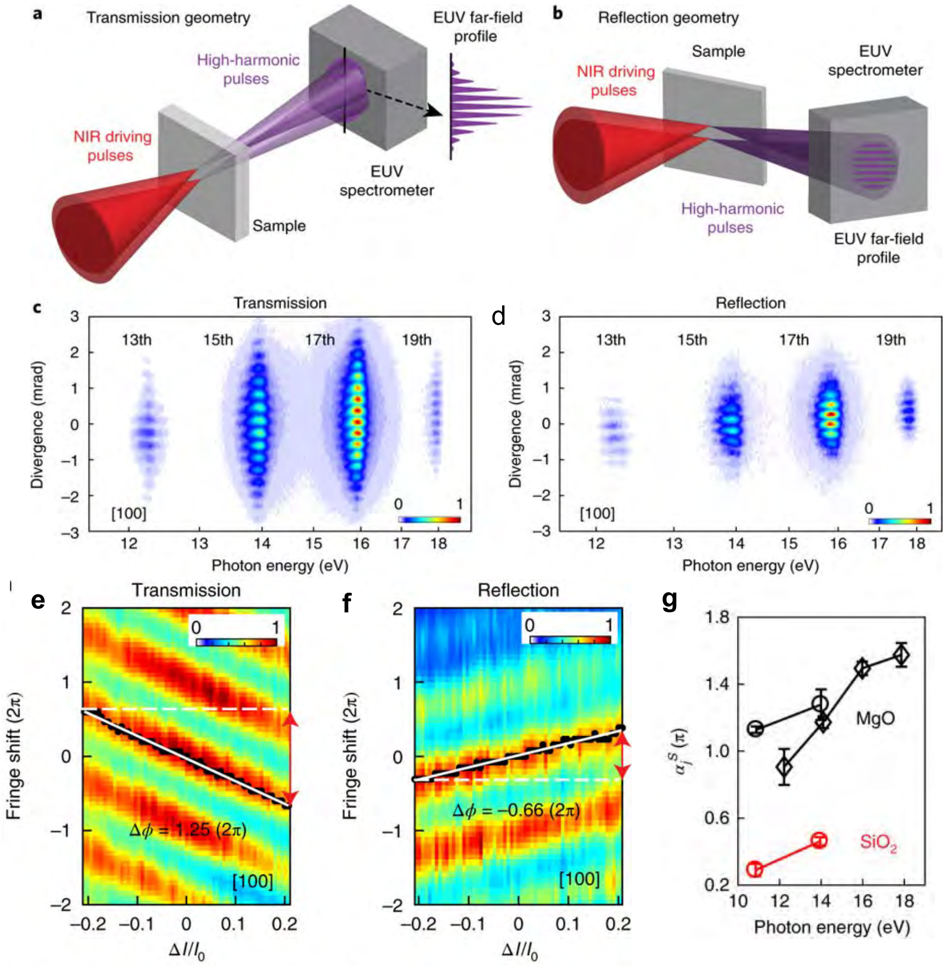

Figure 1: Interferometric measurement of dipole phase of high-harmonics from bulk crystals using **a)** transmission and **b)** reflection geometries. NIR laser beam is split and focused onto a sample to generate EUV high-harmonics radiation. The EUV high-harmonic beam overlaps in the far field and produce interference pattern as seen in **c)** in transmission mode and in **d)** in reflection mode. **e)** and **f)** show the recorded shift in the fringe position as we vary the relative intensity between two laser spots in transmission and reflection mode respectively. The source material dependence (MgO and SiO_2) is plotted in **g)**

Our paper titled, "*Crystal orientation-dependent polarization state of high-order harmonics*" is published in *Optics Letters*. In this paper, we analyze the orientation-dependent polarization state of extreme-ultraviolet high-order harmonics from bulk MgO crystals subjected to intense linearly polarized NIR laser fields. We find that only along high-symmetry directions, do high-order harmonics follow the polarization direction of the laser field. In experiments, we fix the laser polarization direction and rotate the crystal around its normal. We find that as we rotate the crystal the polarization of harmonics rotates in a non-trivial manner. The deviations depend on harmonic order, crystal angle, and the peak field strength of the laser pulse. To understand the origin of such an anomalous deviation, we extend the real-space electron trajectory model [You2017a], where we analyze electron collision angles --the angle between the direction of the laser field and the direction of the group velocity of the electron at the time of the collision to atomic cores. In MgO, two conduction bands have opposite energy-momentum dispersion relation, which causes such rotations in opposite directions. If harmonics are originated from conduction bands of opposite dispersion, they would rotate in the opposite directions. This conclusion supports our previous prediction, where we attributed the role of higher-lying conduction band on the origin of the secondary plateau [You2017b].

Our review article titled, "*High-harmonics from solids*" is published in *Nature Physics*. In this paper, we summarized ongoing activities since the experimental discovery of this phenomenon in 2010. Collaborative work with internal groups such as the NLX-Reis and EDN-Heinz, and external groups such as the Gaarde group, LSU can be seen in our publications.

Planned Research

This is the final year of the Early Career Award. We have proposed a new sub-task titled HHG in ultrafast chemical sciences FWP, which is led by Phil Bucksbaum. In that sub-task, we have proposed multi-dimensional high-harmonic spectroscopy and element-specific transient absorption spectroscopy using attosecond X-ray pulses at the LCLS. This new effort will be complementary to other exiting sub-tasks; ATTO, NLX and EDN, and together we make use of existing local infrastructures such as the table-top soft-X-ray HHG source that is under construction.

Journal Publications (17-19)

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2. Jian Lu, Eric Cunningham, YongSing You, David A. Reis and Shambhu Ghimire, " ***Interferometry of dipole phase in high harmonics from solids***". Nature Photonics 13,96-100, 2019.
3. YongSing You, Jian Lu, Eric Cunningham, Cristian Roedel and Shambhu Ghimire, "***Crystal orientation-dependent polarization state of high-order harmonics***", Optics Letters 44, 3, 53-533, 2019

4. Shambhu Ghimire and David Reis "***Review: high-order harmonic generation from solids***", Nature Physics, 15, 10-16, 2019
5. Shambhu Ghimire, "***Locking the waveform with a quartz crystal***" NATURE PHOTONICS 12 (5), 256-257, 2018
6. YongSing You, Eric Cunningham, David Reis and Shambhu Ghimire, "***Probing periodic potential of the crystal via strong-field re-scattering***", J. Phys. B: At. Mol. Opt. Phys. 51, 114002, 2018
7. Giulio Vampa, YongSing You, Hanzhe Liu, Shambhu Ghimire, and David Reis, "***Observation of backward high-harmonic emission from solids***" Optics express 26 (9), 12210-12218, 2018 (ECA not lead)
8. Mengxi Wu, YongSing You, Shambhu Ghimire, David Reis, DA Browne, Kenneth J Schafer, and Mette Gaarde, "***Orientation dependence of temporal and spectral properties of high-order harmonics in solids***", Physical Review A 96 (6), 063412, 2018 (ECA not lead)
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11. Yong Sing You, David A. Reis, and Shambhu Ghimire, "*Anisotropic high harmonic generation in bulk crystals*", Nature Physics 13, 345-349, (2017)
12. 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 (ECA not lead)

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4. [Liu2017] Liu et al., "Observation of high harmonics from an atomically thin semiconductor", Nature Physics 13, 262, 2017
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Early Career: Time-resolved imaging of non-equilibrium electron dynamics with novel X-ray holographic approaches

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Scope of the program

The ability to follow transient structural changes is essential for understanding and controlling non-equilibrium phenomena such as catalytic reactions, ultrafast phase transitions, and energy transfer from light to matter. These processes often evolve from a complex interplay between rapid electronic and nuclear motions at the nanoscale, which are hardly accessible with conventional microscopic methods. State-of-the-art imaging tools often require long exposure times to achieve high spatial resolution and thus, their sensitivity to short-lived phenomena is limited. Ultrafast spectroscopic methods can provide valuable information about transient states, but the signal ambiguity often increases with the complexity and heterogeneity of the sample. The capabilities offered by current and next-generation X-ray laser facilities, such as the Linac Coherent Light Source (LCLS) and its successor, LCLS II, offer the potential to directly visualize ultrafast dynamics with high spatial and temporal resolutions. This research program will develop and apply novel ultrafast X-ray diffraction imaging approaches that exploit these cutting-edge X-ray sources to advance the fundamental understanding of non-equilibrium processes in complex nanoscale systems.

Recent Progress

First experiments dedicated to quantum X-ray fluorescence imaging. This year we have focused on simulating, conducting and analyzing two experimental campaigns exploring the potential of quantum imaging with X-ray fluorescence. We used an in-house beamtime shift at LCLS to estimate the signal and sample damage levels in collaboration with the X-ray Pump Probe (XPP) team. Later, we carried out a 5 x 12 hours experiment at the Spring-8 Angstrom Free Electron Laser facility (SACLA) in Japan. While the data analysis is still ongoing, we have clearly identified two crucial bottlenecks in our previous experimental settings. We should be able to overcome both using sub-fs X-ray FEL pulses and new large area X-ray detectors soon available at LCLS. A follow-up experiment is scheduled for February 2020 at SACLA FEL in Japan and a LCLS proposal has been submitted for run 18. A detailed description of the project follows below.

A very recent theoretical publication suggest that incoherent diffraction imaging (IDI) with X-ray fluorescence will eventually enable create three-dimensional (3D) maps of nanospecimen with atomic resolution, high chemical contrast, and sub-fs time resolution. In addition, IDI bears the promise of overcoming several fundamental limitations inherent to coherent X-ray diffraction imaging (CDI) as there are three major potential advantages compared to CDI [Classen2017]. First, the structure is determined from fluorescence, which has orders of magnitude higher cross sections than elastic scattering in the hard X-ray domain. Second, fluorescence is being emitted into 4π so that in theory the full 3D structure can be determined without rotating the sample and without the need of high dynamic range detectors. Third, the method carries a spectroscopic dimension as it is highly element selective and very sensitive to changes in the fluorescence line shape. Overall, IDI bears the potential to increase the state-of-art capabilities of hard X-ray diffraction imaging. However, it has not been experimentally demonstrated yet (to the best of my knowledge).

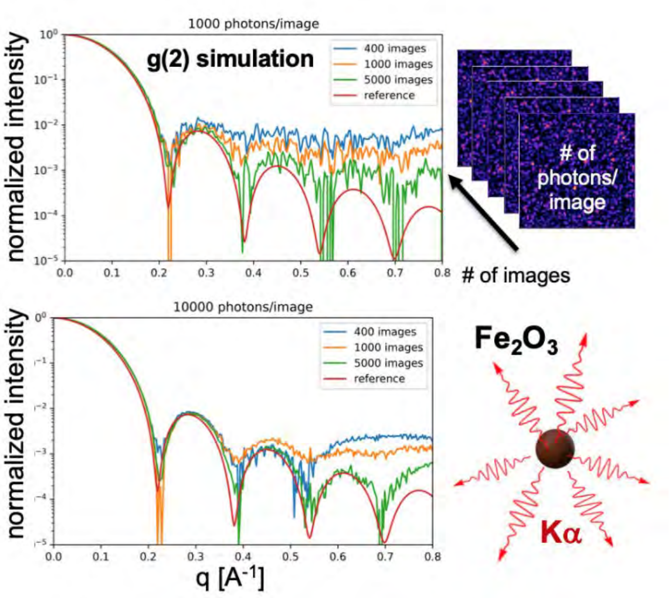

Figure 1: Simulation of g(2) for iron oxide nanospheres with around 8 nm diameter emitting K_α fluorescence. First speckle patterns for a number of incoming photons is calculated, second the g(2) is calculated from series of several exposures.

One crucial requirement for IDI is spatially incoherent, but temporally coherent radiation, such as monochromatic thermal light or X-ray fluorescence excited by ultrashort FEL pulses on a timescale comparable to the fluorescence coherence time. If the fluorescence photons are being recorded within their coherence time on a photon detector, the relative phases of the scattered photons can be considered as stable, allowing the observation of stationary speckle pattern similar to the observation of Hanbury Brown and Twiss [Hanbury1956, 1956a]. The patterns will fluctuate and spatially vary over several exposures, yet the autocorrelation of the intensity distribution calculated for each short exposure is insensitive to the random phase variations of the emission, and will continuously build up for several exposures [Classen2017]. By calculating the second order correlation function g(2) of the speckles over the multitude of exposures, the structure factor of the sample (or the Fourier transform the sample´s structure) will appear demonstrated in Figure 1. Our main strategy for the proof-of-principle experiment is to use simple and symmetric samples. Figure 1 show radial plots of g(2) calculated from a number of K_α fluorescence speckle patterns from uniform Fe_2O_3 nanospheres with 8 nm diameter. The detector has 512 X 512 pixel, 70 μm sized pixels and is placed at 10 cm distance from the sample (similar to currently available detectors at LCLS and SACLA). The g(2) graphs displayed on the left side of Figure 1 indicate that the structure factor of the spheres would emerge after about 1000 exposures with 5000 fluorescence pixels on average.

We also have identified that it is crucial to increase the overall fluorescence yield per pixel and thus, the number of possible two-photon cross correlations. The benefits are obvious by considering two extreme cases. If only two photons are recorded per exposure, the number of two-photon correlations will be proportional to N exposures. In contrast, if all the photons are recorded within a single exposure at different detector positions, the two-photon correlation number is N^2. Thus, the best samples for a proof-of-principle experiment are dense specimen with a highly regular structure, which will generate a large fluorescence yield. In our SACLA experiment, we have recorded fluorescence from 10 nm small metal nanoparticles such as Fe_2O_3 nanospheres dispersed in a polystyrene film and single crystals films such as GaAs or GaN. Under ideal conditions, we would require around fluorescence 10^7 photons in total (which corresponds to only about 10 shots) in order to reconstruct the Bragg peaks of Ga atoms in a GaAs crystal as shown on the right side of Figure 2. However, the SACLA FEL pulses are much longer than the Ga K-shell fluorescence lifetime and thus, we expect a reduction of contrast by at least a factor 50. In addition, we could only use a small detector and thus, the speckle patterns were subject to some undersampling. We recorded several hours of data to correct for these signal degradation factors, however our measured g(2) seems to be still dominated by noise as demonstrated in Figure 2, left panel. Overall, we expect some improvement of contrast in our next scheduled experiment and almost ideal conditions in a potential LCLS beam time with sub-fs pulses.

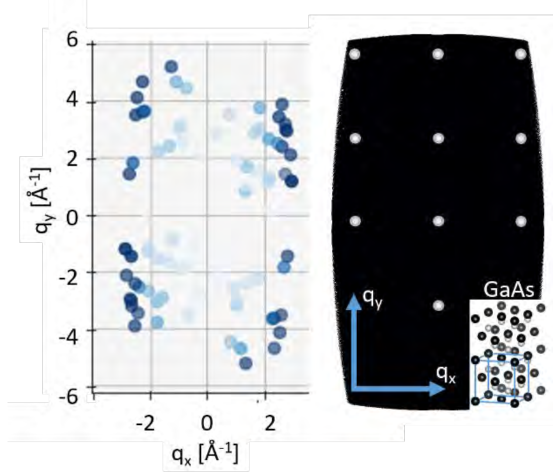

Figure 2. Left side: first results from the 2019 SACLA measurement of GaAs. Right side: the corresponding simulation of the Ga structure factor.

Planned research

As mentioned above, the next quantum imaging beam time in February 2020 is currently being prepared. In addition, we are preparing holographic diffraction imaging experiments with a table-top higher harmonics source in collaboration with G. Shambhu and D. Reis. We have also submitted a holographic imaging proposal to the FERMI FEL in Italy, which is currently under review.

Peer-Reviewed Publications Resulting from this Project (project start date 09/2018)

No publications to report

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

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Program 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 and organic photovoltaics, electrons are injected from a photo-excited 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 main 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/surface interfaces. An ancillary objective is also developing the required instrumentation.

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. Angle-resolved photoemission (ARPES) provides momentum-space information about molecular orbitals of adsorbates, energy dispersion of surface states at the interface, the band structure of the underlying solid. The quasi-CW nature of synchrotron radiation ($\sim$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.

The ideal XUV light source for extending photoemission techniques to the time domain would have the flux and multi-MHz repetition rate of a synchrotron, but with ultrashort pulse durations. Many groups around the world have been working towards this goal using a variety of platforms. At Stony Brook, we have developed this ideal light source using cavity-enhanced high-harmonic generation and now have achieved a setup with sufficient flux, tuning range, and (most important) reliability to enable challenging surface science experiments at the endstation. We have summarized the details and the performance of the instrument in two breakthrough papers acknowledging DOE support [1, 2].

The light source has been running with few problems since Jan. 2018. We consider the XUV light source development phase of the project now essentially finished (although we do continue to make improvements in the visible pump arm of the pump/probe setup). Most of the work in the past year has been on implementing a new photoelectron analyzer.

Our first results demonstrating the capabilities of the 80 MHz cavity-enhanced HHG light source for photoemission made use of an antiquated single-channel hemispherical analyzer (VSW HA100) [1, 2]. This single-channel hemisphere detects the photoelectrons very inefficiently, recording only one voxel of the 3D (k_k, k_y, E) dataset at a time. With the support of the DOE and the Stony Brook Foundation Discovery Prize, we have now implemented a new photoelectron analyzer based on time-of-flight (TOF) momentum microscopy (k-mic), as pioneered by the Schönhense group at

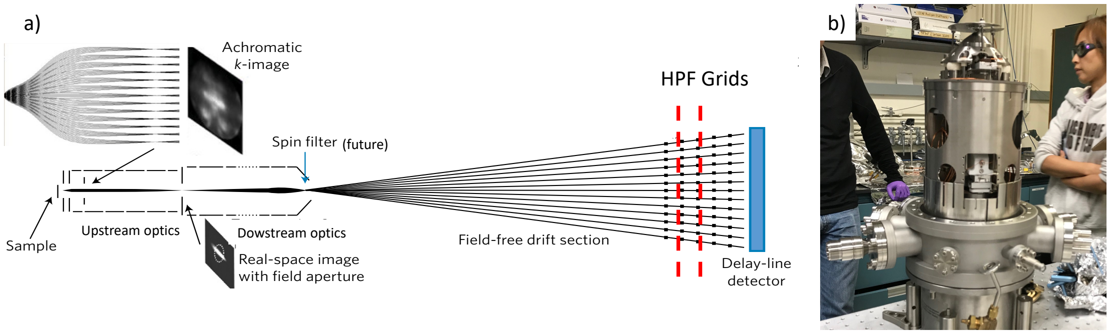

Figure 1: **The TOF momentum microscope analyzer** a) Illustration of the TOF-k-mic concept. Photoelectrons at the sample are first collected with full 2π collection efficiency using a cathode lens objective, which forms an achromatic k-space image at the objective back focal plane. Subsequent optics relay image the electrons to a time- and position-sensitive detector at the end of a field-free TOF region. Two high-pass filter grids can reject unwanted low-energy electrons and reduce detector saturation. b) A photograph of the microscope column shortly after its arrival in Stony Brook in Fall 2018.

Johannes Gutenberg Universität in Mainz, Germany. This new analyzer detects all electrons in parallel for rapid acquisition of the full 3D data set, as detailed in [3]. We have collaborated with the Schönhense group on this.

Figure 1 illustrates the basic principle of the analyzer, which combines photoemission electron microscopy (PEEM) with time-of-flight detection. Electrons are first collected from the sample with a cathode lens objective biased up to 8 kV. Additional electron optics of the microscope column relay image the electrons to a time-resolving delay-line detector (DLD) at the end of a field-free TOF tube. The electron optics can be divided into the “upstream” optics and the “downstream” optics. In all modes of operation, the upstream optics form a real-space image at the field-aperture plane, where an adjustable aperture can be inserted to limit the field of view (FOV) of the microscope. The downstream optics can be adjusted to form either a real-space or momentum-space image at the DLD.

In real-space mode, we have so far only achieved a resolution of 2.6 μm, limited by sample vibration with our long sample manipulator. We expect this to improve to < 1 μm when we upgrade to the new hexapod manipulator described below. Inserting a small aperture at the field-aperture plane, we can use this resolution to record ARPES (momentum-space) data from a $\sim$3 μm region of the sample, as discussed below.

Figure 2 shows some results from operating the microscope in momentum-space mode. In all figures, it is the Fermi surface that is displayed, or more precisely a DLD image corresponding to one 200 ps TOF slice. The corresponding energy resolution is currently approximately 100 meV, limited either by the TOF window/resolution or the fact that all spectra have been recorded at room temperature. Figures 2a) and 2b) show results for Au(111). Figures 2c) and 2d) show results from highly-ordered pyrolitic graphite (HOPG). The accumulation time for each full 3D (k_k, k_y, KE) data set (of which the Fermi surface is only one component) is just a few minutes. Figures 2c) and 2d) illustrate the ability of the PEEM system to perform ARPES measurements with high-spatial resolution at the sample (i.e. μ-ARPES [4, 5]). Figure 2c) shows the Fermi surface of the HOPG sample without any field aperture inserted, such that signals from three crystal domains of the HOPG are visible. Upon inserting a field aperture to select at 5 μm region

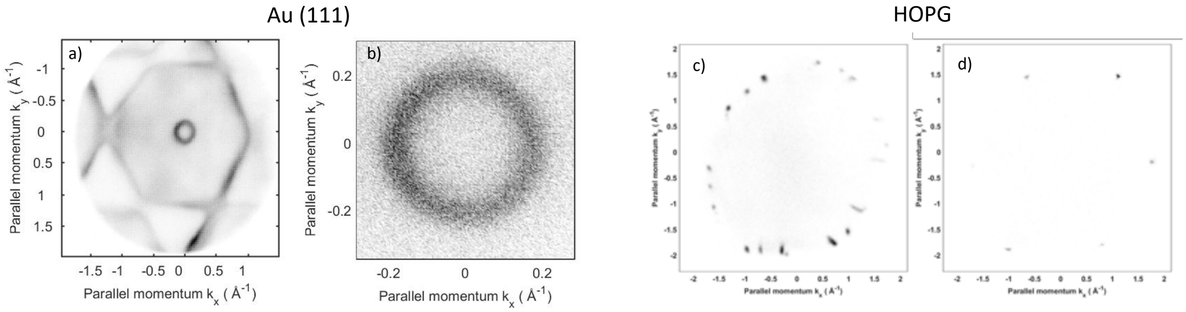

Figure 2: **Fermi surface recorded with the momentum microscope** a) Fermi surface of Au(111) recorded with 18 eV photon energy. b) Zoom-in of the Au(111) surface state. c) The Fermi surface of a highly-ordered pyrolytic graphite sample recorded with 25.2 eV photon energy from the full ∼100 μm XUV spot. Multiple domains are observed. d) Same as c) but with a field aperture selecting 5 μm of sample region. Only a single domain is observed, with 6 Dirac points at the Fermi level.

of the sample, only a single hexagonal pattern from a single domain is visible. This ability enables us to study spatially inhomogeneous samples, such as deliberately nano-patterned surfaces or many 2D materials produced by exfoliation. To our knowledge, no other time-resolved ARPES setup has demonstrated this ability.

We have very recently recorded our first time-resolved data using the momentum microscope, momentum-resolving the dynamics of electrons excited above the Fermi level in our HOPG sample with a single domain selected using the field aperture. Pump/probe measurements additionally require high dynamic range in addition to fast acquisition, and this has required us to modify the microscope to include aggressive high-pass filtering of the electrons that reach the DLD. Optimizing the microscope for pump/probe measurement remains an on-going project but we have a setup now that is workable using two fine mesh grids for the high-pass filter. Accumulation times remain a few minutes per pump/probe delay. We are working now on concluding these demonstration experiments with the plan of publishing several papers about the performance of the system, particularly, for the new ability of time-resolved μ-ARPES, soon.

While we have not yet written up these demonstration results, former postdoc Chris Corder and graduate student Jin Bakalis have presented these demonstration results at the VUVX and Surface Dynamics Gordon Conferences in summer 2019, respectively, and received enthusiastic responses. Graduate student Peng Zhao successfully defended his Ph.D. thesis about the development of this instrument this past summer as well.

Future Plans

There is still some technical work to be done before the instrument is fully optimized for pump/probe measurements. Some work still needs to be done to optimize the high-pass filtering such that TOF k-mic data achieves ultra-high dynamic range. Without high-pass filtering, or with sub-par high-pass filtering, the signal dynamic range is limited by detector saturation from low-energy electrons. We are also working to implement a resonant $f_{\text{rep}}/2$ pulse picker for fast differencing (lock-in) detection in pump/probe measurements. Additionally, we have received the cryo-cooled hexapod manipulator and repaired damage that occurred in shipping such that it is ready to install - but we decided to first get papers out using the current manipulator before completing this technical upgrade.

In addition to this technical work, we also plan to go beyond demonstration experiments in the coming year. Two postdocs are coming to Stony Brook this fall and winter to do just that. After writing up the current demonstration experiments, we hope to proceed to running three classes of experiments with the instrument:

- Ultrafast dynamics at $TiO_2(110)$ and other photocatalytically active surfaces, as described in our initial proposal.
- Ultrafast dynamics in molecular films relevant to organic photovoltaics, as described in our last DOE abstract report.
- Time-resolved μ-ARPES in 2D materials uniquely enabled by the capabilities of our instrument.

In the longer term, we are also considering the possibility of upgrading our polarization mode-locked Yb:fiber oscillator (currently the weakest link of the system) with a dispersive-wave shifted Er:fiber comb, and also implementing OPAs for tunable pump pulses with variable repetition rate. We have made this switch on other projects and found it to be quite reliable.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

C. Corder, P. Zhao, J. Bakalis, X. L. Li, M. D. Kershis, A. R. Muraca, M. G. White, and T. K. Allison. Ultrafast extreme ultraviolet photoemission without space charge. *Structural Dynamics* **5**, 054301 (2018). DOI:10.1063/1.5045578

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Early Career: New correlated numerical methods for attosecond molecular single and double ionization

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Project Scope

Continuous advances in the XUV and soft-x-ray ultrafast technologies, pursued at large free-electron-laser facilities as well as in several attosecond laboratories around the world, have extended the range of attosecond-pulse parameters to shorter durations, larger intensities, energies, and repetition rates. New XUV-pump XUV/soft-x-ray-probe schemes, in which the duration of both light-matter interaction stages is short, have drastically enhanced the time resolution with which ionization can be steered and monitored. Soft-x-ray probes can excite core electrons, thus monitoring the valence dynamics with high spatial resolution. X-ray pulses in the water window have extended the scope of attosecond spectroscopy to aqueous matrices. Photoelectrons from core orbitals are scattered by neighboring nuclei, thus encoding the geometry of the target molecule. In molecules with tightly bound pairs of equivalent atoms, such as N_2 or C_2H_2, core photoelectrons give rise to characteristic double-slit interference fringes that mirror the evolution of molecular geometry and charge migration. XUV pulses can even release two or more electrons, which, if detected in coincidence, give direct information on the concerted motion of electrons in the ground as well as in excited states. The theoretical description of these processes is essential to track the motion of correlated electron pairs, and, ultimately, to control ultrafast dynamics in matter. Until computational tools for molecular single and double ionization will be available, the "attosecond revolution" will remain incomplete.

We will merge hybrid-basis close-coupling approaches with state-of-the-art numerical techniques for the single- and double-ionization continuum, and for correlated parent-ion bound states, to describe both single- and double-escape processes from poly-electronic molecules. No general method to solve the secular problem above the second ionization threshold has been established yet. Whereas recent interfaces of quantum-chemistry codes to hybrid Gaussian-B-spline close-coupling (CC) space are promising, more advanced methods are required to describe the multi-photon double-ionization processes targeted by upcoming attosecond experiments. For this reason, we will develop and integrate the numerical tools for the representation of free-electron pairs with electronic-structure molecular packages to lay the foundation of a new hybrid CC program for the time-dependent description of molecular single and double-ionization processes, with a quantitative account of light-driven static and dynamic electronic correlation. Most of the fundamental quantities needed to carry out this program (hybrid integrals and high-order transition density matrices) are not available yet. Computing and incorporating them in scalable programs is a major theoretical, computational and algorithmic challenge. Successfully tackling this challenge will allow us to directly image correlated motion in matter, thus opening the way to a transformative expansion of attosecond science.

Recent Progress

The project has started on September 1 2019. The outline of the code architecture is already well defined. In the recent weeks, we have started developing the two basic pillars of the method. The first pillar is the calculation of one-, two-, and three-body transition density matrices between correlated bound states with arbitrary symmetry and multiplicity, based on the LUCIA general Configuration Interaction code, developed by Dr. Jeppe Olsen, a close collaborator of the PI. The second pillar is the hybrid basis for mono- and bi-electronic integrals. We are currently tuning the routines for the one-body integrals between FEDVR functions and molecular orbitals, in collaboration with Dr. Barry Schneider. The search for a postdoctoral fellow who will work at the implementation of the hybrid integrals and of the matrix elements between close-coupling states is under way.

Future Plans

By the end of the first year, we anticipate to be able to integrate the hybrid basis and the density matrices from the quantum chemistry package in a secular solver, and reproduce accurate dipole transitions matrix elements between diffuse Rydberg states of benchmark molecules.

Peer-Reviewed Publications Resulting from this Project (Project start date: 09/2019)

None

Attosecond dynamics driven by ultrashort laser pulses

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Project Scope

The quest for studying dynamics in matter on ultrashort timescales has driven the development of a variety of technologies in ultrafast science. The most prominent among these are ultrashort electron pulses, femtosecond laser pulses, X-ray free electron lasers, and currently one of the shortest of all these probes, attosecond light pulses (1 as = 10^{-18} s). Substantial progress in controlling electron dynamics and the coupling between electron and nuclear dynamics in highly nonlinear processes driven by femtosecond laser pulses enabled the first realization of sub-femtosecond pulses in 2001. Nowadays, the controlled electron dynamics over a subcycle of the driving laser pulse allows for the emission of coherent light at extreme ultraviolet and soft X-ray wavelengths on a suboptical cycle time scale, i.e. on the attosecond time scale, through the process of high-harmonic generation.

Measurements on the attosecond timescale have been under ongoing rapid development for about a decade. One of the open challenges is the realization of a conventional pump-probe spectroscopy set-up using two isolated attosecond laser pulses, in which time resolution would be achieved by the delay and durations of the two pulses. So far, the intensity of attosecond laser pulses has however been too low to achieve significant attosecond pump-probe signals. Using the knowledge how to manipulate and control electron dynamics with laser pulses, a variety of spectroscopic techniques with and without the application of attosecond pulses has been developed and applied to temporally resolve dynamical processes on the attosecond time scale [DOE3].

With the work in our projects we seek to provide theoretical support related to the establishment of ultrafast optical techniques as tools to uncover new insights in the temporal resolution of ultrafast dynamics in atoms and molecules and strong-field nonlinear processes, such as excitation, ionization and high harmonic generation, in general. One of the exciting recent developments in this area is the development of a polarization control over the generated ultrashort pulses. This creates new possibilities for imaging on ultrafast time scales and has renewed, in general, the interest in the interaction of atoms and molecules with laser light of variable polarization, ranging from linear via elliptical to circular.

Recent Progress

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

A. Attosecond Streaking Time Delays

Our efforts over the last few years in analyzing attosecond spectroscopic techniques were mainly directed towards the analysis of the attosecond streaking method. In this method a 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 review of our theoretical analysis and interpretation of the method summarizes the recent results in this project [DOE8]. Briefly, this includes an analytical model formula that provides insights into various aspects of the streaking time delay: for example, an alternative justification of the widely used decomposition of the streaking time delay into a Wigner–Smith time delay and a Coulomb–laser coupling term [DOE2] or the role of the attochirp of the ionizing XUV pulse [DOE4].

We further presented in the review [DOE8] an analysis of a recent related proposal [1], which has been put forward for the interpretation of RABBITT experiments. Since it has been shown [2] that RABBITT and streaking measurements provide equivalent information concerning the time delay, we could relate our numerical simulations to the RABBITT work. Our results support two main assumptions of the proposal [1]. First, the time delay is essentially obtained within the first half-cycle of the streaking field after the transition of the photoelectron in the continuum. Second, information about the differences between short-range parts of different atomic potentials is incorporated in the streaking time delay accumulated over the first quarter cycle of the streaking field after emission of the photoelectron in the continuum.

B. Excitation with Strong Field Pulses

Excitation of atoms (and molecules) is known to play an important role in many strong-field processes. Past theoretical (and experimental) studies of the excitation mechanism in strong fields mainly consider the distribution of the population as a function of the principal quantum number, while theoretical analysis of the distributions over the orbital angular momentum and magnetic quantum numbers in the populated Rydberg states is less advanced.

Utilizing solutions of the time-dependent Schrödinger equation based on recently developed single-active-electron potentials we have found that for linearly polarized laser pulses the parity of the populated angular momentum distributions agrees with the selection rules for multiphoton resonant absorption at low intensities [DOE6]. Additionally, it has been found that population trapping in low excited states suppresses population in states with low angular momentum quantum numbers. In contrast, the parity effect cannot be observed for ultrashort pulses as well as for long pulses at high intensities. It has been proposed that this is due to the fact that Rydberg states are in resonance with photon processes of different orders for a significant time during the rising and trailing parts of the pulse.

We have then extended these studies towards an analysis of the excitation process in bichromatic circularly polarized laser pulses. The interest is spurred by a recent experiment [3] which has shown that the probability to ionize an atom is significantly enhanced if the two fields are counter-rotating as compared to co-rotating. The experimental observations were interpreted as due to the increased density of excited states accessible for resonant enhanced multiphoton ionization in the case counter-rotating fields. With our project we intend to provide insights into the excitation process via resolution of the excited state distributions over the quantum numbers (principal, angular momentum, magnetic).

Numerical simulation of these kind of processes involves several challenges, namely the resolution of Rydberg states which extend over large radial distances as well as the inclusion of angular momentum states with large orbital and magnetic quantum numbers. So far, our results have revealed patterns in the distributions that we relate to the spin-angular momentum selection rules for the absorption of circularly polarized photons. Furthermore, clear differences in the population of the excited states for co-rotating and counter-rotating pulses have been observed which appear to provide footprints of the excitation pathways. Currently, we study the dependence of the excited state distributions on the ratio of the intensities of the two pulses to test our tentative conclusions about the pathways.

C. Interaction with Ultrashort Pulses

We recently focused part of our work on the interaction of atoms with ultrashort pulses. First, we studied the effect of the difference between the central frequencies of the spectral distributions of the vector potential and the electric field of an ultrashort laser pulse on various light induced processes, such as excitation, ionization and high harmonic generation [DOE7]. The results of our study and the related analytical estimate of the frequency shift is relevant for numerical calculations in which it is often useful to define the laser pulse via the vector potential and the related central frequency. It is shown that the shift has to be accounted for to avoid potential misinterpretation of numerical results for processes induced by few-cycle pulses.

We have then turned our attention to few-photon ionization processes induced by ultrashort pulses in view of the ongoing technological quest in shortening pulses at extreme- and deep-ultraviolet wavelengths towards the single-cycle regime (e.g., [4]). The broad spectral width of such pulses can give rise to the competition of few-photon processes at different orders, as mentioned e.g. in [5]. Our numerical results show that at photon energies below the first ionization threshold there is a transition from dominant single-photon ionization to two-photon absorption over a rather small window of pulse duration. The impact of the different processes and their interference is currently studied via the anisotropy parameters β_i in the photoelectron angular distributions. Related previous experimental studies have so far mainly focused on two-photon absorption [6] and our analysis will provide insights and limits for interaction with pulses having shorter duration.

D. Resolution of Electron Dynamics with Pulses of Variable Polarization

One of the exciting recent developments in attosecond laser pulse technology is the development of polarization control for the generated ultrashort pulses [7]. This creates new possibilities for imaging electron dynamics on ultrafast time scales and has renewed, in general, the interest in the interaction of atoms and molecules with laser light of variable polarization. In order to study the prospects of the application of these pulses for time resolution we have recently started to analyze ultrafast imaging schemes in which the superposition of states in an atom is probed via the interference between few-photon transitions of different photon order. We are specifically interested in superposition of excited states which lead to a so-called ring current in the atom, that is characterized by the circulation of electron density about the center of the atom. Such ring currents have recently attracted much attention in theory and experiment in strong-field physics. A goal of our current numerical calculations and analysis is to investigate if and how a temporal resolution of these ring currents can be achieved.

Future Plans

We plan to continue our studies in the different projects outlined above. For the interaction of atoms with bicircular laser pulses we intend to apply our insights in the excitation pathways towards a potential control over the population in the excited states. To this end, we exchange results with the local experimental group at JILA (Kapteyn/Murnane) for further interpretation of excitation and ionization with structured laser beams, such as bicircular pulses. Concerning the interaction with ultrashort pulses we plan to extend our analysis by studying how our theoretical predictions depend on various pulse parameters, e.g. the carrier-envelope phase which is often difficult to control during the generation of an ultrashort pulse. Such study may enhance the impact of our results for potential future experiments with table-top laser systems or free-electron laser sources. Concerning the application of spectroscopic techniques for the resolution of ultrafast processes we intend to continue our analysis of ring current dynamics pumped and probed by laser pulses of variable polarization. Furthermore, we plan to analyze how the fact that the attosecond streaking techniques strongly depends on the oscillating electric field of the streaking pulse can be used towards imaging of ultrafast dynamical changes in an atom or molecule.

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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 ultrafast 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 and attosecond 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)** Time-resolved molecular dynamics investigations using x-ray pump-x-ray probe techniques using free electron lasers (FELs), such as the LCLS x-ray FEL at SLAC National Laboratory but also at SACLA, Japan, FLASH-II, and XFEL in Hamburg, Germany. Our current experiments allow us to probe physical and chemical processes that happen on femtosecond time scale. **2)** The study of non-linear and strong field phenomena, particularly in the soft and hard x-ray regime. **3)** We will propose investigations to study attosecond electron dynamics in molecules with the new attosecond XLEAP capability at LCLS-II. We use IR/UV table-top lasers at UConn and the ALS synchrotron facility to prepare our FELs experiments. We present below results completed and in progress this past year and plans for the immediate future.

Recent Progress

1) X-ray multiphoton ionization of molecules: Femtosecond-resolved observation of delayed fragmentation and evaporation of neutral atom using the LCLS FEL.

We have carried out an experimental and theoretical investigation on a large molecule, buckminsterfullerene, exposed to 640 eV X-ray pulses with 20 fs pulse duration, using the X-ray Linac Coherent Light Source (LCLS) at the SLAC National Accelerator Laboratory. The goal of this project was to examine the role of chemical effects, such as chemical bonds and charge transfer, on the fragmentation following multiple ionization of the molecules. We performed femtosecond-resolved X-ray pump/X-ray probe measurements to provide time resolution. The investigation was made possible by the fresh slice technique developed at LCLS by Alberto Lutman [a] that provided the two X-ray pulses. The experiment was accompanied by advanced simulations performed by Zoltan Jurek and Robin Santra (DESY). The experiment and simulations revealed that despite significant ionization induced by the ultrashort X-ray pump pulses, the fragmentation of C_{60} is surprisingly significantly delayed. In fact, the investigation uncovered for the first time the persistence of the molecular structure, which thwarted fragmentation over a timescale of about 600 femtoseconds. Furthermore, the results demonstrate that a substantial fraction of the ejected fragments are neutral carbon atoms.

Proteins have chemical bonds of similar strength to C_{60}, and, under imaging conditions, experience a similar degree of ionization as C_{60} does in our investigation. Our findings reveal that during the entire 20 fs X-ray pulse, the C_{60} structural changes remain below the critical resolution of 2 Å, considered sufficient in biomolecular studies (such as for example, in the context of distinguishing peptides from a protein or the bases of a nucleic acid).

The impact of this work is that delayed fragmentation will play a critical role in most other X-ray multiphoton ionization of molecules. With the dawn of LCLS-II which is being upgraded to provide more intense pulses, as well as attosecond pulses at a high repetition rate, our findings lay the foundation for a new understanding of large systems. Our results, in press with Nature Physics [1], may also have implications regarding the role of chemical effects in reducing radiation damage of all molecules, including biological systems imaged at XFELs [1].

2) Photoionization and fragmentation of $Sc_3N@C_{80}$ following excitation above the Sc K-edge using the SACLA FEL.

Endohedral fullerenes are of great interest to use as samples due to their unique properties, such as electron transfer between the encaged species and the carbon cage [b]. The goal of the experiment was to measure electron transfer dynamics between the encapsulated species and the carbon cage using X-ray pump-X-ray probe technique. We performed the ionization and fragmentation of the metallo-endohedral fullerene, $Sc_3N@C_{80}$ using ultrashort (10 fs) x-ray pulses from the SACLA FEL in Japan. Following selective ionization of a Sc (1s) electron with photon energies of $h\gamma = 4.55$ keV, an Auger cascade leads predominantly to either a vibrationally cold multiply charged parent molecule or leads to multi-fragmentation of the carbon cage following a phase transition. We probed the system by using a time-delayed, hard x-ray pulse energy of $h\gamma = 5.0$ keV.

We measured the mass spectra that provided evidence for two processes leading to distinct signatures in the ion distributions: (i) multiple ionization of the parent molecular ion via Auger cascades that transfer sufficiently little energy to vibrational excitation of the molecule to survive intact during the microsecond timescale of the mass spectrometer and (ii) high-energy transfer to the cage followed by cage break-up and the production of small, predominantly singly-charged fragment ions. In contrast to table-top intense laser studies, no intermediate regime of C_2 evaporation from the carbon cage was observed.

We observed a small but significant change in the intensity of Sc-containing fragment ions as well as in the coincidence counts for a time delay of 100 fs compared to 0 fs. We also observed an increase in the yield of small carbon fragment ions, which could be indicative of incomplete charge transfer from the carbon cage on the 100 fs timescale. We had planned to measure several time delay, but the alignment at SACLA for the X-ray pump-probe measurements took a considerable amount of beamtime, preventing the measurement of the experimental program we had planned [2].

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Future Plans.

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

1) Write and submit the manuscript for publication on time-resolved ionization dynamics of the molecular fragments chains resulting from C_{60} multiphoton ionization since the data has already been analyzed. **2)** Continue the data analysis of our 2018 experiment on solvated molecules carried out at the FERMI FEL in Trieste, Italy. The experiment investigated intermolecular interactions of molecular iodine solvated in small water clusters. **3)** Conduct and analyze the FLASH-II FEL data on time-resolved ultrafast dynamics, subsequent to the ionization of giant C_{60} resonances in the XUV regime. These resonances consists of strongly correlated electrons, thus measuring the electrons and ion momenta might reveal new understanding. The experiment will be carried out Oct, 2019. **4)** Analyze the FLASH-II data on time-resolved double and single H-migration in ethanol. The experiment was conducted in April 2019. These last two projects were carried out at DESY, Hamburg, Germany, using high repetition laser pulses paired with a Reaction Microscope (REMI/COLTRIM) instrument similar to the one being built at LCLS-II, called DREAM. Thus the last two projects carried out at FLASH-II will prepare us for the research we plan to conduct at LCLS-II with the high repetition rate using the DREAM and the LAMP end-stations.

Peer-Reviewed Publications Resulting from this Project (2017-2019).

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Imaging Structural Dynamics in Isolated Molecules with Ultrafast Electron Diffraction

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Program Scope or Definition

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.

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

Over the last year we have continued with data analysis of three previous gas phase UED experiments, we have done significant work to upgrade the MeV UED gas phase setup at SLAC, collaborated in the design and implementation of a new liquid phase MeV UED experiment at SLAC, and made key improvements in the keV UED setup in Lincoln.

Data analysis. The data analysis was carried for three previous experiments: Photodissociation of $C_2F_4I_2$, isomerization of Stilbene and proton transfer in 2-Nitrophenol. In the case of these three experiments, the analysis benefits from a collaboration with the theory group of Todd Martinez at Stanford. The data analysis on the photodissociation dynamics of $C_2F_4I_2$ was completed and the manuscript submitted and recently published. These results were described in the previous year report so will not be described here. The UED experiment with Stilbene at SLAC in 2018 was not successful, so we tried to extract as much information as possible from the data from 2016, but we have now determined that there isn't enough data to retrieve time-dependent information. We are planning to submit a proposal for beam time at the SLAC MeV UED to repeat the experiment, we believe with the upgraded gas phase setup (described below) there will be a reasonable chance of success.

We are currently analyzing the results on UED of the proton transfer reaction in 2-Nitrophenol (2NP). In this reaction, we aim to capture the structural dynamics that follow a proton transfer from the hydroxyl to the nitro group. Previous results have reported multiple channels, including dissociation of the nitro group, and rotations and vibrations of the nitro group [Ernst et al, J. Phys. Chem. A 119, 9225 (2015)], but these spectroscopic measurements did not have direct access to the structure. Based on our preliminary analysis of the UED data, we have established that only a small fraction of molecules undergo dissociation, and observed coherent dynamics which are most likely caused by out of plane motion of the nitro group after proton transfer. From the diffraction signal at times larger than 5 ps, we have established that less than 5% of the excited molecules undergo dissociation, in good agreement with simulations. The UED signal shows evidence of coherent NO_2 rotation and/or twisting. These motions are reflected as amplitude oscillation in internuclear distances between 1 and 5 Angstroms with periodicities in the 200 fs to 400 fs range. Figure 1 shows the difference pair distribution function as a function of time. Additionally we have observed a depletion of the internuclear distances below 2.5 Angstrom that is delayed by several hundred femtosecond with respect to the start of the oscillations. We are still working to interpret these time dependent signals in terms of structural changes.

New gas phase UED chamber at SLAC: In collaboration with the SLAC MeV UED team at SLAC led by Xijie Wang, we have designed and constructed a new gas phase UED target chamber. This chamber will be used in the first run of the instrument in a user facility mode of operation. The new target chamber will provide several improvements and more flexibility in the sample delivery, which was the main challenge during the last UED run. The new setup includes an additional differential pumping stage and more pumping capacity in the sample region. This will give us more flexibility in delivering samples using either a seeded gas beam or a flow cell. The gas delivery system has been redesigned to reduce the chance of clogging and will include the possibility of having the sample reservoir inside or outside the target chamber depending on the sample properties.

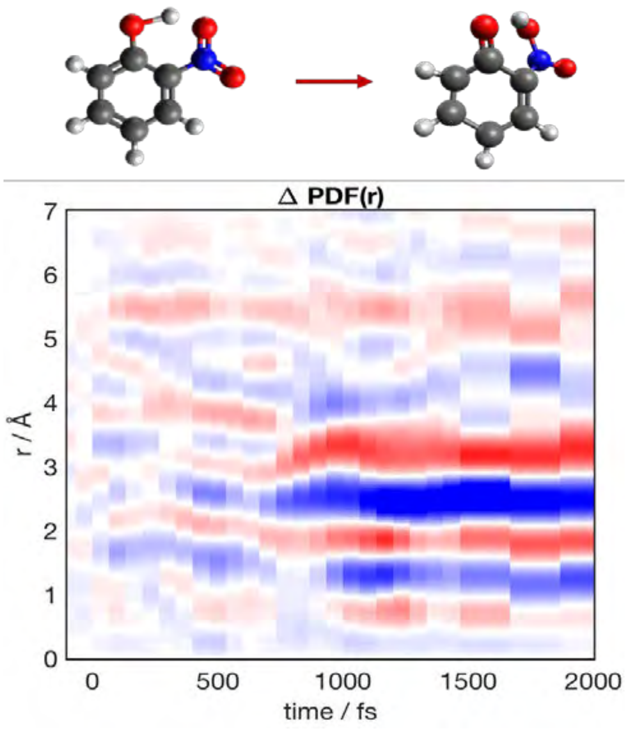

Figure 1. Top graph: Two model structures of 2NP, the left corresponds to the ground state and the right corresponds to the excited state after proton transfer and rotation of the nitro group. Bottom graph: Changes in the interatomic distances extracted from the UED data. Blue corresponds to a decrease and red to an increase. Two regimes are observed, with a change in character of the dynamics taking place after 700 fs.

Gas phase UED setup at UNL: We have made significant improvements in our setup to overcome a longstanding issue of timing drifts. Timing drifts are caused by instabilities in the timing synchronization between the laser and the RF compression cavity, and by changes in the laboratory conditions (air flow, humidity, etc). We have redesigned the synchronization loop and seen significant improvements in pulse compression and synchronization. We have now reached pulse durations below 200 fs, and have repeatedly measured timing drifts around 300 fs over several hours. This stability, however, is only reached one or two hours after the lab is closed with no movements inside. Thus, we have now set up the experiment so that it can be operated remotely.

Liquid phase UED at SLAC. In collaboration with the SLAC MeV UED team, and with the groups of Kelly Gaffney and Amy Cordones-Hahn at Stanford, we have designed, constructed and implemented a new instrument to perform liquid phase UED experiments using the MeV electron gun at SLAC. A successful commissioning run took place this year. We demonstrated static diffraction from liquids, with electron pulse conditions compatible with 200 fs resolution. We have also measured the instrument response to be at or below 200 fs by looking at a signal generated by ionization of water. In addition, a time-resolved experiment on the photoexcitation of iodine in solution was carried out successfully. Further experiments with other solvents were not successful in this first run due to insufficient signal to noise ratio in the data. There are plans to address this issues for the next run, possibly in 2021.

Future plans

Over the next year, we will plan to repeat the Stilbene experiment either at SLAC or UNL. For this, we will submit a proposal for beam time in the first user run of the SLAC MeV-UED which will take place April-August 2020. We will also participate in the commissioning of the new UED target chamber at SLAC. We are planning to perform preliminary experiments with nucleobases with the UED setup at UNL. We will also submit a proposal for ultrafast x-ray diffraction at SLAC in collaboration with Thomas Wolf of Stanford. In this case, we will take advantage of the higher photon energy (up to 20 keV) to capture a larger momentum transfer in the scattering, and thus better spatial resolution. We will complete the data analysis on 2NP and submit the results for publication. We will also analyze the water diffraction data from the liquid phase UED to compare with previous results on x-ray diffraction.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

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Capturing Ultrafast Electron Driven Chemical Reactions in Molecules

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Program Scope

The goals of this project, which started on September 15, 2018, are to develop experimental tools to investigate the dynamics of dissociative electron attachment (DEA) reactions in real time. In a DEA reaction, the attachment of a low energy electron to a molecule results in bond breaking and the fragmentation of the molecule. A new instrument has been designed and is under construction to perform time resolved photoelectron spectroscopy and coincidence measurements of the photoelectron and the reaction fragments. The experiments proposed here will establish the experimental tools to interrogate the dynamics of dissociative electron attachment on the fundamental timescales of the nuclear motion, by simultaneously probing the valence electronic structure and the fragmentation pathways.

Introduction

Low energy (few eV) electrons are readily generated in the interaction of radiation with matter, and these electrons can in turn interact with molecules and drive a large number of chemical processes in atmospheric, radiation and plasma chemistry. One of these fundamental processes is dissociative electron attachment, where a low energy electron attaches to a molecule and causes bond breaking and fragmentation. The metastable transient anion system evolves from the electronic continuum, so dissociation competes with autodetachment of the electron. These reactions can take place on femtosecond time scales and exhibit strong coupling between electronic and nuclear motion. The breakdown of the Born-Oppenheimer approximation makes it challenging to accurately describe the dynamics with existing quantum chemistry models. It is also challenging to observe these reactions experimentally on the relevant timescale, due to the difficulty in delivering few-eV electron pulses on a sample to trigger the reaction with femtosecond resolution.

We are developing a new instrument to do momentum- and time-resolved measurements of dissociative electron attachment reactions by combining two experimental methodologies: time resolved photoelectron imaging spectroscopy and coincidence momentum imaging of the photoelectron and the mass-resolved reaction fragments. The experiments proposed here will establish the required tools to interrogate these dynamics on the fundamental timescales of the nuclear motion. Initial experiments will focus on anion fragment mass spectrometry and fragment momentum imaging, followed by time resolved photoelectron spectroscopic measurements of photodetached electrons. Near-future developments include momentum imaging experiments of photoelectrons with charged and neutral fragment in coincidence. The coincidence measurements will allow us to assign the measured valence electron binding energies to specific fragmentation channels. The experiments will be supported by theoretical calculations of the electron attachment and dissociation processes.

Recent Progress

Work in the first year of the project has focused on the design and construction of a new experimental apparatus. The setup comprises three modular systems: The anion source chamber, the time of flight (TOF) module, to mass-select target anions, and the velocity map imaging (VMI) and detector chamber. The design of the different elements has been guided by numerical simulations of charged particle trajectories and by the literature on mass-selected anion beam instrumentation. Figure 1 shows a CAD drawing of the three connected modular systems. The first chamber (A in Fig. 1) will produce an anion beam by intersecting an electron beam with a molecular beam formed by a supersonic co-expansion of a noble gas and the target molecule. At the connection between the first and second chambers there is a skimmer and steering optics to guide the beam towards the accelerating electrodes in the TOF module (second chamber, labeled B in Fig. 1). The TOF uses pulsed electrodes to accelerate the anions to an energy of a few keV, followed by steering and focusing ion optics (see inset in Fig. 1). A mass gate will be implemented at the temporal focus of the TOF to select the anions of interest, which will pass through to the laser interaction region (C in Fig. 1). At the laser interaction region, a VMI spectrometer will be installed to measure detached electrons. This VMI would serve a dual purpose. First, we will use it to perform photo-detachment spectroscopy of mass-selected anions to measure the electronic structure. Second, we will use it for time-resolved photodetachment spectroscopy of the transient anion complex in order to map the changes in the potential energy surface during the dissociation reaction. A second TOF spectrometer and position-sensitive detector will be used to measure the momentum of mass-resolved anion fragments and energetic neutral fragments resulting from the laser interaction. In the following, we describe the progress so far in the design, fabrication and testing of all the components.

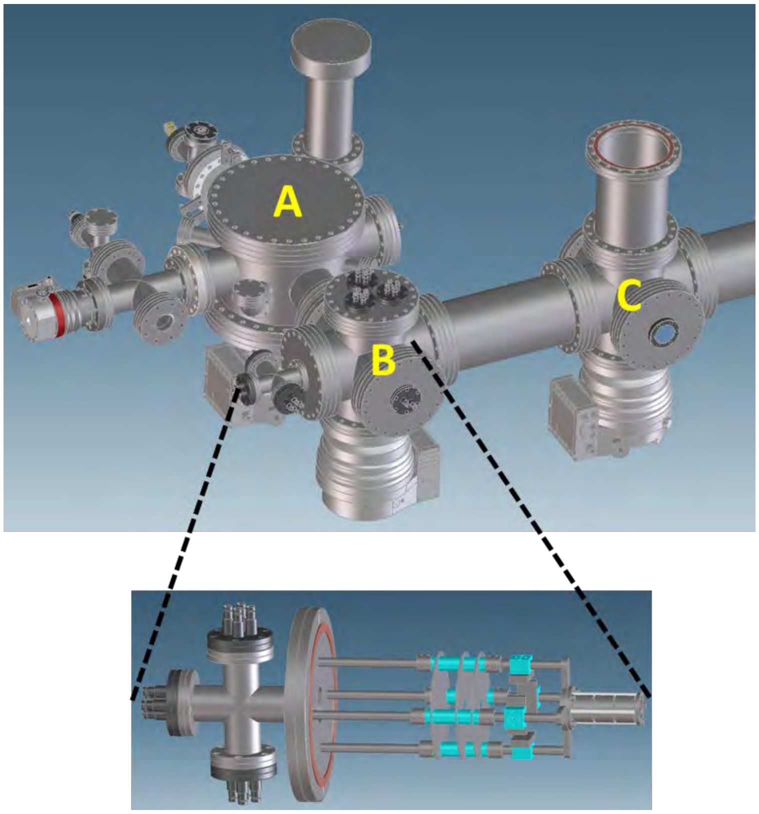

Figure 1. CAD design of the setup with three modular chambers. A: Source chamber, B: TOF module, C: Detector and VMI. The inset below shows the design of the TOF electrodes and the following focusing and steering electrodes with everything mounted on a single flange.

A. Source Chamber. The design and fabrication of the source chamber has been completed. Figure 2(a) shows a photograph of the source (A) and TOF (B) chambers in the laboratory. In the source chamber, an electron beam intersects a molecular beam to generate the desired anion beam. Figure 2(b) shows a top view of the chamber showing the electron gun (C), the nozzle assembly (D), Faraday cups to measure the electron and ion beam currents (E) and a connection point for a liquid nitrogen cooled cold finger. We have designed and fabricated a continuous electron gun to produce an electron beam with tunable energy up to 2 keV. This will allow us to tune the energy to optimize the desired anion formation channel. The electron gun is differentially pumped to maintain a high vacuum when the nozzle is in operation. We have tested the differential pumping to produce a two orders of magnitude pressure difference between the electron gun and source chambers. On first test, the electron gun has produced a beam current of more than 250 microA, which is sufficient for our purposes. Currently we are testing the optimal focusing and steering parameters of the gun. The gun has so far only been tested for beam energies up to 240 eV and it will operate at up to 2 keV once we receive the appropriate power supply within the next few weeks. A pair of concentric faraday cups was built to characterize and optimize the electron beam. The target gas will be introduced with a pulsed valve (Even-Lavie) which operates at a repetition rate of up to 1 kHz, which matches the repetition rate of the laser system. The position and direction of the nozzle can be adjusted manually from outside during operation, without breaking vacuum. The nozzle has been installed and is currently being tested. A cold finger has been designed and fabricated to cool the nozzle down to the optimal temperature to form the cluster that produce the anions. The nozzle is connected through braided copper wire to a copper cold finger. The cold finger is thermally connected to a liquid nitrogen reservoir outside the chamber.

B. Time of flight (TOF) spectrometer. The TOF chamber includes three sets of electrodes, the first are to steer and focus the anion beam onto the acceleration region, the second are the TOF electrodes to accelerate the beam, and finally a second set of steering and focusing electrodes. The inset in Figure 1 shows the acceleration electrodes followed by the focusing and steering electrodes, which are all mounted as a single assembly. The TOF chamber has been purchased and is in the process of assembly in the laboratory (labeled B in Figure 2(a)). The first set of steering and focusing electrodes has been designed and is currently being fabricated. The design of the electrodes for the TOF has been finalized, while the last set of steering and focusing electrodes is currently being optimized to deliver the appropriate beam waist at the interaction region.

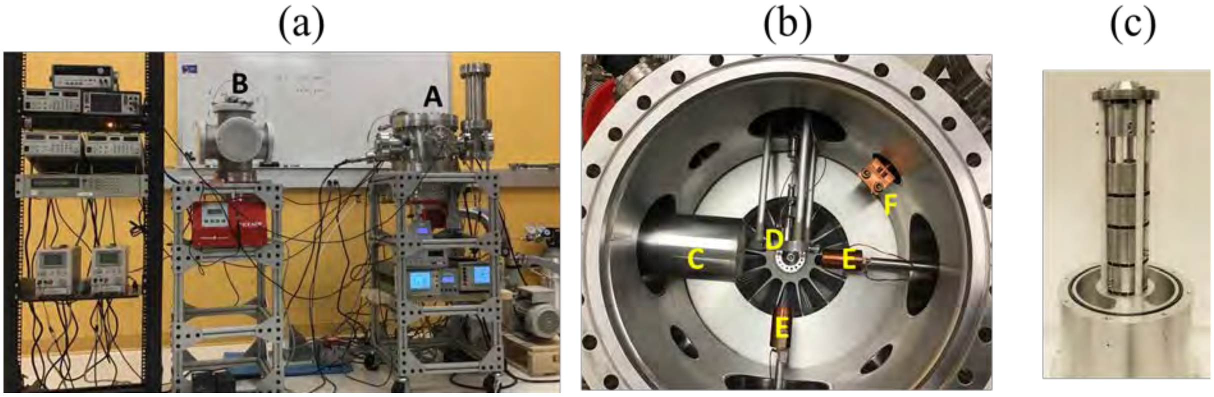

Figure 2. (a) Source chamber (A) and TOF chamber (B). b) Top view of the source chamber showing the compact electron gun (C), gas nozzle (D), Faraday cup (E) and connection for the cold finger.

C. VMI and detector chamber. The third module is still in the design phase. A first design for the VMI has been produced but needs to be optimized after the final parameter of the anion beam are known. A channel electron multiplier detector will be used initially to capture the anion fragments to analyze the constituents of the anion beam by their TOF mass spectra. The detector mount and electronics are currently being designed and tested.

Future plans

The immediate next steps in this project will be to intersect a molecular beam of CO_2 molecules with the electron beam to generate an anion beam consisting of CO_2^- and cluster anions. This preliminary experiment will be used to optimize the electron beam pointing and focusing on to the gas jet and to test the ion optics that collimate the beam before moving to more complex targets. In parallel, we will finish the design and fabrication of the anion TOF, focusing and steering optics, and install the anion beam detector for early experiments to analyze the stable electron-cluster interaction products. The early goals of the project are to measure the fragmentation due to dissociative electron attachment using the laser based method in which an electron is transferred by the laser pulse from an iodine atom to the molecule. First experiments will focus on nitromethane-iodide anion complexes because the dimer has already been demonstrated as an experimentally tractable target for time-resolved photoelectron spectroscopy experiments [Kunin *et al.* **2016** Phys. Chem. Chem. Phys. 18 33226-33232]. The complexes will be created by crossing the electron beam with a molecular beam containing nitromethane, argon and iodomethane. Inelastic electron collisions in the molecular beam will release low energy electrons that will be captured to form several species of molecular and cluster anions. The gas expansion and electron beam parameters will be optimized for $CH_3NO_2{\cdot}I^-$ yield. In the photodetachment stage, a 4.6 eV laser pulse, being above the vertical detachment energy of the $CH_3NO_2{\cdot}I^-$ atom-molecule cluster, may transfer the outermost electron within the dimer from I^- to CH_3NO_2, forming the $CH_3NO_2^-$ $^2B_1$ shape resonance [Walker and Fluendy **2001** Int. J. Mass Spectrom. 205 171–182]. The molecule will then either return to the ground state of the neutral nitromethane CH_3NO_2 by autodetachment of the electron, or dissociate into $CH_3+NO_2^-$. The influence of the iodine atom on the dissociation will be investigated by comparison with complementary DEA experiments using the anion fragment momentum imaging reaction microscope at LBNL. There the DEA reaction will be initiated by the interaction of a pure nitromethane molecular beam with a monoenergetic, tunable beam of low energy electrons. The comparison of the two experiments will reveal, for the first time, how the electron transfer within a dimer anion, from iodide to a molecule, compares with the process of capturing a free electron, and will allow us to determine the validity of using iodide as an ultrafast source of low energy electrons for triggering reactions driven by electron attachment.

Peer-Reviewed Publications Resulting from this Project (Project Start Date: 09/2019)

None.

Probing nuclear and electronic dynamics in ultrafast ring-conversion molecular reactions

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Program Scope or Definition

This project, which started on August 15, 2019, is in collaboration with the groups of Daniel Rolles and Artem Rudenko at Kansas State University, Peter Weber at Brown University and Kenneth Lopata at Louisiana State University. This project will investigate a series of ultrafast photo-triggered ring-opening and ring-closing reactions with the goal of developing general rules that can be applied to understand and predict the outcome of a large class of reactions. We will do this by focusing on a set of exemplary reactions and by applying multiple complimentary time-resolved pump-probe techniques to capture a complete picture of the dynamics. The work over the first two years will focus on the strained multi-ring reaction in the conversion of quadricyclane to norbornadiene and the formation of a four-membered ring in the conversion of cycloocta-1,3-diene to bicyclo [4.2.0]oct-7-ene. A unique aspect of this project will be the combination of multiple state-of-the-art probing methods that provide complementary information along with theoretical support to interpret experiments and build a more complete picture of the dynamics,

Introduction

One of the research priorities for the Chemical Sciences, Geosciences, and Biosciences Division within the US DOE Basic Energy Sciences Program is to develop and implement novel tools to probe the dynamics of electrons and nuclei that underlie chemical bonding and reactivity, and to elucidate structural dynamics responsible for chemical transformations. After many successful proof-of-principle studies performed with a variety of ultrafast methods in recent years, the next big strategic step to push the field into a new phase is a concerted effort to employ several competing and complementary techniques on a specific class of photochemical reactions in order to gain significant new insights into their reaction dynamics and pathways. Here, we propose to study several important electrocyclic ring-transformation reactions using multiple time-resolved probing methods and advanced theoretical modeling to follow the nuclear and electronic dynamics in real time. The interconversion between different ring structures is an important theme in organic synthesis. Ring conversion reactions change the number of carbon or heteroatoms in organic ring structures, and are therefore essential in the creation of a large number of cyclic molecular structures. Photochemical electrocyclic reactions are widely seen in nature in the synthesis of natural products, and have tremendous commercial applications in the synthesis of pharmaceuticals. They featured prominently in the development of the Woodward-Hoffman rules that aim to explain pericyclic reactions, and play an important role in the photo-induced vision mechanism and the light-induced formation of previtamin D. Yet only a few model systems have been studied using advanced time-resolved spectroscopic and scattering methods. Consequently, many aspects of their nuclear and electron dynamics remain unknown.

We will perform ultrafast electron and X-ray diffraction experiments that are directly sensitive to the nuclear structure, complemented by ionization-based methods that are sensitive to both the electronic and nuclear structure. The ultrafast ionization-based experiments will include ion mass spectrometry, Coulomb explosion imaging, photoelectron spectroscopy, and Rydberg fingerprint spectroscopy. Experiments will be carried out in the PIs laboratories and also at large-scale facilities such as the XFEL and MeV electron sources at SLAC National Lab and the XFEL at DESY in Hamburg.

Recent Progress

To investigate the strong-field-induced fragmentation of qudricyclane and norbornadiene as a first step towards subsequent time-resolved experiments, we have recently performed strong-field ionization experiments using the COLTRIMS coincidence momentum imaging system at KSU. Data analysis is in progress. From the theory group at LSU, we have made recent progress towards computing observables for interpreting the experiments. This includes the ground state geometries of the reactants and products (used as inputs for scattering calculations), as well as their UV absorption cross-sections using time-dependent density functional theory (TDDFT). From a methods development standpoint, we have also begun work on a new technique for computing photoelectron spectra using TDDFT with Gaussian basis sets. This will allow for hybrid DFT all electron simulations for both valence and core photoelectron processes. At Brown University, we have taken time-resolved photoelectron spectra to determine the lifetime of norbornadiene upon excitation at 200 nm.

We have performed calculations of the expected difference scattering signals for the quadricyclane and cyclooctadiene reactions, where the initial and final structures were calculated using B3LYP/def2-SVP level of theory. Three proposals have already been submitted for XFEL beamtime, and a MeV-UED proposal will be submitted in October. One beam time proposal was submitted to the European XFEL: "Coulomb explosion imaging of ultrafast ring-conversion reactions" focused on the toluene cation, and one to FLASH: "Probing Ultrafast Electronic Dynamics during a Ring-Opening Reaction by Time-Resolved Valence Photoelectron and Ion Spectroscopy". A proposal has also been submitted to LCLS run 18: "Molecular Nuclear and Electron Dynamics on Complex Energy Landscapes" which will focus on X-ray scattering of measurement of both the quadricyclane and cyclooctadiene reactions.

Future plans

During the first year of the grant, we will submit multiple proposals for beam time at electron and X-ray facilities, carry out experiments in our local laboratories and perform numerical simulations of the experimental observables and molecular dynamics. The proposals for beam time will focus on quadricyclane, norbornadiene and cyclooctadiene with the goal of performing the experiment under identical excitation conditions. At KSU, the fourth harmonic generation setup will be commissioned for first experiments. COLTRIMS pump-probe experiments will be performed on photoexcited quadricyclane, norbornadiene and cyclooctadiene. At Brown, the fourth harmonic generation system will be installed, Rydberg photoelectron spectra of cyclo-octatriene and quadricyclane will be acquired as a function of excitation wavelength and exploratory experiments will be carried out with the toluene cation. At UNL, the TOPAS will be purchased, installed and commissioned, and the setup will be prepared for preliminary UED experiments. The TOPAS will be purchased, installed and commissioned at KSU. The data from the different experiments will be analyzed together not only to have a better understanding of the reaction dynamics but also to characterize the relative advantages/disadvantages of the different experimental tools. Quantum Dynamics calculations will be carried out for the reaction dynamics of cyclo-octatriene. TDDFT simulations will be carried out to generate the spectra for given molecular geometries for photoelectron, inner shell and Rydberg spectroscopic measurements. This will initially focus on the reactant and product geometries, before moving on to intermediate geometries computed via quantum dynamics simulations. Additionally, development of methods for computing PES will continue and will be validated against the experiment.

Peer-Reviewed Publications Resulting from this Project (Project Start Date: 08/2019)

None.

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Early Career: Probing Attosecond Bound Electron Dynamics Driven by Strong-Field Light Transients

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Program Scope

The measurement and control of ultrafast dynamics in electronically-excited states of molecular systems have opened new frontiers in the study of internal energy conversion, charge transfer, and coupling of electronic and nuclear degrees of freedom. Recently, such control has been extended to the attosecond (1 attosecond = 10^{-18} seconds) regime, owing to the development of carrier-envelope phase-stabilized few-cycle lasers and isolated attosecond extreme ultraviolet (XUV) pulses. This project aims to use innovative laser techniques to reconstruct the time-dependent quantum mechanical wave packets initiated by strong-field excitation in bound electronic states of gas-phase atoms and molecules, and to control their dynamic evolution on attosecond to few-femtosecond (1 femtosecond = 10^{-15} seconds) timescales.

Recent Progress

Measurement and control of electronic motion requires time-resolved spectroscopic techniques with attosecond precision. In this project, coherent wave packet dynamics will be triggered using strong-field near-infrared light transients lasting only a single optical cycle. The dynamics will be followed using optical spectroscopies based on the interference of the coherence emission with an isolated attosecond pulse produced via high-order harmonic generation.

As a first step towards our goal, we have successfully developed a source of sub-two cycle near-infrared pulses based on nonlinear compression of a Yb:KGW amplifier (400 μJ pulse energy, 280 fs pulse duration, 50 kHz repetition rate). While Yb-based laser technology offers significant advantages over other femtosecond laser platforms in terms of high average power, excellent power and pointing stability, and low thermal load, the long pulse durations (typically ~300 fs) have prevented their

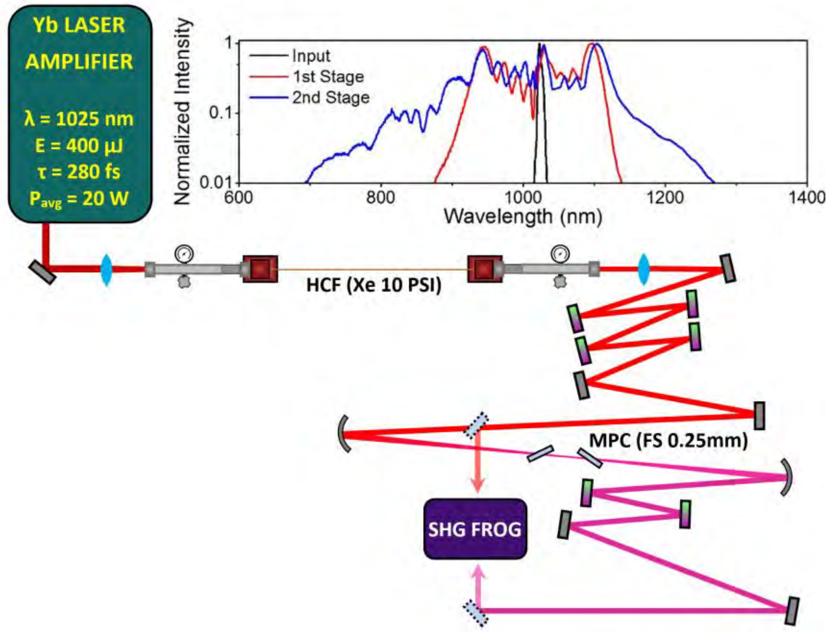

Figure 1: Schematic of the pulse compression setup.

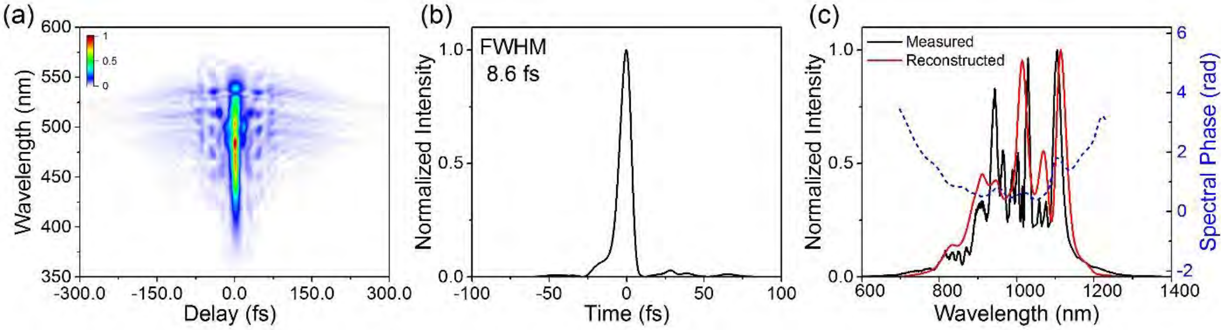

Figure 2: Characterization of two-stage pulse compressor. *Left:* Experimentally measured FROG trace. *Center*: Reconstructed pulse with FWHM duration of 8.6 fs. *Right:* Comparison of the retrieved spectrum to an independently measured spectrum.

widespread application to attosecond science. Few-cycle compression of Yb-based lasers can be accomplished using traditional nonlinear compression schemes, relying on spectral broadening in gas-filled hollow-core fibers[1] or dielectric solids[2]. However, reaching durations close to a single cycle has required very long interaction lengths[3] or multiple compression stages[4,5].

In the last year, we have successfully demonstrated compression to 8.6 fs (2.5 optical cycles at the central wavelength of 1030 nm) in a two-stage compressor consisting of a Xe-filled hollow-core fiber followed by a set of thin glass plates[6] (Figs. 1 and 2) and more recently to 6 fs (1.7 optical cycles at the central wavelength of 1135 nm) by taking advantage of enhanced optical nonlinearity in molecular gas-filled fibers. In both cases, the total energy throughput is 60%, providing sufficient pulse energy of 240 μJ for generating high-order harmonics and attosecond pulses in gases.

Additionally, we have completed the design of our experimental setup for time-resolved attosecond spectroscopy. While the design phase took somewhat longer than planned, it has yielded a versatile instrument, shown in Fig. 3, which will allow us to perform the proposed

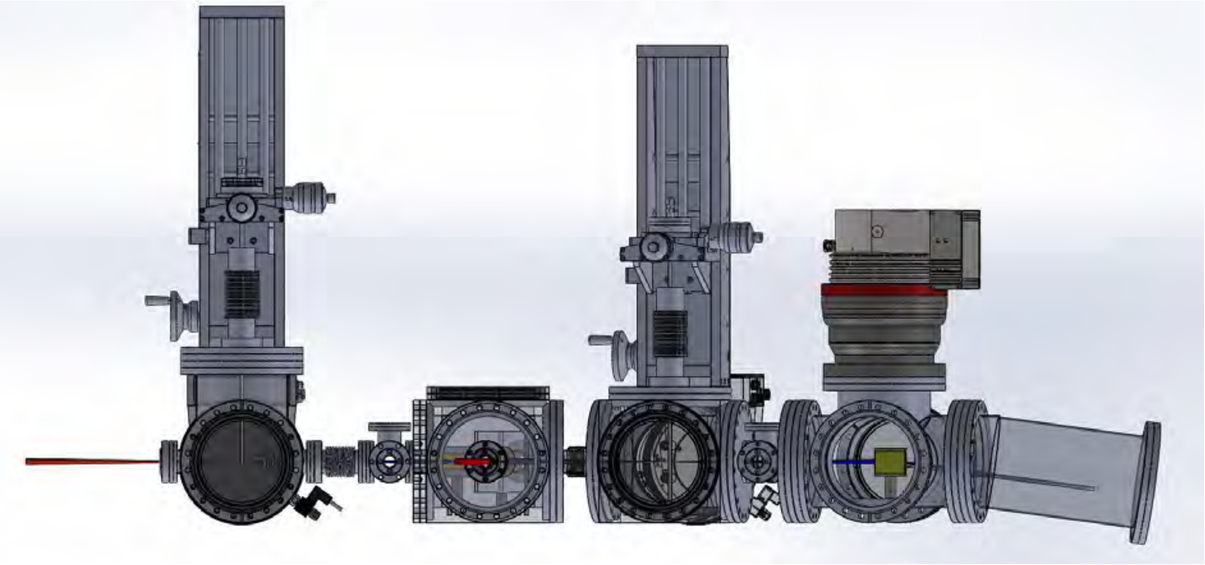

Figure 3: Experimental setup for attosecond time-resolved spectroscopies.

attosecond strong-field transient interference spectroscopy (ASTIS) measurements, as well as attosecond experiments in transient absorption[7], interferometry[8], and photoelectron imaging[9] modes.

Future Plans

In the next year, we aim to complete the characterization of the near-infrared source and to use the sub-two cycle pulses to generate isolated attosecond pulses and XUV coherences. This primarily involves characterizing the carrier-envelope phase (CEP) stability of the compressed pulses, and measuring the CEP dependence of the high-order harmonic spectrum. In addition, we aim to characterize the CEP-dependence of XUV free-induction decay for short pulses. These measurements can be completed using our existing XUV spectrometer. Finally, we will construct and test our new experimental setup for time-resolved attosecond spectroscopy.

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Peer-Reviewed Publications Resulting from this Project (Project start date: 08/2018)

No publications to report.

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Understanding and Controlling Strong-Field Laser Interactions with Polyatomic Molecules

DOE Grant No. DE-SC0002325

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1. Program Scope

Advances made over the past two decades in our understanding of laser-matter interactions allow us to start thinking about strategies for not only observing, but also *controlling* the different processes and reactions that these interactions cause. Our program focuses on the chemical processes occurring in polyatomic molecules under intense laser excitation. Efforts on quantum control of electronic, vibrational, and rotational dynamics of molecules prior to and during strong-field interactions are in line with the Grand Challenge questions that have been proposed in recent DOE- and NSF-sponsored workshops. Recently, we have sharpened our focus towards better understanding and controlling of ultrafast hydrogen migration processes occurring in organic molecules under strong fields. These processes include the formation of neutral hydrogen molecules, and exotic chemical processes involving making and breaking of multiple chemical bonds that result in the formation of H_3^+, H_2O^+, H_3O^+, and CH_5^+. Our studies have provided the first evidence for roaming chemical reactions initiated by ion precursors. Our work, in collaboration with other groups within the DOE AMOS group, is improving the quantum mechanical descriptions of relatively unknown chemical reactions that involve roaming of neutral fragments.

2. Recent Progress

(a) Discovery of neutral H_2 roaming chemistry occurring under strong fields

N. Ekanayake, M. Nairat, B. Kaderiya, P. Feizollah, B. Jochim, T. Severt, B. Berry, K. 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 "Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields," *Nature Scientific Reports*, 7, 4073 (2017)

Strong-field laser-matter interactions have been found to involve exotic chemical reactions. H_3^+ formation from organic molecules is one such case that requires multiple bonds to break and form. In this study, conducted in collaboration with the James R. Macdonald Laboratory at Kansas State University, we present evidence for the existence of two different reaction pathways for H_3^+ formation from organic molecules irradiated by a strong-field laser. The mechanistic details and timescales were experimentally determined by femtosecond time-resolved time-of-flight mass spectroscopy and photoion-photoion coincidence momentum measurements carried out on methanol isotopologues, ethylene glycol, and acetone. *Ab initio* molecular dynamics simulations suggest that H_3^+ formation occurs via a two-step mechanism in which a neutral H_2 molecule is formed, and then roams about the doubly-charged intermediate until it abstracts a proton from the remaining $CHOH^{2+}$ fragment. This reaction, proton abstraction by a roaming H_2 molecule, is reminiscent of the well-known Hogness and Lunn reaction for H_3^+ formation in the universe. These exotic chemical reaction mechanisms, involving roaming H_2 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.

(b) H_2 roaming chemistry and the formation of H_3^+ from organic molecules in strong laser fields

N. Ekanayake, T. Severt, M. Nairat, N. P. Weingartz, B. M. Farris, B. Kaderiya, P. Feizollah, B. Jochim, F. Ziaee, K. Borne, K. Raju P., K. D. Carnes, D. Rolles, A. Rudenko, B. G. Levine, J. E. Jackson, I. Ben-Itzhak, and M. Dantus, *Nat. Commun*. **9**, 5186 (2018).

With the goal of understanding H_3^+ formation and enhancing its yield, we studied its formation from alcohols with different chain lengths (see Fig 1 left). The mechanistic details and femtosecond time-resolved dynamics were obtained through a combination of strong-field laser excitation studies, photoion-photoion coincidence measurements, and *ab initio* molecular dynamics simulations. For small alcohols, four distinct pathways involving hydrogen migration and H_2 roaming prior to H_3^+ formation were uncovered (see Fig 1 right). In principle, one might expect the yield would be proportional to the number of hydrogen atoms. However, we find that methanol has the highest efficiency while *tert*-butanol has the lowest. We explain the observed reaction timescales and yields with the aid of molecular dynamics simulations. Collaboration with JRML.

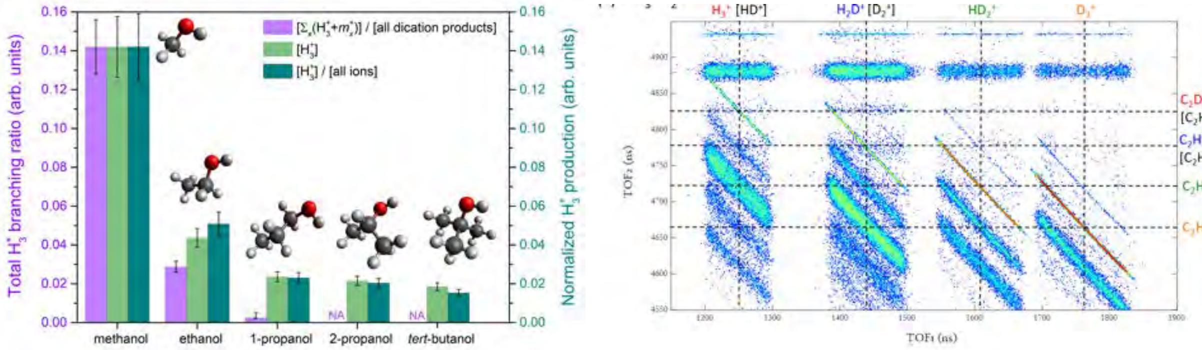

Fig. 1 (Left), Total H_3^+ branching ratios ($[\Sigma_x(H_3^+ + m_x^+)]$/[all dication products]) together with normalized H_3^+ ($[H_3^+]$), and fractional H_3^+ ($[H_3^+]$/[all ions]) production from dissociative ionization of methanol, ethanol, 1-propanol, 2-propanol, and tert-butanol in a linearly polarized laser field with a peak intensity of 2.0×10^{14} W/cm^2. The $[H_3^+]$ and $[H_3^+]$/[all ions] yields were obtained through the time-of-flight technique, and each of them is normalized with respect to the corresponding branching ratio of methanol, $[(H_3^+ + HCO^+)]$ / [all dication products], determined by the coincidence time-of-flight (CTOF) method. Due to the complexity of quantitative analysis, CTOF measurements were not performed for large molecules (2-propanol and tert-butanol) and are indicated by 'NA' at the corresponding positions in the figure. (Right) Truncated CTOF maps focused only on H_3^+ production from dissociative ionization of CH_3CD_2OD in a linearly polarized laser pulse centered about 790 nm, 23-fs long with a peak intensity of 3.0×10^{14} W/cm^2. The labeled dashed lines indicate the two-body breakup ion pairs related to H_3^+ formation from the ethanol dication. The logarithmic color scale depicts the number of ion pairs recorded.

(c) Substituent effects on H_3^+ formation via H_2 roaming mechanisms under strong-field photodissociation of organic molecules

N. Ekanayake, M. Nairat, N. P. Weingartz, M. J. Michie, B. G. Levine, and M. Dantus, *J. Chem. Phys.* **149**, 244310 (2018).

In this study, we investigate the photodissociation and H_3^+ formation from organosulfur compounds (thiols) and compare them with their alcohol counterparts. Thiols have a lower ionization potential and higher acidity relative to alcohols. Therefore, we expect thiols to produce a higher H_3^+ compared to alcohols. Contrary to expectations, the H_3^+ yield was found to be an order of magnitude lower for thiols compounds at certain laser field intensities(see Fig 2). We present an in-depth analysis of experimental findings, supported by *ab initio* quantum mechanical calculations.

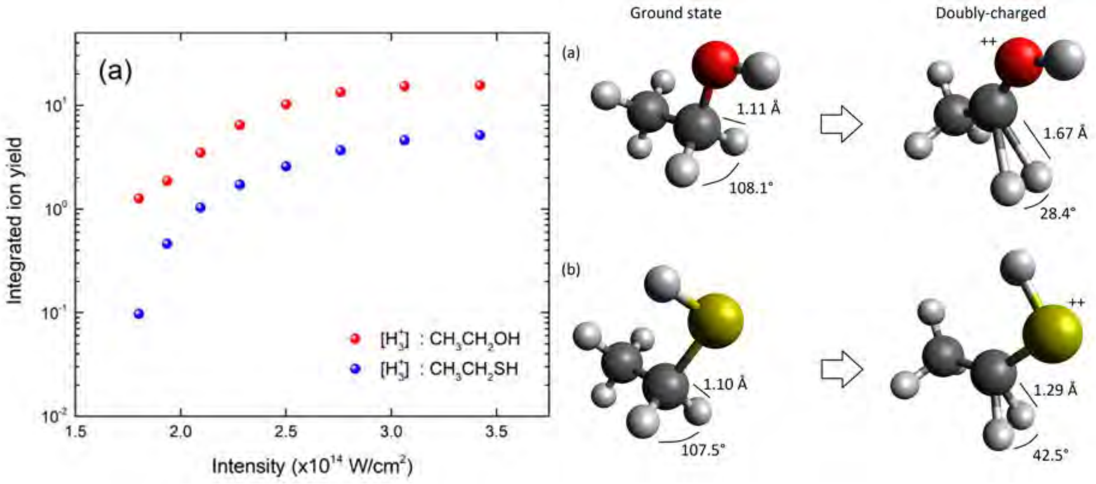

Fig. 2 (Left) Experimental photodissociation H_3^+ yields for CH_3CH_2OH are an order of magnitude greater than for CH_3CH_2SH, after ionization by an 800-nm 40-fs pulse. (Right) Neutral and doubly-charged structure minima for (a) ethanol and (b) ethanethiol carried out at the CCSD/aug-cc-pVDZ level of theory. Bond angles and bond lengths relevant to H_2 formation are shown. Doubly-charged ethanol shows longer αC−H bonds and smaller H–αC–H angles allowing H_2 ejection to be more efficient. In addition, unlike in ethanethiol, the hydroxy hydrogen in ethanol is pointing towards the nascent H_2.

(d) Quantum Coherent Control of H_3^+ Formation in Strong Fields

M. Michie, N. Ekanayake, N. P. Weingartz, J. Stamm, and M. Dantus. Manuscript to be submitted in October 2018.

Strong-field laser-matter interactions are well understood for isolated atoms and diatomic molecules, yet our understanding falls short when polyatomic molecules are involved. Similarly, quantum coherent control (QCC) of laser-matter interactions is well known for two- and three-photon resonant transitions, but not understood in cases with higher order transitions. Here, we consider the simplest approach to QCC, namely the use of a single spectral phase step, on a chemical process requiring strong-field double ionization. The goal is to determine if QCC can be used to control strong-field laser-matter interactions involving higher order 7- to 16-photon excitation. We find that indeed the spectral phase step provides a significant and unexpected method to control the yield of H_3^+ and its coincidence ion HCO^+ following the double ionization of methanol (see Fig. 3).

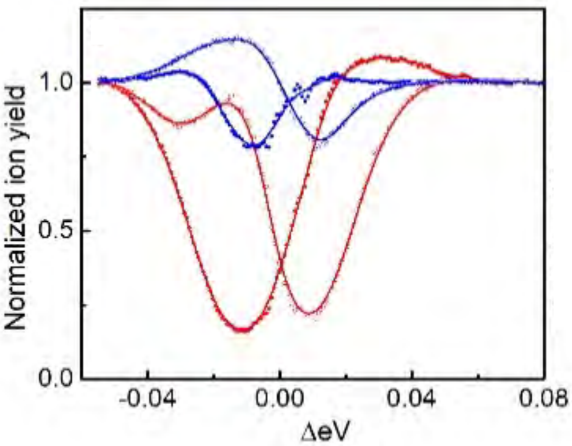

FIG. 3. The yield of H_3^+(red) and its coincidence ion HCO^+ (blue) detected as a function of scanning a positive or negative 3π/4 phase step phase across the spectrum. The ion yields are normalized to their value when TL pulses are used. Notice that in some cases the ion yield exceeds that obtained for TL pulses.

3. Future Plans

The proposed research addresses Grand Challenge questions related to quantum control of electrons in matter. We focus on coherent control of excited electronic states, taking advantage of higher energies, broader bandwidth and shorter times afforded by shape femtosecond lasers. We plan to continue our work on elucidating and controlling hydrogen migration mechanisms occurring under strong-field excitation. We have a manuscript under review in Communications Physics, collaboration with I. Ben-Itzhak, addressing the effect of phase control on ethane and the product ions resulting from non-sequential double ionization. Recently we obtained time resolved data on ethane where we observe coherent vibrations associated with the formation of H_3^+. We plan to write a comprehensive review about the lessons learned regarding hydrogen migration. Our findings are important because they include the first time-resolved roaming chemical processes, which happen to be the first roaming process recorded in ion chemistry. Understanding hydrogen atoms, their chemistry, and dynamics is important given that they make up the majority of atoms in the universe, therefore, the chemical dynamics we are observing teach us about timescales of fundamental chemical processes leading to hydrogen containing molecules in the universe.

Following up on the results obtained when scanning a ±¾ π phase step across the spectrum of the laser while detecting the resulting ions we have found some very interesting results, for example see Fig. 3 above. To understand these results at a more fundamental level we have been studying the nonlinear optics of these pulses. In Fig. 4 we show experimental second harmonic spectra and theory for similarly shaped pulses. The data shows excellent agreement, giving us confidence that we can begin to address higher order processes such as those involved in strong field laser matter interactions.

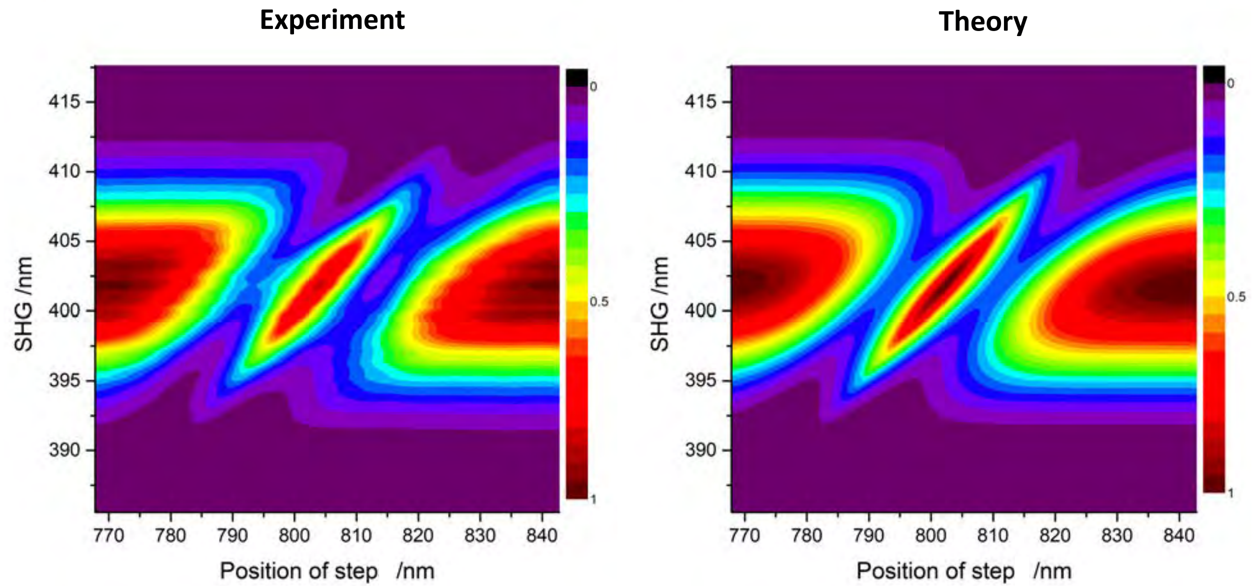

FIG. 4. Second harmonic spectra (vertical axis) as a function of the position of a positive phase step (horizontal axis). The experimental data is in very good agreement with the multiphoton intra pulse interference theory we derived in 2002-2006, and now part of my book, publication #5 here.

Following the departure of two wonderful graduate students and one wonderful postdoc in 2017, and one more excellent student and an excellent postdoc in 2018, I have been rebuilding my research group. This year, I was able to hire two great students and one great postdoc, so I am optimistic about our progress. We will continue to take advantage of our expertise in pulse shaping, a new OPA that allows us to tune from 234 -2100 nm, and data from our PEPICO instrument.

5. Peer Reviewed Publications Resulting from this Project (2017-2019)

1. M. J. Michie, N. Ekanayake, N. P. Weingartz, J. Stamm, and M. Dantus, "Quantum coherent control of H_3^+ formation in strong fields" *J. Chem. Phys*. **150**, 044303 (2019).

2. N. Ekanayake, M. Nairat, N. P. Weingartz, M. J. Michie, B. G. Levine, and M. Dantus, "Substituent effects on H_3^+ formation via H_2 roaming mechanisms from organic molecules under strong-field photodissociation" *J. Chem. Phys*. **149**, 244310 (2018).

3. N. Ekanayake, T. Severt, M. Nairat, N. P. Weingartz, B. M. Farris, B. Kaderiya, P. Feizollah, B. Jochim, F. Ziaee, K. Borne, K. Raju P., K. D. Carnes, D. Rolles, A. Rudenko, B. G. Levine, J. E. Jackson, I. Ben-Itzhak, and M. Dantus, "H_2 roaming chemistry and the formation of H_3^+ from organic molecules in strong laser fields," *Nat. Commun*. **9**, 5186 (2018).

4. N. Ekanayake, M. Nairat, B. Kaderiya, P. Feizollah, B. Jochim, T. Severt, B. Berry, K. Raju P., K.D. Carnes, S. Pathak[2], D. Rolles, A. Rudenko, I. Ben-Itzhak, C. A. Mancuso, B. S. Fales, J. E. Jackson, B. G. Levine, and M. Dantus "Mechanisms and time-resolved dynamics for trihydrogen cation (H_3^+) formation from organic molecules in strong laser fields," *Nature Scientific Reports* **7**, 4073 (2017)

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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, we explore and exploit fundamental aspects of generation and measurement of high harmonic and attosecond pulses 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 the field-driven electron wave packet as an alternative route for spatial-temporal imaging in the gas phase. In 2011, the viability of this approach for achieving femtosecond timing and picometer spatial resolution was demonstrated in 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, x-ray nonlinear optics and the development of methods for time-resolved x-ray physics. Our overall aim 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 four projects: (1) a demonstration of the foundations of simulating strong field physics using attosecond pulses, (2) dynamical spatial-temporal imaging of the C_{60} fullerene, (3) the measurement of the spectral phases around multiple autoionizing states and (4) investigations utilizing the attosecond capabilities of the LCLS.

1.2 PROGRESS IN FY2019

Our strong field program over the last several years has focused on using long wavelength generated harmonics. We are interested in addressing three basic questions related to attosecond physics. First, can high harmonic and attosecond spectroscopy extract atomic/molecular structure? Second, what is really being measured? Finally, can attosecond techniques simulate basic strong-field physics?

The Strong Field Simulator. In typical strong field ionization experiments, a single high-intensity laser allows bound electrons to tunnel into the continuum, ionizing the atomic or molecular target, and drives the trajectory of that electron far from the parent ion. Electron trajectories that return to interact with the parent ion are of particular interest due to the many physical phenomena attributed to them: elastic (LIED) and inelastic (NSDI, RESI) scattering or recombination (HHG). Here, we are interested in simulating these processes in Helium and other systems. Helium provides an ideal platform for studying electron-electron interactions in strong-field processes since it is most accessible to theoretical investigation.

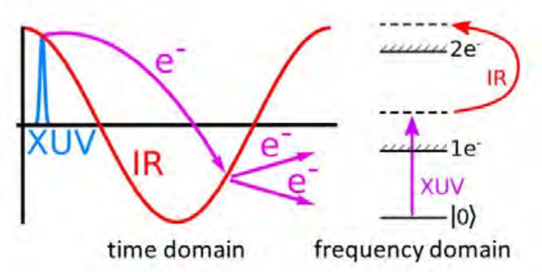

Figure 1: The strong field simulator conceptualized for the (e,2e) process. In the time domain, a photoelectron is excited to the 1*e* helium threshold by an XUV attosecond pulse (see frequency domain). The electron accelerated by a phased locked low-frequency field can recollide with the He^+ core, freeing a second electron.

Normally there is a direct correspondence between the ionization and propagation steps, as the same low-frequency strong field drives both steps. This significantly constrains our ability to control these processes. To counter this, we employ the strong field simulator (SFS) scheme, which replaces the tunnel ionization with photoionization by an attosecond XUV pulse (Fig. 1). The decoupling of ionization and propagation allows selection of any ionization phase, so that new classes of quantum trajectories can be studied by controlling the time delay between the XUV pulse and the strong field. Tuning other properties of the XUV pulse opens additional avenues for investigation.

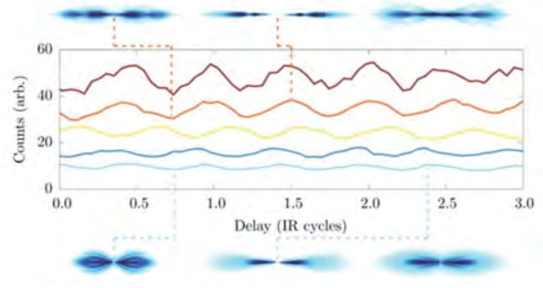

Figure 2: Total electron counts measured at 1.3 μm for different ponderomotive energies (U_p) as a function of the time delay. Dark Red 26.5 eV, Orange 19.5 eV, Yellow 13.0 eV, Blue 8.0 eV, and Light Blue 3.5 eV. Above (U_p=19.5 eV) and below (U_p=3.5 eV) the figure are the momentum distributions for delays corresponding to a peak in the count number (left), a dip in the count number (middle), and for the NIR-only case (right).

We have performed a set of preliminary measurements to demonstrate the SFS approach. Using an existing attosecond beamline not optimized for this experiment, photoelectron spectra were collected as a function of the delay between the XUV and strong field pulses. The delay spectra exhibit an overall structure, which repeats with frequency 2ω, or twice each cycle of the strong field. There is also an energy dependence to the phase of this oscillation. Our collaborators, Prof. Ken Schafer and Dr. Jens Egebjerg Bækhøj (LSU), performed theoretical modelling of the SFS scheme. Their work reproduced the primary features of our experimental results and provided a physical explanation for an unexpected enhancement in total count rate that oscillated with delay. As shown in Fig. 2, the fluctuating count rate was present for all ponderomotive energies of the MIR field tested. This feature was explained as a changing angular distribution of the outgoing photoelectrons, as a result of certain trajectories (corresponding to specific delays) spending additional time near the atomic core of the Coulomb potential. Thus, we concluded that we had achieved the quantum path control key to the SFS scheme.

Ultrafast dynamical imaging of C_{60} fullerene. The 1985 discovery of C_{60} 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 C_{60} - the archetypical fullerene - remains the focus of ongoing scientific studies.

The interaction of C_{60} 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 efficient transferred into C_{60}'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 (10^{14} W/cm^2).

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 visualizing a C_{60} cage elongation of ~5% under irradiation with 80 TW/cm^2, 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). The results are published in PRL [7A].

RABBITT measurements on interfering autoionizing states. To date, experimental reconstruction of electronic wave packets generated in the vicinity of autoionizing states has been limited to isolated atomic resonances, *i.e.,* to the case in which only one of these states is accessible in between two consecutive harmonics. But in general, many-electron atoms and molecules do not have isolated resonances, so the former circumstance is the exception rather than the rule. On top of that, performing ab initio full-electron time-dependent theoretical calculations for such complex systems, which would be necessary to guide experiments, is very often difficult, if not impossible, since a correct description of the autoionization decay requires an accurate treatment of electron correlation in the continuum.

In this thrust, we have determined spectral phases of Ne autoionizing states from extreme ultraviolet and mid-infrared attosecond interferometric measurements and ab initio full-electron time-dependent theoretical calculations in an energy interval where several of these states are coherently populated. The retrieved phases exhibit a complex behavior as a function of photon energy, which is the consequence of the interference between paths involving various resonances. In spite of this complexity, we showed that phases for individual resonances can still be obtained from the experiment by using an extension of the Fano model of atomic resonances. As simultaneous excitation of several resonances is a common scenario in many-electron systems, this work paves the way to reconstruct electron wave packets coherently generated by attosecond pulses in systems larger than helium. The RABBITT measurements were performed at OSU in collaboration with Dr. Pascal Salieres (CEA Saclay) and Prof. Fernando Martin (Madrid). The results appear in Phys. Rev. Lett. [9A].

Investigations using the LCLS XLEAP. We participated in a beam time awarded in November 2018 for “Time-resolving correlated continuum electron and core-excited state wavepackets by photoemission streaking”. The run was led by Dr. James Cryan (SLAC) and Dr. Ago Marinelli, and focused on the attosecond capabilities of the LCLS. The streaking results are still under analysis.

1.3 FUTURE PLANS

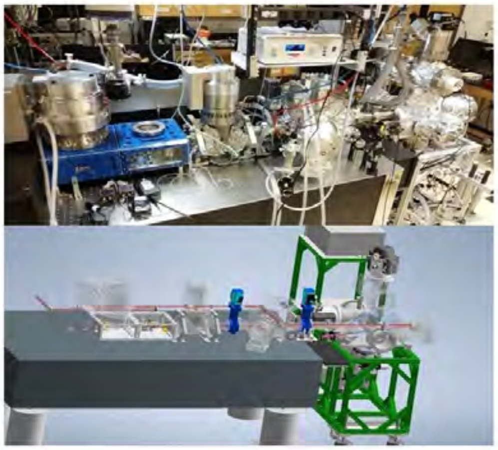

Figure 3: An image of the SFS beamline above and the corresponding CAD drawing. The key design elements include the use of a pulsed gas valve, narrower vacuum apertures, spherical dielectric XUV mirrors, and a low profile with respect to the optical table.

Strong field simulator: Based on the encouraging results described above, we decided to design a new attosecond beamline optimized for strong field simulator measurements. As shown in Fig. 3, we have completed the design and assembly of a new beamline optimized for SFS experiments. We focused on improving three criteria which limited our previous experiments: (1) XUV flux in the interaction region (increasing signal), (2) background contamination in our detection chamber (reducing noise), and (3) passive interferometric stability (improved temporal resolution). Criterion (1) is addressed by the addition of a pulsed gas valve which will allow for higher pressures for the gas used in HHG to produce the XUV light. In addition, Xenon gas will be used for HHG which typically provides a factor of 10 increase in XUV light produced, as compared to the Argon gas used previously. Previously, the largest contaminant in the detection chamber was the gas used in HHG. As such, (2) is resolved by a combination of the pulsed gas valve – reducing the amount of gas entering the vacuum system – and tighter vacuum apertures to choke the gas flow through the apparatus. (3) Is aided by keeping this apparatus closer to the laser system and building the entire beamline at a lower height profile with respect to the optical table. We have also added a new capability by using a dielectric spherical mirror to focus the XUV pulse. These mirrors are engineered to have a narrow band reflection efficiency (~5 eV FWHM), with a central energy of 25, 35, or 45 eV depending on choice of mirror. This will allow us to selectively filter the photon energies of the XUV pulse train, and correspondingly the initial kinetic energy of the photoionized electrons adding another dimension to explore in the SFS scheme.

Using the newly constructed beamline, we will be able to perform a series of novel experiments along the SFS scheme. (i) To study NSDI in Helium, the dielectric mirror centered at 25eV – close to Helium's ionization potential at 24.6 eV – will be used to closely approximate the typical strong field tunneling step, with ion spectra being recorded to measure changes in the rate of double ionized Helium. This will be a multi-dimensional study with the MIR wavelength, XUV photon energies, interferometric delay, and laser intensity all being independent tunable parameters. (ii) We will also study the rate of electron recollision using elliptically polarized MIR light. In this scenario, a delay scan will modulate the relative angle between the XUV polarization, and therefore the initial momentum vector of the photoelectrons, and the instantaneous direction of the MIR field vector. Ken Schafer (LSU) will provide theory support for this program.

Imaging: The goal for FY20 is the application of LIED/FABLES to study ultrafast molecular dynamics using pump-probe geometries. (1) Work will continue on hydrocarbon chains. 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}.

1.4 PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2017-2019)

1A. *"Precise access to the molecular-frame complex recombination dipole through high-harmonic spectroscopy"*, S. Schoun *et al.*, Physical Review Letters **118**, 033201 (2017).

2A. *"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.

3A. *"Tunable orbital angular momentum in high-harmonic generation"*, D. Gauthier *et al.*, Nat. Comm. **8**, 14971 (2017). doi: 10.1038/ncomms14971.

4A. *"Tunable mid-infrared source of light carrying orbital angular momentum in the femtosecond regime"*, A. Camper *et al.*, Opt. Lett. **42**, 3769 (2017). doi: https://doi.org/10.1364/OL.42.003769.

5A. *"Probing electronic binding potentials with attosecond photoelectron wavepackets"*, D. Kiesewetter *et al.*, Nat. Phys., **14**, 68 (2018). doi: 10.1038/NPHYS4279.

6A. *"Femtosecond profiling of shaped x-ray pulses"*, M. Hoffmann *et al.*, New J. Phys. **20**, 033008 (2018). doi: https://doi.org/10.1088/1367-2630/aab548.

7A. *"Diffractive Imaging of C_{60} Structural Deformations Induced by Intense Femtosecond Midinfrared Laser Fields"*, H. Fuest *et al.*, Physical Review Letters **122**, 053002 (2019). doi: 10.1103/PhysRevLett.122.053002.

8A. *"Probing the interplay between geometric and electronic-structure features via high-harmonic spectroscopy"*, T. T. Gorman *et al.*, J. Chem. Phys. **150**, 184308 (2019). doi: 10.1063/1.5086036.

9A. *"Disentangling Spectral Phases of Interfering Autoionizing States from Attosecond Interferometric Measurements"*, Lou Barreau *et al.*, Phys. Rev. Lett. **122**, 253203 (2019). doi: 10.1103/PhysRevLett.122.253203.

Electron Quantum Correlation with EM Fields

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Project Scope

Recent and current interest in AMO science has been triggered by availability of ultra-short (fs and sub-fs scale) laser pulses having intensities in the range near and well above $I = 0.1$ PW/cm^2, and in wavelengths both longer and shorter than near-visible. We believe it continues to be important to improve understanding of the fundamental process whereby photons excite electrons in atoms as well as in more complex materials where an electric dipole interaction activates the principal photon interactions.

Our work, through the development of the virtual numerical detector (VND) method, has been providing a unique avenue of theoretical access to still-mysterious quantum details of ionization initiation via tunneling. The perceived value of this work is indicated by the reception of our ISI Highly Cited invited review [1], the invitation to contribute to M. Vrakking's special issue of Journal of Physics B [2], and the invitation to deliver the opening plenary address [3] at the 2017 International Conference on Matter and Radiation at Extremes, held in Beijing.

Going forward we will continue to develop the VND approach while opening an attempt to deepen our understanding of coupled field + material system correlation physics in the highly quantum domain of few, rather than infinitely many, photons in cavity environments. We expect a role for strong probing of electronic-photonic dressed states and modes, a quantum light-matter domain engaging entanglement, previously disregarded almost entirely.

Recent Progress

Two avenues of *ab initio* evolution have enabled recent progress, and our calculations have followed both tracks, leading in 2017 and 2018 to a PhD thesis and three peer-reviewed publications [2, 4, 5, 6].

Cooperation through J. Biegert has let us contribute theoretically on questions about the intriguing transition zone between non-sequential and sequential double ionization in multi-electron systems (see results of the Barcelona-Heidelberg experimental teams [6]), which were previously largely overlooked. Our approach is partially analytical via extension of the "Simpleman" model. This allows to follow longer-than-optical wavelength experiments being used to uncover new phenomena or enable more detailed studies.

A prominent instance of the value of Simpleman calculations [5] is the ability to systematically and self-consistently include post-release ion-core Coulomb effects on outgoing electrons, which have captured experimental attention in the recent past. What has still 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). A need for attention to this point has existed since it was described a decade earlier - see Ivanov, Spanner and Smirnova [7] where they said: "Identifying the wavepacket dependence on [exit velocity] 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." They point out that it is virtually impossible to separate the initial velocity distribution from the distortions caused by the laser field. In an adiabatic tunneling model, the electron does not gain or lose energy during the tunneling process. This assumption is simply not valid, especially for longitudinal momentum distributions. For example, as we have shown, effects of temporal oscillations will be missed.

Future Plans

Ongoing and future work will see a competition between two different priorities. One priority is obvious - the extension of our SENE application (see Tian, et al. [4, 5]) of the Feuerstein-Thumm idea, leading to our development of the VDN (virtual numerical detector) [8]. A specific task is a challenging directional smoothness issue. We expect to replace the numerical detector ring with an "onion" type detector that accepts information from more than one layer of cells, and this brings complications needing to be resolved concerning three-dimensional detection.

A competing second priority, newly arisen, will be exploration of quantum electronic coherences in truly photonic aspects of the interaction of an electric dipole with one photon. Possibly more interesting will be vacuum interactions with no photons. Cavity containment makes related questions for molecules experimentally accessible and photonic entanglement (see specialized overview [9]) of field modes and molecular states must be expected. Extended theoretical work is anticipated (see, for example, [10, 11, 12]). The well-known Jaynes-Cummings theory [13] is at the simplest level of interaction, engaging only a single atom and single field mode. As the expected starting point for quantum photonic dynamics it immediately introduces an instance of polaritonic quantum entanglement [14]. Extending it beyond its traditional single-atom close-resonance approximation raises fascinating questions for field-induced molecular dynamics, and our experience (see [15]) with the related strong-field two-atom Tavis-Cummings cavity interaction will be important.

Publications supported in recent grant periods are marked with * in the References listing.**

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Peer-reviewed Publications Resulting from this Project (2017-2019)

“Virtual Detector Theory for Strong-Field Atomic Ionization”, Xu Wang, Justin Tian and J.H. Eberly (invited),
J. Phys. B **51**, 084002 (2018). https://doi.org/10.1088/1361-6455/aab5a4.

“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). doi:10.1103/PhysRevLett.118.213201.

“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 Schroeter, Joachim Ullrich, Thomas Pfeifer, Robert Moshammer, J. H. Eberly and Jens Biegert,
Phys. Rev. A **96**, 033401 (2017). DOI: 10.1103/PhysRevA.96.033401 .

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), X-ray second harmonic generation (XSHG), nonlinear two-photon Compton scattering (2PCS) and two-photon absorption (TPA). 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. We have also extended our studies to investigations of parametric mixing interactions, including higher-order optical X-ray mixing and four-wave mixing process.

Recent Progress

Non-parametric Two-Photon Hard X-ray Scattering

The first observation of nonlinear Compton scattering has resulted in an unexpected result: the energy of the generated photon from the simultaneously nonlinear scattering of two 9 keV X-ray photons in a beryllium target was measured to be significantly lower than expected. More specifically, the observed spectrum is redshifted from 18 keV by ~800 eV *in addition* to the expected nonlinear Compton shift. This energy shift is incompatible with the approximation of electrons interacting as quasi free in solids (impulse approximation) for hard X-ray – matter interactions far from atomic resonances. The experiment was performed at extremely high X-ray intensities of ~4×10^{20} W/cm^2.

In order to further investigate this effect and rule out trivial causes for the redshift we have performed a more detailed study. Part of the experiment was extending the measurement of the nonlinear signal into the forward scattering direction. In addition to the angular distribution, we were also able to extend the lower bound of the additional energy redshift to >2 keV by simultaneously investigating the effect for a wider photon energy range of the incoming beam.

Through linear Compton scattering spectroscopy, we were able to infer the temperature of the sample during the interaction. An additional redshift of 800 eV requires an extremely hot plasma temperature with an electronic temperature of kT > 320 eV. The spectrum of the linear Compton scattering does not show a significant broadening, which indicates that the there is no appreciable heating (kT < 10 eV) during the interaction. The unexpected small temperature can be explained by the X-ray interaction generating ~10 keV photoelectrons that propagate outside of the 100 nm focus before depositing most of their energy.

The experiment also included different target materials, namely a metal (Be) and dielectric (diamond). As described below, we will continue the investigation of the dynamics of non-resonant inelastic X-ray scattering from X-ray -heated beryllium plasmas.

The observed emission pattern has a double-peaked shape with an asymmetry in intensity peaked at higher (backward) scattering angles. The asymmetry is increasing with increasing intensity. Although a quadrupole-like pattern is expected for a free-electron interaction, the position of the peaks and the minimum cannot be explained by a free-electron model. An initial model of this process consists of a previously unobserved scattering mechanism that includes the whole atom in the process. In this model, the missing momentum and energy can be transferred to the third body. The process occurs through pA and A^2 scattering processes via a virtual intermediate electronic state, where p is the momentum operator and A the electromagnetic vector potential. However, the observed angular distribution can also not be explained by a simple model that uses the scattering from a virtual intermediate electronic state following photo-ionization.

In a recent experiment performed at the SACLA free-electron laser, we have observed a comparably strong nonlinear signal through the interaction of two photons with energy near the K absorption edge in iron. An initial analysis showed that the cross sections are approximately six orders of magnitude higher than what was expected from the LCLS experiment (far from atomic resonances) in Be. The cross section strongly increases as the photon energy is increased above the K edge. This is in contrast to Cu and Al targets where at the same photon energies (around 7.1 keV) the cross section were significantly smaller than in Fe and had varied only little as a function of with photon energy. This is additional indication that the whole atom participates in the process rather than a free-electron interaction.

In a follow-up experiment, we were able to verify the effect and to obtain spectral information on the nonlinear signal. We have measured the signal as a function of incoming photon energy ranging from below the K edge to well above. The spectrum of the observed signal is very rich. A preliminary data analysis shows two non-dispersive lines around 12.9 and 13.5 keV that have a strong intensity-dependence with the incoming photon energy. We also observe at least one dispersive signal. The signal has a clear threshold behavior. Currently we speculate that 2-electron relaxation-1 photon emission and hyper-Raman scattering could be potential candidates for the effects.

Despite this progress, the detailed mechanism of these fundamental nonlinear processes is still not fully understood, neither far from resonance, nor near-resonance. The further investigation of the process requires performing additional experiments including a complete measurement that has the ability to observe not only the photons but also the momentum distribution of the electrons and ions involved in the process.

Core-resonant Coherent Raman Scattering

The goal of the experiment was the observation of X-ray coherent anti-stokes Raman scattering (XCRS) in the X-ray range. In order to enhance the signal, the core resonance of the Si L-edge was used. To this end, the LCLS was operated in two-color mode and the pulses were temporally and spatially combined at the suitable angles to satisfy the phase-matching condition using a split-and-delay in combination with a Laue and Bragg reflection. The FEL is used in two color SASE mode at photon energies around 10 keV, with the energy difference matching the silicon L-edge (99.4 eV). The tuning of the photon energy difference across this edge will allow the first measurement of the third-order susceptibility at a core resonance. The observation of this signal would constitute the proof of principle of XCRS in the hard X-rays.

We have also taken an initial step in this direction performing a degenerate four-wave mixing experiment. Here two crossed X-ray pulses of the same color generate a transient grating from which an optical pulse gets diffracted.

This experiment is a follow-up experiment on an earlier beamtime at LCLS, where the machine had problems and was not able to deliver sufficiently intensity pulses in the two-color mode. The experiments were performed only recently and the data analysis is still going on.

Higher-Order X-ray - Optical Wave Mixing

The goal of the experiment is the investigation of higher-order X-ray-optical sum-frequency generation (XSFG) as a means of measuring the microscopic, nonlinear induced charge density in optically excited materials. XSFG represents a direct route to investigate the dynamics of *local* linear and nonlinear induced charges with atomic resolution. These induced charges ultimately give rise to the macroscopic induced polarization; however, the local atomic response to external fields is experimentally and theoretically largely unexplored. Our preliminary simulations show that microscopic effects induced during the interaction of a crystal with an optical pulse are indeed much more complex than the resulting macroscopic polarization. The short wavelength of X-rays make it possible to investigate aspects of the interaction that cannot be resolved by optical wavelengths. Note that microscopic currents are induced even when the optical second harmonic generation is symmetry-forbidden in the electric dipole approximation. XSFG allows the investigation of these nontrivial microscopic effects induced by an optical pulse inside the unit cell. We expect that the results can provide a completely new view on the charge dynamics in light-matter interactions. In the experiment the XFEL beam is highly monochromatized to a bandwidth of ~0.5 eV. We used 1 μm optical radiation. As target we used GaAs due to a large second-order (optical) susceptibility. An crystal-based analyzer with a high spectral resolution was used. The experiment was performed at SACLA in December 2018 and data analysis is still ongoing. A follow-up experiment at SACLA is scheduled for December 2019 (see below).

Scientific Opportunities with an X-ray Free-Electron Laser Oscillator (XFELO)

We have studied opportunities for an X-ray Free-Electron Laser Oscillator (XFELO) in the field of nonlinear X-ray – matter interactions. The XFELO characteristics provide exciting opportunities in X-ray nonlinear optics and coherent spectroscopy. Its narrow bandwidth, high coherence, and widely tunable photon energy range are features of particular interest in nuclear nonlinear spectroscopy. The increased coherent bandwidth (i.e. shorter pulses) and peak power of an XFELO would be of interest for coherent electronic and vibrational spectroscopies. These applications could exploit the possibility of tailoring the electric-field temporal profile spanning eV bandwidths. The XFELO characteristics are well suited for a variety of two-photon processes, including X-ray parametric down-conversion (PDC) and various up-conversion processes. Both can involve lower - frequency components in addition to X-rays. This allows the electronic and/or lattice modulations induced through a lower-frequency resonance to be studied with atomic spatial resolution given by the X-ray wavelength because the frequency-shifted signal is diffracted from the crystal lattice. These processes can also be stimulated in which case they are referred to as sum and difference frequency generation. This provides access to the atomic-scale polarization arising from the induced local fields, and not just the long- wavelength dielectric response.

Future Plans

In the future, we will expand on our observations of nonlinear effects at X-ray wavelengths. To this end, we will further investigate nonlinear non-parametric processes near and far from resonance in solids and more specifically its wavelength dependence. From this we expect to get invaluable insights into the process that are necessary to a theoretical description. We will also investigate the process in different states of matter, such as the gas phase. This will be a step towards performing a complete experiment 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.

We will further investigate high-field X-ray – matter interactions. Specifically we have proposed to investigate the unexpected low instantaneous electronic temperature during the FEL interaction that we have observed during the nonlinear Compton scattering experiments. We will extend these observations by observing the linear Compton signal from two-color X-ray pulses focused at different focus sizes in a X-ray pump X-ray probe arrangement. This will allow us to investigate the spatio-temporal energy transport in the electronic system during high-intensity X-ray – matter interactions (proposal at LCLS pending)

We will further explore parametric higher-order nonlinear processes and the possibility of imaging the local induced charge distribution. To this end we will perform an experiment to investigate second-order optical and X-ray mixing, which has been awarded beamtime at the SACLA XFEL in December 2019. In a further experiment we will investigate the scaling of the mixing signal with optical wavelength and the impact of two-photon absorption on the scattering signal (proposal at European XFEL pending).

We will also use nonlinear effects to investigate and measure the temporal structure of hard X-ray FEL pulse structure. In particular, the temporal pulse structure of XFELs operating in the self-amplified spontaneous emission (SASE) regime is very complex since it is composed of many uncorrelated intensity spikes that have a width of only few hundred attoseconds. We will investigate hard X-ray FEL pulses using techniques similar to those routinely used in the optical wavelength range. In particular, we propose to perform intensity autocorrelations of LCLS pulses with high resolution to investigate the temporal structure of the SASE spikes (proposal at LCLS pending).

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.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

Roadmap of Ultrafast X-ray Atomic and Molecular Physics: Hard X-ray Nonlinear Optics
M. Fuchs and D. A. Reis
J. Phys. B **51**, 3 (2018).

Multiple Fourier Component Analysis of X-ray Second Harmonic Generation in Diamond
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Scientific Opportunities with an X-ray Free-Electron Laser Oscillator
B Adams *et al.* (arXiv:1903.09317)

Studies of Autoionizing States Relevant to Dielectronic Recombination

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Project Scope

Initially, 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 Rydberg state.[1-3] 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. Because Rydberg states are involved, DR rates are profoundly influenced by charged particle collisions and small electric and magnetic fields.[2,4-6]

Our initial approach was the isolated core excitation (ICE) of bound Rydberg atoms to their autoionizing analogs,[7] for example , driving the Ba 6snd to 6pnd transition. In this excitation the nd Rydberg electron is a spectator while the Ba^+ ion core is excited.[7] The laser frequency is scanned across the 6snd→6pnd transition, and the width of the observed peak in the resulting ionization signal gives immediately the autoionization rate of the 6pnd state. ICE is precisely the inverse of DR, and we have used it to measure the effects of electric and magnetic fields on autoionization, and therefore, DR rates. We have developed a second approach, which we term DR from a continuum of finite bandwidth.[8] The essential idea is as follows. The Ba $6p_{3/2}11d$ state straddles the Ba^+ $6p_{1/2}$ ionization limit. If the laser driving the 6s11d to $6p_{3/2}$ 11d ICE transition is tuned below the $6p_{1/2}$ limit the 11d electron can deexctite the $6p_{3/2}$ core to the $6p_{1/2}$ state and be captured into a Rydberg state converging to the $6p_{1/2}$ limit. If this Rydberg state decays radiatively to a bound Rydberg state, DR has occurred. Using these two approaches we have explored many aspects of DR, providing insights which have, in addition, been directly applicable to zero kinetic energy (ZEKE) spectroscopy. [9]

In our experiments with DR from a continuum of finite bandwidth we introduced a microwave field, to mimic electron collisions, and discovered that in the presence of a microwave field recombination can be observed even when the laser is tuned an integer multiple of the microwave frequency above the Ba^+ $6p_{1/2}$ ionization limit.[10] Although the resulting spectra resemble those seen in above threshold ionization, the physics is more like that of half cycle pulse ionization.[11] We have developed a simple model which accounts quantitatively for our observations and indicates that recombination occurs when the laser excitation occurs at the phase of the microwave field at which the field removes energy from the electron as it departs from the ion core, resulting in recombination of the electron with the ion.[15] Our experiments are analogous to those in which a ground state atoms are excited by an attosecond pulse train of XUV pulses in the presence of an intense infrared (IR) field, a problem investigated by several research groups.[12-16]

Recent Progress

To verify our model for the frequency domain recombination experiments we have conducted time domain experiments. Specifically, we have excited Li atoms to the vicinity of the ionization limit in the presence of a microwave field. We have used several laser sources, the first being a mode locked laser producing 5 ps pulses, a duration short compared to the 17 GHz microwave period. We used an optical delay line to vary the microwave phase at which laser excitation occurred and recorded the number of atoms remaining after the laser and microwave pulses (the recombination signal). We observed a clear phase dependence for the recombination signal, with two maxima in each microwave cycle. There are two maxima per cycle since the laser excitation leads to electrons ejected both parallel and antiparallel to the microwave field. Those losing energy to the microwave field are detected, irrespective of the direction in which the electrons are ejected by the laser excitation.

We replaced the ps laser with a laser intensity modulated at twice the microwave frequency, which enabled us to tune the laser closer to the ionization limit and observe the effect of tuning the laser both above and below the limit. As the intensity modulated laser was delayed relative to the microwave field we again observed two maxima in the recombination signal in each microwave cycle. These results and those obtained with the ps laser are analogous to those observed in the XUV/ IR experiments.

When we detect the recombination signal after the laser and microwave pulses the two half cycles of the microwave field are indistinguishable. However, if a small static electric field is added, they are easily distinguished, and, as the optical delay line is scanned only one maximum is observed in each microwave cycle. As expected, the phase of the recombination signal is reversed if the static field is reversed, and there is no phase dependence if the static field is perpendicular to the microwave field. A surprising observation is that when the laser is tuned below the ionization limit the modulation not only changes sign when the static field changes sign, but changes sign again as the amplitude of the positive or negative field amplitude is increased.

Finally, we have observed the recombination in the microwave field using frequency modulated laser excitation. By first exciting bound Stark states in combined static and microwave fields we established the phase relation between the frequency modulation of the laser and the microwave field felt by the atoms. Tuning the laser frequency to the vicinity of the limit we then observed the recombination signal as the frequency modulated laser was delayed relative to the microwave field. We observed two maxima in the recombination signal which occur when the laser frequency extrema match the positive and negative maxima in the microwave field felt by the atoms.

Using microwave spectroscopy we have measured the quantum defects of the Yb 6sns, 6snd, 6sng, 6snh, and 6sni states. They are of interest since the high angular momentum bound Rydberg states of Yb are now used for cold atom research,[17] and Yb^+ is an atomic clock candidate. [18] From the 6snh and 6sni quantum defects we have extracted the Yb^+ dipole polarizability, $\alpha_d = 60.33(10)\ a_0^3$. Ours is the first measurement of this polarizability, and it is important for the the black body frequency shift of the clock. We have, in addition, completed a study of the forced autoionization of the preturber in the Yb 6snd $^1D_2$ series at n==26.

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Physics of Correlated Systems

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Project Scope

For the past few decades, research in multiple fields, including condensed matter physics, nuclear physics, and atomic, molecular, and optical physics, has been confronted by a severe challenge, namely improving our ability to theoretically describe the coupling between multiple degrees of freedom, also known as correlations. Theory would be easier and simpler if the motion of one electron would not affect what another electron does in a many electron atom or molecule, i.e. if they were effectively uncorrelated. And, somewhat surprisingly, that is often a fairly reliable starting point in atomic and molecular physics calculations to neglect correlation in such systems, which is the reason why most calculations of atomic processes begin with a Hartree-Fock zeroth-order starting point. Then if some phenomena appear to require inclusion of some correlations in order to describe them, theory usually attempts to build them on to uncorrelated starting point as corrections, often perturbatively as is the case with many-body perturbation theory.

This research project concentrates on developing theoretical treatments of systems, primarily in atomic, molecular, and optical physics, where two or more degrees of freedom exhibit nonperturbatively coupling. Such coupling, which produces correlations between those degrees of freedom, also produces entanglement. It is important to remember that correlations are not merely an annoyance for theorists: they have a key role in all forms of chemical reactivity and energy transfer. Major challenges still remain even for simple systems such as electron dynamics in an individual atom, negative ion, or small molecule, or in the coupling of electronic and dissociative degrees of freedom in molecules. Hence it is frequently desirable to tackle highly correlated phenomena using a method that builds in the key correlations from the outset. Our studies develop such theoretical techniques and then apply them to problems where the coupling of multiple degrees of freedom has a controlling influence on the phenomena of interest. Some of our theoretical projects are aimed at interpreting experiments that have been carried out which have no satisfactory theoretical interpretation or understanding, while others attempt to predict new opportunities for future experiments relating to photofragmentation, chemical reactivity, and energy transfer.

Recent Progress

(i) Few-body collisions in molecular physics and frame transformation theory

Remarkably, many regimes of the simplest neutral molecule H_2 are still challenging for theory to understand to this day, despite tremendous conceptual and computational progress over the past decades. Some of the difficult issues include the need for a fully quantitative description of electron-nuclear correlation that shows how energy gets interconverted between electronic and nuclear degrees of freedom. From a more global perspective, these questions extend to diatomics and polyatomics throughout the periodic table. Yet another question relates to how strongly are the electron-nuclear correlation phenomena occurring in H_2 dependent on the large mass ratio between the heavy and light particles in the system. Reference [1] by the P.I. with graduate student Michael Higgins in the list of publications below explored this by tackling one of the most extreme mass ratios where the Born-Oppenheimer approximation is likely to be unsuccessful, where the protons are replaced by positrons. In that study, both elastic and inelastic collisions between positronium 1s and positronium 2s atoms were treated in a 4-particle hyperspherical coordinate treatment. This is a fundamental collision process that could be relevant to the eventual creation of a positronium gamma ray laser.

While the rovibrational frame transformation can be viewed as a treatment of correlated electronic and nuclear motions, the correlation of an electron with the fields of two fixed ions or one ion and one atom, e.g. in highly excited states of a diatomic molecule, is a purely electronic problem to an excellent approximation. With postdoc Teri Price, we formulated a first treatment [2] of this class of correlations using the local frame transformation which involves a transformation between spherical and prolate spheroidal coordinates. That study built on experience that we gained by developing methods to treat an unusual regime of very high energy states of the H_2^+ molecule, and at very large internuclear distances on the micron scale.[3]

The next topic considered in the context of our molecular physics studies, indirect dissociative recombination, might initially seem simple, when the target of the incident electron is a small diatomic or triatomic molecular ion. But it is challenging for standard theoretical methods because there is no simple, direct dissociative pathway to visualize or compute, in contrast to ordinary dissociative recombination or attachment collisions that follow the Bates-type mechanism. One of the prototype collision systems is an electron collision with HeH^+ at low energies where there is no identifiable direct dissociative Born-Oppenheimer potential curve.

We have benchmarked the simplest version of the frame transformation theory of such collisions involving electron-nuclear correlations, by comparing a semi-realistic model of e-H_2^+ collisions with an essentially exact calculation.[5] The upshot of that study was that in the low energy range, extending over approximately 1 eV or thereabouts, the frame transformation theory combined with multichannel quantum defect theory does reasonably well in describing the complex resonance structures that an exact calculation produces in a dissociative recombination calculation. The most significant discrepancies are somewhat infrequent isolated occurrences of a low principal quantum number perturbing state that is sometimes located at a slightly shifted incorrect energy, and our current efforts, almost ready to submit for publication, indicate that this small shift can be made nearly exact by implementing an improved energy-dependent frame transformation treatment. In addition to the value of this study [5] in benchmarking the approximate frame transformation theory, it has at the same time provided the first estimate of the ungerade contribution to the H_2^+ dissociative recombination cross section. We view this as a prototype system that will also pay dividends in the study of other systems, especially polyatomic dissociative recombination.

In our 2017 article on the HeH^+ system [6], we implemented a new treatment of the low temperature collision regime, 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 confirmed reassuringly that equivalent results could 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. Those calculations agreed reasonably well with older experiments. But an exciting development is that new results have been obtained for the first time with a very cold (<10K) ion storage ring experiment at the Cryogenic Storage Ring (CSR) in Heidelberg. This is expected to yield the sharpest test of theory yet, including low energy data with sufficient resolution to observe individual resonances. Our new variant of the energy-dependent frame transformation theory will soon complete a test of this hypothesis, in collaboration with the Prague research group of Roman Curik.

(ii) Extreme correlation regime in negative ion photodetachment

Atomic negative ions, even comparatively simple ones possessing just two valence electrons, have for many years served as prototypical systems for the observation of strong electron-electron correlations. One of the most dramatic regimes arises in processes where a negative ion absorbs a photon that excites two or more electrons to a high degree of excitation, after which the system decays by autodetachment, with one electron ejected and the remaining neutral atom left in a highly excited state. [4] An impressive series of experiments in such systems, specifically the alkali-metal negative ions, has been undertaken in recent years by the group of Dag Hanstorp in Gothenberg, Sweden. [See, e.g., Phys. Rev. Lett. 108, 033004 (2012); Eur. Phys. Lett. 106 (2014); Phys. Rev. A 88, 053410 (2013);] Some of their most striking experiments were carried out in the series of negative ions K^-, Na^-, and Cs^-, where absorption of an ultraviolet photon produces high double excitation and autodetachment

These calculations carried out by the P.I. and graduate student Matt Eiles (who completed his PhD in May, 2018) required a significant enhancement of our two-electron R-matrix computer codes, in a number of ways.[4] First, to get more (and more accurate) radial basis states, which were needed to reach convergence in these larger box sizes and higher degrees of excitation, we switched over to a B-spline method to solve for the box-confined radial atomic eigenfunctions. This change allowed us to include up to 100 radial functions per partial wave, a major improvement. Second, we implemented an R-matrix propagation scheme to handle the very strong long-range couplings in the Hamiltonian outside the R-matrix box radius, where exchange could be neglected. Ref.[4] achieved quantitative agreement with experiment, even on the comparatively small and sensitive partial photodetachment cross sections that leave the residual atom in states of high energy and angular momentum, and also a detailed physical interpretation.

*(iii)*Fano resonance model in the time domain

As one of our recent projects, we initiated some explorations in an attempt to find other scenarios in collision physics where Fano line shapes or even more complicated multichannel line shapes can be modified through ultrafast phase control. This study led to a publication [7] that formulated and explored a model study of this phenomenon.

Future Plans

A new graduate student, Yimeng Wang, has begun to develop a theoretical treatment of 2-photon and 3-photon ionization of atoms with two valence electrons, concentrating on photoelectron angular distributions and also on novel polarization dependences. Our aim is to have a first exploration implemented soon for atomic helium, in the region of the even parity doubly excited states. Once our methodology is verified, we hope to broaden the treatment into the alkaline earth atoms and treat the combination of autoionizing intermediate and final states, whose decay is mediated by either electron-electron interaction or spin-orbit coupling.

A major project that expected to get finished within the coming year is a quantitative implementation and test of the recently improved rovibrational frame transformation theory. This will build on some of our preliminary evidence that a variant of the theory which incorporates the energy-dependence of the fixed nuclei scattering parameters can give improved cross sections for processes such as dissociative recombination and inelastic excitation over a broader energy range. While the simplest (energy-independent) variant of frame transformation theory has given excellent results over small energy ranges, in comparison with other theories as well as experiment, and permitted the solution of some highly challenging problems such as indirect dissociative recombination in diatomics and polyatomics with up to 5 atoms, its quantitative limitations are still not well understood. Moreover, we anticipate completing a more extensive implementation of the spherical-to-spheroidal coordinate frame transformation to treat highly excited long range states of the Sr_2^+ molecule.

For another project related to ultrafast science, 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. Our group has begun an exploration of this phenomenon, in collaboration with the Rost group, to understand its wider applicability as well as its limitations. Preliminary results suggest that there is a quantum mechanical interference of two dominant pathways, which can be sometimes constructive and sometimes destructive.

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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 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. This motion occurs over attosecond to picosecond timescales. Ultimately, we hope to obtain a more complete picture of correlated multi-particle dynamics in molecules and other complex systems.

In our principal experiments, gas phase atoms and molecules are exposed to short pulses of electromagnetic radiation with frequencies ranging from THz into the XUV spectral regions, and with durations from picoseconds to attoseconds. The pulses coherently induce and/or probe dynamics in the electronic, vibrational, and rotational degrees of freedom of the targets. In one line of experiments, we hope to clarify the roles of both electron correlation and coupled electronic-nuclear dynamics in directional multi-electron dissociative ionization of small molecules. In another, in collaboration with the DiMauro-Agostini group at Ohio State, we are developing novel techniques for directly probing the effective electronic potential experienced by an outgoing attosecond photoelectron wavepacket during the first femtosecond, or so, after its release. Lastly, we are exploiting large electric field enhancements near nano- and micro-structured metals to produce high-energy (>5 keV) electron bursts which might serve as fast probes of molecular structure and dynamics.

II. Recent Progress

A. Electron field emission from nano-tipped wires for sub-wavelength probing of THz waveforms

Previously, we showed that high-energy (> 5keV) electron bursts could be produced by exposing nano- and micro-structured metals to intense, single-cycle THz pulses [1]. Local electric-field enhancements of greater than 3000x where achieved at the surface of nanotips, enabling tunneling emission and subsequent acceleration of the electrons over subpicosecond time-scales. We are continuing to characterize the emission as a potential source of localized subpicosecond electron pulses for inducing or probing dynamics in molecules, or on surfaces. In addition, we are exploring the use of field emission from nanotips as an *in situ*, sub-wavelength probe of the time-dependent electric field in a focused THz beam in vacuum.

Our scheme for sub-wavelength probing of THz waveforms utilizes two THz pulses and takes advantage of two key features of high-energy electron field emission driven by intense (near) single-cycle THz pulses. First, the emission of the highest energy electrons is temporally confined to a brief window near the peak of one half-cycle of the THz field. Second, the maximum energy, E_{max}, of the emitted electrons is proportional to the peak THz field at the tip. Accordingly, we use one (relatively intense) "source" THz pulse to generate electrons from a nanotip, and measure the changes in E_{max} in the presence of a second (relatively weak) THz pulse. The fractional variation in E_{max} is proportional to the field amplitude in the weak pulse at the location of the nanotip and at the instant that the high energy electrons are released by the source. By scanning the position of the nanotip and the delay between the two THz pulses, we can map out the spatio-temporal waveform of the weaker THz pulse. We are currently working to reduce the time, and number of measurements, required to use this method to fully characterize a focused THz beam in vacuum.

B. Attosecond Photoelectron Probes

We recently showed that when an attosecond photoelectron wavepacket is created in the presence of an oscillating field, its momentum and acceleration (averaged over the first quarter-oscillation of the dressing field) are directly mapped to the final electron energy spectrum as a function of the delay between the ionizing pulse and the dressing field [a]. Thus, for attosecond XUV photoionization in a near-infrared field, the coarse characteristics (in particular, the average depth U and gradient α) of the binding potential traversed by the electron during the first femtosecond, or so, after its birth can be recovered from the delay-dependent photoelectron spectrum. In collaboration with the DiMauro-Agostini group at OSU, we demonstrated this measurement concept using RABBITT+, a modified version of a standard technique originally developed to characterize XUV attosecond pulse trains [2]. Specifically, we employed photoelectron wavepackets, produced by an attosecond XUV pulse train, to characterize the differences in the effective binding potentials for two different atoms, He and Ne, as a function of photoelectron energy [a]. Not surprisingly, the results showed significant differences in the effective potentials for the two atoms, reflecting the dissimilar degree of correlation between the departing and remaining electrons in the two species.

Notably, our previous measurements with atoms did not take advantage of the full power of the approach, namely, that the departing photoelectron captures information on the binding potential during a brief, ~1 fs, interval. Indeed, using the same basic approach, it should be possible to monitor changes in molecular binding potentials resulting from additional electronic or nuclear dynamics taking place over longer, or comparable, time scales. Accordingly, we have been planning experiments that can exploit this short measurement window to measure changes in a molecular binding potential due to coherent nuclear dynamics induced by a preceding laser pulse. The measurements will be enabled by the improved electron energy resolution, increased harmonic flux, and enhanced low-energy electron collection efficiency of an updated attosecond beam line at OSU.

We will consider I_2 as an example. We will use a visible, OPA-generated, ~50fs pump pulse at 513 nm to resonantly (and efficiently) excite I_2 molecules in the X $^1\Sigma_g^+$ ground state to the B $^3\Pi_u^+$ level [3]. The pump will launch a vibrational wavepacket for which the internuclear separation, R, changes by nearly a factor of 2 (from approximately 5 to 9 a.u.) as the B-state vibrational wavepacket oscillates with a period of 700 fs. The coarse characteristics, U and α, of the electronic binding potential will be probed by performing RABBITT+ measurements at different time delays during the wavepacket evolution. Low energy photoelectrons (and RABBITT+ sidebands) resulting from ionization of the X and B states will be distinguished by the differences in their energies using the improved resolution of the new TOF electron spectrometer. Overlapping TOF signals will be minimized by tuning the wavelength of the OPA generated infrared pulses used for the XUV generation and dressing fields.

Several features make this system an excellent test case for exploring the effectiveness of the time-resolved RABBITT+ probe method. First, the long vibrational period ensures that the wavepacket will be nearly stationary during the 50fs infrared-dressing and XUV ionization pulses available for the RABBITT+ probe. Second, the large changes in R should result in significant, readily detected, changes in the relevant potential parameters. Third, due to the angular dependence of the X→B transition moment, molecules that are excited will be preferentially aligned along the 513nm pump laser polarization. By employing a TOF electron spectrometer with a narrow angular acceptance, and rotating the pump laser polarization, we can choose to measure electrons that are ejected along or perpendicular to the internuclear axis as a function of time delay. Correspondingly, we can characterize the effective potential along, perpendicular to, or at any intermediate angle relative to the molecular axis. Unlike in the previous measurements in Ne and He for which a separate reference atom was used to determine the XUV phase, here we will only determine changes in U and α by comparing the photoelectron spectra as a function of pump-probe delay and/or pump laser polarization.

III. Future Plans

First, as noted above, we will continue working to improve our method for sub-wavelength, *in situ* probing of focused THz waveforms. We also plan to characterize the spatial distribution of the high-energy electron emission from THz irradiated nanotips, to determine the utility of this ultrafast electron source for initiating and/or probing molecular dynamics. Second, in collaboration with the DiMauro-Agostini group, we intend to initiate the time-resolved RABBITT+ measurements described above, demonstrating the possibility for directly probing changes in the molecular binding potential occurring during vibrational motion. Third, we hope to return to our investigation [4,5] of the roles of electron correlation [6] and coupled electronic-nuclear dynamics in directional multi-electron dissociative ionization of small molecules, through pump-probe experiments with bichromatic fields.

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V. Peer-Reviewed Publications Resulting from this Project (2017-2019)

[a] D. Kiesewetter, R.R. Jones, A. Camper, S.B. Schoun, P. Agostini, and L.F. DiMauro, “Probing Electronic Binding Potentials with Attosecond Photoelectron Wavepackets,” Nature Physics **14**, 68 (2018).

Real-time observation of multi-electron processes in atoms and diatomic molecules

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Project Scope:

The main 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 are currently working on the development of an experimental system, which combines 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) in order to investigate the correlated electron dynamics in atoms and 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:

At the beginning of the current report period, our experimental setup, composed of a laser system, an attosecond source, an XUV/IR interferometer and a velocity-map imaging system was operational. Over the last year, it has been then used for performing preliminary measurements of the electron dynamics in atoms at the attosecond time scale. In addition, we have also pursued some technical development on the setup in order to achieve the required capability for performing long-term experiments with multi-particle imaging techniques. In particular, we have completed the assembling of an XUV spectrometer and we have developed a stabilization system for our XUV/IR interferometer.

1- Completion of the attosecond pump/ IR probe beamline

(a) Finalization of the XUV spectrometer (Project Leader: S. Burrows, graduate student)

The assembling and the calibration of an XUV spectrometer has been completed. The spectrometer consists of a fixed toroidal grating and a microchannel plate/phosphor screen-based detector coupled to a CCD camera. By using the appropriate grating, the spectrometer covers the wavelength region from 10 to 170 nm (10 to 130 eV), with a spectral resolution of the order of

0.1 nm (2.10-4 eV). The spectrometer is primary used to measure the spectrum of the frequency components making up the attosecond pulses for its temporal characterization. It does not only offer a fast data collection (a few tens of millisecond per spectrum), which is well suited for optimizing the attosecond pulse's spectrum prior to any measurement, but also allows for monitoring the spectrum over the course of a given experiment. As a demonstration of its capability, figure (1) shows the spectrum of two different attosecond pulses made of odd harmonics generated with either an 800-nm or a 400-nm field. The spectra were recorded with an exposure time of 10 ms.

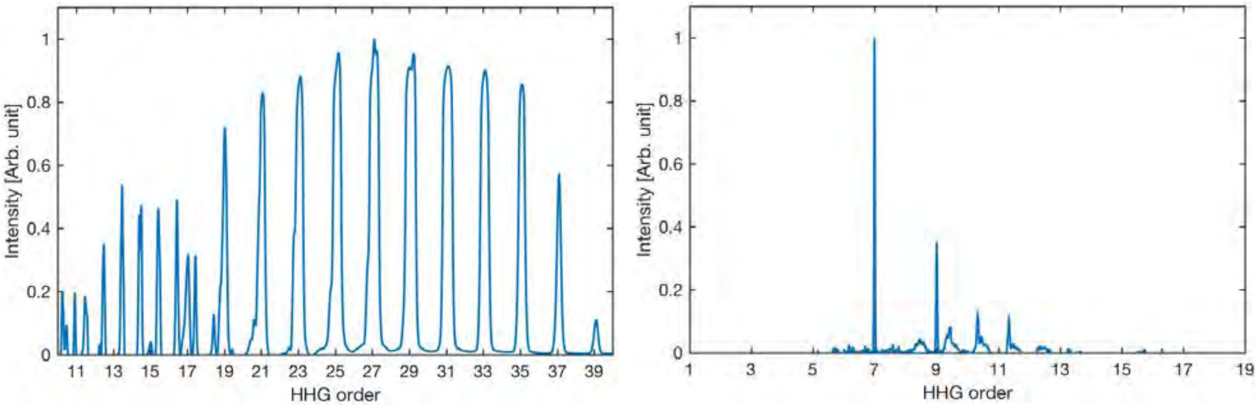

Figure 1: Spectral components of two attosecond pulses produced with an 800 (left) and 400-nm (right) IR field.

(b) Development of an optically-locked interferometer for long-term attosecond measurements (Project Leader: J. Vaughan, graduate student).

In this project, the temporal characterization of a given electronic process is measured by exposing the target to both an attosecond pump pulse (~100 as) and a phase-locked optical IR probe field, with a variable time delay between the two. To fully exploit the temporal resolution of attosecond pulses for time-resolved study using such a pump-probe approach, the time delay between the pump and probe pulses must be controlled with an attosecond resolution as well. This requires the ability to linearly vary the delay with time steps of the order of the pulse duration (or less), and, more importantly, to maintain it to any desired value over extended periods of time. The major difficulty to achieve such temporal resolution comes from the fact that the spatial extent of an attosecond pulse is of the order of a few tens of nanometers (~30 nm for a 100-as pulse). As a consequence, any nanometer-scale fluctuations of the path length difference between the paths followed by the pump and probe beams inevitably lead to a timing jitter of the order of magnitude of the pulse duration itself. Such nanometer-scale fluctuations are generally inherent in any attosecond experimental setup due to beam pointing instabilities, thermal expansion of the optical table, or vibrations of the mechanical structure of the optical system resulting from the surrounding environment (air flow, vacuum pumps, chillers ...). To allow for precise measurements at the attosecond timescale, we have developed a stabilization system for our Mach-Zehnder-type XUV/IR interferometer. It is based on a CW laser propagating coaxially with the pump and probe beams in the interferometer. At the exit of the interferometer, an optical system is used to align coaxially the CW beams in order to produce an on-axis interference pattern that can be captured with a fast photodiode. Such a design presents several advantages over other methods. First, it offers a large stabilization bandwidth, which is mainly limited by the resonance frequency of the piezoelectric transducer used to adjust the interferometer path length. And, more importantly, it allows for a high stability as the relative phase between the two CW waves is directly measured from the photodiode signal without the need of any retrieval procedure. With such a design, we obtained a time delay jitter in the interferometer of the order of 10-as rms over several hours (see figure 2) and a feedback frequency close to 300 Hz.

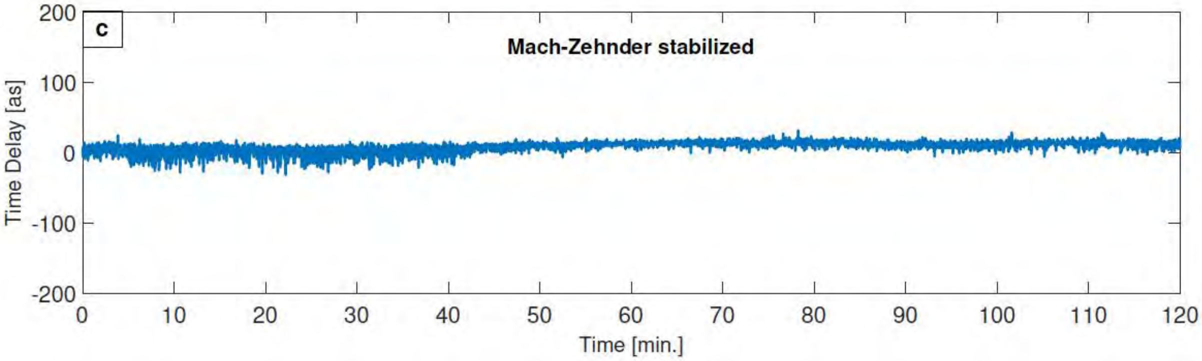

Figure 2: Long-term time delay jitter in the stabilized XUV/IR interferometer.

2- Attosecond control of the photoemission process in atoms (Project Leader: B. Unzicker, undergraduate student)

Using the experimental approach developed in this project, we are currently investigated ways to observe and control the photoemission process at the attosecond time scale. An asymmetric electron emission from atoms is generated and controlled by combining an attosecond pulse train (APT) composed of both odd and even harmonics and a weak IR field (10^{11} W/cm^2) [11]. Electron wave-packets are formed by ionizing argon gas with such APT in the presence of the IR field. Consequently, a mix of energy-degenerate even (*s*,*d*) and odd (*p*,*f*) parity states is fed into the continuum by one- and two-photon transitions. These interfere, leading to an asymmetric electron emission along the polarization vector. At some appropriate time delay between the APT and IR fields, the even and odd angular continuum wave function resulting from one- and two-photon transitions, respectively, add constructively on one side (up) of the polarization vector direction and destructively on the other side (down), thus creating a strong up-down asymmetry in the angular emission of the photoelectrons.

It is known that the direction of the emission can be controlled by varying the time delay between the two pulses [8]. In this study, we show that the direction of emission can also be controlled by tailoring the temporal profile of the APT. Figure (3) show the asymmetric electron emission as a function of the photoelectron energy and the time delay between the attosecond pulse and the IR field, for two different temporal profiles of the attosecond pulse. It can be observed by comparing the figures on the left and right that the direction of emission of an electron with a given energy is varied as the temporal profile of the APT changes.

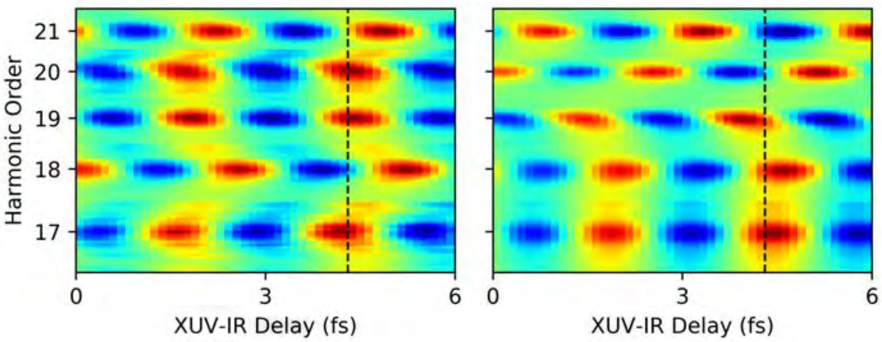

Figure 3: Electron emission as a function of the photoelectron energy and the time delay between an attosecond pulse and the IR field, for two different temporal profiles (left and right) of the attosecond pulse.

Future Plans:

For the upcoming year, we plan to complete the current study on the control of electron emission at the attosecond time scale. In addition to its scientific value, this study will also serve as a reference study in the future when multi-particle imaging detector will be installed on our beamline. The second main goal for the next period is to implement and calibrate the multi-coincidence particle's momentum spectrometer in the presence of EUV and IR pulses. As soon as such a detection system will be completed, we will be all set to perform measurements of the correlated electron dynamics at the attosecond time scale.

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Peer-Reviewed Publications Resulting from this Project (Project start date: 08/2017)

1- *"Design of an optically-locked interferometer for attosecond pump-probe setups"*, J. Vaughan, J. Bahder, B. Unzicker, D. Arthur, M. Tatum, T. Hart, G. Harrison, S. Burrows, P. Stringer, and G. M. Laurent. Optics Express, *in press* (2019)

2- *"DAVIS: A Direct Algorithm for Velocity-map Imaging System"*, G. R. Harrison, J. C. Vaughan, B. Hidle, and G. M. Laurent, Journal of Chemical Physics, **148**, 194101 (2018)

Early Career: First-Principles Tools for Nonadiabatic Attosecond Dynamics in Materials

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Project Scope

The response of molecules and materials to intense and/or high energy light underpins a wide range of important processes such as light harvesting, radiation damage, and energy storage. At the atomistic level, many of the underlying mechanisms are poorly understood, especially the electron dynamics during and immediately following interaction with a laser pulse, as well as the resulting electron/lattice dynamics. There are strong ongoing efforts towards measuring these processes using time-resolved X-ray spectroscopy at free-electron laser facilities such as LCLS, due the ability to make short intense pulses, and the elemental specificity of X-ray absorption. The resulting time-resolved spectra are complex, however, and can be difficult to interpret as they involve features such as intensity modulation, subtle edge energy shifts, and transient pre-edge features. Going from observables as a function of time delay to actual electron dynamics in the system requires first-principles simulations. To address this, the overarching goal of this project is to develop quantum chemistry techniques for simulating both the attosecond electron dynamics and X-ray observables in solid state materials. This includes both electronic dynamics as well as non-adiabatic electron/lattice effects.

Recent Progress

During the previous year of this project we focused primarily on developing and validating time-dependent density functional theory (TDDFT) approaches for computing X-ray observables such as transient inner-shell absorption for measuring attosecond dynamics. We have made significant progress towards this goal, including development of relativistic TDDFT for cases where spin-orbit coupling is significant, finite bulk-mimicking cluster models for capturing field-modulated XAS in solids, and simulated X-ray transient absorption for reconstructing electron dynamics in molecular systems.

I. Relativistic TDDFT for Core Spectroscopy and Electron Dynamics

Relativistic effects can play an important role in X-ray driven/probed processes, as the spin-orbit coupling of p states can be on the order of a few eV or more for transition metals and beyond. Simulating dynamics as well as transient spectra of molecules and materials containing moderate and heavy elements thus requires an electronic structure method capable of capturing this. In collaboration with Niri Govind (PNNL), in the past year we completed implementation and validation of a spin-orbit TDDFT code in the NWChem software suite. This is two-component method [1] based on the zeroth-order regular approximation (ZORA) with SO potentials constructed from four-component atomic densities [2]. It has been extensively validated against a range of core-level and UV-Visible absorption spectra and gives excellent agreement with experiment (see Fig. 1). This is a critical development for simulating dynamics and time-resolved spectra in transition metal oxides and similar systems (work in progress). A manuscript is under preparation [3].

II. Field-Modulated X-Ray Absorption in Metal Oxides

As a first step towards simulating strong-field processes in solids, we have also recently developed cluster models for titania (TiO_2) subjected to weak and strong static electric fields. We use a covalent embedding procedure to construct $Ti_xO_yH_z$ clusters [4], with boundary partially charged “hydrogens” to passivate the cluster. Bulk-mimicking clusters using atom-centered basis sets have numerous advantages over planewaves or grids as they are natural for all-electron simulations, and allow for efficient evaluation of hybrid functionals, which has been shown to give significantly improved band gaps and near-edge X-ray absorption (XANES) spectra versus traditional DFT functionals.

To compute the XANES spectrum, the single particle density matrix is propagated in time following a broadband excitation pulse using our two-component spin-orbit TDDFT with the hybrid B3LYP functional. To facilitate convergence, we use Padé approximants to the Fourier transform, built from the sum of occupied/virtual dipole contributions [5]. This technique significantly reduces required simulation times and is readily extended to time-resolved XAS.

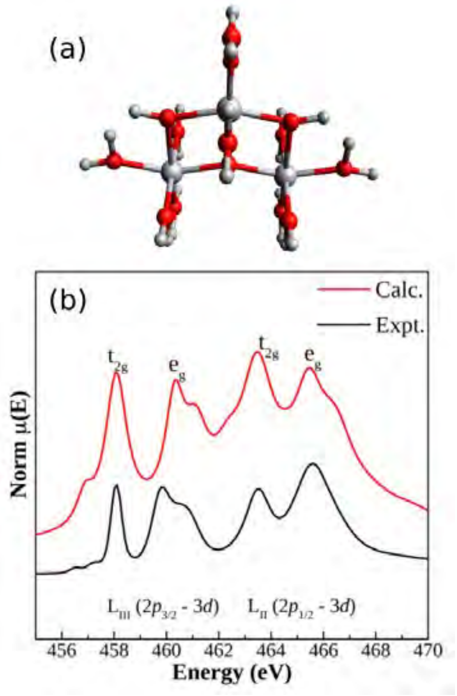

Figure 1: (a) $Ti_3O_{14}H_{24}$ bulk-mimicking cluster of anatase TiO2. (b) The simulated Ti L-edge XANES spectrum using spin-orbit TDDFT matches experiment well.

Before tackling transient spectra, we first validated the XANES spectra versus experiment in collaboration with James Dorman (LSU Chemical Engineering). The resulting L-edge XANES spectrum is shown in Fig. 1. The spectrum agrees well with the experiment [6], including the L_2/L_3 splittings as well as the t_{2g}/e_g gaps. We have also made progress towards simulating the effects of weak and strong fields on these materials. Weak static fields due to surface ligands, for example, have been shown to modulate XANES via band hybridization [6], which manifests as a broadening of the e_g peak in the spectrum. Additionally, as a first step towards transient absorption in these systems, as have also elucidated the effect of strong static laser fields on XANES in TiO_2. This is similar to using very low frequency (adiabatic) IR light to transiently dress the system. In this strong-field regime, there is a pronounced red-shift of the edge with increasing field intensity arising from band tunneling/hybridizing as well as Stark effects. A manuscript draft has been completed and will be submitted shortly [7].

III. Reconstructing Electron Dynamics from Time-Resolved X-Ray Absorption

We have also recently developed a TDDFT method or transient XAS based on a sudden excitation pump with a time-delayed broadband probe. This builds on our previous successes with core-level linear-response spectra and lays the foundation for first-principles TR-XAS for systems containing everything from 1st-row elements to heavy elements.

Before studying more complicated systems such as solids, we first applied this method to simple molecules. This both serves as validation for the theory, and also will help guide future experiments LCLS and other XFEL facilities by determining how electron dynamics can be reconstructed from transient X-ray absorption spectra. For interpretation, we draw on a density-based picture, where rather than referring to particular excited states, we instead relate modulations in the X-ray spectrum to local densities around particular absorbing atoms (e.g., N, O, S, etc).

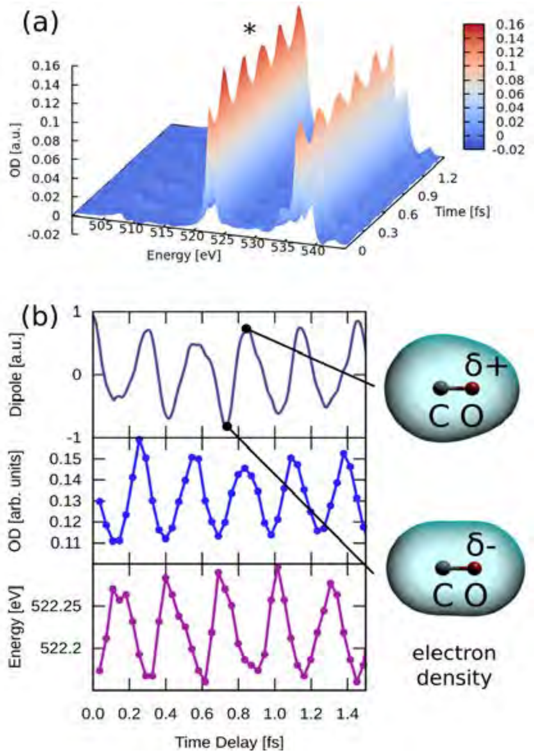

Figure 2: (a) Time-resolved O K-edge XAS in carbon monoxide during valence electron oscillations. For the transition at 522 eV, the absorption decreases and the edge energy blue-shifts with increasing density around the O atom..

Fig. 2 shows TR-XAS results for a single excited carbon monoxide (CO) following a valence excitation. Since resonant excitation with TDDFT is challenging due to local-in-time functionals, instead we emulated a UV pump by perturbing the density of the molecule at t=0. The resulting dynamics are very simple, as the electron density oscillates between either carbon or oxygen with a single dominant frequency (see Fig. 2(b)). While this process is likely too fast to measure with the existing attosecond capabilities of facilities such as LCLS, the results are illustrative and easy to interpret. Fig. 2(a) shows the resulting transient X-ray absorption as a function of time delay between a sudden UV pump and the weak probe. The attosecond O K-edge TR-XANES shows both pronounced absorption modulations as well as more subtle X-ray edge energy shifts. Looking at the lowest energy O K-edge peak (marked *) shows these two effects that are correlated with the density around the O atom: The absorption intensity decreases with increasing local density around the O, and the edge energy blue-shifts with increasing density around O. For this peak, there is modulation of ±16% for the absorption and ±0.05 eV for the edge shifts, and these modulations are specific to the various peaks in the XANES. Similar effects have been seen in polyatomic molecules (work in progress). Additionally, Fano-shaped pre-edge sideband-like features [8] appear, which are due to 1s→HOMO transitions. Overall, the information-rich nature of these spectra suggest that complicated dynamics can be potentially be reconstructed from TR-XAS, albeit with simulations for interpretation. A manuscript detailing this approach is being prepared [9].

Future Plans

In the coming year, we will further validate our XANES approach for the case of low TiO_2 with low concentrations of dopants. In parallel, we will continue to validate our TR-XANES approach for molecules, for which future experimental data is likely to be more readily available than for solid state systems. This will include checking the dependence on initial state and DFT functional, as well as studying other diatomics (e.g., NO) and polyatomic molecules (aminophenol, formamide). We will also link up with future experiments towards measuring attosecond impulsive-ionization triggered electron dynamics with attosecond XFEL pulses (e.g. submitted LCLS proposal, PI James Cryan). In parallel, given our promising results for static fields as well as TR-XANES in molecules, we will also adopt our approaches to describe attosecond dynamics in both TiO_2 as well as SiO_2, which has been studied previously in experiments [10]. This will involve both explicit off-resonant infrared pumps, as well as core-holes created using via a sudden ionization.

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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 photoemission) 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 areas of attosecond time delay in photoemission (including negative ion photodetachment), outer-shell photoemission in the vicinity of inner-shell thresholds and confined systems. The primary areas of programmatic focus are: many-body and relativistic effects in photoionization; photoabsorption of inner and outer shells of atoms and atomic ions (positive and negative); dynamical properties of atoms endrohedrally confined in buckyballs, primarily C_{60}; studies of Wigner time delay on the attosecond scale in photoemission of free and confined atomic systems. Flexibility is maintained to respond to opportunities as they arise.

Recent Progress

A number of aspects of attosecond motion of electrons in the photoemission process, as revealed by Wigner time delay [1,2] 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 [3] 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. It was also 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. In addition, we 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 [4] 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 [5]. It has also been found that in the vicinity of autoionizing resonances, the time delay spectrum can become quite complicated, exhibiting both positive and negative delays across the resonance profile [6]. A model was introduced that indicated that the shape of the time-delay spectrum is related to the Fano *q* parameter [7]. And aside from the complex energy dependence of Wigner time delay across a resonance profile, our calculations indicate that the angular distribution is also quite complex [8], even to the point that at certain energies, the time delay can be positive in one direction of photoemission, and negative in another direction, a most peculiar result from a physical point of view.

Multielectron correlations in the form of interchannel coupling have been found to crucial determinants of time delay for outer subshells in the neighborhood of inner thresholds [9]; this suggests that time delay measurements can be used as a sensitive indicator of many-body interactions. Since Wigner time delay near the photoionization threshold is dominated by the long-range Coulomb interaction between the photoelectron and residual ion [4-6], 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 long-range Coulomb interaction is obviated and the effects of near-threshold shape resonances are emphasized in the time-delay spectrum. For Cl^- 3*p*, the results show significant differences, both qualitative and quantitative, between the time delays for Cl^- and Ar photoemission at low photoelectron energy [10]. In particular, the Wigner time delay in Cl^- exhibits dramatic energy dependence just above threshold, and a rapidly increasing time delay in the vicinity of the shape resonance. A strong angular dependence of time delay has also been found near the threshold region for the Cl^- case, and is absent for Ar. And we have also initiated investigations of valence photodetachment near inner-shell thresholds. Wigner time delay in photodetachment from the $3p_{3/2}$ and $3p_{1/2}$ subshells of Cl^- has been studied in the vicinity of the $2p_{3/2}$ and $2p_{1/2}$ thresholds, using the relativistic random phase approximation (RRPA). The results show time delay spectra dominated by many-body correlations along with very complicated dependence on the energy over a broad spectral range. In addition, the time delay spectra of the two spin-orbit split 3*p* subshells differ significantly from one another, thereby revealing the importance of relativistic effects even in the case of a low-*Z* system.

It has also been found that confinement resonances in the photoionization of endohedrals induce significant resonances in the attosecond time delay of photoelectron emission [11], which suggests that time-domain spectroscopy might be efficacious in studying endohedrals and clusters. And in high-Z atoms, it was found that spin-orbit induced confinement resonances [12] 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 $Xe@C_{60}$ and various new phenomena have been uncovered including a new kind of Cooper-like minima in certain of the photoionization channels which can lead to huge time delays and great sensitivity to the details of the confinement [13]; confined Xe 4d was chosen because its cross section has already been studied experimentally [14], thereby suggesting the possibility of experimental study of the Wigner time delay of $Xe@C_{60}$.

Investigation of confined atoms is a rapidly growing field. Theoretical investigations of various atoms endohedrally confined in C_{60} [15,16] abound, but experimental studies are sparse [14]. Our theoretical program is aimed at mapping out the properties of such systems, especially photoionization, to guide experiment and uncover new phenomena. We have found a huge transfer of oscillator strength from the C_{60} shell, in the neighborhood of the giant plasmon resonance, to the encapsulated atom for both Ar@C_{60} [17] and Mg@C_{60} [18]. And confinement resonances [19], 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 and confirmed experimentally [14]. 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 [20]. 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 [12], 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.

Future Plans

We will continue investigating attosecond time delay in photoemission, including a focus on how electron-electron correlation effects become important in the vicinity of inner-shell thresholds (interchannel coupling), particularly in negative-ion photodetachment, and we will work to further our understanding of how confinement affects 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 many-body interactions alter the simple behavior of photoionization; preliminary indications are that this can be very significant. In addition, the search for cases where nondipole effects are important, as a guide for experiment, and quadrupole Cooper minima, will continue, along with studies of nondipole effects in time delay. 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. 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 (2017-2019)

- “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).
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Resolving femtosecond photoinduced energy flow: capture of nonadiabatic reaction pathway topography and wavepacket dynamics from photoexcitation through the conical intersection seam

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Project Scope

The dynamics that take place within just tens to hundreds of femtoseconds following the photoexcitation of a molecular chromophore can play a critical role in how the absorbed energy is directed, allowing it to be used for a specific function (photoinduction) or dissipated harmlessly (photoprotection). Underlying these dynamics is the presence of electronic energy degeneracies in the relaxation pathways of the excited chromophores, known as conical intersections (CIs), which mediate nonradiative electronic transitions known as nonadiabatic transitions.

There is already compelling data that nonadiabatic dynamics underlie the energy-managing function of numerous molecules of importance. For example, they are a mediating factor of photochemical energy flow in electrocyclic ring opening reactions, in which the steep potential energy surfaces surrounding the CIs produce swift light-induced chemical action, allowing the envisioning of laser-controlled “molecular motors” at the nanoscale [1,2]. Important examples in biology include the highly effective ultraviolet photoprotection mechanism of DNA [3–5], the efficient phototransduction process of the vertebrate vision response [6], and the photoisomerization of the retinal chromophore underlying channelrhodopsin activation [7,8]. Ultrafast and efficient “photoswitches” based on these natural processes may someday allow controlled manipulation of solar energy or optical control of a wide range of energy management functions, through artificial and biomimetic systems employing optimized nonadiabatic transitions.

Experimental methods, however, have not yet allowed a precisely resolved and complete measurement of the electronic structure during its rapid evolution along the reaction pathway during a nonadiabatic transition – all the way from the Franck-Condon point to the CI seam and finally to the photoproduct. This constitutes a major obstacle to progress in the field, as knowledge of the topography of the reaction pathway and the wavepacket dynamics near the CI will be essential to verifying ab initio theories and to explaining chromophore function, milestones that would inform a wide body of research aiming to efficiently harness the energy of light for practical purposes.

We aim to solve this long-standing problem by establishing a method for direct and complete optical interaction with the evolving electronic structure of a molecule during a nonadiabatic transition, made possible by a multi-octave-spanning light source technology recently developed by our team and capable of providing energetic few-femtosecond probe pulses from visible through mid-IR wavelengths [9]. With a ~10-15-fs instrument response function (IRF), we aim to use visible, near-IR, and mid-IR pulses to measure the changing optical transition frequency across the full reaction pathway, which varies over several octaves during the few hundred femtosecond transition. Once the primary measurement has been established, we plan to expand the approach to 2D electronic spectroscopy, allowing pump-frequency-resolved (and thus wavepacket-kinetic-energy-resolved) investigation of the complete nonadiabatic reaction pathway.

We plan to use this approach to explore nonadiabatic transitions in three well known photochemical systems with known CIs in the photoreaction pathway and essential and complex femtosecond timescale energy flow dynamics: visual rhodopsin, channelrhodopsin and its mutants, and the DNA nucleobases in monomer and oligomer form. Comparison to ab initio modeling through collaboration with theorists in the field will aid this attempt to empirically provide and explain the reaction pathway topography and complete femtosecond timescale wavepacket dynamics of these samples in solution. If successful, this will help to allow a full physical explanation of their branching ratios and time constants, and will inform a next generation of research aiming to harness and control photoinduced energy flow on a molecular level.

Future Plans

The initial phase of our program includes instrumentation development using the capital equipment funding provided by this grant program and preliminary experiments to assess and optimize the IRF of our transient absorption pump-probe setup. The instrumentation to be developed encompasses both the pulsed source and spectrometers to be used for detection. On the laser side, we will add to existing ~10-fs sources of visible (~450-510 nm), near-IR (~670-1010 nm), and mid-IR pulses (~2000-4000 nm) two new beam-lines covering visible/near-IR (~500-700 nm) and near-IR (~1200-2200 nm) ranges, using the same adiabatic frequency conversion technique that produces our existing visible and mid-IR sources [9]. This will enable nearly three octaves of near-continuous spectral coverage for probing the dynamical transition energy of the chromophore system.

On the spectrometer side, we are adding two spectrometers with fast array detectors and high dynamic range. In addition to an existing 2D LN2-cooled HgCdTe array (128 x 128 pixel, 2-11 µm sensitivity) detector-based spectrometer, we are adding a dual-port spectrometer housing low noise and fast acquisition Si CCD (128 pixel, 200-1000 nm sensitivity) and TE-cooled extended InGaAs CCD (256 pixel, 1000-2200 nm sensitivity) detectors. To allow measurements with adequate sensitivity to resolve a $|\Delta T/T|$ of 1×10^{-4}, we have chosen detectors with high enough well depth, low enough readout noise, and low enough dark noise integrated over 100 µs (our laser pulse interval) to achieve a single-shot dynamic range of 10^4 above the noise floor. Moreover, all three detectors are capable of ≥10 kHz readout speeds – the Si and InGaAs linear arrays at full pixel number, and the 2D HgCdTe array when acquisition is binned down to 96 x 16 pixels. These spectrometers will be integrated into our computer controlled pulse shaping and detection system.

To assess the IRF, we are testing a dispersion-scan technique [10,11] for full pulse amplitude and phase characterization, a method that will allow in situ pulse characterization and avoids the need for an interferometer (as it employs an inline programmable pulse shaper instead). For an “in-practice” assessment of the IRF as we work towards our initial chromophore target, we will test the pump-probe spectroscopy method on test samples with high oscillator strength and broad spectral response (e.g., graphene).

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Peer-Reviewed Publications Resulting from this Project (Project start date: 08/2019)

None

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NEGATIVE ION FORMATION IN COMPLEX HEAVY SYSTEMS

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PROJECT SCOPE

The project's primary objective is to gain a fundamental theoretical understanding of the near-threshold electron attachment mechanism in low energy electron elastic scattering from complex heavy systems through the calculation of integral and differential cross sections and extract reliable electron affinities (EAs). The complex angular momentum (CAM), also known as Regge-pole methodology wherein is fully 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 the fundamental level near threshold, thereby uncovering new manifestations, including the mechanism of nanocatalysis, and determine reliable EAs. Low-energy electron elastic scattering total cross sections (TCSs) for the lanthanide and actinide atoms and the fullerene molecules are calculated. From the TCSs ground, metastable and excited states anionic binding energies (BEs) are extracted and compared with the available measured and/or calculated EAs. Significantly, our calculated ground state anionic BEs correspond to the theoretically challenging to calculate EAs.

RECENT PROGRESS

The determination of unambiguous and reliable EAs for complex heavy systems such as the lanthanide and actinide atoms as well as the fullerene molecules represents one of the most challenging problems in atomic and molecular physics and, to date it still plagues both experiment and theory alike. The EAs provide a stringent test of theory when the calculated EAs are compared with those from reliable measurement. Recently, a theoretical breakthrough was achieved in low-energy electron scattering from complex heavy systems through our novel and robust Regge pole methodology. Entirely new in the field of electron-cluster/fullerene collisions, the Regge pole methodology was benchmarked on the measured EAs of the C_{60} and C_{70} fullerenes [1, 2] and the Au and Pt atoms [3]. Consequently, this report focuses mainly on the unprecedented accomplishments of the Regge pole methodology in the investigation of negative ion formation in low-energy electron elastic scattering from complex heavy systems such as the lanthanide and actinide atoms as well as the fullerene molecules. From the characteristic sharp peaks in the calculated electron elastic TCSs, the anionic BEs are extracted; *for ground state scattering these BEs yield the theoretically challenging to calculate EAs.* This theoretical feat has never been accomplished before and the Regge pole methodology requires no assistance whatsoever from either experiment or other theory to achieve the remarkable results presented here. Indeed, this innovative approach to extracting reliable EAs of complex heavy systems from the ground state electron elastic TCSs calculations represents an unprecedented theoretical achievement and provides a robust and reliable method of calculating unambiguous EAs for the first time.

Many existing experimental measurements and sophisticated theoretical calculations have considered the anionic BEs of the stable metastable and/or excited negative ion formation to correspond to the EAs of the considered lanthanide and actinide atoms. This is contrary to the usual meaning of the EAs found in the standard measurement of the EAs of such complex systems as atomic Au, Pt [3] and At as well as of the fullerene molecules [1, 2]. In these systems, the EAs correspond to the ground state BEs of the formed negative ions. For fullerenes existing theories continue to struggle to obtain reliable EAs.

II.1 Fullerene Molecules

Fortunately, for the fullerene molecules excellent measured EAs are available in the literature from C_{20} through C_{92}. Benchmarked on the measured EAs of C_{60} and C_{70} [1, 2], the Regge-pole methodology was then used to calculate the ground state anionic BEs of the fullerene molecules from C_{20} through C_{240}. Our calculated ground state anionic BEs matched excellently the available measured EA values of C_{20} through C_{92}. Indeed, these results provided great credence to the ability of the Regge-pole methodology to extract from the calculated TCSs reliable EAs for the fullerene molecules for the first time. The obtained agreement represented an unprecedented accomplishment by the Regge-pole methodology in electron-cluster/fullerene collisions. For the fullerene molecules other theories are still struggling to go beyond the theoretically simple C_{20} and C_{60} fullerene molecules. It is noted here that the fullerene TCSs are very rich in metastable and excited anionic resonances, revealed for the first time in our papers 1 and 10. Thus, the careful delineation and identification of the various resonances in the TCSs, particularly for the anionic ground states are essential for the reliable calculation of their EAs. Once the ground state negative ions of the fullerene molecules have been identified, the metastable and excited negative ion formation can be delineated and identified readily. This is important because the electron elastic scattering TCSs for complex heavy systems are characterized generally by Ramsauer-Townsend (R-T) minima, shape resonances and ground, metastable and excited negative ion formation. These fullerene negative ions could be useful in *inter alia* nanocatalysis, organic solar cells and sensor technology.

Some specific accomplishments in the fullerene investigations are: We have determined the EAs of many large fullerenes such as C_{100} and C_{136}. These EAs are needed for use in the model potentials which are currently being used in calculating the Wigner time delay in A@C_n (A is an atom and n=80, ---).

II.2 Lanthanide Atoms

II.2.1 Low-energy electron scattering cross sections for the large lanthanide atoms Ho, Er, Tm, Yb, and Lu and Hf

The robust Regge-pole methodology has been used to explore negative ion formation in the large lanthanide atoms Ho, Er, Tm, Yb and Lu as well as in atomic Hf through the electron elastic TCSs calculations. The objective is to assess the reliability of the existing measured and/or calculated EAs and recommend new ones. In the electron impact energy range $0.0 \leq E \leq 10.0$ eV, we find that the TCSs are characterized generally by R-T minima, shape resonances and dramatically sharp resonances manifesting ground, metastable and excited negative ion formation during the collisions. The novelty and generality of the Regge-pole approach is in the extraction of the negative ion BEs of complex heavy systems from the calculated electron TCSs, with *those for the ground states yielding the unambiguous EAs*. The extracted anionic BEs from the ground state TCSs for the Ho, Er, Tm, Yb, Lu and Hf atoms are 3.51 eV, 3.53 eV, 3.36 eV, 3.49 eV, 4.09 eV and 1.68 eV, respectively. The ground, metastable and excited anionic states BEs are compared with the available measured and/or calculated EAs. From the existing inconsistencies and ambiguity in the meaning of the EAs of these atoms among the various measurements and/or calculations, we conclude that the EAs correspond to the ground state BEs of the formed negative ions. This resolves the ambiguous and confusing meaning of the EAs now permeating the literature.

II.2.2 Conundrum in Measured Electron Affinities of Complex Heavy Atoms

Low-energy electron scattering from the lanthanide atoms Eu, Tb, Tm, Gd, and Nd including Nb has been investigated through the calculated electron elastic TCSs using our robust Regge-pole methodology. The extracted BEs of the resultant ground and metastable anions formed during the collisions have been contrasted with the measured EAs. It has been concluded that the measured EAs for these atoms require reinterpretation and new recommended values have been presented, see our paper 3. Indeed, the calculated EAs of atoms and molecules provide a stringent test of theoretical methods when the results are compared with those from reliable measurements. And our revolutionary Regge-pole methodology will certainly provide reliable and definitive EAs for complex heavy systems without the experimental and/or other theoretical assistance.

II.3 Actinide Atoms

II.3.1 Low-energy electron scattering from atomic Th, Pa, U, Np and Pu: Negative ion formation

Here we investigate ground and metastable negative ion formation in low-energy electron collisions with the actinide atoms Th, Pa, U, Np and Pu through the elastic TCSs calculations. For these atoms, the presence of two or more open d- and f- subshell electrons presents a formidable computational task for conventional theoretical methods, making it difficult to interpret the calculated results. Our robust Regge-pole methodology which embeds the crucial electron correlations and the vital core-polarization interaction is used for the calculations. These are the major physical effects mostly responsible for stable negative ion formation in low-energy electron scattering from complex heavy systems. We find that the TCSs are characterized generally by R-T minima, shape resonances and dramatically sharp resonances manifesting ground and metastable negative ion formation during the collisions. The extracted from the ground states TCSs anionic BEs are found to be 3.09 eV, 2.98 eV, 3.03 eV, 3.06 eV and 3.25 eV for Th, Pa, U, Np and Pu, respectively. Interestingly, an additional polarization-induced metastable TCS with anionic BE value of 1.22 eV is created in Pu due to the size effect. We also found that our excited states anionic BEs for several of these atoms compare well with the existing theoretical EAs including those calculated using the relativistic configuration-interaction method. We conclude that the existing theoretical calculations tend to identify incorrectly the BEs of the resultant excited anionic states with the EAs of the investigated actinide atoms. This has led to the proliferation of incorrect EAs for complex heavy systems in the literature, suggesting a need for an unambiguous definition of the EA.

II.3.2 New manifestations in low-energy electron scattering from the large actinide atoms Cm and No

The Regge-pole calculated low-energy electron elastic TCSs for Cm and No, characterized generally by negative-ion formation, shape resonances and R-T minima, have been found to exhibit both atomic and fullerene molecular behavior near threshold. Also, a polarization-induced metastable cross section with a deep R-T minimum near threshold has been identified in the Cm TCSs, which flips over to a shape resonance appearing very close to threshold in the TCSs for No. We attribute these novel manifestations to the size effects and orbital collapse impacting significantly the polarization interaction. This provides a new mechanism of tuning a shape resonance and R-T minimum through the polarization interaction. The comparison between the Regge-pole calculated ground, metastable and excited states anionic BEs with the existing theoretical EAs demonstrates that those calculations tend to obtain metastable and/or excited states BEs and equate them incorrectly with the EAs, leading to ambiguous and unreliable EA determination. Unambiguous and definitive meaning of the EA of complex heavy systems has been recommended, namely, as corresponding to the ground state negative ion BEs of the formed negative ions during the collisions. Similar results are being obtained for the large actinide atoms, from Cm to Lr.

The radioactive nature of the actinide atoms makes them difficult to handle experimentally. However, the recent experimental determination with high precision of the BE of the least-bound electron in atomic No and the very recent (ICPEAC 2019) EA measurement of the radioactive At atom promise the measurement of the EAs of the actinide atoms. Incidentally, the measured EA of the At atom is within 4% of our predicted ground state BE of the At negative ion. For the actinide atoms Am through Lr we have now extracted their EAs from our calculated electron TCSs; they are of the order of 3 eV.

II.4. Negative ion binding energies in complex heavy systems-a Review paper

The determination of unambiguous and reliable EAs of complex heavy systems, such as the lanthanide and actinide atoms, including the fullerene molecules is one of the most challenging problems in atomic and molecular physics, when exploring negative ion formation in low-energy electron scattering.

Here we review briefly the recent progress in the determination of accurate and reliable EAs of complex heavy systems, such as the lanthanide and actinide atoms as well as the fullerene molecules, with the view of assessing the reliability of the existing measured and/or calculated EAs of these systems. We demonstrate using slow electron collisions with these systems a novel and robust approach to the determination of unambiguous and reliable EAs from negative ion formation. From the Regge-pole calculated electron elastic TCSs, characterized generally by R-T minima, shape resonances and dramatically sharp resonances manifesting anionic formation, we extract the anionic BEs for the ground, metastable and excited anionic states formed during the collisions. Importantly, the ground state anionic BEs located at the absolute values of the R-T minima are identified with the systems' EAs. Results for various complex heavy systems, including fullerene molecules are compared with the available measurements and calculations. We conclude by confirming the high quality measured EAs for the C_{20} through C_{92} fullerenes; other theories experience difficulties obtaining reliable results. However, for the lanthanide and actinide atoms, measurements and sophisticated theoretical calculations tend to identify incorrectly the BEs of the metastable and/or excited anions with the EAs, see our paper 18.

FUTURE PLANS

1) Complete the low-energy electron scattering TCSs calculations for the large actinide atoms from Cm to Lr and extract the ground, metastable and excited states anionic BEs. Also new polarization-induced phenomena due to the size effect will be explored and identified
2) Complete the low-energy electron scattering TCSs calculations for the fullerene molecules between C_{32} and C_{58} as well as between C_{140} and C_{250} and extract the anionic BEs and EAs
3) Use the Belfast R-matrix code to calculate the fine-structure BEs for the complex heavy systems as well as construct the attendant elaborate wave functions
4) Complete the extensive review paper on the electron affinities, R-T minima and anionic BEs for the investigated heavy complex systems.

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Theory and Simulation of Nonlinear X-ray Spectroscopy of Molecules

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Program 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 detecting strongly coupled electron-nuclear dynamics in molecules through electronic coherence observed in multidimensional broadband stimulated X-ray Raman signals, multidimensional diffraction with coincidence detection, improving resolution by wavelet analysis and probing time dependent molecular chirality.

Recent Progress

X-ray sum-frequency generation diffraction. A nonlinear time-resolved X-ray technique, sum frequency generation, carried out with a broadband X-ray diffraction pulse (Fig. 1a) scattering off a previously excited molecule, allows the direct imaging of ultrafast electron dynamics [1, 2] and yields snapshots of the transition charge densities, which represent the electron density variations upon optical excitation. Signals were calculated to image transition charge densities from a superposition of valence excited states generated by a short UV pump pulse [1,2]. X-ray diffraction signals from the time-evolving molecular charge density induced by selective core excitation of chemically inequivalent carbon atoms have been calculated [9]. As shown in Fig. 1, an initial narrowband X-ray pulse is used to selectively excite the carbon K-edge of the $-CH_3$ or $-CH_2F$ groups in fluoroethane ($CH_3–CH_2F$). This imaging technique can monitor the characteristic femtosecond charge migration induced by core–valence coherence.

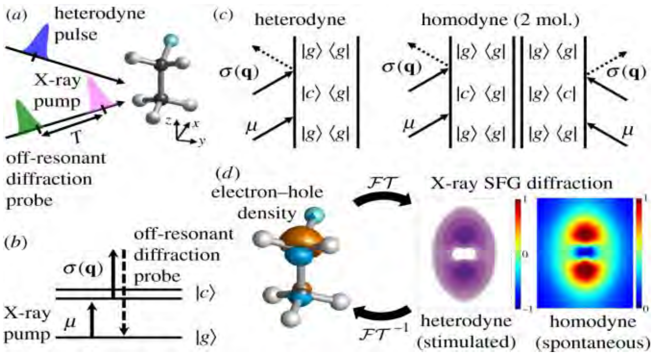

Figure 1: X-ray sum frequency generation imaging of fluoroethane.

Covariance spectroscopy. We have collaboratively studied experimentally and theoretically the effect of frequency dependent phase fluctuations on femtosecond stimulated Raman signals [10]. The interplay of frequency dependent phase fluctuations and the resulting temporal broadening of the applied pulse was established. Covariance spectroscopy of frequency resolved signal offers a powerful tool to overcome difficulties, resulting from the limited ability to define the probe's time for noisy pulses.

X-ray two photon-coincidence diffraction A spectroscopic measurement based on multidimensional photon-coincidence X-ray diffraction, which probes the correlation functions of the charge densities in momentum space was proposed [11]. In the inelastic scattering regime, the signal dynamics is determined by the transition charge densities rather than the diagonal elements of the charge-density matrix and reveals more information about the electronic excitations than conventional X-ray diffraction. The inverse Fourier-transformed signal in real space, which is a combination of correlation functions of transition charge densities, allows to identify the various scattering pathways that dominate the signal in momentum space and provides most valuable information on spontaneous electron-density fluctuations and correlations.

Quantum measurements of X-ray diffraction Monitoring spontaneous charge-density fluctuations by single-molecule diffraction of quantum light was proposed [12]. Homodyne X-ray diffraction signals produced by classical light and classical detectors are given by the modulus square of the charge density in momentum space $|\sigma(q)|^2$. However, such detection does not provide the phase, which is required in order to invert the signal to real space. We showed that quantum detection of the radiation field yields a *linear* diffraction pattern that reveals σ(q) itself, including the phase. We further demonstrated that repeated diffraction measurements with variable delays constitute a novel multidimensional measure of spontaneous charge-density fluctuations in molecules. Classical diffraction, in contrast, only reveals a subclass of even-order correlation functions. Simulations of two-dimensional signals obtained by two diffraction events were carried out for the amino acid cysteine.

Chiral signals using orbital angular momentum of light The nonlinear chiral response of molecules to circularly polarized XUV and X-ray pulse sequences and to angular-momentum-carrying light was investigated [8, 13]. In particular, X-ray pulses carrying orbital-angular-momentum provide novel probes for molecular chirality since, in the X-ray regime, the short wavelength and helical structure of the OAM beam ensure that the light field variation across the molecule is significant [13]. We have demonstrated that the combined spin and orbital angular momentum of the X-ray beam give rise to circular-helical dichroism (CHD) signals, which are stronger than ordinary circular dichroism (CD) signals and may serve as a sensitive tool for the study of molecular chirality. These results are shown in Fig. 2. A nonlocal response description of the matter-field coupling was employed to account for the short wavelength and the structured spatial profile of the field.

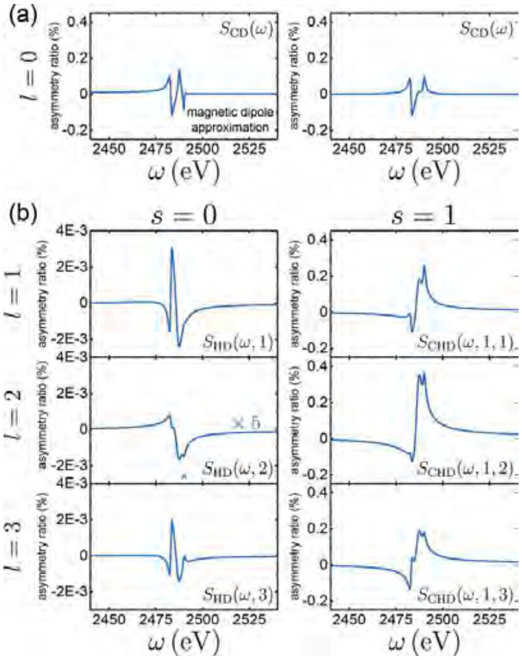

Figure 2: (a) Circular dichroism, (b) helical dichroism (HD), and (c) circular helical dichroism (CHD) signals at the sulfur K-edge of cysteine.

Multiscale wavelet decomposition of time resolved x-ray diffraction signals in cyclohexadiene

We demonstrated how the wavelet transform, which is a powerful tool for compression, filtering, and scaling analysis of signals, may be used to separate large- and short-scale electron-density features in X-ray diffraction patterns [5]. Wavelets can therefore isolate the electron density associated with delocalized bonds from the much stronger background of highly localized core electrons. The wavelet-processed signals clearly reveal the bond formation and breaking in the early steps of the photoinduced pericyclic ring opening reaction of 1,3-cyclohexadiene, which are not resolved in the bare signal.

Imaging electron-density fluctuations by multidimensional X-ray photon-coincidence diffraction

The ultrafast spontaneous electron-density fluctuation dynamics in molecules was studied theoretically by off-resonant multiple X-ray diffraction events. The time- and wavevector-resolved photon-coincidence signals give an image of electron-density fluctuations expressed through the four-point correlation function of the charge density in momentum space. A Fourier transform of the signal provides a real-space image of the multipoint charge-density correlation functions, which reveal snapshots of the evolving electron density in between the diffraction events. The technique was illustrated by ab-initio simulations of the momentum and real-space inelastic scattering signals from a linear cyanotetracetylene molecule.

Future Plans

Recent effort has focused on the investigation of time-resolved off-resonant ultraviolet/X-ray sum-frequency diffraction to image ultrafast electron dynamics. These studies exploit a nonlinear sum-frequency setup, whereby the first ultraviolet pulse creates an electronic wave packet consisting of a superposition of valence states. Subsequent diffraction of an off-resonant broadband X-ray pulse at variable delays provides time- and space-resolved snapshots of the evolution of transient charge densities. A related all-X-ray setup has also been proposed to probe the dynamics of core electronic wave packets generated by an initial X-ray pump pulse [9]. We shall extend these off-resonant XSFG studies [1,2] to core-resonant x-ray pulses. Resonant light tuned to specific cores offers an additional degree of control in multidimensional and diffraction measurements and provide valuable local dynamical information.

Inspired by the rapid experimental progress on orbital-angular-momentum-(OAM-) carrying X-ray beam and our preliminary study of the OAM-based chiral signals, we plan to utilize the OAM of light to detect the chirality of molecules, and simulate the time-resolved helical dichroism and circular helical dichroism signals of electronic and nuclear dynamics. Achiral molecules can be transformed into chiral enantiomers by interaction with linearly or circularly polarized light. The control of molecular chirality using OAM of light is most promising in the X-ray regime, where the beam varies appreciably across the molecule. We shall start by looking at how an achiral molecule, for example the planar formamide in the ground state, is transformed into chiral excited state conformations by the interaction of OAM light.

Time-, frequency-, and wavevector-resolved X-ray diffraction from single molecules as well as photon coincidence detection of multidimensional femtosecond X-ray scattering will be simulated. Our goal will be to simultaneously record structural and temporal matter information, and assign real-space geometric properties to the corresponding quantum dynamics. Existing SASE hard XFEL sources, while reaching ultrashort time and length resolutions, are noisy due to their SASE origin. They are statistically chaotic in higher orders of coherence, and monitoring the real time dynamics of molecules is a challenge.

We shall extend the results of [10], which demonstrated spectral resolution enhancement using covariance, to ultrafast diffraction. Consistent with the frequency-dependent fluctuating-phase model for the stochastic probe, we expect that frequency dispersion of diffraction signals will add valuable information. This stems from the fact that correlated frequencies add up constructively, while statistically distant contributions add up destructively in the signal. Since off resonant diffraction requires one interaction with the probe-pulse and another with the scattered mode (initially in the vacuum state), only one random phase factor per interaction seems to contribute to the signal according to our preliminary results. This suggests that covariance computation of the diffraction signal may result in noise cancellation.

Peer-Reviewed Publications Resulting from the Project (2018-2019)

1. *"X-Ray sum frequency generation; direct imaging of ultrafast electron dynamics", J. R. Rouxel, M. Kowalewski, K. Bennett, S. Mukamel. Phys. Rev. Lett. (2018) DOI: 10.1103/PhysRevLett.120.243902*
2. *"Diffraction-detected sum frequency generation; novel ultrafast x-ray probe of molecular dynamics", J. Rouxel, M. Kowalewski, and S. Mukamel. JPCL, 9, 3392-3396 (2018)*
3. *"Entangled two-photon absorption spectroscopy", F. Schlawin, K. E. Dorfman, and S. Mukamel. Acc. Chem. Res., 51, 2207-2214 (2018)*
4. *"Monitoring Ultrafast Spin Crossover Intermediates in An Iron (II) Complex; Transient Absorption vs. Broadband Stimulated X-ray Raman Spectroscopy", Y. Zhang, K. Bennett, and S. Mukamel. Journal of Physical Chemistry A, 122 (32) 6524-6531 (2018)*
5. *"Multiscale wavelet decomposition of time resolved x-ray diffraction signals in cyclohexadiene", V. Osipov, M. Kowalewski, and S. Mukamel. PNAS, 115 (41) 10269-10274 (2018)*
6. *"Impulsive UV-pump/x-ray probe simulation of vibrational dynamics in glycine", R. Mincigrucci; M. Kowalewski; J. Rouxel; F. Bencivenga; S. Mukamel and C. Masciovecchio. Scientific Reports, 8, 15466 (2018)*
7. *"Towards accurate simulation of two-dimensional electronic spectroscopy", J. Segarra Marti, S. Mukamel, M. Garavelli, A. Nenov, and I. Rivalta. Topics in Current Chemistry, 376, (2018)*
8. *"X-ray Raman optical activity of chiral molecules", J. R. Rouxel, Y. Zhang, and S. Mukamel. Chemical Science, 10, 898-908 (2019)*
9. *"Imaging of transition charge densities involving carbon core excitations in fluoroethane (CH3-CH2F) by X-ray sum-frequency generation". D. Cho, J. R. Rouxel, M. Kowalewski, J. Y. Lee, and S. Mukamel. Philosophical Transactions of the Royal Society A 377, 20170470 (2019)*
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11. *"Imaging electron-density fluctuations by multidimensional X-ray photon-coincidence diffraction", L. Ye, J. R. Rouxel, D. Cho, and S. Mukamel. PNAS, 116, 395-400 (2019)*
12. *"Monitoring Spontaneous Charge-Density Fluctuations by Single-Molecule Diffraction of Quantum Light", K. Dorfman, S. Asban, L. Ye, J. Rouxel, D. Cho, S. Mukamel. Journal of Physical Chemistry Letters, 10, 768-773 (2019)*
13. *"Probing molecular chirality by orbital angular momentum carrying X-ray pulses", L. Ye, J. R. Rouxel, S. Asban, B. Rösner, and S. Mukamel. Journal of Chemical Theory and Computation (JCTC), 15, 4180-4186 (2019)*

Theory and Simulation of Ultrafast Multidimensional Nonlinear X-ray Spectroscopy of Molecules

DE-SC0019484

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Project Scope

Emerging X-ray free electron laser (XFEL) beam sources offer new types of probes of matter with unprecedented spatial and temporal resolutions [Schoenlein 2015, Amann 2012, Allaria 2013, Marcus 2014, Pellegrini 2016]. These experimental advances must be met by robust theoretical and computational tools that provide predictive modeling capacity of the underlying electronic and structural dynamics. The latter are essential for the design of sophisticated multi-pulse experiments and for their interpretation. The research effort focuses on developing cutting-edge simulation tools for nonlinear multidimensional X-ray/optical spectroscopies. These techniques combine sequences of X-ray and optical pulses, to provide a unique experimental toolbox for probing the dynamics of core and valence electronic excitations, as well as material structure. These challenges are addressed by three research thrusts, as outlined below.

The team spans the broad and necessary expertise in theoretical spectroscopy, nonlinear optics, quantum chemistry, molecular non-adiabatic dynamics and code development. The nonlinear spectroscopy, real-time electron dynamics, molecular nonadiabatic dynamics focuses on computing the nonlinear response to X-ray pulse sequences, using multidimensional Raman signals as well as X-ray time resolved diffraction to study nonadiabatic dynamics at conical intersections. Four-wave mixing (e.g., double quantum coherence, see below) techniques will be used to study multi-core excitations and electron correlations. Such experiments were so far reported experimentally in the XUV and soft X-rays (at the Fermi facility) providing proof-of-principle for such experiments. LCLS-II will extend these results to the tender and hard X-ray regimes with much finer spatial and temporal resolutions.

XFEL pulses can launch and monitor desired non-equilibrium dynamics of electronic and structural degrees of freedom in molecular systems. Thanks to their broad bandwidth (10 eV for a 100 attosecond pulse), X-ray pulses can prepare coherent superpositions involving a large number of electronic and vibrational states that are localized at a target atom, and monitor their evolution on a fast time scale. The upcoming X-ray pulses are uniquely suitable for carrying out novel multidimensional nonlinear spectroscopic techniques, first developed in nuclear magnetic resonance, and gradually extended to higher frequency (infrared, and optical) regimes, which probe the electronic structure and nuclear dynamics of molecules through their response to sequences of short pulses with variable, carefully timed delays (Figure 1). Multidimensional techniques, which combine sequences of X-ray (and possibly optical) pulses, should offer a versatile and powerful experimental toolbox for probing the dynamics of both core and valence electronic excitations, nuclear motions and material structure. The ability of two-dimensional 2D X-ray four wave mixing spectroscopy to investigate the interactions between core excitations is illustrated in Figures 2 and 3. Since core energy levels are highly element specific, this technique can provide structural and dynamical information with high spatial, temporal, and spectral resolutions not feasible with optical pulses. Apart from the direct study of core excitations, core resonant excitations offer a fast and versatile way to trigger valence electronic excitations impulsively at selected positions and times via a stimulated Raman process and monitor their subsequent dynamics. [Biggs 2013, Kowalewski 2017]. Notable advantages of Raman techniques are that they do not require phase control of the pulses and their ability to probe valence excitations that are more chemically relevant than core excitations. Moreover, while resonant core transitions provide a short observation time window, limited by the core lifetime, valence excitations prepared by a Raman process provide a much longer window. Ultrafast decay processes such as internal conversion and intersystem crossing are ubiquitous in complex molecules, but have evaded complete understanding due to the extreme temporal and spectral parameter regimes necessary for their observation. Tunable, intense X-ray pulses hold the promise to directly probe such ultrafast processes, as well as to image the evolving electronic wave function and density matrix, ultimately revealing the very nature of elementary photophysical and photochemical events.

While sequences of coherent broadband X-ray pulses offer novel probes into the dynamics of nuclei and electrons in molecules and materials, such as electron/energy transfer in molecular complexes, predictive modeling capability for the design and interpretation of such experiments has not been developed yet. This will require a rigorous theoretical framework for connecting nonlinear spectroscopy techniques with specific dynamics to be probed. This framework needs to be interfaced with robust *ab initio* computational methods tackling numerically costly simulations of dynamics beyond the Born-Oppenheimer regime at an affordable price.

This program aims at creating modeling capabilities and making them available to the broad XFEL (e.g LCLS-II) user community to support existing and inspire new innovative experiments. X-ray pulse sequences and experiments for probing core and valence electronic excitations will be designed. With the development of efficient simulation protocols for the description of multiple-core excited state energetics and dynamics and for the interpretation of their spectroscopies, nonlinear spectroscopy techniques widely used in the visible and the infrared regimes (e.g. time-resolved photoelectron spectroscopy, time-resolved broadband stimulated Raman, and four-wave mixing) will be extended to the X-ray regime and applied to important molecular systems, thus establishing XFEL-based multidimensional spectroscopies as a novel diagnostic tool for tracing electronic and structural dynamics in molecular materials.

Recent Progress

- **Thrust 1:** *Methods/Software development and implementation*

  1. Development (UNIBO-PNNL) of a SPECTRON – NWChem/OpenMolcas interface, which will be made available in the next few months [Segatta 2019b]

  2. Development and testing (UNIBO) of a practical protocol for the computation of single- and double-core excitations in OpenMolcas (RASSCF/RASPT2 methodology) [Segatta 2019a, Nenov 2019]

  3. Development and validation (PNNL) of two-component real-time time-dependent density functional theory (RT-TDDFT) including spin-orbit (SO) and relativistic effects in NWChem [Govind 2019a]

4. Transfer of advanced algorithms and software for excited-state nonadiabatic molecular dynamics simulations from the NEXMD code developed at LANL to NWChem [Nelson 2011, Tretiak 2019]

- **Thrust 2:** *New multi-pulse experiments designed to make use of LCLS-II capabilities*
  1. We have explored (UNIBO-UCI) the information content that can be extracted from a novel proposed experiment, namely a two-dimensional coherent X-ray spectroscopy (2DXCS) technique, first introduced by Mukamel [Schweigert 2007] and further developed here [Nenov 2019]
  2. We (UCI-PNNL) are currently studying resonant X-ray sum-frequency generation, highlighting the different spectral information, which can be gained by addressing different atoms in the molecule with core-resonant X-ray pulses [Bruner 2019]
  3. We (PNNL) are exploring the emergence of novel spectral signatures in prototypical organic molecules upon creation of a heteroatom core-hole [Nascimento 2019]
- **Thrust 3:** *Applications to specific molecular systems*
  1. We have studied (UNIBO) X-ray signature of the azobenzene photoinduced dynamics via simulations of optical pump X-ray probe experiments at the Nitrogen K-edge [Segatta 2019a], and 2DCXS signals (UNIBO-UCI) of the ESCA molecule at the Carbon K-edge [Nenov 2019]. This is a benchmark molecule in photoelectron spectroscopy.
  2. Unraveling the dynamics and Fe K-edge x-ray signatures of the photoaquation reaction of ferrous hexacyanide [Govind 2019b]

Thrust 1: Methods/Software development and implementation

The focus of Thrust 1 is on the integration of the capabilities of different software developed by the different groups, and on the development of new software, to produce a collection of state-of-the-art numerical techniques for the simulation of photo-induced dynamics and different spectroscopic signals on a large variety of systems.

1. We have developed an interface that allows to extract from the output of quantum chemistry codes, e.g., NWChem and OpenMolcas, all the relevant information necessary to build an input for the Spectron code developed at UCI, and thus to simulate linear and nonlinear spectroscopy. At the current stage of development, linear and nonlinear spectra with both phenomenological broadening and more realistic line shapes (via spectral densities) are available. These require the computation of energy levels and of transition dipole moments between these levels. Moreover, to go beyond the phenomenological treatment of the spectral line shape, the coupling between the electronic states and the system intra-molecular vibrations have to be evaluated: in the framework of the displaced harmonic oscillator model, frequency computations on the optimized ground state minimum and excited states gradients at the same optimized geometry, produced by either NWChem or OpenMolcas at the desired level of theory, are the necessary and sufficient inputs [Lee 2016] used to produce intra-molecular spectral densities, later employed by the Spectron code for the line-shape. We are currently working on a pedagogical paper to advertise the capabilities of the interface by using it to produce the linear and nonlinear vibronic spectrum of the pyrene molecule, at both RASSCF/RASPT2 and TDDFT level of theory. (UNIBO-PNNL)
2. We have established (UNIBO) a protocol to simulate single- and double-core excitations of organic molecules, employing the accurate multi-reference RASSCF/RASPT2 methodology, and a new projection technique that allows one to focus precisely on selected lower-lying valence- and core-excited states. This projection technique, recently

implemented in OpenMolcas, is based on a selective removal of all configuration state functions (CSFs) with a certain occupation from a given subspace: as an example, one can set to zero all CSFs with the maximum occupation in the selected core orbitals, thus effectively projecting out all undesired valence transitions preceding energetically the core transitions. This methodology therefore allows for the simulation of linear and nonlinear signals in the X-ray domain in the framework of RASSCF/RASPT2 methodology. In particular, we have applied this technique to study the photo-induced dynamics of the azobenzene molecule via the simulation of an UV pump–X-ray probe near-edge X-ray absorption fine-structure (NEXAFS, or also XANES) experiment, as described in the Thrust 3 section, and the information content of 2DCXS signals at the carbon K-edge of the ESCA molecule (see Thrusts 2 and 3).

3. We (PNNL) have developed an initial implementation of two-component RT-TDDFT in NWChem including relativistic and spin-orbit effects (RT-SO-TDDFT). Our implementation can accommodate both effective core potentials (including spin-orbit core potentials) and all-electron relativistic calculations seamlessly. Relativistic effects have been implemented within the zeroth-order regular approximation (ZORA) via the model-potential approach. To overcome the long propagation time and peak assignment challenges of RT approaches, we have used Padé approximants instead of Fourier transforms to reduce the simulation times, and the molecular-orbital (MO) pair approach to analyze the spectral peaks. As part of our initial validation, we have applied this new development to study the UV-vis and X-ray $L_{2,3}$ edge of a range of small molecular systems including transition metal complexes. This work is in collaboration with Ken Lopata at LSU. He is also a BES-AMO PI.
4. At LANL, the advanced suite of numerical algorithms able to model mixed quantum-classical dynamics with various accuracies was implemented in the semiempirical NEXMD software, which is a powerful tool to study molecular nonadiabatic dynamics. This includes previously developed improved Surface Hopping (SH) approaches [Nelson 2011] as well as the recently implemented accurate Multiconfigurational Ehrenfest *ab-initio* multiple-cloning (MCE-AIMC) formalism [Tretiak 2019]. Altogether, this constitutes a powerful and unique platform for comparing the accuracy of various theoretical approaches such as SH, Ehrenfest and MCE-AIMC for the modeling of critical spectroscopic observables such as the dynamics of electronic coherences. To simulate multiple-core excited-state dynamics, these functionalities are being implemented in full-TDDFT, based on the NWChem software. In particular, the SH methodology is already transferred to the NWChem SH function. The NWChem SH function contains the ability to handle decoherence corrections to alleviate inconsistencies due to the classical treatment of nuclei, and advanced algorithms for tracking trivial (unavoided) crossings between noninteracting states [Nelson 2011]. These capabilities are significant improvements for the accuracy of the SH simulation and to maintain the “on-the-fly” capability. The programming progress in LANL is speeding up after we harmonized the relevant function codes between NEXMD and NWChem. Suitable interfaces are also created to enable the implementation of the SH function in developing RT-TDDFT in the near future.

Thrust 2: New multi-pulse experiments designed to make use of LCLS-II capabilities

1. Resonant X-ray four-wave mixing experiments were simulated, elucidating the information that can be extracted in such experiments. We have shown (UNIBO-UCI) that the origin of

the coupling between different core excitations at the carbon K-edge of the ESCA molecule, that shows up through the appearance of off-diagonal features in 2DCXS maps, is mainly due to effects which follow the creation of a core-hole in the first excitation(s). This strongly affects the subsequent excitations. Exciting a second core electron to a virtual orbital in the spatial proximity of an already excited core requires less energy. In contrast, exciting a second core electron from the same core orbital involves a dramatic increase in energy cost. These trends have been rationalized and described in the Ref. [Nenov 2019].

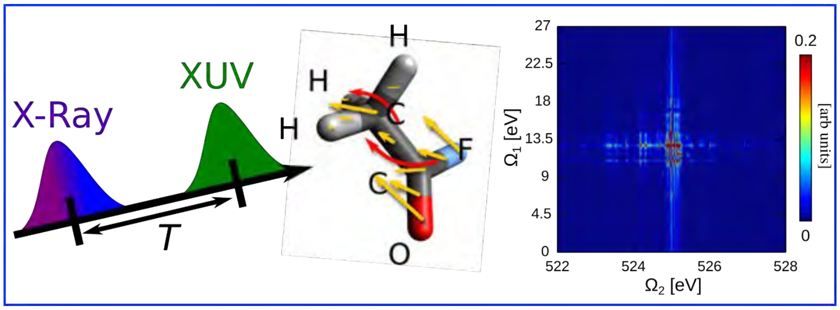

Figure 1: XSFG setup with two excitation pulses inducing current densities in acetyl fluoride, and associated 2D XSFG spectrum for an X-ray pulse tuned to the O K-edge, as a function of the X-ray pulse frequency Ω_2 and the frequency Ω_1 conjugated to *T* [Bruner 2019].

2. We (UCI and PNNL) are currently studying resonant X-ray sum-frequency generation (XSFG) in acetyl fluoride. In a two-pulse setup, an initial superposition of valence-excited states is generated by an XUV pulse, and subsequently probed by a precisely delayed, broadband X-ray pulse. This induces a stimulated X-ray Raman scattering, with core-resonant excitation followed by the emission of the X-ray signal. We elucidate the information which can be extracted from the two-dimensional SFG signal, which depends on the dispersed X-ray pulse frequency and on the time delay between XUV and X-ray pulse. Simulations were performed in acetyl fluoride, which contains well-separated K-edges (due to F, O, and C atoms) which can be resonantly excited in order to select specific dynamics. The RT-TDDFT module in NWChem is used to calculate the evolution of the system and of the current density in time and space, and obtain the associated resonant X-ray SFG signals. In order to properly model X-ray-induced double excitations with RT-TDDFT, we took advantage of a two-step protocol [Fischer 2015, Bruner 2017]. By tuning the X-ray pulse to different core transitions at the F and O K-edges, the resulting 2D spectra reveal how different nearby cores can select and couple to specific valence dynamics, and thus provide information about the properties of the molecular orbitals contributing to the valence electronic wavepacket. A manuscript on resonant X-ray SFG in acetyl fluoride has been submitted for publication [Bruner 2019].
3. We (PNNL) are currently studying the emergence of novel spectral signatures in prototypical organic molecules upon creation of a heteroatom core-hole. By preparing the molecular system in a nonstationary initial state followed by field-free propagation and a probe pulse to study excited-state response at different times, RT-TDDFT can be used to track the ultrafast valence electronic dynamics and spectroscopy. As an illustrative scenario, we are investigating how the creation of a core-hole on the oxygen atom affects the carbon K-edge features on a set of three small ketones/aldehydes, namely pentanal, 2-pentanone, and 3-pentanone. These molecules are interesting because their only difference is in the position of the oxygen atom, such that one can explore symmetry-breaking effects on the carbon K-edge spectra as the oxygen substituent—and thus the core-hole—is moved from a central (3-pentanone) to a terminal (pentanal) carbon atom. Core-hole creation results in the emergence of well separated spectral features that could be used to differentiate systems

otherwise indistinguishable. Since these new features are separated by at least 1 eV, they could, in principle, be observed experimentally. These simulations are performed with the RT-TDDFT module in NWChem. A manuscript is in preparation [Nascimento 2019]

Thrust 3: Applications to specific molecular systems

1. The photoinduced dynamics of azobenzene in its first excited-state (an nπ* state) potential-energy surface has been investigated via the simulation of time-resolved NEXAFS signals. First, we have shown that, far from crossing regions, NEXAFS signals from the nπ* state are qualitatively different with respect to signals in the GS. From the GS, core excitations of the nitrogen 1s orbital can be promoted only to unoccupied valence orbitals. Instead, when an optical pulse is initially used to prepare the system in one of its valence excited states (e.g. the nπ* state), a hole in created in the valence shell, which can be filled by the subsequent core-excitation. This translates in a clear and distinct additional transition in the NEXAFS spectrum from the nπ* state, red-shifted with respect to the GS signals. By simulating NEXAFS signals along the minimum energy path that connects the Franck-Condon point of the nπ* *trans*-azobenzene geometry to the CI with the GS, we have demonstrated that these signals are sensitive to specific geometrical changes, and can be used to track the photo-induced dynamics of the system [Segatta 2019a]. This approach has been recently implemented experimentally to study the ππ* to nπ* photo-induced dynamics in thymine [Wolf 2017].

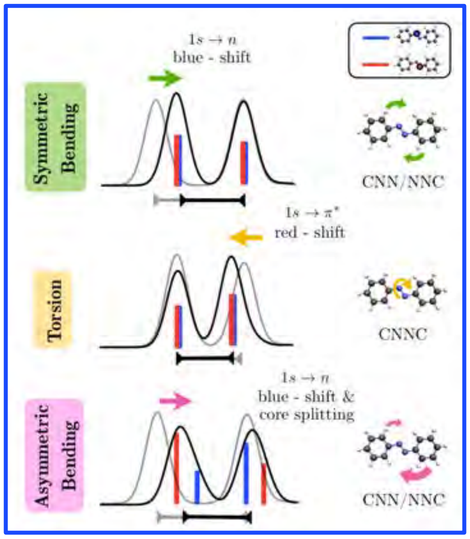

Figure 2: Impact of geometrical changes along key molecular modes on nπ*-NEXAFS spectra of azobenzene.

2. The ESCA molecule (ethyl trifluoroacetate, CF3–CO–O–CH2–CH3), has four inequivalent carbon centers, and is widely employed as a test case for the study of X-ray linear and nonlinear spectroscopy at the carbon K-edge. XANES spectra were produced at both TDDFT and RASSCF/RASPT2 level of theory, showing the same overall spectral shape, characterized by a number of peaks originating from the different core-specific excited states. Each core was observed to contribute to several bands of the total absorption spectrum, at variance with XPS, where each of them was contributing to a different band, well separated from the rest [Travnikova 2012]. Simulation of resonant four-wave mixing experiments in the X-ray domain, namely 2DCXS signals, were also performed at the RASSCF/RASPT2 level of theory: in fact, the previously introduced protocol gives access to both single- and double-core excitations, which are both of paramount importance for describing nonlinear signals. In this first explorative study, the simulation of the 2DCXS maps was performed by reducing the system complexity, i.e. considering only couples of carbon centers, and employing a restricted active space and number of states. The effect of considering signals coming from couple of carbons at a progressively increasing spatial distance has been explored. Our results show that the excitation of one core in the presence of an already excited core may produce a large shift in its excitation energy, producing off-diagonal signals in the simulated maps. The physical origin of these off-diagonal signals was identified with the spatial overlap of the starting core and arrival orbitals, which is

different for π*, σ* and Rydberg orbitals, thereby inducing spectral shifts of varying magnitude. Our results illustrate the potential of 2DCXS to become the X-ray counterpart of 2D-NMR, with its site and structural sensitivity, and show that theoretical computations are essential for the interpretation of the congested 2D maps. [Nenov 2019]

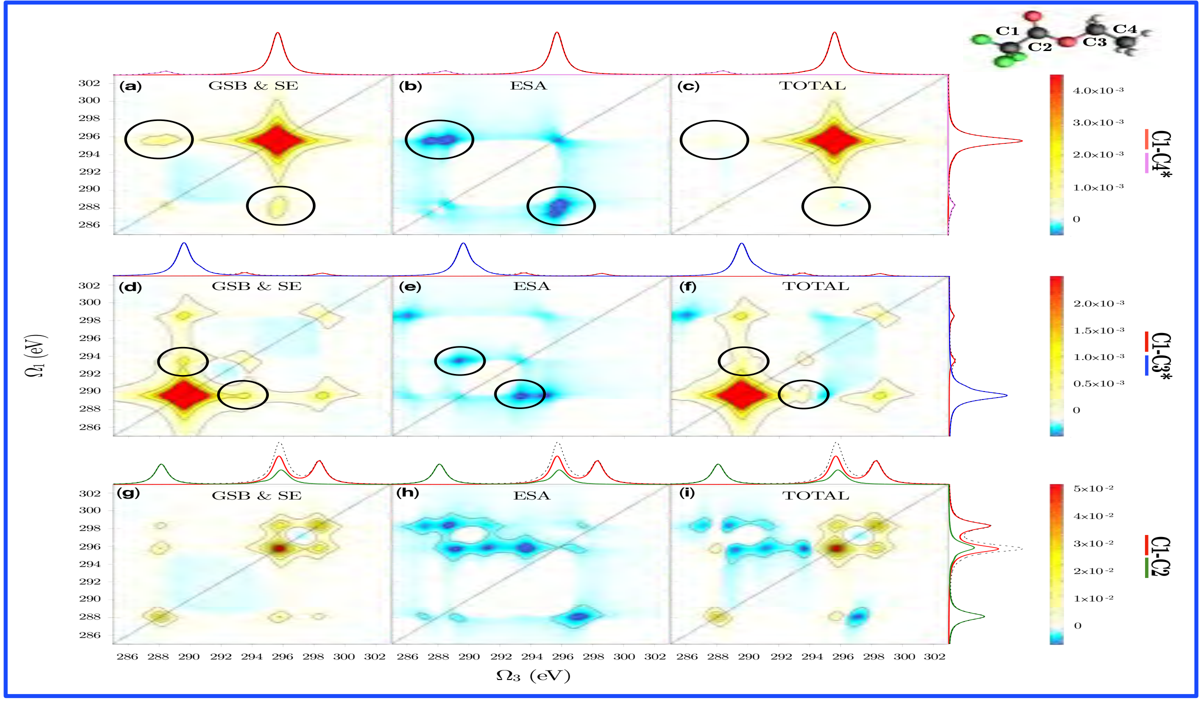

Figure 3: RASSCF-RASPT2 2DCXS spectra at t2 = 0 for different pairs of cores C1-C4 (a-c), C1-C3 (d-f) and C1-C2 (g-i) centers of the ESCA molecule. The linear absorption of the given couple of cores is also shown at the side of each map. (a,d,g) GSB and SE signals, (b,e,h) ESA signals, (c,f,i) total signal, i.e. the sum of GSB, SE and ESA signals. The black circles highlight the deletion of the cross-peaks pertaining non-interacting transitions in distant centers (GSB-SE contributions are cancelled by ESA contributions) [Nenov 2019].

3. Ligand substitution reactions are common in solvated transition metal complexes, and harnessing through initiation with light promises interesting practical applications, driving an interest in new approaches of probing their mechanisms. Using a combination of high precision time resolved x-ray absorption spectroscopy (XAS) measurements, hybrid quantum mechanical-molecular mechanics (QM/MM) molecular dynamics simulations and LR-TDDFT based x-ray absorption near edge spectroscopy (XANES) calculations with NWChem, we have elucidated the photoaquation reaction in the ferrous hexacyanide model system, where UV excitation results in the excitation of a CN^- ligand with a water molecule in the solvent. Our molecular dynamics and spectroscopy calculations support the experimental findings and explain the ~20 ps timescale for the aquation. In addition, we also predict a fluxional pentacoordinated state from our molecular dynamics simulations and the timescale for aquation as involving an interconversion between the square pyramidal (SP) and trigonal bipyramidal (TBP) pentacoordinated geometries, with aquation only being active in the SP configuration. This finding has not been explored experimentally and could be undertaken using ultrashort x-ray pulses available at XFELs. [Govind 2019b]. This work is a collaboration with the experimental BES-AMO group (PIs: A. M. March, G. Doumy, L. Young and co-workers) at the Advanced Photon Source (APS)

at the Argonne National Laboratory.

Future Plans

- **Thrust 1:**
  1. The RASSCF/RASPT2 protocol (UNIBO) will be extended for double-core excitations, designing strategies for splitting the computational complexity of multi-centers molecules over a number of cheaper calculations. This will allow to treat complex system, as e.g. the four-center ESCA molecule, without requiring truncation of the number of considered states. We also want to deliver (UNIBO-PNNL-UCI) an optimized, updated and user-friendly version of the Spectron code, which will be advertised in a separate publication. With this effort, we hope to make the Spectron code, along with interfaces to NWChem and OpenMolcas, available to a broader audience.
  2. We shall further optimize and validate our RT-SO-TDDFT implementation in NWChem. With this effort, we hope to make this capability available to the computational chemistry community in a future release of NWChem.
  3. At LANL, the SH function implemented in NWChem will be further optimized and tested on realistic molecular examples. We (LANL) intend to release this SH function in the future NWChem version, along with a corresponding publication. Moreover, we started to make preliminary studies to transfer the advanced MCE-AIMC formalism from the NEXMD to the NWChem to complete expansion of software packages.
- **Thrust 2:** An extensive study of the 2DCXS class of signals will be carried out (UNIBO-UCI), by employing different *colors* (i.e. energies) of pump and probe pulses, by studying different pulse shapes that may allow to resonantly excite a restricted number of centers, and by simulating other types of 2D signals, as the double quantum coherence signal, which may be used to reveal the single-core excitation composition of doubly excited core states. The ESCA molecule is the natural molecular framework for the application of these techniques.

  (UCI-PNNL-LANL-UNIBO) will test different nonadiabatic-dynamics methods to reveal fingerprints of passage through CIs by the so-called TRUECARS (Transient redistribution of ultrafast electronic coherences in attosecond Raman signals) technique [Kowalewski 2015]. This will be achieved with different electronic structure methodologies ranging from simple semiempirical methods to TDDFT and to high-level *ab initio* approaches, which are able to target systems of different size and complexity.

  Simulations of time- and frequency-resolved X-ray diffraction signals and X-ray sum-frequency generation diffraction imaging of transition charge densities will also be carried out. Off-resonant and resonant X-ray signals will be investigated: While off-resonant diffraction signals provide a space-resolved image of the fast dynamics in molecular systems, X-ray pulses resonant with core excitations will be used to select specific transitions localized at an atom. Stimulated X-ray Raman spectroscopy will be also studied.
- **Thrust 3:** Selected molecular targets were identified as promising systems for the application of the novel multidimensional X-ray spectroscopic techniques described in Thrust 2. Besides the already studied azobenzene and ESCA, thio-uracils (2/4/2-4 substituted), nucleobases, pyrene, porphyrins, azurin are systems of potential interest.

The following applications, that involve all the three Thrusts, are underway.

Monitoring photo-induced dynamics via time-resolved NEXAFS

1. The azobenzene study will be extended by including also ππ*-NEXAFS spectra, then following the signals along the minimal energy path from the ππ* Franck-Condon point, to the ππ*- nπ* CI, and from this CI to the nπ*-GS CI(s) (UNIBO-PNNL).
2. By considering a swarm of trajectories along the studied potential energy surfaces, we will go beyond the evaluation of the X-ray signal at selected molecular geometries, towards a realistic time-resolved simulation of such experiments.
3. The same protocol designed and applied for the UV pump – X-ray probe simulation will be extended to other molecular targets, as nucleobases and thio-uracils (UNIBO).
4. The feasibility of valence-to-core x-ray emission (VtC-XES) and time/frequency-resolved X-ray diffraction signals for transient species will be studied. We would like to predict signatures for possible XFEL experiments. For example, we would like to explore the sensitivity of these approaches to differentiate the two transient pentacoordinated, SP and TBP, species discussed earlier in the photoaquation reaction of ferrous hexacyanide (PNNL-UCI).
5. The conjugated oligomer molecular donor represents a new molecular family successfully used for organic PV. In this system, the excited state dynamics involve a complex manifold of intersecting excited electronic states where the Born-Oppenheimer approximation breaks down. We will use (e.x. p-DTS(PTTh2)2) as testbed systems for applying the new NWChem SH module to study the photo-induced dynamics when used as X-ray chromophores (LANL).

Analysis of 2DCXS signals

Based on the findings of the earlier study of nonlinear X-ray signals on the ESCA molecule, we plan a number of follow-ups (UNIBO-UCI):

- Study the relation between single-core excitation and double-core excitations, by simulating double-quantum coherence signals [Abramavicius 2009].
- 2DCXS simulations similar to what was shown in ref. [Nenov 2019], could be also carried out employing different colors of pump and probe X-ray pulses, shading light on different pieces of information in different spectral regions:
    - A single-color 2DCXS may be used to detect couplings between transitions on different cores, eventually allowing to extract structural information from these maps in a way similar to 2D-NMR spectroscopy.
    - A two-color 2DCXS pumping at the carbon K-edge and probing at ~50 eV higher energies may be used to detect the strongly blue-shifted ESA transitions associated with double-core excitations pertaining the same core, detecting signals in a bleach-free region.
    - A two-color 2DCXS pumping at the carbon K-edge and probing at ~10 eV lower energies may be used to detect de-excitation processes from singly excited cores to valence excited states. These transitions effectively fill the core-hole with a valence electron, thus resolving the electronic structure of the manifold of occupied valence orbitals.
- All the studies described above can be performed in combination with different pulse shapes, enabling the possibility of coherently exciting only selected core centers.
- 2DCXS signals could be used to identify the chemical structure of a given system: we plan to test this possibility by simulating 2DCXS maps on constitutional isomers of the ESCA molecule.

Simulation of stimulated X-ray Raman spectroscopy

Stimulated Raman signals are robust nonlinear optical techniques, which have been recently extended to the X-ray regime via core transitions thanks to the advent of XFELs [Biggs 2013, Weninger 2013, Kroll 2018]. A resonant Raman process can create valence excitations localized in the vicinity of a selected atom (X-ray chromophore) and probe them near another selected atom at a variable delay. Electronic wavepackets can thus be created and subsequently monitored by sequences of X-ray pulses. Implemented with high-quality circularly and linearly polarized beams, this should provide novel probes of time-resolved chirality.

- These multidimensional X-ray spectroscopies will be employed to determine signatures of excitation energy transfer and charge transfer in natural and artificial light-harvesting complexes. Smaller units will be modeled with wavefunction techniques, providing benchmarks for lower-accuracy methods, whereas large systems will be preferably studied using DFT modules in NWChem and semiempirical methods. Stimulated X-ray Raman spectroscopy signals of porphyrin heterodimers with different linkers, bonding structures, and geometries were previously studied [Biggs 2013]. Novel systems of interest will include xanthorhodopsin, porphyrins, or more complex DNA nucleobases and thionucleobases.
- In the light of recent experimental results [Kroll 2018], signals will also be computed for electronic dynamics in transition metal and heavy-element molecular complexes. Heavy-element complexes involving lanthanides and actinides have interesting electronic properties, whose description requires high level quantum chemistry. RT-TDDFT developments combined with advanced models of spin-orbit and relativistic effects in NWChem is expected to provide a unique practical tool for modeling electronic dynamics in these systems in the presence of XFEL probes.

Time- and frequency-resolved X-ray diffraction and sum-frequency-generation imaging

Space-resolved information on quantum dynamics in the molecules and complexes listed above will also be studied via X-ray diffraction imaging. Frequency-, time- and wavevector-resolved diffraction [Bennett 2014] and sum-frequency-generation imaging [Rouxel 2018] with coherent X-ray pulses are powerful techniques, which have been recently studied to access fast light-induced dynamics in molecules with high temporal and spatial resolution. X-ray sum-frequency diffraction imaging is especially advantageous, as it enables access to the transition charge densities, providing a direct image of the electronic excitation in a wavepacket consisting of several valence-excited states.

These diffraction techniques will be extended to account for stochastic light sources or core-resonant X-ray excitations. Applications to relevant specific light-harvesting and heavy-element molecular complexes are foreseen.

- Frequency- and time-resolved diffraction, as well as sum-frequency generation imaging, will be extended to the case of noisy X-ray light sources, such as free-electron lasers, or coherent sources with controllably added randomness. We will investigate how the information contained in the statistical properties of the noise can be exploited in order to restore the temporal resolution of the signals.
- Sum-frequency generation imaging with off-resonant X-ray pulses has been recently investigated for core-resonant excitations [Bruner 2019] in a two-pulse scheme involving a stimulated X-ray Raman process through a single broadband X-ray pulse. A three-pulse setup will be investigated, with two narrow-band X-ray pulses involved in the stimulated

X-ray Raman process. The dependence of the signal on the wavevectors of the incoming pulses will be studied.

- Signals will be simulated, in order to recognize signatures of excitation energy transfer and charge transfer in natural and artificial light-harvesting complexes, or electronic dynamics in transition metal and heavy-element molecular complexes.

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[Govind 2019b] A. M. March, G. Doumy, A. Andersen, A. Al Haddad, Y. Kumagai, M-F. Tu, J. Bang, C. Bostedt, J. Uhlig, D. R. Nascimento, T. A. Assefa, Z. Nemeth, G. Vanko, W. Gawelda, N. Govind, L. Young, "**Elucidation of the Photoaquation Reaction Mechanism in Ferrous Hexacyanide using Synchrotron X-rays with Sub-Pulse-Duration Sensitivity**", accepted in J. Chem. Phys. (2019)

Quantum Dynamics Probed by Coherent Soft X-Rays

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Project Scope

The goal of this research is to develop novel short wavelength quantum light sources, and use them to to understand the dynamic response of quantum systems to short wavelength and strong laser fields. We made exciting advances since 2017, with 17 peer-reviewed publications in top journals such as PRL, Science, Science Advances, Optica, Nature Photonics and elsewhere. Students and postdocs from our group have recently moved to DOE Laboratories (Sandia (2) and Los Alamos (2)).

Recent Progress

Light with a Self-Torque: Extreme-Ultraviolet Beams with Time-Varying Orbital Angular Momentum [1]: Light beams can possess orbital angular momentum (OAM) when the spatial shape of the beam of light rotates around its own axis. OAM beams are enabling unique applications in optical communications, microscopy, quantum optics and microparticle manipulation. To date, however, all OAM beams—also known as vortex beams— have been static i.e. the OAM does not vary in time. In recent work published in Science and featured on the cover in 2019, we experimentally validated a new property of light beams, manifested as a time-varying OAM along the light pulse: the self-torque of light. Although self-torque is found in diverse physical systems (e.g. electrodynamics and general relativity), to date it was not realized that light could possess such a property, where no external forces are involved. Extreme-ultraviolet (EUV) self-torqued beams naturally arise when the extreme nonlinear process of high harmonic generation (HHG) is driven by two ultrafast laser pulses with different OAM and time delayed with respect to each other. HHG imprints a time-varying OAM along the EUV pulses, where all subsequent OAM components are physically present. In the future, this new class of nanometer-wavelength, dynamic-OAM beams can be used for manipulating and probing the fastest magnetic, topological, molecular and quantum excitations at the nanoscale.

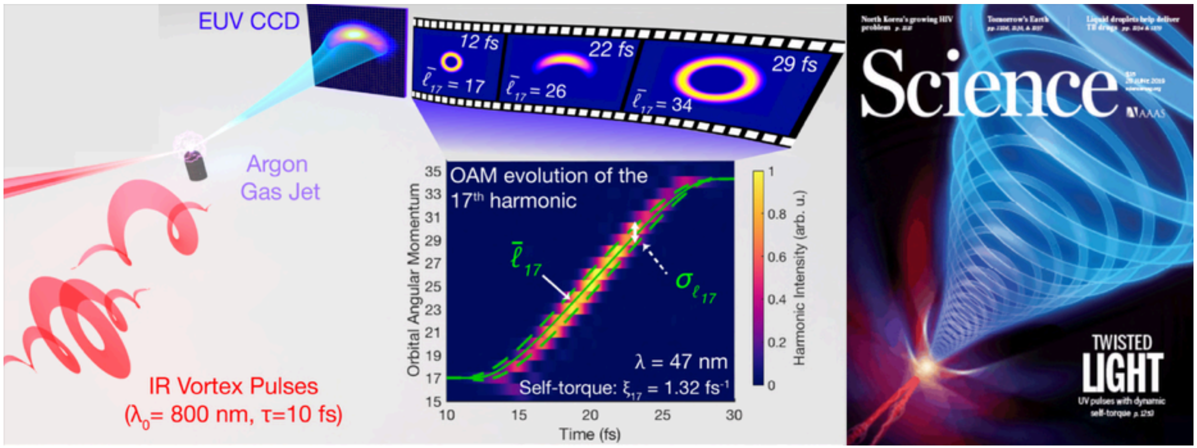

Figure 1: Unique OAM-SAM beams in new intensity and wavelength regimes - generation of EUV beams with self-torque. Two time-delayed, femtosecond infrared pulses with different OAM are focused into a gas to produce self-torqued EUV beams through HHG. The unique signature of self-torqued beams is their time-dependent OAM, as shown for the 17th harmonic (47 nm, with self-torque ξ_{17}=1.32 fs^{-1}). The self-torque imprints an azimuthal frequency chirp, which enables its experimental measurement.

Control of the Divergence, Polarization and Vortex Charge of Attosecond HHG Waveforms via OAM-SAM [2,6,7,11]: Light-matter interactions are governed by both spin and angular momentum conservation laws, which serve as a tool for controlling light-matter interactions or elucidating the dynamics and structure of complex systems. In recent work published in Nature Photonics in 2019, we uncovered a new form of simultaneous spin and orbital angular momentum conservation and showed that this allows for unprecedented control over the divergence and polarization of EUV vortex beams. High-harmonics with controlled shape, divergence and spin and orbital angular momenta are produced, which allows for manipulation of the polarization of attosecond pulses—from linear to circular—, and for the generation of circularly polarized vortices with tailored orbital angular momentum, including harmonic vortices with the same topological charge as the driving laser beam. This has important applications in the use of structured short wavelength light for nanoscale imaging and spectroscopy, particularly in view of the lack of good optics in this region of the spectrum.

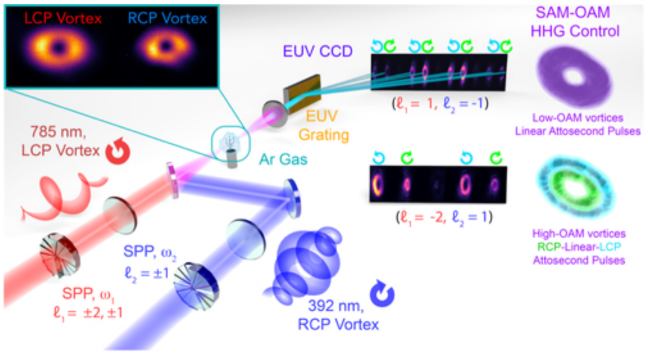

Figure 2. EUV beams with adjustable OAM-SAM can be generated by adjusting the OAM-SAM of the driving lasers using spiral phase plates or spatial light modulators. This can generate EUV beams with light-programmable structure, divergence and size.

VV probing of molecular and material dynamics [9,10,13,16]: Highly excited states of neutral molecules behave qualitatively differently than the lower excited states that are more 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. We combined vacuum-UV (VUV) femtosecond laser sources with an imaging photoelectron-photoion coincidence spectrometer to directly probe the surprisingly fast (10 - 25 fs) reaction pathways of several molecules. We also studied excited state mixing in acetone.

More recently, we developed a new method to produce ultrashort VUV pulses through low-order cascaded harmonic generation, and applied it to identify products from a pyrolysis microreactor. We demonstrated three essential capabilities: the ability to differentiate isomers, the ability to distinguish thermal products from dissociative ionization products, and the ability to study stable molecules with high ionization energy. This work harnessed cascaded four-wave mixing to generate 5MHz repetition rate VUV harmonics spanning from 3 to 18 eV, which is ideal for applications in angle-resolved photoemission from quantum materials, and photoionization mass spectrometry of molecules. We are now collaborating with Nicole Labbe from CU Boulder Mechanical Eng. and Sandia National Labs on this research. It has important implications for understanding the fastest femtosecond-to-attosecond charge transfer reactions, for understanding the interaction of light with next-generation photoresists, and for more efficient combustion.

Future work

We will extend polarization-shaped high harmonics from the EUV into the soft x-ray regions and use them to probe dynamics in molecular, nano and materials systems. Ultra-broad bandwidth, ultrafast HHG will be used implement dynamic x-ray spectroscopies in gas, solid and liquid-phase samples excited using mid-IR – UV light. We will also capture dynamics in molecules and nanosystems using photoelectron spectroscopies.

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DYNAMICS OF FEW-BODY ATOMIC PROCESSES

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PROGRAM 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. *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 (nonoverlapping), 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 [P1] in the list of project publications below.)*

B. *Kinematical Vortices in Double Photoionization of Helium by Attosecond Pulses*

By means of first-order perturbation theory analysis and solution of the six-dimensional two-electron time-dependent Schrödinger equation, two-armed helical vortex structures are predicted in double photoionization of the He atom by a pair of time-delayed elliptically-polarized attosecond pulses with opposite helicities. Originating from Ramsey interference [10] of the created pair of two-electron wave packets, each carrying a total angular momentum of unity, the predicted vortex-shaped patterns appear in the two-electron momentum distribution (i.e., the six-fold differential probability) for any energy partitioning between electrons, and are exquisitely sensitive to the time delay between the two pulses, their relative phase, their ellipticity and handedness. These kinds of vortices are found to occur for both in-plane and out-of-plane detection geometries; however, they only occur when the angular separation between the electron momenta $\mathbf{p}_1$, $\mathbf{p}_2$ is held fixed. Such vortex features are also shown to occur in the fourfold differential probability (i.e., the six-fold differential probability averaged over the emission angles of one electron). The occurrence of kinematical vortices in ionized electron momentum distributions is thus found to be a general phenomenon that can occur for any ionization process. *(See publication [P2] in the list of project publications below.)*

C. *Discontinuities in the Electromagnetic Fields of Vortex Beams in the Complex Source-Sink Model*

In investigating the description of the electromagnetic fields of a tightly-focused intense laser vortex beam (i.e., a laser beam carrying orbital angular momentum), we discovered an analytical discontinuity in what was thought to be the discontinuity-free exact non-paraxial vortex beam phasor generated from the complex source/sink model. 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 have delineated the source of the discontinuities, and provided graphical evidence of the discontinuous real electric fields for the first and third orbital angular momentum modes. A simple means of avoiding these discontinuities was deduced and presented. *(See publication [P3] in the list of project publications below.)*

D. *Dynamical Electron Vortices in Attosecond Double Photoionization of H_2*

We study electron momentum vortices in single-photon double ionization of H_2 by time-delayed, counter-rotating, elliptically polarized attosecond pulses propagating along $\mathbf{k}$ either parallel or perpendicular to the molecular axis $\mathbf{R}$. For $\mathbf{k}$ parallel to $\mathbf{R}$, kinematical vortices occur similar to those found for He. For $\mathbf{k}$ perpendicular to $\mathbf{R}$, we find dynamical vortex structures originating from an ellipticity-dependent interplay of ${}^1\Sigma_u^+$ and Π_u^+ continuum amplitudes. We propose a complete experiment to determine the magnitudes and relative phase of these continuum amplitudes by varying pulse ellipticities and time delays. *(See publication [P4] in the list of project publications below.)*

E. *Perturbative Representation of Ultrashort Nonparaxial Elegant Laguerre-Gaussian Fields*

An analytical method for calculating the electromagnetic fields of a nonparaxial elegant Laguerre-Gaussian (LG) vortex beam is presented for arbitrary pulse duration, spot size, and LG mode. This perturbative approach provides a numerically tractable model for the calculation of arbitrarily high radial and azimuthal LG modes in the nonparaxial regime, without requiring integral representations of the fields. A key feature of this perturbative model is its use of a Poisson-like frequency spectrum, which allows for the proper description of pulses of arbitrarily short duration.

This model is thus appropriate for simulating laser-matter interactions, including those involving short laser pulses. *(See publication [P5] in the list of project publications below.)*

F. *Analytic Generalized Description of a Perturbative Nonparaxial Elegant Laguerre-Gaussian Phasor for Ultrashort Pulses in the Time Domain*

An analytic expression for a polychromatic phasor representing an arbitrarily short elegant Laguerre-Gauss (eLG) laser pulse of any spot size and LG mode is presented in the time domain as a nonrecursive, closed-form perturbative expansion valid to any order of perturbative correction. This phasor enables the calculation of the complex electromagnetic fields for such beams without requiring the evaluation of any Fourier integrals. It is thus straightforward to implement in analytical or numerical applications involving eLG pulses. *(See publication [P6] in the list of project publications below.)*

G. *Molecular Symmetry-Mixed Dichroism in Double Photoionization of H_2*

The angular distributions resulting from double photoionization (DPI) of achiral atomic and molecular targets are dichroic, i.e., sensitive to the handedness of the circularly- or elliptically-polarized incident light. Dichroism in DPI of hydrogen molecules by elliptically-polarized extreme ultraviolet pulses is formulated analytically as a sum of atomic-like dichroism (AD) and molecular symmetry-mixed dichroism (MSMD) terms. The MSMD, unique to the molecule, originates from the interference of transition amplitudes to states of different molecular symmetries. For experimental detection geometries in which the AD vanishes, numerical results for the sixfold differential probabilities for opposite pulse helicities show that the MSMD is significant in the electron momentum and angular distributions and is controllable by the pulse ellipticity. *(See publication [P7] in the list of project publications below.)*

FUTURE PLANS

In addition to preparing recently completely research for publication, we are currently investigating three research problems that should be completed in the remainder of the project period:

- We are investigating how the occurrence of both *kinematical vortices* [1,2,P2] and *dynamical vortices* [P4] produced in resonant two-photon double ionization of the tritium molecule (by time-delayed, oppositely circularly-polarized attosecond pulses) are affected by molecular doubly-excited states that are produced by the first absorbed photon. In two-photon double ionization of He atom, doubly-excited states were found to break the fourfold symmetry of the kinematical vortices, as well as to lead to attosecond quantum beats in the angular and energy distributions [P1]. By considering a fixed-in-space heavy hydrogen molecule, we are thus studying how these doubly-excited state effects depend on the target as well as on the light propagation direction with respect to the molecular axis.

- We are investigating the occurrence of quantum beats in attosecond pulse double ionization of a superposition of ground state and excited He* atoms.

- We are completing our investigation of harmonic generation of the Be atom in order to elucidate the cause of the unusual plateau structure we found previously in the multiphoton regime when doubly-excited and singly-excited states are on resonance with the driving laser field [3].These investigations include the study of the sensitivity to the initial state to determine whether doubly-excited state resonance can support a plateau structure, the use of chirped driving laser fields in order to avoid scanning the driving laser field frequency, and the use of elliptically-polarized driving laser fields to study the ellipticity dependence of this multiphoton regime plateau structure. Our preliminary findings show that the multiphoton regime harmonic generation plateau occurs when singly-excited states are on resonance with the driving laser field.

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PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2017-2019)

[P1] 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 **19**, 124003 (2017) (DOI: https://doi.org/10.1088/2040-8986/aa8fc0). This is an invited contribution to a special issue on emerging attosecond technologies.

[P2] 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).

[P3] 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).

[P4] J.M. Ngoko Djiokap, A.V. Meremianin, N.L. Manakov, L.B. Madsen, S.X. Hu, and A. F. Starace, "*Dynamical Electron Vortices in Attosecond Double Photoionization of* H_2," Phys. Rev. A **98**, 063407 (2018).

[P5] A. Vikartofsky, A. F. Starace, and L.-W. Pi, "*Perturbative Representation of Ultrashort Nonparaxial Elegant Laguerre-Gaussian Fields,*" Phys. Rev. A **98**, 043820 (2018).

[P6] A. Vikartofsky, E. C. Jahns, A. F. Starace, "*Analytic Generalized Description of a Perturbative Nonparaxial Elegant Laguerre-Gaussian Phasor for Ultrashort Pulses in the Time Domain,*" Phys. Rev. A **99**, 053832 (2019).

[P7] J.M. Ngoko Djiokap, A.V. Meremianin, N.L. Manakov, L.B. Madsen, S.X. Hu, and A. F. Starace, "*Molecular Symmetry-Mixed Dichroism in Double Photoionization of* H_2," Phys. Rev. Lett. (Accepted 28 August 2019; in press).

"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 atomic and molecular physics involved in low-energy (5-250 eV) electron as well as soft x-ray (20-950 eV) interactions with complex molecular targets that have biological relevance and significance. These interactions involve deep and shallow core ionization, Auger processes, interatomic and intermolecular Coulomb decay (ICD), transient negative ion (TNI) formation, dissociative electron attachment (DEA) and shape resonances (SRs). TNIs, ICD, DEA and SRs are inelastic energy-loss events which are extremely sensitive to many body effects and changes in local potentials. All of these energy-loss channels likely contribute significantly to the chemical transformations that occur as a result of the interaction of ionizing radiation. This program uses i) energy-resolved inelastic electron scattering to examine the roles of TNIs, DEA, SRs and ICD in radiation damage of adsorbed/condensed complex biologically relevant molecules as well as ii) strong-field ionization/time-resolved x-ray transient hole absorption and x-ray emission experiments. The latter examines the dynamics of energy exchange and dissipation in complex solutions containing solvated ions.

Recent Progress:.

Task 1. X-ray and low-energy electron induced damage of DNA and RNA nucleotides: We have continued our collaboration on x-ray and low-energy electron induced damage of adsorbed molecules of biological relevance[1-5] and completed experiments at the Advanced Photon Source (APS) at Argonne National Laboratory. Specifically, the radiation damage and stimulated desorption of nucleotides 2'-deoxyadenosine 5'-monophosphate (dAMP), adenosine 5'-monophosphate (rAMP), 2'-deoxycytidine 5'-monophosphate (dCMP) and cytidine 5'-monophosphate (rCMP) deposited on Au have been measured using x-rays as both the probe and source of low energy secondary electrons. The fluence dependent behavior of the O-1s, C-1s, and N-1s photoelectron transitions were analyzed to obtain phosphate, sugar and nucleobase damage cross sections and reported in Ref. 1. The observed damage and bonding changes were dominated by the inelastic energy-loss channels associated with secondary electron capture and transient negative ion decay. Growth of the integrated peak area for the O-1s component at 531.3 eV corresponds to cleavage of the C-O-P phosphodiester bond. This yielded effective damage cross sections of 23 Mb and 32 Mb

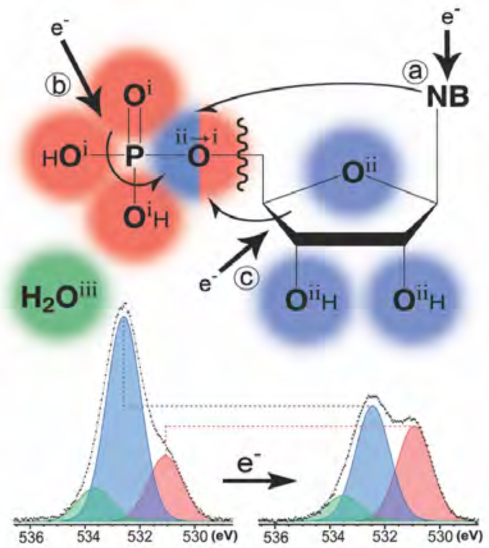

Figure 1. Depiction of the primary chemical transformation observed, annotated with XPS assignments. The cleavage of the phosphoester bond between the carbon and 5' oxygen is denoted by a wavy line. The 5' oxygen, initially assigned as O^{ii}, shifts in binding energy upon cleavage and is subsequently assigned as O^i. The damage can involve several pathways: a) nucleobase capture followed by resonant excitation, b) phosphate capture followed by direct dissociation, and c) sugar capture followed by resonant excitation. Fig. from Ref. 1.

(1 Mb = 10^{-18} cm^2) for AMP and CMP molecules, respectively. The cross sections for sugar damage were slightly lower (about 20 Mb) and statistically similar for the r- and d- forms of the nucleotides. The C-1s component at 287.6 eV, corresponding to carbons in the nucleobase ring, showed a small initial increase and then decayed slowly yielding a low damage cross section (~5 Mb). The damage process is shown schematically[1] in Figure 1. Though there is no statistical difference between the sugar forms, changing the nucleobase from adenine to cytidine has a slight effect on the damage cross section, possibly due to differing initial electron capture and transfer probabilities.

We have also extended this work at Georgia Tech. by directly irradiating multilayers of dAMP deposited on Au films with a mono-energetic low-energy (3-25 eV) electron beam. The damage induced by these electrons was examined using an x-ray photoelectron spectrometer equipped with a low flux impinging x-ray source. Comparison of the O–1s, N–1s and C–1s spectral profiles indicated decomposition of the base and sugar as well as cleavage of the glycosidic and phosphate bonds after 3-25 eV irradiation. Comparison of photoelectron spectra for all incident energies studied show that *all observed chemical changes can ultimately be attributed to the formation and decay of transient negative ions (TNIs), particularly shape resonances at or below 3 eV.* [2]

Task 2. Low energy electron induced damage of vapor condensed histidine on magnetized cobalt substrates: Radiation damage and stimulated desorption of enantiopure L-histidine on a magnetized Co film have been measured at the APS using x-rays to produce low energy secondary electrons which interact with the deposited amino acid.[6] In particular, the fluence dependent behavior of the C-1s, and N-1s photoelectron transitions were analyzed to determine damage cross sections as a function of the electron spin-polarization direction. The histidine was vapor deposited onto the substrate to a coverage of 0.5-1.5 monolayers, and the magnetization direction of the Co film could be flipped *in-situ*, meaning the damage cross-section could be directly compared for both spin-up and spin-down magnetization directions. Reversal of the Co magnetization direction was confirmed using x-ray magnetic circular dichroism (XMCD), and the damage cross-sections

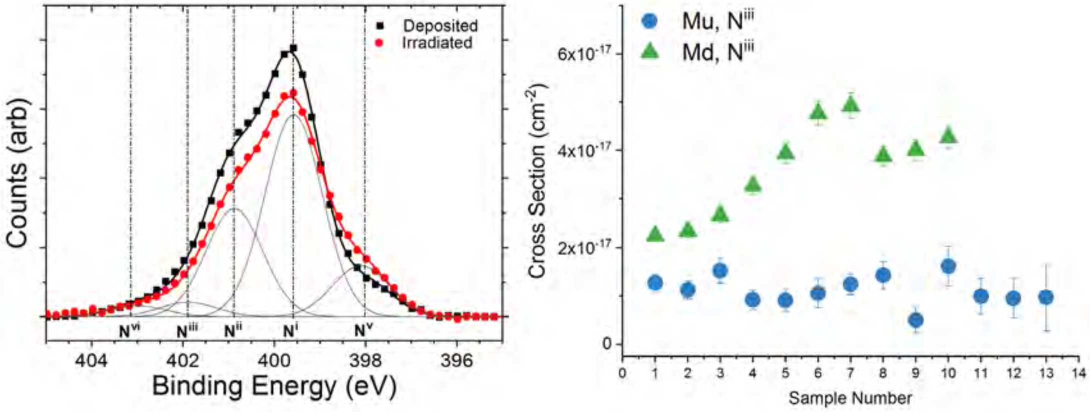

Figure 2: (left) N-1s photoelectron envelope before and after exposure to 695 eV x-ray photons. (right) Calculated cross-sections for spin-up (Mu) and spin-down (Md) configurations showing that there is a significant difference in the averages.

were determined by monitoring the strength of the photoelectron peak components as a function incident x-ray fluence. Statistical analysis of the calculated damage cross-sections for >10 points per sample showed a significant difference depending on the magnetization direction. These results show a preferential reaction of spin-down electrons with the L-histidine, with calculated cross-sections on average 2 -10 times larger under spin-down conditions.

Task 3. Investigating intermolecular Coulomb decay (ICD) at weakly interacting interfaces: We have continued studies of intermolecular Coulomb decay (ICD) on or within condensed interfaces composed of weakly interacting polyatomic molecules such as water and ethane with rare gases. Specifically, we probe ICD at interfaces by monitoring the ejected ion masses and kinetic energies as a function of incident electron energy. When using Ar, the ICD is initiated by ionization of the Ar-3s level. We have extended this work to help examine the role of boehmite, a weakly interacting but chemically relevant substrate being studied in the IDREAM EFRC as an active ICD substrate.[7] When water is adsorbed on boehmite, an efficient ICD process occurs after ionization of the Al-2s level at ~ 120 eV. We are now examining ICD with physisorbed Ar and N_2.

Task 4. Developing a cold molecular beam source for attosecond ionization of biomolecules. A technique known as laser induced acoustic desorption (LIAD) has been exploited to introduce liable biomolecules into the gas-phase for ultrafast ionization dynamics studies. We are exploring whether nanostructured metal substrates can be used to efficiently produce well defined molecular beams of nucleotides, nucleosides and short oligomer for attosecond ionization dynamics studies**.**

Future Plans

- We have beam-time allocated at the APS to complete studies on the spin-resolved secondary electron induced damage of amino acids (histidine and alanine).

- We will expand the ICD work to condensed clusters and thin-films of molecules such as water, formaldehyde, and tetrahydrofuran, a nucleotide sugar surrogate. These studies will compliment energy and time resolved studies carried out on clusters by others.[8]

- Low energy electron damage DNA and RNA nucleotides (i.e. dAMP, rAMP, dCMP, and rCMP) adsorbed on substrates that have been functionalized with amino acids will be examined using Raman micro-spectroscopy, XPS and atomic force microscopy. This information will ultimately be valuable to targeted treatment of cancer studies using radiotherapies and nanoparticles.

- A collaboration with the AMOP group at Argonne National Lab. on strong-field ionization/time-resolved x-ray transient hole absorption and x-ray emission experiments to examine the dynamics of energy exchange and dissipation in complex solutions containing solvated ions will begin. Joint proposals for LCLS beam time at will also be pursued.

- LIAD active substrates for generating cold molecuelar beams of biomolecules such as amino acids, nucleobases, nucleotides and short oligomers of DNA and RNA will continue to be developed and tested. If viable, a portable surce will be built and collaborative studies on attosecond ionization and DEA of nucleotides will begin.

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Recent publications acknowledging support from this program (2017-2019)

1. A. McKee, M. Schaible, S. Kundu, R. Rosenberg and T. M. Orlando, "Low energy secondary electron induced damage of condensed nucleotides", *J. Chem. Phys*. 150, 204709 (2019) https://doi.org/10.1063/1.5090491

Presentations acknowledging support from this program

1. T. M. Orlando, "Very low energy (<5 eV) electron induced damage of DNA and RNA nucleotides", Argonne National Laboratory Colloquium, May 1, 2018.
2. T. M. Orlando, "Very low energy (<5 eV) electron induced damage of complex biomolecules", "Miller Conference on Radiation Chemistry", Oct. 7- 11, Sicily 2017.

Structure from Fleeting Illumination of Faint Spinning Objects in Flight

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Project Scope

The advent of intense, ultrashort pulses of X-rays and electrons has made it possible to obtain two-dimensional snapshots of molecular machines performing their native function. The resulting datasets are, in general, noisy, incomplete, and recorded with substantial timing uncertainty.

We are developing a new generation of data-analytical algorithms to recover three-dimensional structure and dynamics from noisy, incomplete data recorded at highly uncertain time points. Combining concepts from machine learning, differential geometry, general relativity, graph theory, and diffraction physics, these techniques promise to revolutionize our understanding of molecular function at the atomic level.

Recent Progress

1. Extracting Spatio-temporal Information from Complex Dynamical Systems (with D. Giannakis, J. Slavinska, and Zhizhen Zhao)

Decomposition of signals into their principal components is one of the most widely used techniques for recovering - and understanding - complex phenomena. Singular Value Decomposition [1] is a celebrated example. The vast majority of these so-called eigen-decomposition techniques are linear, in the sense that they assume the data lie on a flat manifold, which is rarely the case. The extension of these approaches to the nonlinear domain [2] has provided unanticipated access to important new insights into the structure [3, 4] and dynamics [5] of molecular machines.

Essentially all eigen-decomposition techniques, whether linear or nonlinear, assume the input data can be expressed as the tensor product of temporal and spatial modes. These approaches function poorly, when the signal is not separable into such modes. We have developed a data-driven framework for extracting complex spatiotemporal patterns generated by ergodic dynamical systems [6]. This approach is able to deal efficiently with manifestly non-separable signals (Fig. 1). It is thus now possible to express dynamical information in terms of a small number of modes, even for complex signals with intermittency in both space and time.

The algorithm is based on eigen-decomposition of a kernel integral operator acting on a Hilbert space of vector-valued observables of the system, taking values in a space of functions (scalar fields) on a spatial domain. This operator combines the theory of operator-valued kernels for multitask machine learning, with delay-coordinate maps of dynamical systems. The new kernel construction naturally quotients out dynamical symmetries in the data, and asymptotically commutes with the Koopman evolution

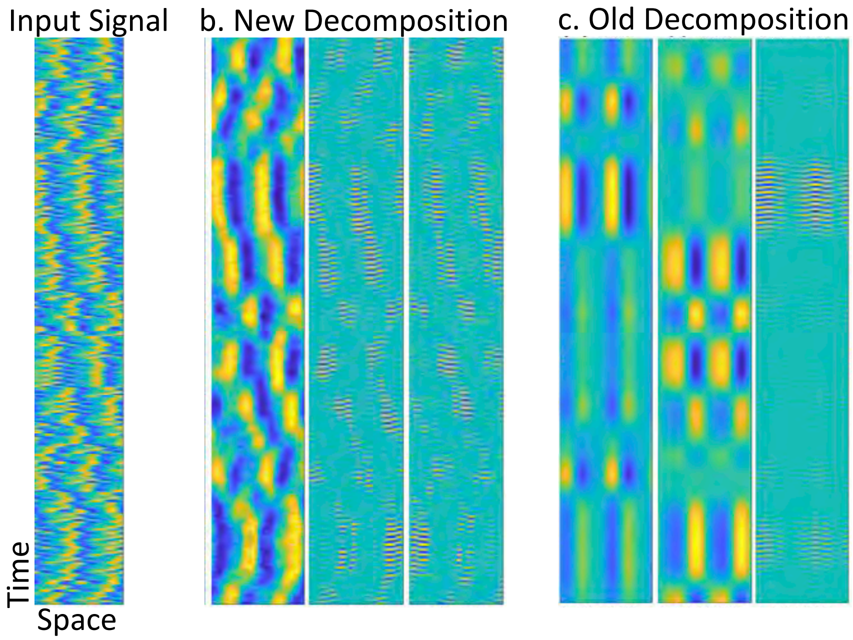

Fig. 1. Comparison of the new eigen-decomposition algorithm [6] with standard techniques [1, 2]. **a.** Input signal displaying a complex spatio-temporal behavior. **b.** Decomposition by new approach efficiently captures the signal characteristics. **c.** Standard decomposition approaches (here, NLSA [2]) cannot efficiently capture the signal characteristics.

operator of the system, enabling efficient decomposition of multiscale signals into dynamically intrinsic patterns. As shown in Fig. 1, application of this approach to the highly complex Kuramoto–Sivashinsky model demonstrates significant gains in efficient and meaningful decomposition over existing techniques based on scalar-valued kernels.

2. Conical Intersections in Large Molecular Systems

(with A. Hosseinizadeh, R. Fung, P. Schwander, and M. Schmidt)

Processes thought to involve conical intersections are ubiquitous in chemistry and biology (see, e.g., [7], [8], and references therein), if only because they represent a vital mechanism for redistributing energy in molecular systems before the onset of irreversible damage.

Spectroscopic studies of processes involving conical intersections have reached an unprecedented level of sophistication [see e.g., [9], and references therein]. But such experiments have been mainly limited to small molecules. The recent advent of time-resolved serial femtosecond X-ray diffraction (tr-SFX) has dramatically extended the range of amenable systems from simple, few-atom molecules to macromolecules, such as the Photoactive Yellow Protein (PYP)[10, 11], and Bacteriorhodopsin [12]. The resulting molecular movies reveal, in unprecedented detail, difference electron density maps before and after passage through a conical intersection. However, the time-resolutions of these molecular movies have been limited by the need to merge 2D diffraction snapshots (each inevitably recorded at a different timepoint) into 3D diffraction volumes. Due to XFEL timing jitter, the time-resolution of such molecular movies is limited to ~100fs, which is considered long compared with the time needed to pass through a conical intersection.

We have developed an approach able to recover the full diffraction volume at each timepoint without the need for merging data obtained at different (inaccurately known) times. This work is in progress, but preliminary molecular movies reveal, with single-femtosecond and near-atomic resolution, the structure-dynamical changes associated with passage through a conical intersection. These changes appear to be accomplished in ~10fs, well beyond the ~100fs time resolution achieved with standard data-analytical techniques.

Future Plans

the new eigen-decomposition approach not based on factorizing the signal into spatial and temporal modes must be evaluated in terms of computational expense and validated with experimental data. The improvement in time resolution (from 100 to ~ 1 fs) of molecular movies of passage through a conical intersection must be verified with synthetic data. If successful, these capabilities would offer unprecedented data-driven routes to understanding, and ultimately controlling the structural dynamics of ultrafast processes at near-atomic level.

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2. Time-Resolved Serial Femtosecond Crystallography at the European XFEL, S. Pandey et al. **Nature Methods** (accepted, in press).
3. Spatiotemporal Pattern Extraction by Spectral Analysis of Vector-Valued Observables, D. Giannakis, A. Ourmazd, J. Slawinska, Z. Zhao, **J. Nonlinear Science**, https://doi.org/10.1007/s00332-019-09548-1 (2019).
4. Enzyme intermediates captured "on the fly" by mix-and-inject serial crystallography, J.D. Olmos Jr. et al., **BMC Biology 16**, 59 (2018).
5. Free-electron laser data for multiple-particle fluctuation scattering analysis, K. Pande et al. **Scientific Data**, 5:180201, DOI: 10.1038/sdata.2018,201 (2018)
6. 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 14**, 878 (2017).
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Control of Molecular Dynamics: Algorithms for Design and Implementation

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A. Project Scope:

Activity in quantum control is wide-ranging, from selectively breaking chemical bonds out to rapidly growing initiatives in quantum information science. This research project addresses several key topics in optimal control of molecular dynamics. Specifically, the collective planned studies aim at exploring a number of issues at the foundation of laser control over quantum phenomenon. There is great need to design, simulate, and understand the complex dynamical phenomena involved. The collective planned studies aim at exploring a number of issues at the foundation of laser control over quantum phenomenon.

B. Recent Progress:

During the current DOE grant period, from October 2018 to September 2019, a broad variety of research topics were pursued in the general area of understanding and controlling quantum dynamics phenomena. A summary of these accomplishments is provided below:

[1] An Upper Bound on the Time Required to Implement Unitary Operations: In this study, we successfully derived an upper bound for the time needed to implement a generic unitary transformation in a "d" dimensional quantum system using d control fields. We showed that given the ability to control the diagonal elements of the Hamiltonian, which allows for implementing any unitary transformation under the premise of controllability, the time T needed is upper bounded by $T \leq \pi d^2(d-1)/2g_{\min}$ where $g_{\min}$ is the smallest coupling constant present in the system. We proved the tightness of the bound by numerically investigating randomly generated systems, with specific focus on a system consisting of d energy levels that interact in a tight-binding like manner.

[2] Ultrafast Photofragmentation of $Ln(hfac)_3$ with a Proposed Mechanism for Forming High Mass Fluorinated Products: In this work, we studied the photo-induced dissociative-ionization of lanthanide complexes $Ln(hfac)_3$ (Ln = Pr, Er, Yb) using intense ultrafast transform limited (TL) and linearly chirped laser pulses in a time-of-flight (TOF) mass spectrometry setup. We have observed various fluorine and Ln-containing high-mass fragments in this experiment, including the molecular parent ion, which were not seen in previous studies relying on relatively long-duration laser pulses (i.e., ns or longer). These new high-mass observations provide important formerly missing information for deducing a set of photo-fragmentation mechanistic pathways for $Ln(hfac)_3$. As a result, we have proposed an overall ultrafast control mechanism by combining insights from earlier studies and the fragments observed in this research to result in three proposed main distinct photo-fragmentation processes: (a) ligand-metal charge transfer, (b) CF_3 elimination, and (c) C-C bond rotation processes. We thus conclude that ultrafast dissociative-ionization could be a promising technique for generating high-mass fragments for potential use in material science applications.

[3] Generalized functional Analysis of Variance (ANOVA) for Computer Experiments with Multiple Distributions: This work provides the basis for applying the generalized functional ANOVA expansion to perform global analysis for computer experiments in the presence of multiple distributions. Specifically, we have provided a thorough analysis of the methodological aspects, assessing the consequences of using mixtures of product and non-product distributions. Numerically, we have studied the generalized function ANOVA effects on the D-MORPH regression and compared the resulting approach, methodologically and through numerical experiments, against two previously implemented alternatives in the literature. We have applied the findings to the identification of the key-uncertainty drivers of a well-known integrated assessment model.

[4] Singularity-free quantum tracking control of molecular rotor orientation: Quantum tracking control aims to identify applied fields to steer the expectation values of particular observables along desired paths in time. The associated temporal fields can be identified by inverting the underlying dynamical equations for the observables. However, fields found in this manner are often plagued by undesirable singularities. In this work, we studied a planar molecular rotor and derived singularity-free tracking expressions for the fields that steer the expectation of the orientation of the rotor along the desired trajectories in time. Simulations have been performed utilizing two orthogonal control electric fields to drive the orientation of the rotor along a series of designated tracks.

[5] On Lifting Operators and Regularity of Nonsmooth Newton Methods for Optimal Control Problems of Differential Algebraic Equations: This work presented a detailed study on nonsmooth Newton methods of optimal control problems governed by mixed control–state constraints with differential algebraic equations. In contrast to previous results, we analyzed lifting operators involved in nonsmooth Newton methods and establish corresponding convergence results. We also provided sufficient conditions for regularity of generalized derivatives of systems of nonsmooth operator equations associated with optimal control problems.

[6] Quantum control landscape of bipartite systems: In this study, we considered the control landscape of a quantum system *A* interacting with another quantum system *B*, assuming only system *A* is accessible through time dependent controls, while system *B* is not accessible. The objective was to find controls that implement a desired unitary transformation on *A*, regardless of the evolution on *B*, at a sufficiently large final time. The freedom in the evolution on *B* was used to define an *extended control landscape* on which the critical points were investigated in terms of kinematic and dynamic gradients. We showed that even if the dynamic gradient with respect to the controls alone is not full rank, the additional flexibility due to the parameters that define the extended landscape still can allow for the rank condition of the extended landscape to hold. Moreover, we observed that satisfaction of the latter rank condition subsumes any assumptions about controllability, reachability and control resources, as demonstrated by two common examples for which the rank condition holds.

[7] Quantum optimal control of multiple weakly interacting molecular rotors in the time-dependent Hartree approximation: In this study, we have performed quantum optimal control simulations, based on the Time-Dependent Hartree (TDH) approximation, for systems of three to five dipole-dipole coupled OCS rotors. The goal in the simulations was to explore the utility of the TDH approximation to model the field-induced dynamics of multiple interacting rotors in the weak dipole-dipole coupling regime. A stochastic hill climbing approach was employed to seek an optimal control field that achieves the desired objectives at a specified target time. We first showed that multiple rotors in chain and polygon geometries can be identically oriented in the same direction; these cases do not significantly depend on the presence of the dipole-dipole interaction. Additionally, we demonstrated that individual rotors in particular geometrical arrangements can be uniquely manipulated toward different objectives with the same field. For example, we showed that the two end rotors in a three-rotor chain can be identically oriented in a specific direction while keeping the middle rotor in its ground state, and any two rotors in an equilateral triangle can be identically oriented in a specific direction while the third rotor is oriented in the opposite direction. These multirotor unique objective cases exploit the shape of the field in coordination with dipole-dipole coupling between the rotors. We have made comparisons to numerically exact calculations, utilizing the TDH-determined fields, for all optimal control studies involving systems of three rotors.

[8] <u>Dual coherent and incoherent two-photon luminescence in single gold nanorods revealed by polarization and time resolved non-linear autocorrelation:</u> It is well known that gold nanorods (AuNRs) readily emit two-photon luminescence (TPL) when excited by a broad bandwidth laser pulse that is tuned to the AuNRs' localized surface plasmon resonance. The nature of the mechanism (i.e., especially its degree of coherence) is under active debate. In this work, we measured the TPL emission from single nanorods while varying the angle θ between the linearly polarized laser electric field and the nanorod's orientation. Data were best fit with a linear combination of $\cos 4\theta$ and $\cos 2\theta$ functions. While the former function may represent TPL signals arising from both coherent and incoherent processes, the later function is indicative of a purely incoherent process. To further validate this assessment, we measured TPL emission from single nanorods in a time-resolved collinear autocorrelation setup. The autocorrelation signal exhibited a large peak at zero delay, which is characteristic of coherent two-photon absorption and two lower intensity wings extending to a few picoseconds, which demonstrates the existence of a long-lived intermediate state that contributes to a two-step incoherent absorption process. We concluded that TPL in AuNRs can result from a combination of coherent and incoherent absorption processes.

C. Future Plans:

In the coming year, in addition to our continuing effort to obtain a deeper understanding of the topology of fundamental control landscapes, we plan to expand our studies on controlling quantum dynamics phenomena, with a particular emphasis on many-body molecular dynamics control. Current studies are limited to only small molecules of a few atoms and we aim to break through this key limitation. In this regard, we are especially concerned with the efficiency to find the accurate solution of the high-dimensional time-dependent Schrödinger equation, which takes precedence over the determination of an optimal control field. The limitation here arises as the Schrödinger equation is generally a high dimensional partial differential equation with spatial coordinates in N dimensions (i.e., N degrees of freedom), leading to the computational effort growing exponentially with N. To this end, we will apply the time-dependent Hartree (TDH) approximation that we have developed in the past year and also explore new avenues, including the Magnus expansion and artificial neural networks (ANN), for performing large-scale molecular optimal control simulations. Specifically, the research plan for the next reporting period aims to determine the scaling of effort involved utilizing the TDH, the Magnus and the ANNs, and to demonstrate both mathematically and numerically that the scaling is no longer exponential but rather polynomic in N, at least for practical values of N of chemical interest.

D. Peer-Reviewed Publications Resulting from this Project (2017-2019)

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[3] Control landscapes are almost always trap free: a geometric assessment, B. Russell, H. Rabitz, R.-B. Wu, J. Phys. A. Theor. **50**, 205302 (2017).

[4] Searching for an optimal control in the presence of saddles on the quantum-mechanical observable landscape, G. Riviello, R.-B. Wu, Q. Sun, H. Rabitz, Phys. Rev. A **95**, 063418 (2017).

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[18] Operational dynamical modeling of spin ½ relativistic particles, R. Cabrera, A. Campos, H. Rabitz, and D. Bondar, Eur. Phys. J. Special Topics, 227, 2195 (2019).

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"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) correlations between two electrons in highly excited states or in double continua, (2) processes for one electron in time dependent or non-separable potentials, and (3) the interaction of atomic electrons with strong electromagnetic fields. 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 (Publications 10/2018-9/2019)

Two electron physics: In Ref. [5], we applied the developments in Ref. [3] where we investigated the post-collision interaction in Auger processes to the case where the two electrons are ejected in a deliberate, time dependent fashion. The process was a pair of time separated laser pulses where each pulse ejects one electron into the continuum. By controlling the timing of the two pulses and the energy of the ejected electrons, the electron-electron interaction could be tuned. We numerically solved the time dependent Schrodinger equation over a large spatial region to accurately obtain the energy and angular correlations between the two electrons. By comparing the quantum results to those from classical calculations, we were able to identify interference that arose from two classical paths going to the same position. Properties of the interferences were studied in detail with respect to laser pulse time widths, laser frequency chirp, and ionization time delay.

One electron physics: The strong field ionization behavior of a Rydberg atom exposed to a terahertz single-cycle pulse was studied in Ref. [6]. We solved the fully three-dimensional time-dependent Schrodinger equation and the classical equations of motion to understand the limits of semiclassical approximations. For crude semiclassical calculations, there can be substantial differences in the results even for relatively large principal quantum number, n. Interference was found in the differential ionization probability and was traced to specific pairs (or more) trajectories going to the same final position.

Scattering in a cold plasma: An experimental and theoretical study of the evolution of an ultracold plasma was presented in Ref. [4] when Rydberg atoms were embedded in the plasma. The collisions between the plasma electrons and the Rydberg atoms could lead to heating or cooling depending on the principal quantum number, n. We obtained the condition that divides the heating regime from the cooling regime. In addition, we obtained estimates for the amount of heating or cooling which occurs when the Rydberg binding energy does not satisfy the crossover condition. In order to understand this system, the effect of multiple electron-Rydberg collisions needs to be correctly modeled. There was good agreement between the measurements and the numerical modeling which allowed the development of a simple and intuitive picture of how the

Rydberg atoms affect the plasma. This picture supports the concept of a "bottleneck" in the Rydberg state distribution of atoms in equilibrium with a coexisting plasma.

The graduate student supported by this grant, Xiao Wang, successfully defended his PhD during the past year. During his graduate research, he was first author on 4 papers supported by DOE. Xiao finished his last research project in 2018. The student replacing him, Akilesh Venkatesh, started research in January 2019 and has been able to very quickly come up to speed. He has finished a project involving strong field X-rays with an electric field of 107 a.u. and frequency ω=340 a.u. to understand non-linear Compton scattering seen at the LCLS and is now working on his second project.

Future Plans

X-ray physics: The graduate student Akilesh Venkatesh has lead a project to understand the non-linear Compton scattering of X-rays from bound electrons. Recent experiments at the LCLS found an anomalous wavelength shift of the 2ω photons corresponding to an extra several 100 eV transferred to the electron. We solved the time dependent Schrodinger equation for an electron interacting with ~4 X 10^{20} W/cm^2 X-rays of ~9 keV. The properties of the scattered photon was investigated using 1st order perturbation theory in the quantized electromagnetic field. We attempted to reproduce the angular dependence of the scattered X-rays as well as the wavelength as a function of scattering angle. While we were able to reproduce the angular dependence, the shift in wavelength did not match the LCLS results. The calculated shift was blue compared to free electrons instead of red and more than an order of magnitude smaller than seen at the LCLS. The results are available on the arXiv and have been submitted for publication. Akilesh is exploring the possibility for further calculations of strong field X-ray/atom interactions.

Atom-atom scattering: The graduate student Akilesh Venkatesh will lead a project to understand how a pair of atoms interact, leading to ionization. For highly excited atoms, there are quasi-conserved quantum numbers which can govern how (or, even, whether) ionization will occur. Recent experiments explore this regime so modeling the interaction is timely.

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 (2017-2019)

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Generation of Bright Soft X-ray Laser Beams

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Project Scope: The project goal is to demonstrate new compact soft x-ray lasers emitting high energy ultrashort pulses at high repetition rates by amplification in atomic transitions in high density plasmas. The combination of an increased pumping efficiency with increased repetition rates can yield soft x-ray laser beams with an unprecedented average power on a table-top for applications demanding a high photon flux. In a very recent result we have demonstrated that the efficiency of plasma-based laser-pumped soft x-ray lasers can be significantly increased by detailed pulse shaping of the pump laser using a new synthesizer. Other recent results include the demonstration of 18.9 nm wavelength laser operation at a record 400 Hz repetition rate, and the extension of repetitive gain-saturated plasma-based table-top x-ray lasers to the shortest wavelength to date, 6.85 nm *(Optica, 5, 257, (2018))*. Laser amplification was also observed at wavelengths as short at 5.8 nm by isolectronic scaling in Ni-like lanthanide ions. The work conducted under this program also includes the use of compact soft x-ray lasers in applications to problems of chemical interest, such as isotopic composition mapping of micron-size U particles with nanoscale resolution, and nanoscale resolution depth profiling analysis of a CoNCN-coated electrodes for water oxidation catalysis.

Recent Progress: Demonstration of increased efficiency of table-top soft x-ray lasers sources by pump laser pulse shaping. During this reporting period we have succeeded in demonstrating a significant increase in the efficiency of table-top soft x-ray lasers by precise tailoring of the pump pulse. Previous research has shown that control of the rate at which the pump pulse energy is deposited to create and heat the plasma can greatly influence the magnitude of the gain, as well as its duration and spatial spread. However, precise control of the shape and duration of the entire pump pulse sequence has never been attempted in spite of its significant potential to improve the performance of soft x-ray lasers. This has been the case due to the difficulty of creating joule-level pulses of arbitrary shape simultaneously having picosecond features and total pulse duration spanning several nanoseconds.

To overcome this limitation we have developed a pulse shaping technique with programmability for the generation of Joule-level pulses and pulse trains of arbitrary shapes up to 9 ns in duration. The pulse synthesizer is based in pulse stacking, a technique based on pulse splitting and recombination that has been used before, but that to the best of our knowledge had not been shown to be capable of generating synthesized pulses of Joule-level energy with a record length greater than a few hundred picoseconds and with a resolution of a few picoseconds. Our new pulse synthesizer generated 1 J pulses of up to 9 ns in duration with a temporal resolution of 8 ps. The pulse synthesizer, illustrated in Figure 1, was inserted into a cryogenically cooled high power diode-pumped Yb: YAG laser system. It can generate trains of ten sub-pulses with peak powers of > 10 GW when all the sub-pulses are of equal amplitude. The pulse synthesizer consists of three functional modules: a two-stage cylindrical telescope, an array of liquid crystals, and a set of sliding retro-reflectors inserted into a high power cryogenically cooled diode-pumped Yb: YAG laser system composed of two room temperature regenerative amplifiers and a sequence of two cryogenically cooled Yb: YAG high power amplifiers. The pulse synthesizer was placed at the output of a first regenerative amplifier. The pulse entering the pulse synthesizer is linearly polarized, and the direction of polarization can be tuned using a $\lambda/2$

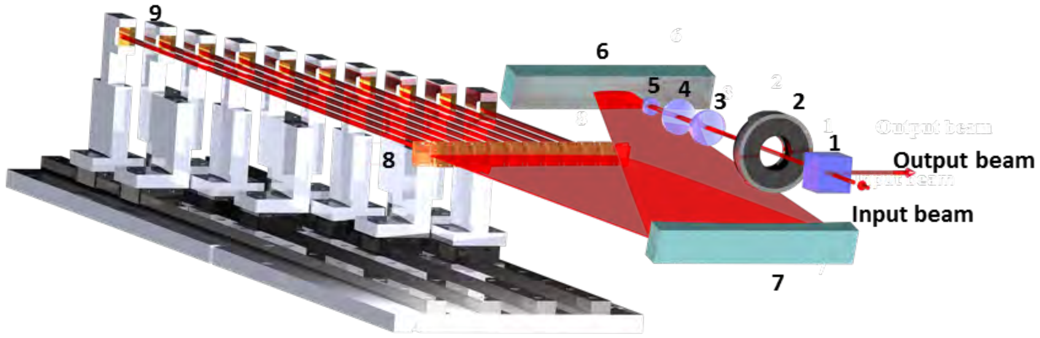

Figure 1 3-D schematic diagram of the pulse synthesizer for the generation of high energy laser pulses of arbitrary shape 1. Polarizing cube, 2. half-wave plate, 3. negative cylindrical lens, 4. positive cylindrical lens, 5. positive cylindrical lens, 6. flat mirror, 7. concave cylindrical mirror, 8. liquid crystals, 9. mobilized retroreflectors.

wave plate. The polarization state of each sub-pulse changes after it passes through a liquid crystal twice-can be controlled by selecting the voltage applied to liquid crystal.

The synthesized pulses are injected into a second regenerative amplifier which increases their pulse energy to compensate for loses in the pulse shaper ,improves their beam quality, and makes the sub-pulses co-linear as required for efficient further amplification and use. The synthesized pulse train is first amplified to ~100 mJ by the first of two cryogenically-cooled Yb: YAG amplifiers and is subsequently further amplified to 1.3 J by the second amplifier. This two stages of high power cryogenically-cooled Yb: YAG amplifiers are similar to those we demonstrated before as part of this project (C. Baumgarten et at, Optics Lett. **41**, 3339, (2016)). They are based on liquid nitrogen-cooled active mirror slabs operating in a multi-pass configuration. Another advantage of this pulse shaping technique is that the synthesized high energy pulses are chirped and can be compressed into sub-pulses of picosecond duration by a grating pulse compressor. The cryogenically cooled Yb: YAG amplifiers have a bandwidth of ~ 0.3 nm, sufficient to allow compression into pulses of sub-5 ps duration.

Using this new pulse synthesizer we tailoring the high energy pump pulses with an unprecedented degree of freedom. We are finding, as we expected, that the soft x-ray laser output energy is very sensitive to the shape of the pump pulses and that it can be optimized to achieve maximum conversion efficiency. This is illustrated for an 18.9 nm wavelength Ni-like Mo laser in Figure 2, in which the a pump pulse sequence consisting of an early train of 8 picosecond duration pre-pulses precedes a low intensity nanosecond plateau followed by a sequence of two closely separated 8 picosecond pulses. The output energy 18.9 nm soft x-ray laser is measured to depend greatly on the characteristic of the early picosecond pulse train. In all cases the early picosecond pulse train contains 5 % or the total pump energy. However, when this pulse trains increases in complexity from a single pulse to three pulses separate by 50 ps, the soft x-ray laser output pulse energy increases from 0.03 μJ to 3.7μJ. The latter represents a factor of two increase in efficiency and pulse energy over the highest values we had previously achieved. The pump pulse optimization is still ongoing, exploiting the flexibility provided by the control of the amplitude and delay between ten picosecond duration pulses. Comparison with simulations will provide additional insight on the plasma physics and guide further optimization. Nevertheless, the result presented above already represent a record output for this type table-top lasers, and a promising approach to improve the efficiency of compact plasma-based x-ray lasers in general.

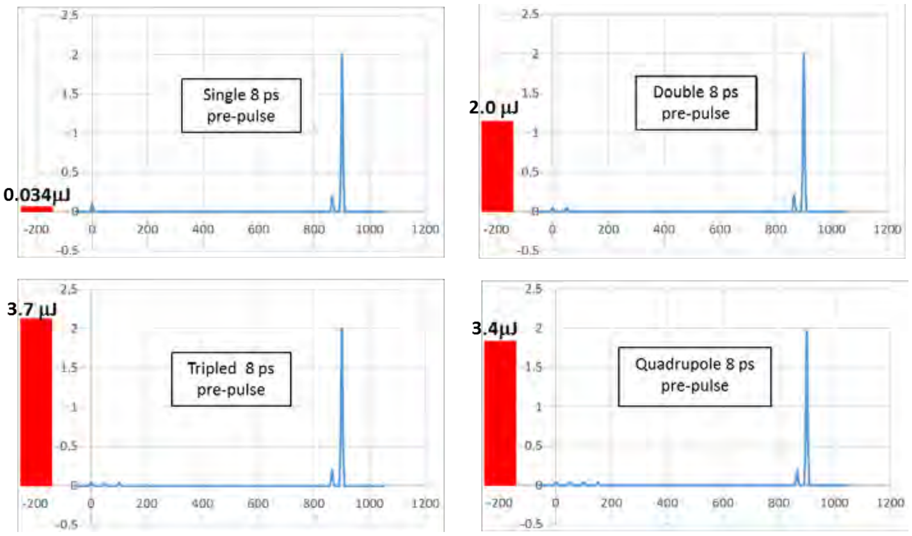

Figure 2. Output pulse energy of an 18.9 nm Ni-like Mo laser excited with different synthetized pulses (red bars). The pump pulses (blue traces) differ on the composition of the early train of 8 ps pre-pulses, that in all cases contains 5% of the total pump energy.

Simulations of atomic x-ray laser amplification in the carbon window. We have conducted simulations to explore the possibility of demonstrating gain saturated atomic x-ray lasers near the carbon K-edge, in the "carbon window" for the first time. Model simulations show that a direct extrapolation of the approach we successfully used to obtain strong lasing in the atomic transitions of Ni-like Gd (λ = 6.8nm) and other lanthanide elements during the present grant period would not provide sufficient gain. A reason for this is that as the degree of ionization of the plasma increases, as required to obtain lasing at shorter wavelengths in Ni-like ions, the electron density required to achieve the necessary electron impact excitation rate also increases. Lasing in atomic transitions with wavelengths in the "carbon window" requires an electron density that starts to approach the critical density, $n_{ec}=1.7\text{x}10^{21}$ cm^{-3} for the λ = 800 nm light from the Ti:Sa pump laser used. Consequently, in plasmas generated with near infrared pump lasers the region where x-ray amplification occurs is too close to the critical density surface. In this region the electron density gradient is too step to allow for the amplified x-rays to travel the necessary distance through the gain medium without being refracted away. This results in very low amplification, leading to a very low output energy pulse (black line in Figure 3) for XRL on Ni-like ions of Ta operating near 4.5 nm.

To overcome this limitation, we are exploring to depart from the traditional approach used in all the atomic plasma-based x-ray lasers demonstrated to date, consisting of using the fundamental wavelength of the pump laser. Instead, will use the second harmonic, λ = 400 nm in the case of a Ti:Sa pump laser. The shorter pump wavelength will increase by 4x the critical density to $6.9\text{x}10^{21}$ cm^{-3}. As a result, the optimum plasma region for x-ray amplification will occur in a

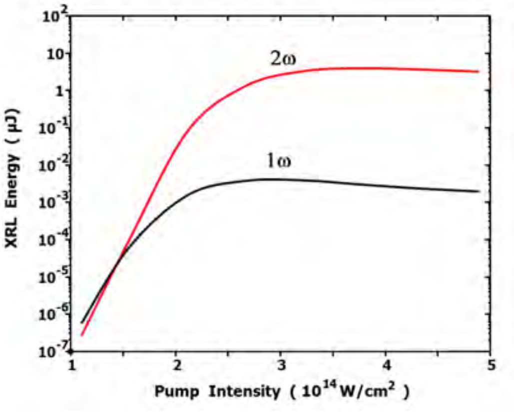

Figure 3. Comparison of the simulated output pulse energies for λ =4.5 nm Ni-like Ta 4d-4p x-ray laser as a function of pump intensity for: λ = 800 nm pump pulse (black curve) and a second harmonic pump pulse (red curve). Second harmonic pumping is key for the successful operation of the laser.

plasma region with the required higher density but further from critical density region and hence reduced density gradient. Hydrodynamic atomic physics simulations we have conducted for a Ni-like lutetium Lu (Z=71) x-ray laser (λ=4.7 nm) in a line focus plasma generated with λ = 400 nm pump pulses of 40 ps duration impinging at near normal incidence onto solid targets at an intensity of $3\text{x}10^{14}$ W cm^{-2} predict a gain coefficient of ~ 50cm^{-1}. This gain is sufficient to saturate the gain medium and generate pulse energies of several μJ. Similar gains are computed for other transitions at wavelengths between 4.26 nm and 5.8 nm from Ni-like ions ranging in Z from Er (Z=70) to W (Z=74). They cover the carbon window, and in the case of W the shortest wavelength transition is in the water window (λ~4.23 nm).

Future Plans: During the next year of the project we plan to complete our study of increasing the pulse energy and efficiency of high repetition rate soft x-ray lasers by temporally tailoring the pump pulse sequence, aiming to higher average power tabletop coherent soft x-ray sources. We will also continue expanding compact plasma-driven soft x-ray lasers to shorter wavelengths using transient collisional excitation of atomic transitions in highly ionized atoms, aiming also to shorter pulse duration. We plan to study approaches to obtain 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. In addition we plan to continue taking advantage of the large energy per pulse, and short wavelength of soft x-ray lasers to study chemistry and material science problems.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

1. S. Wang, C.M. Baumgarten, Y. Wang, B.A. Reagan, A.P. Rockwood, H. Wang, L. Yin, K. Wernsing, H. Bravo, B.M. Luther, C.S. Menoni and J.J. Rocca, "High-Power Ultrashort Pulse Lasers to Pump Plasma-Based Soft X-Ray Lasers," IEEE J. Selected Topics in Quantum Electronics, 25, 8800515, (2019) *(Invited Paper).*
2. A.Rockwood, Y. Wang, S. Wang, M. Berrill, V.N. Shlyaptsev, and J.J. Rocca, "Compact gain-saturated x-ray lasers down to 6.85 nm and amplification down to 5.85 nm". Optica. **5**, 257, (2018).
3. A.Rockwood, Y. Wang, S. Wang, V.N. Shlyaptsev, J. J. Rocca, and M. Berrill, "Compact Gain-Saturated X-ray Lasers Down to 6.85 nm". Optics & Photonics News. **29**, (2018).
4. R. Muller, I. Kuznetsov, Y. Arbelo, M. Trottman, C.S.Menoni, J.J. Rocca, G.R. Patzke, D. Bleiner, “Depth-Profiling Microanalysis of CoNCN Water-Oxidation Catalyst Using a lambda 46.9 nm Plasma Laser for Nano-Ionization Mass Spectrometry,” Analytical Chemistry, **90**, 9234, (2018).
5. V. Vozda, T. Durian, J. Chalupsky, V. Dedic, V. Hajkova, P. Hlidek, L. Juha, M. Kozlova,. M. Kraus, J. Kunc, M. Rejjan, L.Vysin, J.J. Rocca and J. Franc. “Micro-Raman mapping of surface changes induced by XUV laser radiation in cadmium telluride,” J. Alloys and Compounds, **763**, 662 (2018).
6. L. Vysin, T. Burian, E.Ukraintsev, M.Davidkowva, M. Grisham, S. Heinbuch, J.J. Rocca, and L. Juha. “Dose-rate effects in breaking DNA strands by short pulses of extreme ultraviolet radiation”, Radiation Research, **189**, 466, (2018)
7. T. Green et al , “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).

Investigating charge transfer and charge migration on the few- to sub-femtosecond time scale

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Program Scope:

Intramolecular motion of electronic charge is one of the most important primary events in all photoinduced processes in chemistry and biology. Understanding charge dynamics at the microscopic level is essential for achieving fundamental insights into these phenomena and, in a longer-term perspective, for improving technological applications related to energy conversion and storage, which rely on charge motion and separation. This project aims at studying ultrafast charge dynamics (more specifically, charge transfer and charge migration) in gas-phase molecules utilizing novel capabilities provided by the development of the XFEL facilities, and by recent progress in advanced theoretical modelling. This includes time-resolved experiments investigating charge motion triggered by valence and inner-shell photoabsorption, studies of distance-dependent charge transfer processes in dissociating molecules, detailed theoretical simulation of these experiments, and further development of theoretical tools required for the adequate description of the molecular states involved. A basic underlying concept of these studies exploits the fact that X-rays can specifically probe the atomically localized core-level electrons, which makes the XFEL-based techniques sensitive probes of the spatial (element-specific) localization of an electronic wave packet. A particular focus of this project is placed on creating a coherent superposition of molecular states launching a well-defined electron-hole wave-packet, visualizing its evolution in time within the first femtosecond after the photoabsorption, and understanding how subsequent coupling to nuclear motion affects these dynamics. One of the central goals of this program is to identify the observables most sensitive to such ultrafast charge motion [P1, P2, R1] and developing experimental techniques capable of revealing these observables, often relying on a few-particle coincidence measurements [R2, R3]. Technically, this project relies on the recent development of attosecond X-ray pulses at LCLS [R4], which paves the way towards achieving sub-femtosecond temporal resolution, and on the availability of high repetition rate XFEL facilities such as the European XFEL and especially the upcoming LCLS-II, which makes coincident measurements feasible and efficient.

In order to advance our understanding of different aspects of ultrafast light-driven charge dynamics, we identified four main thrusts, on which we have focused our efforts:

Thrust 1: *X-ray pump – X-ray probe measurements aimed at understanding and disentangling charge transfer and charge migration dynamics following X-ray photoabsorption.*

Thrust 2: *UV pump – X-ray probe experiments aimed at studying intramolecular charge transfer reactions triggered by valence-shell photoabsorption.*

Thrust 3: *Studies of distance-dependent charge transfer processes in dissociating molecules*

Thrust 4: *Theory development*

Thrust 1*: *X-ray pump – X-ray probe experiments **(Rudenko, Rolles, Greenman, Santra)**

Recent progress

The final goal of this project is to image in real time electronic dynamics unfolding on the time scale of few hundred attoseconds, before the onset of the nuclear motion The LCLS is currently the only XFEL facility worldwide, which offers attosecond X-ray pulses for user operation. Therefore, because of the current LCLS shutdown, our main efforts in *Thrust 1* of the project during the first year aimed at developing concepts and tools, which would facilitate X-ray pump – X-ray probe experiments with sub-femtosecond resolution once the corresponding X-ray pulses become available, and on extracting complimentary time-resolved information from coincident measurement with a single X-ray pulse. Finally, we contributed our concepts and ideas to the multi-institutional campaign proposal aimed at utilizing the attosecond capabilities during the upcoming LCLS–II runs, in particular, for the early-phase operations with 120 Hz repetition rate. All four PIs of this project contribute to each of the activities outlined in this section.

Detecting coherent core-hole wave-packet dynamics in N_2 by time- and angle-resolved inner-shell photoelectron spectroscopy

To demonstrate the feasibility of mapping ultrafast light-induced charge dynamics in real time, we proposed an experimental scheme to launch and detect core-hole wave-packet oscillations in the nitrogen molecule, and performed detailed modeling of the outcome of such experiment [P1]. In this scheme, a broadband attosecond X-ray pulse core-ionizes the nitrogen molecule, preparing a coherent superposition of two electronic eigenstates resulting from the ionization of the $1\sigma_g$ and $1\sigma_u$ core orbitals. A subsequent attosecond X-ray pulse probes the evolution of the electron dynamics by ionizing the N_2^+ [$1s^{-1}$] molecular ion into a double-core-ionized state. The central photon energies for the first and the second pulse are 430 eV and 440 eV, respectively. As illustrated in Fig. 1, the oscillation of the core-hole between the two atomic sites can be imaged by

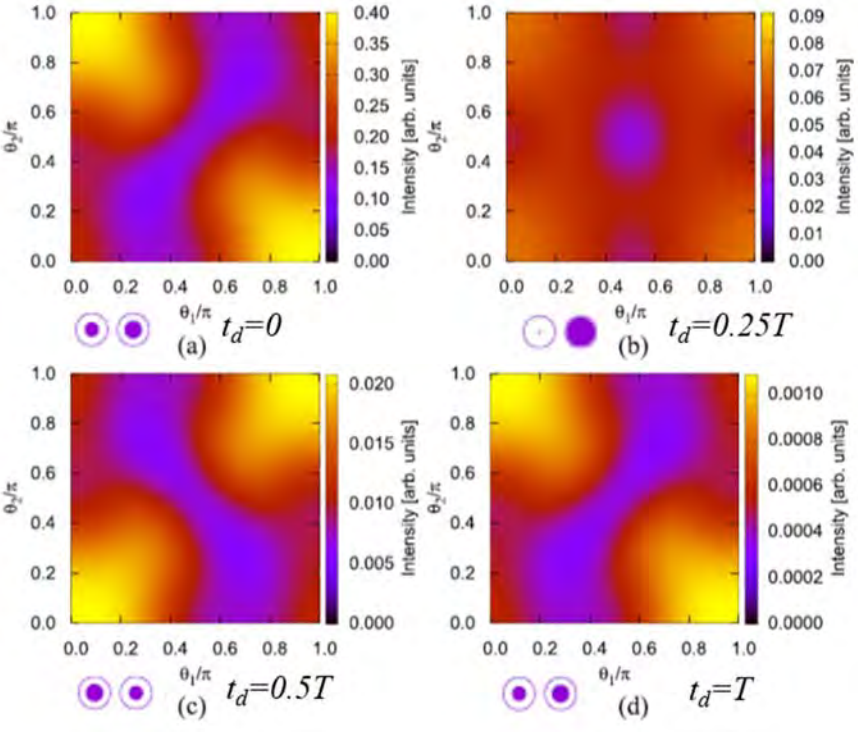

Figure 1: *Intensity of two photoelectrons stemming from core-shell ionization and subsequent double-core-shell ionization of nitrogen molecule as a function of angles θ_1 and θ_2 to the molecular axis for four different delay times t_d between two attosecond x-ray pulses (in units of T, where T is the core-hole oscillation period of 41.4 fs). The data are integrated over azimuthal angles ϕ_1 and ϕ_2 and averaged over the orientation of the molecular axis with respect to the polarization axis. The oscillation of the hole density from the left to the right atom is sketched in each subplot with the filled circle representing presence of the hole.*

measuring the angular correlation between the two photoelectrons at different time delays between the two pulses. As can be seen from Fig. 1(a), the photoelectrons initially tend to be emitted into opposite hemispheres of the molecule. At $t_d = T/4 \simeq 10$ fs, there is an equal contribution for the two photoelectrons to be emitted into the same direction and into the opposite directions (Fig. 1(b). After half a period ($t_d = T/2 \simeq 21$ fs, Fig. 1(c)), the photoelectrons tend to be emitted into same hemispheres of the molecule. As the core-hole state efficiently relaxes via Auger decay and has a lifetime of ≃7 fs, any core-hole wave-packet dynamics in $N_2^+ [1s^{-1}]$ is strongly suppressed at larger times (as can be seen in the changing scale of color palette from Fig1(a) to 1(d)), and only the first half period of such dynamics is therefore of practical relevance.

The feasibility of the experiment presented here relies on the ability to generate synchronized pairs of attosecond X-ray pulses with somewhat different photon energy, to measure the angular correlation between the two photoelectrons detected in coincidence, and to distinguish the photoelectrons resulting from both ionization steps from the contributions of the competing channels (e.g. those corresponding to the 2nd ionization happening after the Auger decay). All these conditions are expected to be fulfilled when the LCLS-II becomes fully operational at a repetition rate of 100 kHz or higher. Moreover, even though the angular correlations between the two electrons still manifest the clear signatures of the core-hole oscillation if both electrons are measured in the laboratory frame, the detection of the electrons in the molecular frame (as shown in Fig. 1) allows for much more direct interpretation of the results [P1]. In the experiment, this can be achieved via coincident detection of the two photoelectrons with one or two ionic fragments. While our count rate estimates suggest that this could also be readily achieved exploiting the expected high repetition rate of LCLS-II, in the following section we discuss the results of the first ion-electron coincident measurements, which demonstrate the feasibility of this kind of experiments already at much lower repetition rate.

Probing ultrafast X-ray induced dynamics via sequential two-photon absorption and ion-electron coincident measurements

Pump-probe spectroscopy is a key technique for time-domain studies of ultrafast light-induced reactions. With the development of FEL technology, a variety of FEL pump – FEL probe experiments in XUV or X-ray domain have been performed over the last decade, largely motivated by the advantages of using a single high-energy photon for both initiating and probing the dynamics [R5]. The temporal resolution of these experiments ranges from few tens to a few femtoseconds, with a realistic hope to enter the sub-femtosecond regime using synchronized pairs of attosecond X-ray pulses recently developed at the LCLS [R4]. However, the retrieval of time-resolved information does not necessarily require a two-pulse pump-probe configuration. In fact, every two- or multiphoton absorption process in the XUV or X-ray domain represents an indirect pump-probe measurement, where the first absorbed photon creates a molecular wave packet (typically in a highly excited or ionic state(s), bound or dissociating), and the following photoabsorption step(s) probe it on the timescale of the pulse. The (average) time delay between the two steps can, in principle, be retrieved from the experimental observables such as the ion kinetic energy release (KER). While several measurements of ion KER resulting from molecular breakup during multiple sequential photoionization have been discussed in this context [R5-R7], an important next step would be to exploit this relation for resolving in time such rich source of information on molecular structure as the emitted photoelectrons.

We made the first step in this direction by measuring in coincidence ions and electrons stemming from two-photon core-shell ionization of N_2 molecule [R2]. The experiment was performed at the LCLS in 2018 (in-house experiment led by P. Walter, SLAC) employing ~80 fs pulses with a few tens of μJ pulse energy and the photon energy centered at 506 eV. The LAMP instrument with the double-sided velocity map imaging (VMI) spectrometer was used to detect photoions and photoelectrons in coincidence [R8]. The main results of this measurement are presented in Figs. 2 and 3. While the 3D momentum vectors of the fragment ions could be calculated from the measured times-of-flight (TOF) and hit positions on the detectors, the TOF range was too short to resolve the corresponding momentum components for electrons, and only 2D momentum distributions have been measured. Core-shell single-photon absorption at this photon energy predominantly produces doubly or triply charged molecular ions. Therefore, both non-coincident and coincident ion spectra in Fig. 2(a) and 2(b) clearly show signatures of two-photon processes. They are also clearly reflected in the photoelectron spectra coincident with N^{3+} ions in Fig. 2(c). While all measured photoelectron spectra manifest a major peak around 96 eV reflecting the core-shell ionization of a neutral N_2 molecule, the electrons detected in coincidence with N^{3+} also exhibit a pronounced peak around 67 eV due to the ionization of molecular dication created by the first ionization and subsequent Auger decay. The electrons corresponding to the two-sided double core hole production considered in the previous section appear as minor contribution at ~81 eV. Because of the moderate pulse energies and the pulse duration being much longer than the Auger lifetime, all double-core hole channels in this experiment are expected to be rather weak.

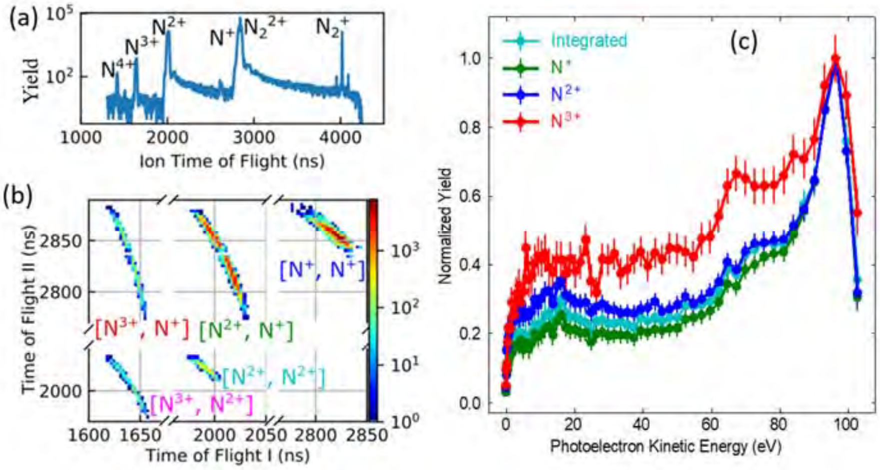

Figure 2: ***(a)*** *The time-of-flight spectrum of detected ionic fragments.* ***(b)*** *Ion-ion coincidence spectrum.* ***(c)*** *The photoelectron spectrum detected in coincidence with a particular nitrogen ion. Since the background resulting from stray electrons and high-energy Auger electrons prevented reliable inversion of the VMI images for electrons, the shown electron data represent the radial distributions obtained from the non-inverted VMI images and rescaled in units of energy.*

In Fig. 3, we focus on a specific ionic final charge state pair ($N^{3+} + N^+$) resulting from the two-photon absorption, and consider its KER distribution (Fig. 3(a)). Intuitively, one can expect that the high KER region should reflect the events where the molecule remains bound after the first photoabsorption, whereas the low KER part of the spectrum is likely due to dissociating molecules. This behavior was clearly observed in an earlier X-ray pump – X-ray probe experiment on N_2 [R9]. The separation between the contributions from the bound and dissociating parts of the nuclear wave packet is also reflected in the two-fold structure of the calculated KER distribution (cyan line and symbols in Fig. 3(a)), where it is more pronounced than in the experiment. In Fig. 3(b), we plot the spectra of the photoelectrons detected in coincidence with [N^{3+}, N^+] ion pairs with low (red) or high (blue) KER. The peak resulting from the second ionization step shows a pronounced

(~2 eV) shift towards larger kinetic energies for smaller KER, i.e., for the ionization of a dissociating molecule.

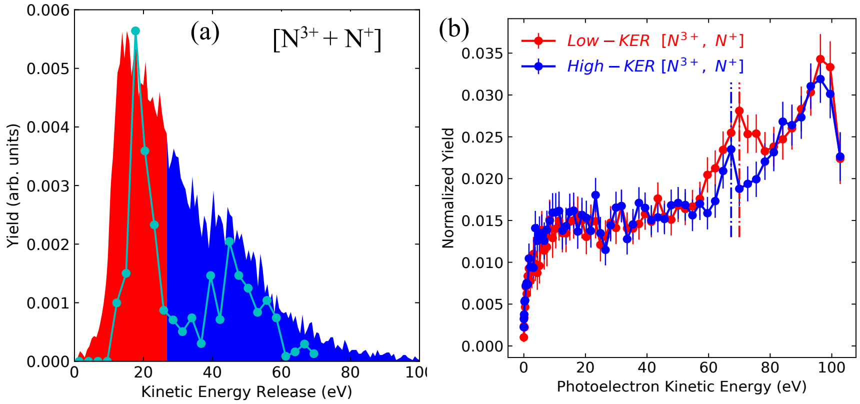

Figure 3: ***(a)*** *Experimental kinetic energy distribution of the [N^{3+}, N^{+}] coincidence channel, divided into 2 regions: low-KER region (0-27.4 eV, red) and high-KER region (27.4-100 eV, blue). The calculated kinetic energy release of the [N^{3+}, N^{+}] coincidence channel obtained for 60 fs pulses is shown by the cyan line with dots.* ***(b)*** *Experimental photoelectron spectra correlated with the two regions in (a). The blue and red dashed lines mark the center of the peak resulting from the second photoionization step (67.3 eV and 70.0 eV, respectively).*

To understand the origin of this shift more quantitatively, the dissociation dynamics of core-ionized N_2 have been simulated using the XMOLECULE package [R10, R11] modified to combine the rate equation approach with gradients from a configuration interaction calculation based on Hartree-Fock orbitals [R3]. Fig. 4(a) depicts the results of this simulation, revealing the relation between the time delay between the two absorption steps, the spatial distribution of the nuclear wave packet (internuclear separation) and the expected KER. These results confirm that filtering on the lower KER part mainly focuses on the dissociating part of the wave packet. Fig. 4(b) shows the simulated evolution of the second-step photoelectron spectrum as a function of the internuclear separation. While this calculation does not include all accessible dicationic states, it clearly reveals a complicated evolution of the photoelectron spectrum from the bound molecular dication to a system of two independent atomic ions. The predicted trend is consistent with the experimentally observed shift of the photoelectron line.

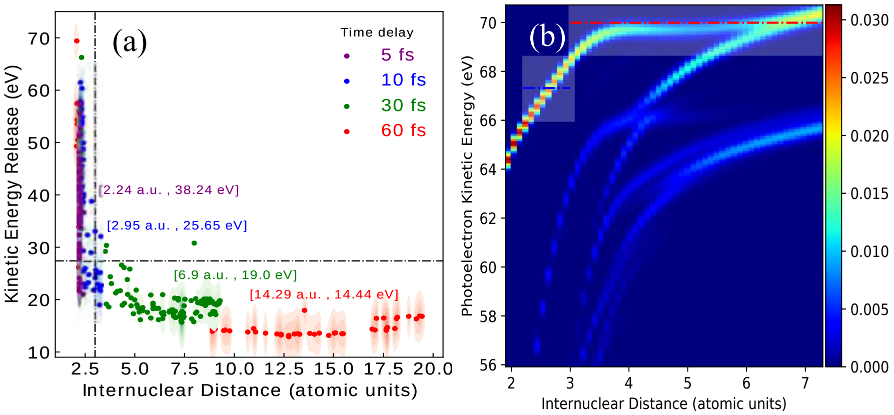

Figure 4: (***a***) *KER distribution for the [N^{3+}, N^{+}] channel as a function of N_2^{2+} internuclear separation at the time of the probe photoabsorption calculated for four different time delays between the two absorption steps. The values in square brackets are the average internuclear distance and KER for each time delay. The horizontal dashed line is the 27.4 eV boundary used in Fig. 3(a). The vertical dashed line marks the bond length of 3 a.u..* ***(b)*** *Calculated kinetic energy of the photoelectron resulting from the ionization of N_2^{2+} ($1^1\Delta_g$) as a function of the internuclear separation. The color encodes the relative probability for a N_2^{2+} photoelectron to have certain energy at different internuclear distances. The experimental peak positions of the photoelectrons from the second ionization step coincident with the high-KER and low-KER [N^{3+}, N^{+}] ion pairs from Fig. 4(b), are marked by the blue and red dashed lines, respectively. The width of the experimental photoelectron peaks are indicated by the shaded rectangles.*

While the results discussed above prove the feasibility of triple coincidence measurements (involving two ions and one electron) in the multiphoton regime at an XFEL facility and, for a simple diatomic molecule like N_2, reveal the evolution of the electronic structure of the molecule during the X-ray induced fragmentation, the low repetition rate of 120 Hz clearly limited the statistical significance of the data and, in particular, precluded the extraction of molecular frame information from this data set. The feasibility of coincidence-based molecular frame measurements at XFELs has been demonstrated in a recent experiment on O_2 at the European XFEL (led by T. Jannke, Frankfurt University), which involved both of the experimental PIs and one of the students (X. Li) supported by this program [R2]. There, the facility operated at an effective repetition rate of 420 Hz (10 pulse trains per second with 42 microbunches each), enabling ion-ion-electron coincidence measurement with enough events to extract molecular frame photoelectron angular distributions (MFPAD). The measured electron spectra where filtered on the KER of the [O^{3+}, O^{+}] channel similar to the nitrogen experiment. The KER-dependent MPFADs of the second-step electron then reflected the distance- and, thus, time-dependent diffraction patterns of a photoelectron wave launched from one and scattering from the other atomic constituent of the dissociating molecule “illuminated from within”.

Future plans

Once the LCLS resumes operations after the shutdown, our main focus in *Thrust 1* will be on utilizing its recently developed attosecond capabilities. Since a large number of experimental and theory groups worldwide (including many within the DOE AMOS program) are interested in the fundamental aspects of ultrafast charge migration and charge transfer, which can be studied using these novel attosecond tools, these overlapping interests resulted in a joint community proposal for a series of experiments aimed at *real-time observation of ultrafast electron motion using attosecond LCLS pulses* – an effort dubbed “the attosecond campaign” [R12]. This projeect, which is led by SLAC researchers J. Cryan, P. Walter and A. Marinelli, is perfectly aligned with the objectives of the *Thrust 1* of our program. If awarded machine time, the attosecond campaing will make use of X-ray sensitivity to charge localization for probing the dynamics, and test two complementary methods for launching a coherent electron : impulsive ionization (core-shell or inner-valence) and impulsive stimulated X-ray Raman scattering (SXRS). Our main contributions to this campaign will be identifying the most promising observables (all PIs), modelling the experiment and specifically those identified observables (Greenman, Santra), and utilizing the broad expertise in charge-particle coincident spectroscopies (Rudenko, Rolles). Since the first two LCLS runs after the shutdown will still be carried out at the 120 Hz repetition rate, the latter part will most likely become relevant within the later stage of the campaign. Therefore, in parallel with attosecond experiments at the LCLS, we will continue performing experiments relying on coincidence techniques elswhere, in particular, at the European XFEL.

Thrust 2: UV pump – X-ray probe experiments **(Rolles, Rudenko)**

Recent progress

While the X-ray driven processes induced by core-shell interactions discussed in the previous section represent attractive test grounds for studies of ultrafast charge dynamics, it is the electronic motion upon valence-shell photoabsorption (in particular, photo-induced electron transfer) that is of more general interest for chemical or biological applications. It would be therefore beneficial for a multidisciplinary community interested in ultrafast photochemical reactions to employ such efficient probing tool as ultrashort, intense X-ray pulses at high repetition rate of LCLS-II to map electron motion triggered by the interaction with visible, UV or XUV light. However, the temporal resolution for studies involving the external lasers at LCLS is much worse than that for X-ray pump – X-ray probe experiment. In the UV regime, it is mainly restricted by the available pulse durations, which typically exceed 80 fs [R13-R15]. Therefore, our initial effort within *Thrust 2* focused on the development of short-pulsed UV source, which will be suitable for operations at the LCLS, and on gathering experience with time-resolved imaging of UV-driven photoprocesses at the JRML. Here, we shortened the pulses delivered by our conventional 266 nm setup (3rd harmonic of the 800 nm Ti:Sa laser generated in a BBO crystal) to <40 fs, and apply them to drive dissociation, elimination and isomerization reactions in halomethanes and in some ring molecules, which are then probed by strong-field ionization and coincident ion momentum imaging. We have also added a 4th harmonic generation setup to our capabilities, and used a similar arrangement for a 200 nm pump – soft X-ray probe experiment at FLASH in Hamburg, led by M. Burt (Oxford University) and D. Rolles.

In parallel, we are exploring schemes to generate significantly shorter (sub-20 fs) UV pulses. The two approaches we focus at right now include a low-order harmonic generation or non-collinear four wave mixing, both in a high-pressure gas cell filled with noble gases [R16, R17]. A test setup, which would allow us to test both of these schemes, is currently under construction. This work is performed in close collaboration with R. Forbes from the PULSE institute, who also establishes the communication between the JRML KSU group and the LCLS laser group.

Future plans

During the next year, we plan to develop a working system delivering sub-20 fs UV pulses at the JRML. In parallel, we will focus the efforts in *Thrust 2* on studying charge transfer dynamics in PENNA cation, which is often considered to be a representative model system for inducing and probing charge motion [R18]. The excitation of a few low-lying cationic states in PENNA is expected to result in charge transfer from the phenyl chromophore through a -CH_2-CH_2- bridge to the methylated amine group, unfolding on a 60-80 fs time scale. We plan to induce these dynamics by impulsive two-photon ionization with a 266 nm pulse, and probe it first with strong-field ionization at the JRML, and later with 1s ionization of a nitrogen atom by at one of the XFEL facilities. The latter scheme is expected to be a very sensitive probe of the local charge density in the vicinity of the nitrogen atom, and the underlying charge rearrangement is expected to be imprinted in the delay-dependent N 1s photoelectron and Auger spectra. The corresponding proposal for the European XFEL will be submitted for the next call.

Thrust 3: Studies of distance-dependent charge transfer processes in dissociating molecules **(Rudenko, Rolles, Santra)**

Recent progress

In the previous sections, we discussed intramolecular charge dynamics occurring in bound molecular system before it undergoes fragmentation. However, in X-ray interactions with molecules, electronic dynamics and Auger decay processes are often accompanied by a rapid molecular breakup, such that charge transfer between different sites of the fragmenting molecule plays an important role for the reaction outcome. A series of recent pump-probe measurements [R14, R19-R21] studied such long-range (up to 20 Å) charge transfer as a function of internuclear separation in a molecule. While the results of these experiments were consistent with the predictions of the classical over-the-barrier (OTB) model developed earlier for ion-atom collisions [R22], limited time resolution precluded a more detailed analysis of the distance-dependence of charge transfer probability. Our main goal for *Thrust 3* is to circumvent this limitation, and to study the functional dependence of the charge transfer rate on distance for several prototypical fragmenting systems.

During the first year of this project, we approached this goal from a slightly different direction, and studied charge transfer transitions in dissociating halomethane molecules after valence-shell XUV ionization. The experiment was performed at the FLASH-II facility in Hamburg employing XUV pump – XUV probe configuration. In contrast to earlier experiments of this type [R14, R19-R21], we have chosen rather low photon energy (23.5 eV) for both, the pump and the probe, well below the core-shell ionization threshold. A decisive advantage of using such photons for the pump step is a rather slow time scale for the dissociation of the populated singly charged states, in contrast to inner- shell interactions resulting in double or triple ionization via Auger decay followed by rapid Coulomb explosion (CE) of the molecule. Using the same XUV wavelength as a probe allows one to consider this problem from a somewhat different perspective on the problem since the XUV pulse interacts with delocalized valence electrons and, thus, the interaction becomes site-specific only at very large internuclear separations, when the molecule has already dissociated, enforcing the electron localization.

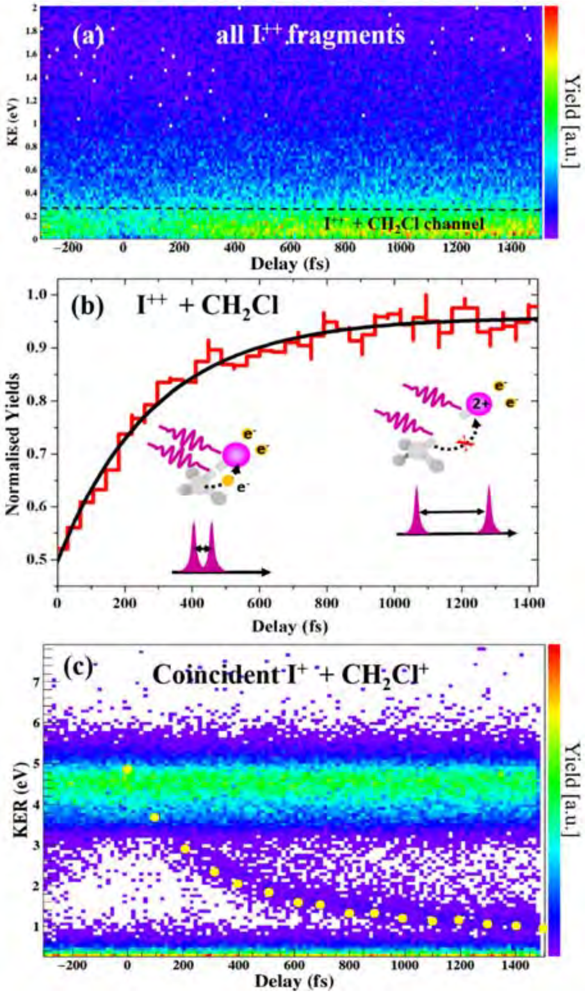

Figure 5: ***(a)*** *Kinetic energy (KE) distribution of I^{++} ions resulting from CH_2ICl fragmentation by a pair of 30 fs XUV pulses as a function of pump-probe delay. The dashed line separates low-energy fragments, which in most cases have a neutral partner.* ***(b)*** *Red line: delay-dependent yield of low-energy I^{++} ions (those within the region below the dashed line in (a)). Black line: exponential fit to the data, yielding the rise time of 285 ± 25 fs.* ***(c)*** *Delay-dependent KER of I^+ + CH_2Cl^+ ion pairs detected in coincidence. Yellow circles depict the results of a Coulomb explosion simulation fit to the dominant dissociation band.*

Similar to previous experiments [R14, R17, R19], we trace the signatures of charge transfer by following the delay-dependent yield of the charge-asymmetric fragment pairs. Specifically, as shown in Fig. 5(a,b) for the CH_2ICl molecule, we monitor the yield of low-energy doubly charged iodine ions, which must have a neutral partner. As can be seen in these figures, the yield of these ions has a pronounced minimum at the region of small delays, where the pump and the probe pulses overlap, and grows towards larger delays. As sketched in the inset of Fig. 5(b), the most likely qualitative reason for this behavior is the efficient charge rearrangement at small internuclear separation, which tends to equalize the charge on both fragments, and which becomes less efficient and, at some point, forbidden, as *R* grows. However, in contrast to the results of earlier experiments employing inner-shell ionization as a probe, where the step-function-like behavior expected from the OTB model was observed, the delay-dependence shown in Fig. 7(b) manifests a steady exponential growth, with a characteristic rise time of ~285 fs, well beyond the temporal resolution of the experiment (~40-45 fs). It remains to be seen whether this qualitative difference simply reflects the improved resolution in *R*, or whether it is determined by a different nature of valence interactions employed here, along with a specific landscape of dicationic potential surfaces involving charge transfer transitions [R23]. For a more quantitative conversion of the delay time into *R*, we fit the most prominent dissociation band in the delay-dependent KER spectrum of coincident I^{+}+ CH_2Cl^{+} ion pairs (shown in Fig. 5(c)) with a simple Coulomb explosion model, which assumes constant dissociation velocity of the fragments after the pump pulse and instantaneous ionization to the final state by the probe. Interestingly, the internuclear separation of 12 a.u., which the dissociating molecule would reach within the 285 fs exponential rise time of I^{++} signal moving with the velocity obtained form that fit, nearly exactly coincides with the predictions of the OTB model for a critical distance, at which the charge transfer from I^{++} to a neutral CH2Cl partner becomes classically forbidden. This suggests a relation between the predictions of the classical OTB model, which coarsely defines the range of the electron transfer between two classical potentials, and the quantum mechanical charge transfer rate in a real molecule, which is expected to depend exponentially on the distance between the two sites, reflecting the spatial overlap of the two wave functions localized at those two sites [R24].

Besides the experiments described above, we have recently considered the role of charge rearrangement and, in particular, electron transfer in multiphoton ionization of molecules by intense X-ray pulses. Following our earlier finding demonstrating that such charge rearrangement can significantly enhance ionization of molecules [R25], we considered (both experimentally and theoretically) how the interplay of multiphoton absorption, nuclear dynamics and electron transfer modifies the pulse parameter dependence of X-ray – molecule interactions at high intensities. We found that because of the distance-dependent charge rearrangement, sequential X-ray ionization of molecules like CH_3I can be enhanced for shorter pulses [R7], which is very different from earlier observations in soft X-ray domain. Extending the theoretical analysis to larger molecules, it was also found that for systems like iodobenzene, the charge transfer can actually enhance ionization of atoms at the largest distance from the absorbing center [P2]. We have recently found signatures of such an effect in data obtained at European XFEL (*R. Boll, T. Jahnke et al. in preparation*), where the charge state distribution of carbon atoms has been measured as a function of their positions in the phenyl ring via three- or four-body coincident momentum imaging.

Future plans

As next steps, we plan to work on developing a more quantitative theoretical picture for the experiments on halomethanes described above, and proceed with a combined experimental and theoretical analyses of the EuXFEL results on intramolecular charge dynamics. Besides that, within the concept of our initial charge-transfer experiments [R14, R19], we developed a scheme aimed at improving our ability to determine the internuclear separation *R* in a dissociating molecule, and to quantify the charge-transfer rate. To achieve this, we plan to use iodosilane (SiH_3I) as a model system for such measurements. Compared to earlier studies, where CH_3I, a prototypical polyatomic system for ultrafast photochemistry, was used, SiH_3I offers two decisive advantages. First, its laser-induced dissociation proceeds considerably slower because of the heavier mass of the silicon atom, significantly improving our resolution in *R* for a given temporal resolution. Second, since the silicon atom has considerably more electrons available for transfer to X-ray ionized iodine than the carbon atom in CH_3I, the use of iodosilane will allow us to quantify the probability to transfer a given number of electrons. Based on the above scheme, we have submitted the beam time proposals for both the European XFEL and the LCLS, which are currently under review.

Thrust 4: Theory development **(Greenman, Santra)**

Recent progress

Identifying observables sensitive to ultrafast charge motion

Since our overall project relies on the use of large-scale XFEL facilities, where machine time is limited and expensive, a detailed planning of the experiment and a proper choice of experimental priorities is crucial for its success. Therefore, one of the central goals of this project from the theory side is to predict the most promising observables, which can reveal the signatures of the charge dynamics of interest, and to identify model systems, which would facilitate observation of these effects, and enable drawing general conclusions from one particular data set. A first step in this direction has been performed in [P1], where, as illustrated in Fig. 1, the observable most sensitive to coherent electronic motion appears to be electron-electron angular correlation observed in the molecular frame. From an experimental point of view, this would require coincident detection of at least three particles (two photoelectrons and one ion determining the direction of the molecular axis). While the calculation performed in [P1] cannot yet be directly compared with experiment, we have recently attempted to perform a calculation describing the existing triple-coincidence LCLS data, in this case ion-ion-electron coincidences (see Fig. 3,4) [R3]. Furthermore, we explored the potential of time-resolved X-ray absorption spectroscopy for probing ultrafast charge dynamics in prototype donor-acceptor systems [P2] and in liquid water [R1] (the later project in collaboration with an experimental team led by L. Young)

Accurate calculation of angular correlations between photoelectrons in attosecond x-ray pump-probe processes

The observables we focused on in [P1], namely the angular correlations between multiple photoelectrons, are among the most sensitive to coherences driving attosecond electron dynamics. We have therefore been spending time on trying to describe the angular correlations more accurately. Rather than using a plane-wave description of the continuum states, which allows for a simple analytical expression for molecular-frame observables (used to obtain the results shown in Fig. 1), we are developing the tools to numerically evaluate these distributions from better continuum-state approximations. While both calculations show the pronounced variations of the angular correlations between the two electrons, which can be directly interpreted as a consequence of the dynamical evolution of the core-hole wave-packet, they also reveal some quantitative differences in the simulated electron emission patterns [P1]. In addition to a greater level of accuracy, we believe that there may be further dynamical effects that can be seen in the angular correlations than predicted by plane-wave approximations. The input to these numerical calculations are photoelectron angular distributions of neutral and singly-ionized species at different levels of approximation (no orbital relaxation compared to the neutral, Hartree-Fock orbitals of the ion), calculated using the ePolyScat photoionization package [R26, R27]. A new member of the Greenman group, S. Chattopadhyay, is leading the effort to develop the codes behind this improved description. These codes are intended to be readily extensible, so that the underlying approximations about the pulses and electronic structure of the neutral and ionic species can be improved stepwise. This improvement will lead to identification of further time-dependent observables, more accurate description of experiments, and importantly to quantum optimal control calculations that can identify the experiments that are most likely to lead to success.

Optimal control requires a relatively quick method of calculating observables, so our developments are made with this goal as well.

The plane-wave approximation, and the approximation that nuclear centers do not couple, have been investigated both in the [P1] and in subsequent calculations. We have found several indications that the additional accuracy provided by molecular continuum state calculations will provide us with additional observables to use as a fingerprint for electronic dynamics. The difference between photoelectron angular distributions for N_2 using the molecular continuum state (blue) and the plane-wave / non-interacting approximations ("model-molecular MFPAD", red) is illustrated in Fig. 6. The contrasts are especially clear for photoelectrons perpendicular to the molecular axis. Additionally, while the σ_u core-ionized angular distribution is relatively accurate, the σ_g distribution shows significant differences. These should be differences that we can exploit to enhance the observable effect of wave packet dynamics between these holes. Preliminary calculations have shown dynamic behavior in, e.g., the single-site double-core-hole that was not present using the previous approximations.

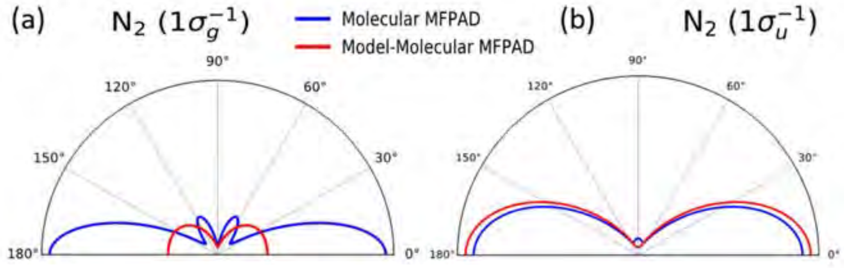

Figure 6: *Molecular-frame photoelectron angular distributions for the core ionization of* $1\sigma_g^{-1}$ *(a) and* $1\sigma_u^{-1}$ *(b) orbitals of* N_2.

Identifying fragmentation pathways following core-ionization

In addition, we have also been performing electronic structure calculations on molecules where preliminary experiments attempt to understand the interplay between core-ionization and subsequent electronic and nuclear dynamics. We have been calculating potential energy surfaces for several systems potentially promising for the experiments within this project, including the thiophenone and the dichloroethane molecules. In each case, core-ionization leads to fragmentation, and the fragments can be correlated with photoelectrons. The resulting photoelectron spectra provide a differential measurement to compare to theory, and to use as a tool in combination with theoretical potential energy surfaces to suggest possible nuclear pathways for experimental observables.

Future plans

A key technical aspect of our recently published work [P1] was the comparison of the continuum state description of variational scattering methods like the Schwinger method implemented in ePolyScat [R26, R27] with the description used in XMOLECULE [R10, R11] and other Monte Carlo X-ray dynamics methods. We will continue to integrate improvements of this type to the XMOLECULE package. By improving the continuum state description, we will make the rates calculated for ionization processes more accurate, and therefore improve the accuracy of the description of the X-ray dynamics. We will also adapt the XMOLECULE package for a broader range of targets, following the efforts started in [P1, P3].

An important aspect of the theoretical work for the next year of the project will be a contribution to the planned "attosecond campaign" at LCLS. This will include adapting XMOLECULE for some of the targets planned to be used within the campaign, simulations of the photoelectron and near-edge transient absorption signals, and further search for correlation-based observables sensitive to ultrafast electron-hole dynamics.

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Peer-Reviewed Publications Resulting from this Project (Project start date: 09/2018)

[P1] L. Inhester, L. Greenman, A. Rudenko, D. Rolles, and R. Santra, "*Detecting coherent core-hole wave-packet dynamics in* N_2 *by time- and angle-resolved inner-shell photoelectron spectroscopy"*, J. Chem. Phys. **151**, 054107 (2019).

[P2] K. Khalili, L. Inhester, C. Arnold, R. Welsch, J.W. Andreasen, and R. Santra, "H*ole dynamics in a photovoltaic donor-acceptor couple revealed by simulated time-resolved X-ray absorption spectroscopy*", Structural Dynamics **6**, 044102 (2019).

[P3] Y. Hao, L. Inhester, S.-K. Son, and R. Santra, "*Theoretical evidence for the sensitivity of charge-rearrangement-enhanced x-ray ionization to molecular size"*, Phys. Rev. A **100**, 013402 (2019).

Light-induced modification of electronic interactions and electron-nuclear couplings

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Project Scope

In this project we aim to characterize the light-induced electronic couplings and use them as a tool to tune the interactions that drive electron dynamics in atoms and molecules. In one thrust, our goal is to quantitatively study how linear and non-linear light-induced couplings manifest in the attosecond transient absorption signals, and how they can be used to monitor and alter the fast dynamics stemming from interaction between electrons, e.g. in atomic and molecular autoionization. The second thrust concerns the light-induced modification of the multielectron processes and electron-nuclear coupling driven dynamics, e.g. near conical intersections of small polyatomics. Attosecond transient absorption spectroscopy, non-collinear four-wave-mixing, and coincident velocity map imaging form the main experimental techniques utilized on this project.

In contrast to our prior efforts on the investigation of electron dynamics in atoms and molecules, this project employs new technical approach based on the tunable wavelength (800-3400nm) laser fields, enabling a systematic study of resonant and non-resonant couplings, leading to new strategies for controlling few-body dynamics in atoms and molecules. The overarching goal of this research effort is to understand and predictably modify the charge and energy redistribution dynamics inside molecules, which are driven by the complex interplay of electronic correlations and couplings between electronic and nuclear degrees of freedom. In this respect, the use of multi-pulse pump-probe scheme with wavelength-tunable fields provides new control knobs while also providing means to disentangle the side-effects of strong fields used in most XUV-IR experiments. The ongoing project then dovetails into our future plans to employ attosecond soft-x-ray pulses to obtain elemental and chemical sensitivity in the study of charge dynamics.

We have successfully completed the tasks associated with Thrust 1 and obtained new results on Thrust 2 that currently being analyzed and modeled. Collaborations with LSU, LBNL, and UCF theory groups have played an important role in the interpretation of results.

Recent Progress

We have published three papers, and results from three more experimental campaigns are currently at various states of modeling or manuscript preparation. The research progress can be divided into following topics:

Light induced electronic couplings: In the first paper [Pub. 1], we employed a transient absorption scheme that uses a fixed-spectrum attosecond pulse train in conjunction with a tunable IR probe laser to demonstrate control over the time-dependent Autler-Townes splitting of the 1s4p absorption line in helium and study its evolution from a resonant doublet to a light-induced sideband. The non-commensurate probe allowed background-free study of Four-Wave-Mixing (FWM) emission in the collinear geometry. Using this capability, we observed two different XUV emission pathways, one prompt and the other delayed. The spectral and temporal structure of emission results from contributions from several excited states (e.g. 3s, 3p, 4p). We identified the electronic couplings underlying these non-intuitive FWM pathways by comparing the experimental results to TDSE calculations conducted by the Schafer and Gaarde group at LSU.

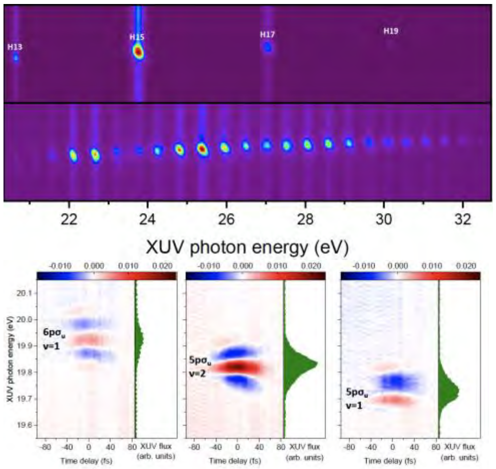

Fig 1. (top panel) In comparison to the typical odd harmonics from Ti:Sa laser, the harmonics from a two-color high order mixing yields much better spectral coverage. (bottom pabel) Easy tunability of XUV allows targeting of specific electronic and vibrational states in O_2.

Following up on this work, we generalized our experimental approach by developed a scheme where we can also generate tunable extreme ultraviolet emission through high-order frequency mixing between a strong near-infrared (780 nm) field and a weak shortwave-infrared pulse whose wavelength can be adjusted. In this two-color driving scheme, new harmonics appear at energies which are linear combinations of photons from the two fields. This method provides a much higher spectral coverage than single color harmonics and allows easy tuning to XUV energy to target resonances of interest. We demonstrated the utility of tunable two-color harmonics by employing them for XUV transient absorption spectroscopy and time-resolved photoelectron spectroscopy [Pub. 3]. We show that the two-color harmonics can be used to address the excited state dynamics which are inaccessible using single-color harmonics. Specifically, we show the ability to switch between excitation of 3p and 4p states in Helium, control of transitions to the light induced states, observe new four-wave-mixing emissions, and selectively address different principal and vibrational quantum numbers of O_2 Rydberg states (Fig. 1).

Using the tools developed above, we progressed towards quantifying the electronic couplings between autoionizing states. We systematically varied the IR wavelength to detuning relative to the two auto ionizing resonances in Argon to gain quantitative understanding how light-induced couplings manifest in the transient absorption signals. The 17th high harmonic was used to excite $(3s^{-1})4p$ state, which autoionizes due to electronic interactions. The external IR field induced couplings to other quasi-bound states and to various continua available in a many-electron system strongly modify the transient absorption line shape associated with this state. We found that by tuning the 4p-3d and 4p-5s couplings we can alter the temporal extent and spectral profile of the transient absorption signal (Fig. 2). The lineshapes are also highly sensitive to the laser ellipticity due the modification of selection rules for transitions. TDSE calculations and modeling of the effect of electronic couplings on lineshapes by Argenti group at UCF verify these results. A

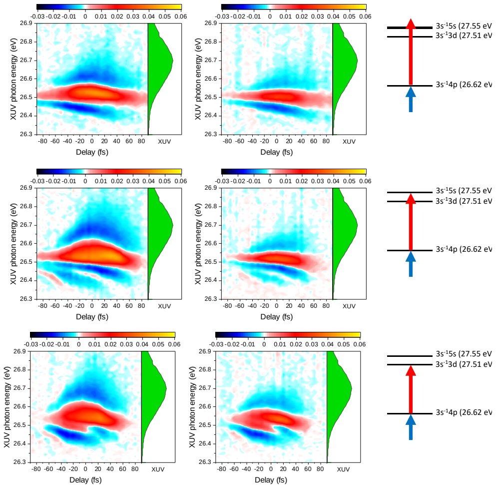

Fig. 2. Top to bottom panels: Tuning the IR wavelength and coupling between the 4p and 5s/3d states in Argon to control the transient absorption line shape. (Left panels) IR polarization parallel to the XUV polarization; (middle) IR perpendicular to XUV; (Right) IR photon energy vis-à-vis location of unperturbed 3d and 5s resonances.

manuscript on these results is under preparation. Our systematic results show that changes to the transient line shape evolution could be used to obtain quantitative information about the underlying matrix elements - information that is often lacking in the case of multi-electron states.

<u>Multielectron processes and dark state dynamics</u>: Our investigation in O_2 explored the fragmentation of highly excited states of using femtosecond transient photoelectron spectroscopy. An XUV pulse populates the autoionizing Rydberg series converging to O_2^+ $c^4\Sigma_u^-$, and a femtosecond IR pulse photoionized these states as they dissociate. The photoelectron spectrogram (Fig. 3) exhibits a signal corresponding to the formation of 4p excited atomic oxygen fragment, which is not an expected dissociation product. In a recent paper [Pub. 2] We show that this fragment results from previously unexplored $(^4\Pi_g)$4p repulsive state and, contrary to expectations, this multielectron excitation pathway presents a substantial cross section. This work was conducted in collaboration with McCurdy group at LBNL. Additional ongoing work aims to use a third pulse to control the fragmentation dynamics of these multi-electron states.

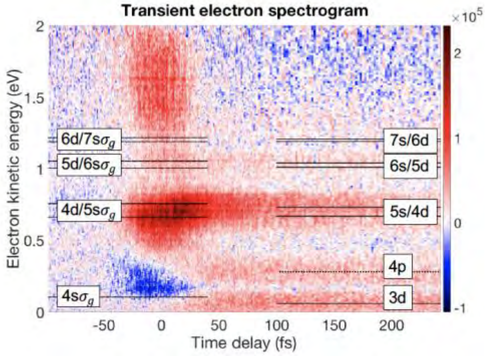

Fig. 3. Photoelectron spectrogram showing the formation 4p excited O atom (labeled on the right side of figure), which we identified with a multielectron excitation channel of O_2.

We also demonstrated the application of non-collinear XUV FWM to target the intermediate dark states in Argon and obtain their lifetime. We designed an experimental setup that allows us to acquire FWM data with two IR pulses, one collinear and one non-collinear, with latter being delayed in time. We have access to various V-type and Ladder-type FWM emissions, by resolving the XUV emission in energy and angle, respectively. In a ladder type FWM process, we excite to 4p state with 17th harmonic and a 1.4 μm photon couples to the optically dark 3d state, whose lifetime we are interested in obtaining. The second IR photon couples the 3d further to 6p, from which we obtain an emission signal corresponding to transition back to the ground state. If both IR photons involved are collinear, we get collinear FWM emission. If one or both IR photons are non-collinear, we get FWM emission at an angle that is determined by the number of photons involved. The temporal extent of the non-collinear FWM signal is expected to contain information on the lifetime of the intermediate dark state, however the information is convoluted with the pulse duration and intensity profile of the IR pulse. We are modeling these results in collaboration with Argenti group at UCF, and we aim to extract the lifetime of dark autoionizing 3d state.

In additional work on this system with photoelectron imaging, we have obtained exciting results on the interference between ionization pathways to the spin-orbit split continuum states. We observed a beat signal associated with ion-core change during photoionization due to inter-channel coupling. The angular distribution also changes dramatically as a function of the beat pattern. We will be conducting further analysis to refine our understanding and control of these dynamics.

<u>Coupled electron-nuclear dynamics under strong fields</u>: We are engaged in the study of light induced modifications of conical intersection dynamics. In past, we have used XUV pump - NIR probe to investigate the conical intersection between the electronic states of CO_2 molecular ion at ~17 eV energy. The electron hole is driven between the σ and π orbitals by the bending and asymmetric stretch vibrations of the molecule. A delayed NIR pulse excites the hole population to a dissociative state and by monitoring the ion-yield we were able to follow the quantum beating of the electron hole density and its decay with time. Now we are using a 'third' IR control pulse to modify the potential energy landscape of conical intersections. We observe that the intensity of the NIR field changes the frequency and amplitude of the coherent electron hole beating between the two vibronic states of $CO_2{}^+$. This is a very striking effect and needs a full theoretical analysis to decode the underlying strong-field modification effect. We are acquiring additional data at different IR intensities and wavelengths to build a comprehensive picture of this light induced modification of conical intersection dynamics.

We have installed a TIMEPIX based coincidence VMI system, which now allow us to conduct coincident imaging of the electrons and ions for deeper insights in coupled dynamics. We have applied it to study Iodobenzene fragments in a pump-probe experiment, which shows interesting dynamics of four carbon fragment formation, relative to the molecular ion signal. We are going to continue this investigation path over the next few months to gather more data.

Future Plans

We made successfully completed several investigations that aim to understand and quantify light-induced electronic couplings and their impact on multi-electron processes. To conclude the ongoing investigations, we will work with our collaborators to finalize the simulations on impact of IR coupled autoionizing resonances on transient absorption signals, the measurement of dark state lifetimes through FWM, and the interference between photoionization pathways associated with ion-core state change. We will also press ahead on two ongoing experimental efforts which aim to study modification of electron nuclear couplings with strong light fields. One of these studies has been conducted in Iodobenzene and another near a conical intersection in CO_2. We will collect additional datasets and establish collaborations for simulating the strong-field modification of potential energy landscape and vibronic couplings in molecules. The tunable, multi-color and multi-pulse spectroscopy techniques developed in these efforts will enhance the attosecond science toolkit by providing new control knobs. We envision that this approach will offer significant advantages in disentangling of the ultrafast dynamics of wave packets traversing the complex manifold of molecular potential energy surfaces and provide means to access the dynamics of optically dark states.

We will also install a new high power, few-cycle MIR laser which will drive the soft-x-ray generation. The additional tunability of light field from 1.6 to 3.4 um will be enabled by this source. The soft-x-ray capability will allow us to conduct elementally specific probing of charge dynamics in complex molecular systems or relevance to light harvesting, energy conversion, and catalysis.

Peer-Reviewed Publications Resulting from this Project (Project Start Date: 09/2017)

Pub. 1) Nathan Harkema, Jens Baekhoj, Chen-Ting Liao, Mette Gaarde, Ken Schafer, Arvinder Sandhu, "Controlling attosecond transient absorption with tunable, non-commensurate light fields", *Optics Letters* **43**, 3357-3360 (2018).

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Pub. 3) Nathan Harkema, Alexander Plunkett, Arvinder Sandhu, "Tunable high-order frequency mixing for XUV transient absorption and photoelectron spectroscopies", Optics Express (2019). In print.

Transient Absorption and Reshaping of Ultrafast Radiation

DE-SC0010431

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Project Scope

Our program is centered around the theoretical study of transient absorption of ultrafast extreme ultraviolet (XUV) radiation by matter interacting with a precisely synchronized near-to-mid infrared (IR) laser pulse, and emphasizes both fundamental theoretical research and a close connection with experimental groups doing attosecond physics [1]. 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 scenarios, 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 laser-matter 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 for atomic systems in the gas phase [2]. More recently we have also started considering attosecond transient absorption and reflection in condensed phase systems [3].

Recent Progress

We have completed a number of research projects, all of them in collaboration with experimental groups carrying out ATA measurements, see [R1-R4] and [3–5]. In this abstract we highlight some of our latest work:

(i) Spatio-temporal coupling in ultrafast light-matter interactions: We have been involved in two types of studies exploiting spatio-temporal coupling: (a) the use of opto-optical modulation (OOM) to explore nonlinear AC Stark phase interactions [R4], and (b) transient grating spectroscopy of ultrafast dynamics of light-induced resonances in helium [R3]. Here we concentrate on the former.

In collaboration with the Mauritsson experimental group at Lund University, Sweden, we have explored OOM of ultrafast XUV pulses in gas-phase media [6], [R4]. OOM is based on IR-controlled spatial redirection of the free-induction-decay radiation initiated by an ultrafast XUV pulse (XFID), as illustrated in Fig. 1(a) and (b). In the presence of a spatially offset IR beam, the IR-imposed AC Stark phase varies across the XFID spatial profile because of the IR intensity variation. This resulting tilted phase front can lead to a redirection of the XFID "beam" so that it appears as emission off-axis in the far field, as seen in Fig. 1(a).

In [R4], we explored the spatial manifestations of bound-state linear and non-linear AC Stark phase accumulations. We found that for some IR parameters, the Stark shift of the helium 1s2p state is highly nonlinear. This manifests as profound changes in the XFID redirection with IR intensity: At low intensities, the 1s2p light is spatially redirected downwards, indicating that the Stark shift of the 1s2p state is toward lower energies. As the IR intensity increases, the 1s2p light first becomes first bi-directional and then eventually is primarily redirected upward, as shown schematically in Fig. 1(b). This is in contrast to the 1s*n*p states for which the XFID is always redirected upward. Both the 1s2p up-and-down and the 1s*n*p up-only redirection can be seen in the experimental spatial-spectral profile in Fig. 1(c). This change in redirection is caused by the intensity dependence of the IR-induced AC Stark phase accumulation of the 1s2p state, as shown in Fig. 1(d). The phase accumulation changes sign near 2 TW/cm^2, from decreasing at low intensity to increasing at higher intensities. This can be understood in terms of a transition from a low intensity regime in which the 1s2p state couples strongly to the 1s3s and 1s3d states, which are in close to one-photon resonance with it, to a high intensity regime, where the electric field strongly distorts the potential and the electron behaves increasingly like a free charge in an oscillating field. In the high intensity regime the 1s2p state accumulates a near-linear phase similar to (but slower than) the higher-lying 1s*n*p states. These results indicate the possibility for the future study of Stark phases in more complicated atoms or molecules, where the states and/or their dipole couplings may be less well known, and even allow for reconstruction of the phase accumulation from the experimental result given tighter control over the experimental parameters.

(ii) ATA of ultrafast exciton dynamics in condensed phase MgO: In collaboration with the Leone/Neumark experimental group at UC Berkeley, we have considered ultrafast exciton dynamics in a condensed phase system interacting with a moderately intense IR pulse, using attosecond transient reflectivity [3]. We are interested in the signature and dynamics of excitonic states in the vicinity of the band gap energy. Although excitonic states are somewhat similar to atomic excited states in the sense that they are localized in space and energy (as opposed to the delocalized excitations characteristic of the conductions bands), they have much shorter lifetimes than atomic states because of the inevitable coupling to the phonon dynamics. As a first foray into calculations of exciton dynamics in the condensed phase, we have developed a simple model in which the excitonic states are described as a three-level system consisting of two bright and one dark state, and the phonon coupling is included as a time-dependent amplitude and phase modulation as described in [7]. We used multi-parameter optimization in comparisons between calculated and measured results in order to extract an estimate for several of the unknown parameters that goes into the model. For example, while the energies of the two bright states are well known from literature (and are clearly visible in the experimental results), both the energy of the dark state and its coupling to the bright states are not. We were able to extract consistent values for these quantities from the modeling coupled with the optimization. The main results of this collaboration were two-fold: Comparison between experiment and theory showed that (i)

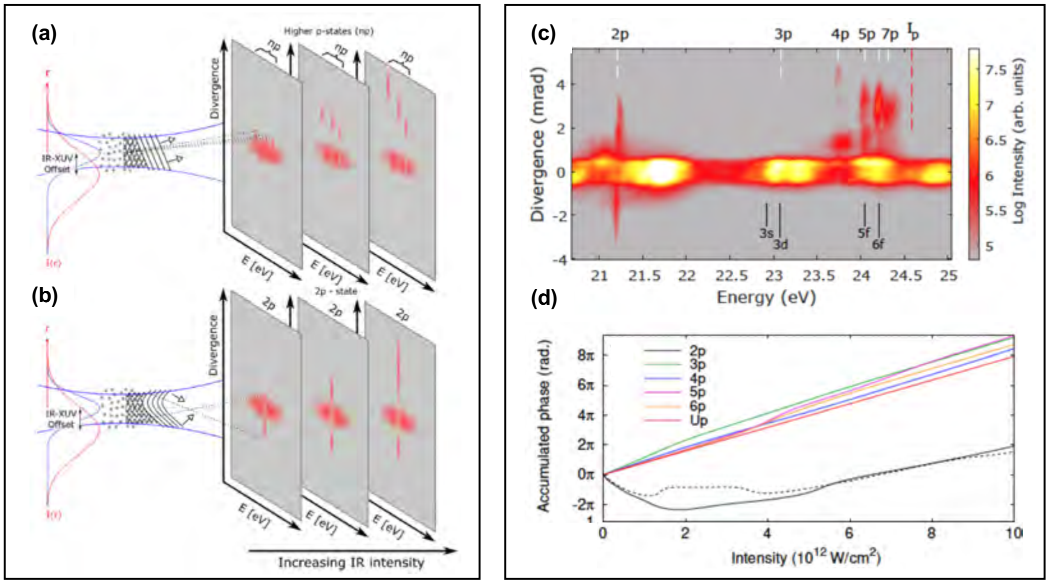

Figure 1: Panels (a) and (b) illustrate the principle of OOM. An XUV beam (in blue) initiates XFID radiation in a gas, and its phase is altered by a time-delayed, spatially offset IR beam. For the 1snp states in (a) the phase shift is proportional to the IR intensity, which tilts the wavefront and directs the XFID upward. The phase shift of the 1s2p state is nonlinear, causing a downward tilt at low intensity and an upward tilt at high intensity (see (b) and (d)). An experimental spatial-spectral profile in shown in (c).

the exciton decoherence times due to coupling to the phonons are incredibly fast - between 1 and 3 fs for both bright exciton states, and (ii) coupling between bright and dark excitonic states strongly influences the (bound) excitonic dynamics.

Future Plans

Several projects are in progress or planned for the near future:

(i) Ultrafast spatio-temporal coupling: Building on both our work using OOM and the ultrafast phase grating, we are continuing our exploration of spatio-temporal coupling in ultrafast light-matter interactions. Topics of current interest are (a) the use of OOM as a phase meter, for both bound and autoionizing state dynamics in helium, and (b) studying the dynamics of autoionizing states in neon using the transient phase grating technique. Both projects represent continuing collaborations with experimental partners.

(ii) Studies with ultrafast free-electron-laser (FEL) light: In two newly initiated experiment and theory collaborations we are in the process of: (a) Studing ATA for core-excited states in neon using intense sub-to-few fs X-ray FEL pulses, with intensities such that both linear and non-linear X-ray processes take place. This is in collaboration with the Young experimental group at Argonne National Lab. (b) Study both the characterization and the use of coherent harmonic radiation from a seeded FEL. This is in collaboration with the Sansone (U. Freiberg) and Mauritsson (Lund U.) experimental goups.

(iii) Condensed-phase ATA: We will continue studies of ATA in condensed phase materials, both expanding on our present work on excitonic ATA, and through the development and application of a larger-scale theory framework based on the semiconductor Bloch equations.

Peer-Reviewed Publications Resulting from this Project (2017-2019)

R1 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).

R2 N. Harkema, J. E. Bækhøj, C.-T. Liao, M. B. Gaarde, K. J. Schafer, and A. Sandhu, *Controlling attosecond transient absorption with tunable, non-commensurate light fields*, Opt.Lett. **43**, 3357 (2018).

R3 A. P. Fidler, S. J. Camp, E. R. Warrick, E. Bloch, H. J. B. Marroux, D. M. Neumark, K. J. Schafer, M. B. Gaarde, and S. R. Leone, *Nonlinear XUV Signal Generation Probed by Attosecond Transient Grating Spectroscopy*, Nat. Comm. **10**, 1384 (2019).

R4 E. Simpson, M. Labeye, S. Camp, N. Ibrakovic, S. Bengtsson, A. Olofsson, K. J. Schafer, M. B. Gaarde, and J. Mauritsson, *Probing Stark-induced nonlinear phase variation with opto-optical modulation*, Phys. Rev. A **100**, 023403 (2019).

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Coherent Probes of Charge Migration

Science Using Ultrafast Probes: DE-SC0012462

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Project Scope

When forced out of equilibrium, electrons in matter can respond exceedingly fast, on time-scales approaching the attosecond. At this time scale, the dynamics are inherently quantum, and they are not yet impacted by the weaker coupling to a system "bath" that involves large numbers of additional degrees of freedom. This response can expose correlations between electrons and holes that are otherwise hidden in the static properties of the system. These correlations, and the dynamics they evoke, are of great importance as they can impact fundamental processes, such as charge transport and photoelectric energy conversion. From the perspective of furthering basic science or a desire to manipulate the outcome of a reaction, one needs to understand how attosecond electron-hole dynamics initiate, drive, or steer physical and chemical processes, which may occur on much longer time scales.

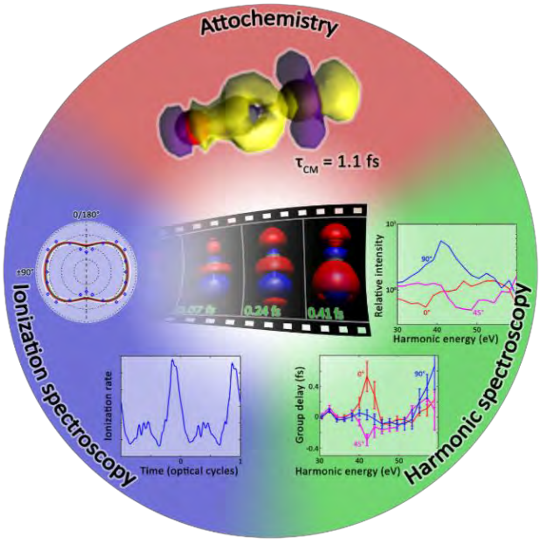

Figure 1: The ATTO-CM network is organized around three main thrusts: (i) attochemistry, (ii) high harmonic spectroscopy, and (iii) frequency-matched ionization spectroscopy. In the figure we illustrate these thrusts with recent experiments and theory on OCS molecules: (top) Calculations of charge migration modes, (right) measurements of the amplitude and phase of harmonics from aligned OCS, and (left) measurements and calculations of ionization from aligned OCS.

The ATTO-CM team is focused on developing and applying coherent probes to directly characterize correlation-driven ultrafast charge migration dynamics that are initiated by different means across molecular families. In this context, charge migration refers to the rapid movement (femtosecond or faster) of positively charged holes in a molecule following localized excitation or ionization. Understanding the mechanisms of this migration, and developing experimental tools for observing it, is crucial to advancing ultrafast science and potential applications across disciplines. 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 experimentalists, as illustrated in Figure 1. Enabled by an integrated relationship between theory and experiment, our emphasis is on the implementation of high-harmonic spectroscopy and frequency-matched ionization spectroscopy as coherent probes of charge migration dynamics in chemical systems. Our ultimate goal is to develop experimental probes that can provide direct access to specific time-resolved information in a manner that does not require sophisticated modeling for interpretation. For practical implementation, our focus has been to identify parameters to probe and control these dynamics, *e.g.*, molecular alignment and/or functionalization of the target. The initial experiments are laboratory based but experiments on large-scale facilities, like LCLS, are envisioned for the future.

Recent Progress

As illustrated in Figure 1, in our effort to understand and observe charge migration (CM, hereafter) with strong laser fields we have focused our efforts on three main thrusts: “Attochemistry picture of charge migration”, “High-harmonic spectroscopy (HHS)”, and “Frequency-matched Ionization spectroscopy (FIS)”. As demonstrated in what follows, all three nodes of the ATTO-CM network are closely involved in each of the three thrusts defining our program. In brief, our key recent results are:

1. Thrust 1: Attochemistry picture of charge migration – We have developed a way to extract CM modes from the simulated time-dependent hole density. This enables us to identify CM modes initiated by sudden ionization, and to relate these modes to experimentally relevant quantities such as migration time and migration length. We have also made progress towards predicting future targets for CM studies based on chemical principles. For example, halogen-functionalized conjugated molecules can be both ionized to create a localized hole, and also support CM through their conjugated π system.
2. Thrust 2: High-harmonic spectroscopy (HHS) – We have explored several instances of how ultrafast dynamical effects manifest in HHS, in particular in the context of two-center interference (TCI). In experiments we have studied TCI at different driving-laser wavelengths and disentangled static vs dynamical contributions to the TCI. In calculations we have shown that transient laser-driven changes in the molecular charge-density influence the appearance of the TCI in both HHG amplitude and phase. In experiments, we have made progress toward implementing HHS of aligned and oriented molecules.
3. Thrust 3: Frequency-matched ionization spectroscopy (FIS) – We have combined experiment and theory to study intensity- and angle-dependent ionization in linear and symmetric top molecules [Sándor 2018, Sándor 2019], demonstrating the effectiveness of alignment-controlled strong field ionization for initiating detectable and interpretable CM. We have used the calculated ionization yields to infer details of the sub-cycle ionization and subsequent hole dynamics that are not directly available from experiment. We have begun measurements comparing the effectiveness of bichromatic laser vs THz pulses for preparing transiently oriented, neutral molecular samples for experiments exploring single and double ionization in strong, directional fields.

Thrust 1: Attochemistry picture of charge migration

The first thrust of the ATTO-CM network focuses on using first-principles simulations to predict CM in molecules, and to interpret these dynamics in terms of chemically-inspired mechanisms. Here we use time-dependent density functional theory (TDDFT) with atom-centered basis sets and hybrid exchange-correlation functionals. Previously, we have shown that TDDFT using hybrid functionals gives quantitative agreement with previously reported experimental and correlated simulation results, for both core-hole and valence-hole triggered attosecond CM times [Bruner 2017]. Moving forward, our main focus is now on quantifying CM in molecules in terms of molecular modes, *i.e.,* simple experimentally-relevant metrics such as migration time, migration length, and the degree of localization. There are two key challenges: identifying the CM modes that result from a particular ionization-trigger and extracting the metrics of this mode.

Charge-migration modes: We have made significant progress on the identification and characterization of CM modes. We take a density-based approach, where we interpret the dynamics directly from the electron density. To identify CM modes in a molecule, we first compute the density following a sudden ionization in a particular region of a molecule. Often this results in the superposition of several modes of excitation in the molecule. We then distinguish between migrating and non-migrating modes using spatio-temporal Fourier

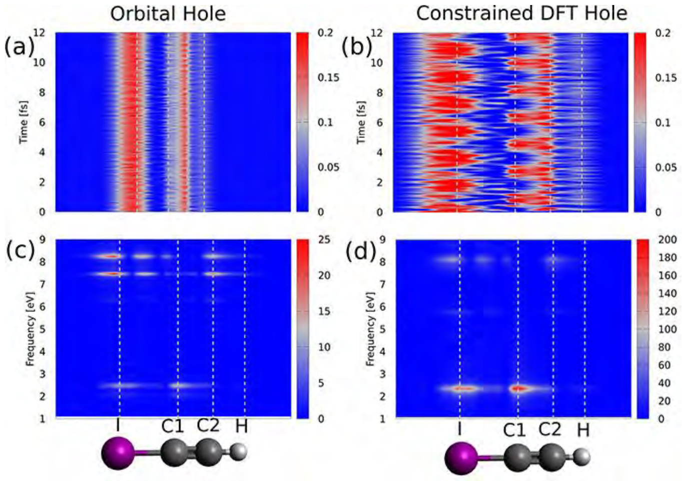

Figure 2: (a,b) Time-dependent and (c,d) Fourier transforms of the hole densities in iodoacetylene following a sudden HOMO hole and a constrained DFT hole.

analysis of the hole density. This allows us to identify the modes that involve "particle-like" CM motion of a hole from one end of the molecule to another. This is in contrast to an "excitation-like" motion which is typically more delocalized and often occurs at higher frequencies.

Recently, we have shown that the resulting CM dynamics are not necessarily sensitive to the specifics of the initial state created, but instead depend mostly on where in space the initial hole is created. This physically intuitive result is much in the spirit of TDDFT where the time-dependent density is the fundamental quantity. Figure 2 (a), for example, shows the time-dependent hole density in iodoacetylene following ionization by removing an electron from the highest occupied molecular orbital (HOMO, left). Here we show the density along the migration axis, *i.e.*, integrated transverse to the molecular axis. CM in iodoacetylene has been previously studied [Kraus 2015] and thus offers a good molecule to validate against. The HOMO hole dynamics are difficult to interpret visually. In contrast, Figure 2 (b), shows the same molecule but this time using constrained DFT (CDFT) to create a localized hole on the iodine atom (right). CDFT solves for the ground state density with a specified constraint that the I atom has a net charge of +1. This can be thought of as an approximation to an adiabatically created hole, as in a low frequency strong field ionization (SFI) experiment. CDFT has been previously shown to give improved electron transfer dynamics in molecules due to reduction in self-interaction errors [Wu 2006]. Looking at the hole density in the CDFT case, the CM dynamics can be seen to oscillate between the I atom and the C≡C bond with a period of 1.8 fs (*i.e.*, a CM time of 0.9 fs). This result is consistent with the experimentally reported migration time [Kraus 2015]. The corresponding Fourier analysis in Figures 2 (c, d) of these two cases both exhibit the same additional mode at 2.3 eV, albeit with different magnitudes. In the context of CM, CDFT thus has the advantage that it is straightforward to create localized initial states which can better emulate a localized hole following strong-field ionization than a delocalized orbital hole. We have found similar results in a selection of different molecules, to be detailed in a forthcoming paper [Bruner 2019].

Attochemistry mode metrics: We have also extended our attochemistry framework to determine the relationship between molecular size and CM in larger linear conjugated molecules. This is a key step towards understanding and ultimately predicting how CM can be modified by the molecular geometry and/or chemical functionalization. Based on our SFI results (see Thrust 3 below), we predict that a hole can be readily localized on a halogen atom, with increasing hole localization as the halogen increases in atomic number from fluorine to iodine [Sándor 2019]. Thus, iodine-functionalized, conjugated molecules are promising for CM, as they are predicted to both support facile hole motion due to their delocalized π system, and can also be ionized via tunneling to create a hole at one end of the molecule. Figure 3 (a) shows the hole dynamics in iodobutadiene (IC_4H_5) following CDFT ionization from the iodine atom. The hole density along the long axis of the molecule shows a clear migration from the I to the C=C bond at the opposite end of the molecule. The corresponding real value of the Fourier transform of the hole density, Figure 3 (b), shows a strong mode at 1.9 eV (period of 2.18 fs, CM time of 1.09 fs) involving primarily the I atom, the C_1, atom, and the C_3=C_4 double bond. Together with the molecular sites involved in a mode, the real part of the Fourier transform can be used to interpret the dynamics directly from the spectrum, as it is related to the relative phase of the dynamics: Positive at one end of the molecule and negative at the other means this particular mode involves a hole travelling from left to right.

Generalizing to longer chain lengths, I(CH$_2$)$_n$H, we have found that migration time increases with chain length, with the effective CM velocity increasing with molecule size. This is likely a result of π-electron delocalization, similar to the case of incoherent molecular conductivity [Evans 2008, Terao 2013]. These results suggest that, in contrast to small molecules, where we observe a regularity in the hole migration speed of 2 bonds/fs, for linear alkenes the effects of size are less trivial. These results have important implications for future CM experiments. Successful measurement of CM requires a molecule that can be experimentally addressed *(e.g.*, put into the gas phase), can be ionized to create a local hole (*i.e.*, strong-field ionization or possibly a core-hole), and supports migration that can be observed within experimental time resolution limitations. Based on these results, studying larger molecules may not necessarily result in significantly slower dynamics. Instead, chemical functionalization may be a more promising path forward, especially using hole donor/acceptor schemes. We are working on incorporating these insights into the manuscript we have been preparing detailing our methodology for identifying CM modes and the implications for experiments [Bruner 2019].

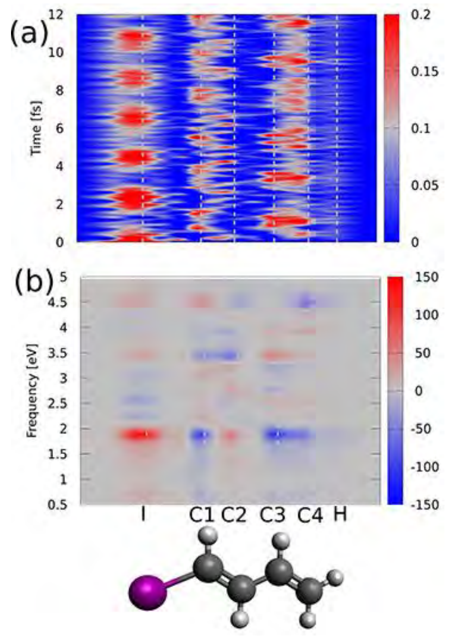

Figure 3: Extraction of charge migration modes in iodobutadiene via Fourier transform analysis. (a) The hole density along the migration axis following sudden ionization from the I atom using CDFT. (b) The real part of the Fourier transform shows a migration from I⟶C$_3$=C$_4$ in 1.1 fs.

Thrust 2: High-harmonic spectroscopy (HHS)

As illustrated in Figure 1, Thrust 2 of the ATTO-CM network focuses on HHG as a spectroscopic tool for probing CM. The study of two-center interference (TCI) in HHG spectra involves all three nodes in the ATTO-CM network. We have made a thorough study on this phenomenon in CO$_2$, OCS, and N$_2$O [Gorman 2019]. We next discuss our continued progress in our understanding of TCI.

Discerning dynamic vs. geometric multi-center interferences using HHS: While completing the study detailed in [Gorman 2019], we observed a discrepancy between the only phase measurement for TCI in CO$_2$ in the literature [Boutu 2008] and our own measurements. Motivated by this discrepancy, we have resolved the inconsistencies between the prior published works and ours, thus revealing two underlying mechanisms leading to TCI in this molecule: a conventional, intensity-independent geometric TCI, and a dynamic, intensity-dependent interference involving multiple molecular orbital channels. By changing the laser wavelength, we can switch between geometric and dynamic interferences, and probe their interplay through HHS measurements, as shown in Figure 4.

In the simplest case, one can think of TCI as that of a recolliding electron-wave-packet scattering on different centers of density in the HOMO channel [Etches 2011]. In this framework, the HHG amplitude and phase are solely determined by the emission energy and should be independent of the laser intensity and wavelength [Gorman 2019]. To test this, in Figures 4 (a-c), we compare the normalized spectral amplitude for various wavelengths with increasing laser intensity. At 1200 and 1300 nm, we indeed observe a static TCI. At 800 nm, however, we clearly see that the TCI moves to higher energies with increasing intensity. This is not consistent with the simple-TCI picture described above, as originally proposed by [Vozzi 2011].

Figures 4 (d-f) demonstrate the key benefit of measuring harmonic phases as well as amplitudes. As for the normalized amplitude, we see a clear intensity dependence of the relative phase at 800 nm, while the phase is intensity-independent at 1200 and 1300 nm. Note the qualitatively different phase behavior at 800 nm, which confirms that the TCI results from a different mechanism than in the mid-infrared (consistent results have been observed at 1500 nm, not shown).

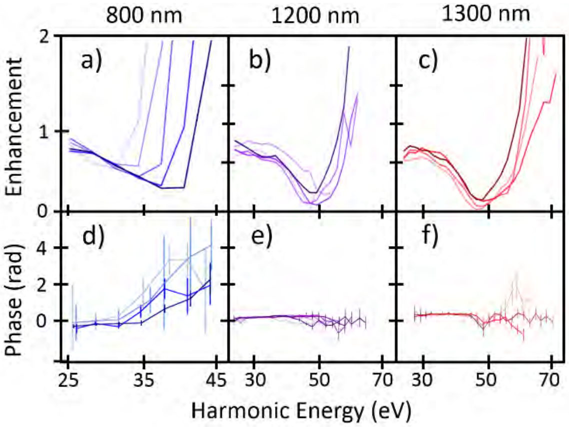

Figure 4: Normalized spectral amplitude (top row) and phase (bottom) in HHS of aligned CO_2 molecules. Here we compare TCI features with varying laser wavelength (see titles) and intensity (on each panel, increasing intensities are labeled with darker curves). We normalize the data by taking the ratio of the 0° and 90° signals with respect to the laser polarization.

Transient two-center interference in HHS: On the theory side, we have done several follow-up investigations to the two-center HHS experiments and calculations presented in [Gorman 2019]. In particular, in [Mauger 2019] we provided the theoretical background supporting our claim that we can calculate experimentally relevant HHG signals from many-electron molecules using theoretical models. We then used these techniques to examine TCI in the asymmetric OCS molecule and found that we could clearly identify transient, *i.e.*, dynamical, effects of the field dressing on the TCI process.

Figure 5 illustrates several aspects of the transient TCI and how it manifests in the HHG spectrum. Panel (a) illustrates the electron recollision process during a *single* half-cycle of the laser field, with the laser polarization oriented either at 40° or at 220° with respect to the molecular axis. The molecule is oriented so that this leads to acceleration away from and recollision on the S-side (40°, red) or the O-side (220°, blue), respectively. Panel (b) illustrates that the harmonic spectra calculated from each of these single-recollision events are quite different: whereas the S-side spectrum has a deep minimum near 35 eV, the O-side spectrum is nearly flat. The black curve represents the signal one would get from an aligned sample (as opposed to up-down oriented), namely the coherent average of the two opposite-orientation spectra, which shows that the TCI-minimum is still visible, although at a slightly different energy.

Figure 5 (c) illustrates the dynamical aspect of the visibility of the TCI minimum. We show the DFT-calculated density of the oriented OCS molecule exposed to a static electric field so that its force points either O-to-S (left, like at the moment of O-side recollision) or S-to-O (right, like S-side recollision). Because the density is biased toward the electron-heavy S atom in the field-free case (middle), the applied field will either exacerbate or diminish this imbalance. This means that a recolliding wave packet on the S-side will “see” two centers with comparable density at the time of recollision, allowing for a very effective destructive interference

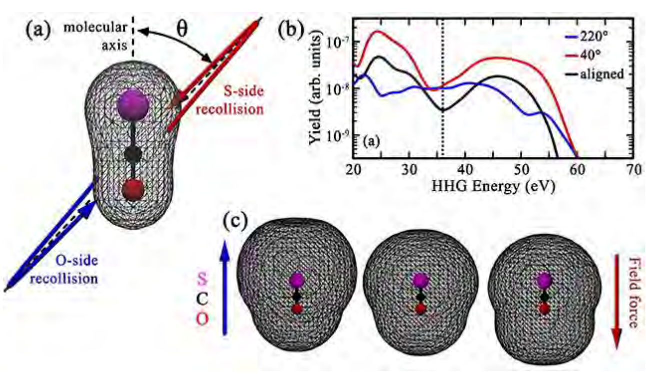

Figure 5: TCI in OCS molecule: (a) Oriented-molecule dynamics during one half-laser-cycle so that the electron recollides only on the S-side (red), or O-side (blue), with the resulting harmonic spectra shown in panel (b). (c) Calculated density of the OCS molecule exposed to a static field with a force pointing either O-to-S (blue, on the left), or S-to-O (red, right), as well as the field-free density (middle). The rebalancing of the asymmetric field-free density by the field in the latter case allows for the effective destructive interference between the contributions from the two centers seen in the red spectrum.

and thereby a deep TCI minimum, whereas that on the O-side will see two very different centers. We have also found that the sign of the group delay feature associated with the TCI minimum provides information on the orientation of the charge-imbalance at the time of recollision, *i.e.*, which center has a more localized density (not shown in the figure). In combination, this means that the measured TCI spectral amplitude and phase of an oriented molecule in a highly controlled laser field provides information about the dynamical charge distribution of the molecule, and as such offer a promising framework to probe ultrafast CM dynamics.

Further progress in our joint effort to coherently probe CM involves deploying methods that can directly verify the theoretical insight we have gained so far. For instance, in molecules likes OCS or the conjugated chains supporting the migration modes identified in Thrust 1, we seek methods that can resolve head-tail asymmetry and different contribution channels. It also means applying quantum-control methods to align and orient those molecules, see Thrust 3 below.

Improved HHS setups: Molecular orientation has been central to our approach for studying CM for some time. As shown in Thrust 3 below, it can lead to site-specific ionization and a subsequently localized hole in molecules. Compared to its aligned-only counterpart, orientation also clarifies HHG fields by (i) removing head-tail averaging and (ii) bringing back the signal from even harmonics. Due to the challenges we have faced with producing molecular orientation so far, we have pursued additional types of spectroscopy.

In previous attempts to achieve molecular orientation using 800-nm pulses, we encountered two types problems: (i) the expected signal in HHS from molecular orientation with this method has been demonstrated to be very small [Kraus 2012], and (ii) the ionization induced while using 800-nm alignment pulses limits the intensities we can use and therefore the alignment/orientation we can achieve. To mitigate this ionization effect, we have demonstrated impulsive alignment with the signal (1100-1600 nm) and idler (1600-2200 nm) beams from the OPA instead of the depleted 800-nm OPA-pump beam previously used. The ionization rate is considerably lower at the longer wavelengths, allowing us to use higher intensities to hopefully achieve better alignment. To date, we have focused on proof-of-principle measurements in CO_2, and have observed similar degrees of alignment to the previous published work at 800 nm [Gorman 2019]. Because nearly all molecules of future study will likely have ionization potentials lower than 14 eV, this represents a useful tool with greater flexibility when molecular alignment and orientation is to be involved in future studies.

Because two-color HHG offers many of the same benefits as molecular orientation, we chose to examine its application and calibration with MIR wavelengths, an unexplored area of study. By generating and overlapping a second harmonic of the fundamental field, the resulting two-color field creates a high-harmonic frequency comb with both odd and even harmonics, effectively doubling the energetic sampling compared to conventional fundamental-field only. For its analysis, we have developed algorithms using the "phase reconstruction by omega-oscillation filtering" (PROOF) method and an improved second-generation iteration (iPROOF) for phase analysis. Preliminary work has focused on measurements of electron correlation delays in argon and helium, and are the topic of an upcoming publication [Scarborough 2020]. The PROOF measurements were performed in collaboration with Prof. Guillaume Laurent (Auburn).

Thrust 3: Frequency-matched ionization spectroscopy (FIS)

Through Thrust 3, the ATTO-CM team seeks to determine if periodic hole motion within a molecule, initiated by strong-field single ionization, can be detected by observing changes in the double ionization yield as the period of the ionizing laser is tuned to match that of the oscillating hole. As such, the underlying focus is on understanding strong-field single and multiple ionization from aligned and oriented molecules. This Thrust plays a central and unifying role across the network, as SFI is the first step in high-harmonic and attosecond pulse generation, and the use of aligned and/or oriented molecules may be essential for effectively inducing, controlling, and probing CM dynamics. Indeed, our development of experimental and theoretical methods to enable direct comparisons of measured and simulated intensity- and angle-dependent

SFI yields critically informs the research performed in Thrusts 1 and 2. As an example, after verification of their TDDFT SFI calculations, using direct comparisons with angle-resolved ionization measurements performed at UVa, the LSU node has been able to predict, with confidence, that molecular alignment plays a key role in the degree of localization of a hole produced through SFI. This insight will guide continuing work on probing CM. In addition, the alignment/orientation expertise developed at UVa will be valuable for the molecular-frame HHS measurements at OSU (see Thrust 2 above). Likewise, interactions between all three nodes have been essential for progress in Thrust 3 and, by extension, for its impact on the overall goals of the network. For instance, the optimal molecular species to be studied in ionization measurements at UVa have been determined through numerous discussions with the LSU and OSU personnel, based on previous experience and prospects for future calculations and HHS measurements.

Ionization spectroscopy of the halomethane family: Following our recent work with linear molecules (OCS) [Sándor 2018], we have measured and computed intensity- and angle-dependent ionization yields in several members of the CH_3X (X = halogen) family, allowing us to investigate the impact of functionalization on the ionization process and subsequent hole localization and dynamics. A manuscript showing the excellent agreement between theory and experiment, and describing what we have learned about the significant differences in the sub-cycle strong-field dynamics across this molecular family, has been submitted for publication [Sándor 2019].

Moving our focus from aligned to oriented species, experiments comparing the effectiveness of bichromatic optical vs THz pulses to transiently orient neutral molecules have begun. Whereas ionization appears to be a substantial drawback for bichromatic optical orientation methods [Znakovskaya 2014], non-ionizing THz-based schemes are currently limited by the magnitude of the permanent electric dipole moment of the molecules and the strength of the THz fields that can be applied [Machholm 2001, Fleischer 2011, Kitano 2013, Egodapitiya 2014]. Ultimately, we intend to test our recent theoretical predictions about the role of the relative orientation of the molecular dipole with respect to the ionizing field polarization for enhancing (or suppressing) molecular ionization and its influence on initial hole-localization.

The effort in Thrust 3 relies on theoretical and experimental tools developed within the network. The LSU node uses TDDFT to simulate molecular SFI. These simulations are a crucial first step towards reliably predicting the channels involved in SFI and, ultimately, CM dynamics. On the experimental side, the UVa node measures ionization yields as a function of delay between non-ionizing "alignment" and more intense "ionization" pulses and extracts angle-dependent strong-field ionization yields [Makhija 2016, Marceau 2017, Sándor 2018] from those pump-probe experiments. Comparison of experimental and simulation results allows for validation of TDDFT algorithms for computing molecular SFI across a wide range of laser intensities and polarizations.

The TDDFT simulations accurately predict the saturation intensities for SFI of CH_3Cl and CH_3Br as well as the angle

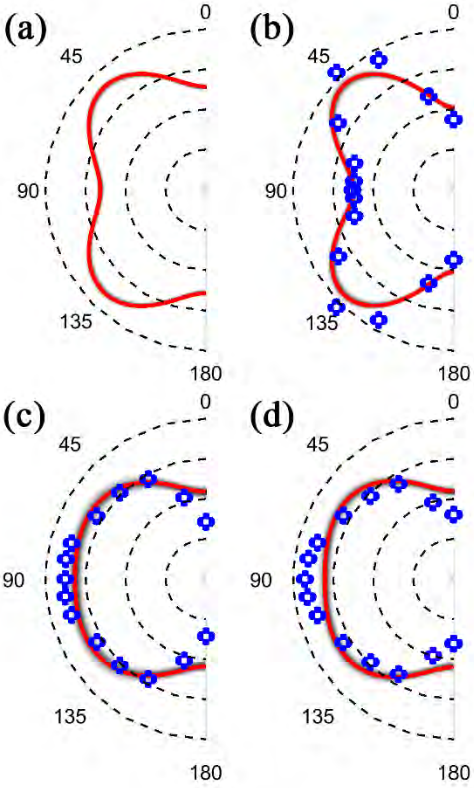

Figure 6: Ionization yields for CH_3Cl^+ at intensities of (a) 46 and (b) 64 TW/cm^2 and for CH_3Br^+ at (c) 45 and (d) 60 TW/cm^2 as a function of the angle between the molecular symmetry axis and the laser polarization. Red curves show measurements with grayscale shaded uncertainties. Blue symbols show TDDFT results.

dependence of the ionization yields for these molecules (Figure 6) [Sándor 2019]. The impressive agreement suggests that theory captures the essential features of the underlying strong-field dynamics and, therefore, that we can rely on the TDDFT simulations to provide insights into aspects of the ionization process that are not yet available from measurement. For example, using TDDFT we can confidently assert that the differences in the angular distributions in Figure 6 are due to molecule-dependent contributions to ionization from more tightly bound orbitals in CH_3Cl, presumably influencing the characteristics of the remaining hole in the cation.

Extending the calculations to CH_3F, we find that despite having identical symmetries and similar frontier orbital shapes, there are substantial differences in the mechanisms of ionization for these three molecules [Sándor 2019]. For instance, SFI in CH_3Br and CH_3F is largely single-channel, dominated by the HOMO. Conversely, SFI of CH_3Cl involves multiple channels, and the predominant contributor depends upon the alignment angle. This case clearly shows that, in general, molecular SFI calculations and interpretations based solely on the shape of a single orbital (*e.g.*, the HOMO) can be problematic. Our simulations also show that with increasing halogen mass, the hole produced during SFI of halomethanes is progressively more localized on the halogen atom (Figure 7).

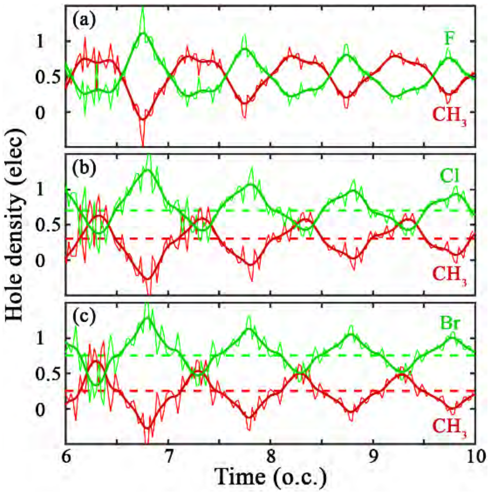

Figure 7: Reconstructed sub-cycle hole density around the methyl (red) and halogen (green) groups for cations with (a) fluorine, (b) chlorine, and (c) bromine functionalization vs optical cycle. Horizontal dashed lines label the cycle average localizations: 50% (CH_3F), 70% (CH_3Cl), and 75% (CH_3Br). In all panels, we use an 800 nm laser pulse with a constant-intensity envelope, six-laser-cycle ramp-up, and 45° alignment angle.

Taken together, our results offer a consistent picture, allowing us to infer other key aspects of the SFI dynamics in halomethanes that cannot be directly obtained from the calculations or experiments [Sándor 2019]. Specifically, ionization of CH_3F is dominated by electrons that are initially localized on the methyl group, and the ionization rate is greatest when the force on the electrons points from CH_3, out of the molecule. In CH_3Br, ionization is dominated by electrons that are initially localized on the Br, and proceeds more rapidly when the force on the electrons points from the Br, out of the molecule. In the intermediate case of CH_3Cl the ionization evolves from CH_3F-like to CH_3Br-like for molecular alignment parallel and perpendicular to the laser polarization, respectively. Thus, while the preferred direction of ionization (relative to the permanent molecular dipole) appears to reverse with alignment angle, the tunneling is always direct. Importantly, for all species and alignment angles, ionization appears to favor direct tunneling of electrons out of the molecule, rather than some intramolecular tunneling process.

Molecular orientation: Moving forward, our SFI picture in terms of orbital contributions and orientation dependent yields should be invaluable for interpreting and guiding experiments with bichromatic fields, aimed at exploring directional ionization and control of CM dynamics in halogen-functionalized oriented molecules. Indeed, our experiments comparing the effectiveness of bichromatic optical vs THz driven field-free orientation schemes are underway and will be followed by measurements of SFI of oriented molecules using directional, bichromatic fields.

To support experimental orientation developments, we have validated a method for computing frequency-dependent molecular hyperpolarizabilities using TDDFT. Dipole moments are computed at various field amplitudes and decomposed into first and second order responses, from which the polarizabilites are recovered [Ding 2013]. We checked and found good agreement with previously reported values in carbon monoxide and paranitroaniline molecules[Spanner 2012]. In conjunction with CM studies (Thrust 1), these first-principles computation will help guide choice for future CM-supporting candidate molecules that can be readily oriented using a two-color fields.

Cross-training and interactions between the network partners

We have maintained continuous communication between all the nodes of the network, including:

- Frequent Skype meetings between all partners, together with frequent, internode email, phone, and Skype communications between smaller working groups that target specific tasks.
- An intranet website (with content access restricted to members of the ATTO-CM network), featuring results of common interest, all meeting notes, and many relevant papers. The network also has a cloud storage facility to share, archive and back up data.

These active exchanges have maintained a strong collaborative community among the PIs, students and postdocs. Results of the ATTO-CM network were showcased in numerous international conferences.

ATTO-CM workshop: The first yearly ATTO-CM workshop was held at LSU on February 21-22nd, 2019. The workshop had oral presentations from all nodes (PIs, students and postdocs) of the network. It also featured contributions from three invited external speakers: Lars Madsen (Aarhus University), Tom Weinacht (Stony Brook), and James Cryan (Stanford/Pulse). These external speakers were selected for their expertise in theory/experiments related to ultrafast phenomena in AMO and CM questions. The workshop concluded with a PIs' meeting during which the long-term directions for the network were reaffirmed and the projects for the next 12-to-18 months were refined. The workshop was very successful (a sentiment that was shared by both collaboration members and external visitors) and we intend to iterate it again next year.

Future Plans

We believe that the continued interactions between the three nodes of the ATTO-CM network is a cornerstone of our success. We fully intend to continue our current interactions, *i.e.*, with regular communication (Skype, emails, etc.) and exchange visits between the nodes. Building upon our Recent Progress, for each thrust (Figure 1) area we intend to focus our efforts as follows:

- Thrust 1: Determine the effect of molecular geometry, bonding, and chemical functionalization on both hole localization and CM dynamics, and elucidate the importance of dephasing on CM.
- Thrust 2: Informed by conclusions from Thrust 1, calculations of HHG in systems exhibiting CM will be undertaken, in parallel with nonlinear dynamics investigation to better control the CM initiation. HHS experiments using two-color fields to improve molecular alignment are in progress, with the aim of controlling the hole-initialization site in future CM studies.
- Thrust 3: Initiate FIS experiments and refine strong-field-ionization computational methods. Optimize field free molecular orientation using bichromatic and/or THz fields. With maturation, these techniques will be transferred to molecular-frame HHS (Thrust 2). Explore frequency-resolved one-photon XUV ionization as a probe of hole localization.

Below we briefly explain the main avenues we intend to pursue to advance our chances of observing CM with strong laser fields.

AN ATTOCHEMISTRY PICTURE OF CHARGE MIGRATION: Based on our observations that the dynamics are primarily dictated by the location of the hole (rather than particular orbitals), we will use constrained DFT and similar techniques to create holes on specific sites in the molecule. The focus will be on hole/donor acceptor schemes to enhance and direct CM, and branching motifs for directing holes across molecules.

We will also begin addressing the role of dephasing on CM. These effects can potentially be exploited to selectively enhance or diminish particular CM modes due to their different dephasing times. To assess the robustness of each CM mode to dephasing, we will first compute the hole dynamics for a range of geometries perturbed along particular vibrational modes. For quantitative predictions, we will use Ehrenfest TDDFT to directly include the interactions between the electronic and nuclear degrees of freedom.

NONLINEAR DYNAMICS OF CHARGE MIGRATION: In the TDDFT framework, electron correlation is modeled by a nonlinear effective-interaction potential that depends on the mean-field one-body density. Deeper understanding of how electron dynamics are organized by these nonlinearities can shed light on CM motions of interest to the ATTO-CM network. The LSU node is planning on applying modern nonlinear-dynamics tools and analyses (for example, frequency-map analysis) to study CMs modes identified in Thrust 1 above. Preliminary investigations, using dimensionally reduced and simplified interactions models, have shown promising results. We will extend the most promising tools and analyses to full-TDDFT-molecular systems.

HHS CALCULATIONS IN SYSTEMS WITH CHARGE MIGRATION: We will be initiating grid-based investigations into HHG in systems that we know exhibit CM. We have reproduced the studies of initiation and characterization of CM in the iodoalkene family, similar to those described in the Thrust 1, but using grid-based TDDFT as implemented in the open-software code Octopus. Doing these calculations on a spatial grid is crucial for the extension to HHG calculations. In initial studies, we will focus on systematic HHG-and-CM calculations in one- and two-dimensional model systems in which we can exert control over the structure and CM dynamics of the system. Our long-term goal is to investigate HHG in the iodoalkene family both with and without initiating the CM prior to the HHG driving pulse.

TWO-COLOR HHG WITH ORIENTATION: Having demonstrated impulsive molecular alignment with MIR wavelengths, we intend to further pursue molecular orientation in a two-color version of this setup. As mentioned above, orientation provides an asymmetry in the molecular sample which can give atomic-site specificity in the point of ionization, increasing measurement precision and overlap with theoretical calculations. Using the additional flexibility provided by the wavelength tunability of our OPA and the lower rate of ionization from longer wavelengths, we will explore orientation using two-color fields in the MIR. A two-color orientation pulse can then be used in conjunction with the two-color HHG driving fields. By combining an up-down asymmetric molecular distribution with an up-down asymmetric electric field, full resolution can be achieved regarding the atomic site of ionization, and a new dimension of specificity can be achieved in the measurement which has eluded our prior efforts.

PROBING CHARGE MIGRATION THROUGH FIS: We are engaged in experiments to directly compare, in the same apparatus and with the same molecules (*e.g.*, OCS and CH_3X), the degree of field- and ionization-free orientation that can be achieved with bichromatic laser and THz techniques, respectively. We have now separately observed transient orientation in OCS with THz and phase-controlled bichromatic optical pulses. Once we have optimized and fully characterized the two approaches, we will employ the better method to explore ionization of oriented molecules using bichromatic pulses that have a pronounced (and known) directional field asymmetry. Through such measurements, we will test TDDFT predictions from the LSU node for the dependence of the SFI rate on molecular orientation relative to the ionizing field [Sándor 2018, Sándor 2019]. Using calculations for the time-scales for principal CM modes in different species (Thrust 1, Figure 2), we will prepare for FIS measurements by experimentally characterizing dissociative and non-dissociative ionization in aligned and/or oriented candidate molecules.

In conjunction with experiments, we will improve our TDDFT methodology for computing SFI yields. One current limitation to our Gaussian basis set approach is the nonphysical "leakage" of charge due to overlap with the complex absorbing potential (CAP). We have developed, and are currently validating, an approach for remedying this problem by "filtering" out the effect of the CAP on bound states. This will give us access to lower intensities in simulations. Additionally, in the coming year we will extend our approach to compute ionization yields of oriented molecules via bichromatic pulses. This will involve either simulating explicit two-color pulses, or alternatively computing sub-cycle ionization rates from analysis of the time-dependent density. Finally, the accuracy of TDDFT for multi-color ionization is less well explored. Thus, in addition to interpreting experiments, this project also offers an ideal opportunity to validate various functionals, especially IP-tuned range-separated hybrids.

MOLECULES AS XUV-DETECTORS: We are now exploring using the molecules of interest as the XUV detection gas. This offers a variety of benefits, both scientific and practical. Using single-XUV-photon ionization as the detector opens up many more potential molecules of study than traditional HHS. A further advantage is that information about individual molecular orbitals can be accessed by studying UV-XUV absorption. In an appropriate experimental architecture, we can begin to probe state-selective phase structures involving dynamics. This ability would add a new dimension to CM studies, as the hole's occupation in a superposition of orbitals may be represented in either amplitude or phase in such measurements.

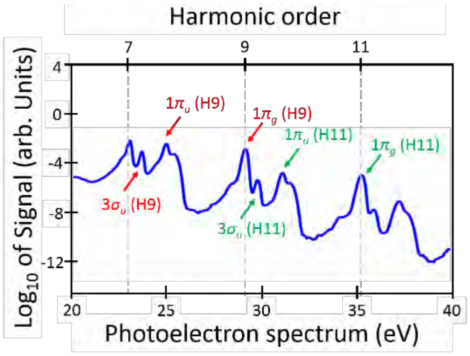

Figure 8: With a 400 nm HHG field, the photoelectron spectrum of CO_2 can be resolved with greater clarity. The shorter wavelength spreads the harmonic comb, allowing orbital-specific measurements. In this case, the 9th and 11th harmonics are shown to create six dominant peaks, from the three highest occupied orbitals of CO_2.

We show a proof-of-principle measurement in Figure 8. By doubling the fundamental Ti:Sapphire laser's wavelength and generating harmonics with a 400-nm HHG pulse, we can energetically spread out the harmonic comb spacing. This provides enough resolution for orbital-specific measurements and may become an interesting path forward for the ATTO-CM project. We may also benefit from a better overlap between theory and experiment, as the computationally-expensive angle-dependent TDDFT could be replaced by simpler multi-photon calculations.

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FEMTOSECOND AND ATTOSECOND LASER-PULSE ENERGY TRANSFORMATION AND CONCENTRATION IN NANOSTRUCTURED SYSTEMS

DOE Grant No. DE-FG02-01ER15213

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1 Program 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 2017-2019 are: [1-8]. Among these publications, the following articles acknowledging this Grant's major support have been published: [1, 2, 4-7]. The following articles have received, as acknowledged, supplementary support of this grant during this Grant period: [3, 8].

2.1 Weyl Semimetals in Ultrafast Laser Fields [7]

We study theoretically the interaction of topological Weyl semimetals with an ultrafast optical pulse. The electron dynamics in such material is coherent and highly anisotropic. For some directions of pulse polarization, the electronic dynamics is irreversible, which means that the residual electron conduction-band population after the pulse is comparable to the maximum conduction-band population during the pulse. For other directions of polarization, the electron dynamics is highly reversible and, after the pulse, the electron system returns to its initial state with almost zero conduction-band population. Such high anisotropy in electron dynamics is related to anisotropy in interband dipole matrix elements. In the reciprocal space, the electron conduction-band population density shows hot spots near the Weyl points. The optical pulse also causes net charge transfer through the system. The direction of transfer is the same as the direction of the field maximum. The transferred charge has highly anisotropic dependence on polarization direction with almost zero transferred charge for some directions

2.2 Topological Resonance and Single-Optical-Cycle Valley Polarization in Gapped Graphene [8]

For gapped graphene, we predict that an intense ultrashort (single-oscillation) circularly polarized optical pulse can induce a large population of the conduction band and a large valley polarization. With an increase in the band gap, the magnitude of the valley polarization gradually increases from zero (for the native gapless graphene) to a value on the order of unity. The energy bandwidth of the electrons excited into the conduction band can be very large (~10 eV for a reasonable pulse amplitude of ~0.5 V/Å). These phenomena are due to the effect of topological resonance: The matching of the topological (geometric) phase and the dynamic phase. Gapped graphene with a tunable band gap can be used as a convenient generic model of two-dimensional semiconductors with honeycomb generic lattice structures and broken inversion symmetry, such as transition metal dichalcogenides.

2.3 Femtosecond valley polarization and topological resonances in transition metal dichalcogenides [5]

We have theoretically introduced the fundamentally fastest induction of a significant population and valley polarization in a monolayer of a transition metal dichalcogenide (i.e., MoS2 and WS2). This may be extended to other two-dimensional materials with the same symmetry. This valley polarization can be written and read out by a pulse consisting of just a single optical oscillation with a duration of a few femtoseconds and an amplitude of ~0.25 V/Å. Under these conditions, we predict an effect of topological resonance, which is due to the Bloch motion of electrons in the reciprocal space where electron population textures are formed due to non-Abelian Berry curvature. The predicted phenomena can be applied for information storage and processing in PHz-band optoelectronics.

2.4 Fundamentally fastest optical processes at the surface of a topological insulator [4]

We have predicted that a single oscillation of a strong optical pulse can significantly populate the surface conduction band of a three-dimensional topological insulator, Bi2Se3. Both linearly- and circularly-polarized pulses generate chiral textures of interference fringes of population in the surface Brillouin zone. These fringes constitute a self-referenced electron hologram carrying information on the topology of the surface Bloch bands, in particular, on the effect of the warping term of the low-energy Hamiltonian. These electron-interference phenomena are in a sharp contrast to graphene where there are no chiral textures for a linearly-polarized pulse and no interference fringes for circularly-polarized pulse. These predicted reciprocal space electron-population textures can be measured experimentally by time resolved angle resolved photoelectron spectroscopy (TR-ARPES) to gain direct access to non-Abelian Berry curvature at topological insulator surfaces.

2.5 Graphene superlattices in strong circularly polarized fields: Chirality, Berry Phase, and attosecond dynamics [1]

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 **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.

2.6 Interaction of crystalline topological insulator with an ultrashort laser pulse [2]

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 routs to ultrafast optical-field control of the CTIs and petahertz-band optoelectronics.

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 focusing on modern two-dimensional solids such as graphene, transitional metal dichalcogenides, boron nitride, the surfaces of topological insulators, and Weyl semimetals. We will focus on the recently introduced effect of topological resonance in two-dimensional solids. We will describe a plethora of optical and electric phenomena due to ultrafast valley- and spin-selective ultrafast excitation of electrons. Among them, currents during and after the pulse, edge currents in topological edge states and emission of THz radiation due to these currents. We will also describe induced ultrafast light reflection and absorption by such systems. Of particular interest is the study of effects of the Bloch band topology and nonlinear anisotropy.

4 Peer-Reviewed Publications Resulting from this Project (2017-2019)

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Complete spectroscopy in the attosecond regime

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Project Scope

The main scope of my research is to perform coherent measurements of the time dependent molecular structure with femto and attosecond time resolution.

Recent progress

New lab infrastructure

On September of 2019 the lab moved to a new location with much better infrastructure thanks to large investments from the university. The new space was designed, from the ground up, as an ultrafast laser laboratory. One key aspect is an HVAC system that controls the temperature and humidity with very tight tolerances all year round using low-speed laminar flow air handlers. In addition, we also have several HEPA filters also with laminar flow, lab-wide chilled water and vacuum lines as well as enclosed closets dedicated for noisy or wet equipment. In addition to this large investment by the university, the college of arts and sciences also provided funds to purchase floating, thick and heavy optical tables to mitigate vibrations plus state-of-the-art pointing correction systems. All of this infrastructure is currently working and installed in the new space. The laser system from Continuum/Amplitude produces 14-16mJ of energy per pulse and pulse durations as low as 16 fs with center wavelength that can be tuned from 750 to 850 nm thanks to a Mazzler-Dazzler combination. This October the system will be upgraded to produce 20mJ of energy per pulse. We can use the laser system to seed a dual high energy optical parametric amplifier that so far has been able to generate 1.5 mJ on each arm.

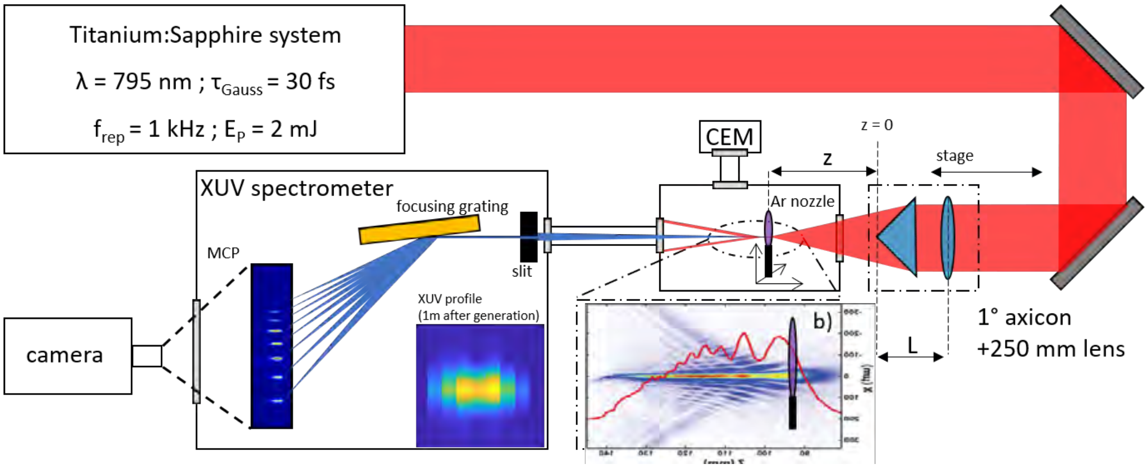

Figure 1: Experimental setup used to study the generation of higher order harmonics with Bessel-like beams generated by the combination of a lens and an axicon. The two main parameters explored in the experiment are the lens-axicon distance and the distance to the gas jet. In unison with the harmonic yield we also measure ionization with a channel electron multiplier (CEM in the figure). The XUV beam profile was measured with a micro-channel plate 1m away from the interacting region. b) Zoom of the spatial beam profile at the interaction region showing the intensity oscillations typical of a Bessel-like beam.

Finally, in the Spring of 2019 we purchased a new laser system that will be placed in another room adjacent to the current lab. This new laser system will have 300 W of average power and will have a tunable repetition rate from 20 kHz to 100 kHz and will be capable of producing pulses as short as 6 fs. Both labs are optically connected to Prof. Nora Berrah's lab so that laser beams can be send from each laser to a all available experimental setups.

Generation of higher-order harmonics with Bessel-like beams

By using a lens-axicon optical system we have demonstrated greater control of the effective Rayleigh range and spot sizes that can be very beneficial for strong-field experiments. We have recently concluded taking experimental data showing how harmonics can be generated with this optical system. The experimental setup is shown in Fig. 1 v

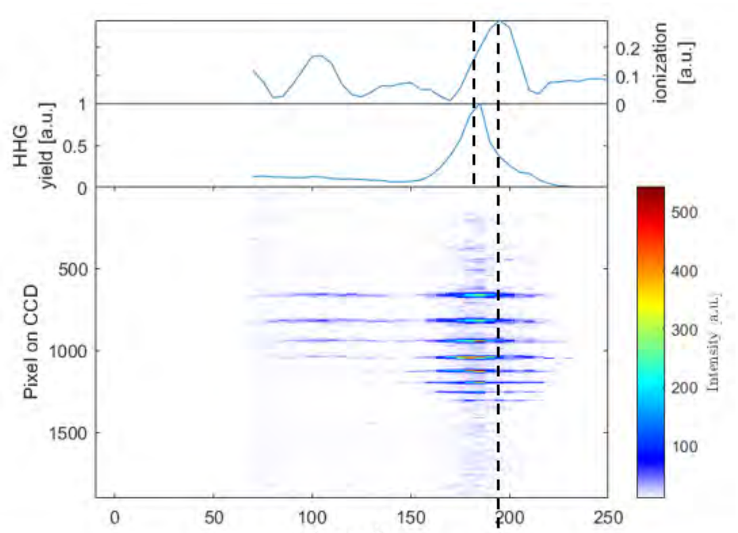

Figure 2: Ionization and harmonic yield generated in Ar with a combination of lens and axicon as shown in Fig. 1. All measurements are as a function of the distance of the gas jet to the tip of the axicon. Top, ionization yield. Center panel integrated harmonic yield. Bottom panel lineout of harmonics 11 to 23rd. The dashed vertical lines indicate the maximum harmonic and ionization yield.

This work aims to produce harmonics from Bessel-like beams and study the relative intensity of the harmonics across the focal profile of the beam. Further, we measure ionization yield in conjunction with the HHG signal to provide insight into the local phase matching conditions that mediate the two competing effects. A schematic of the experimental setup is shown in Fig. 1. Argon gas is injected into the source chamber as a thin gas jet produced by a hollow core (250μm core diameter) capillary approximately 5 cm from the entrance window of the chamber.

Experimental results are shown in Fig. 2. In all panels the x axis is the distance from the tip of the axicon to the gas jet measured in mm. Top panel shows the ionization signal, medium panel shows the integrated harmonic yield and the lower panel shows harmonic lineouts, as recorded by the spectrometer camera. The two vertical dashed lines indicate where the maximum of the ionization and integrated harmonic yield occur. Ionization follows strictly the intensity of the field whereas the harmonics depend also on the phase matching conditions. It is evident from the figure that while harmonics can be generated at multiple positions where the field becomes intense, by far the highest yield is obtained in the first intensity oscillation. The XUV yields obtained with these Bessel beams are comparable with yields obtained with Gaussian beams of the same pulse energy and similar peak intensities. However, the geometry needed to maintain phase matching is more compact in this approach.

Generation of non-interfering Bessel-like beams

One of the ultimate goals of our research is to develop heterodyne spectroscopic methods for phase and amplitude measurements of dynamic quantum processes in molecules. One step in that direction is to perform measurements with XUV beams in the absence of strong fields. As such we have first demonstrated the generation of two Bessel-like beams whose relative optical phase , or CEP, can be controlled independently with the aid of a spatial light modulator (SLM). As in the previous setup, we also make use of a lens and axicon but with the addition of an SLM that induces a tilt in the incoming wavefront as we demonstrated in our recent publication (Opt. Exp. **27**, 22960-22969, (2019)). This combination results (see Fig. 3) in the generation of two Bessel beams that can be focused to generate an intense region for both CW and femtosecond pulses for z=50 to 130 mm from the tip of the axicon whose relative optical phase can be controlled.

A second feature of the beam profiles is observed for distances greater than z¿ 130mm. As it is typical for Bessel beams, in the far field they develop a donut mode with almost zero field in the center. As can be seen from the experimental results we recover this behavior as well. However, as can be seen from the Fig. 1 and Fig. 2, the HHG beam profile remains phase matched in the forward direction. Thus, these field-free regions of the fundamental are ideal for spectroscopy with XUV beams. Panels c) and d) show lineouts of the same figures for femtosecond pulses or CW lasers respectively, as marked by the red lines in panels a) and b), from this panels, it is obvious that a marked field-free region is formed for z¿150mm and the aperture of this zone is controlled with the SLM.

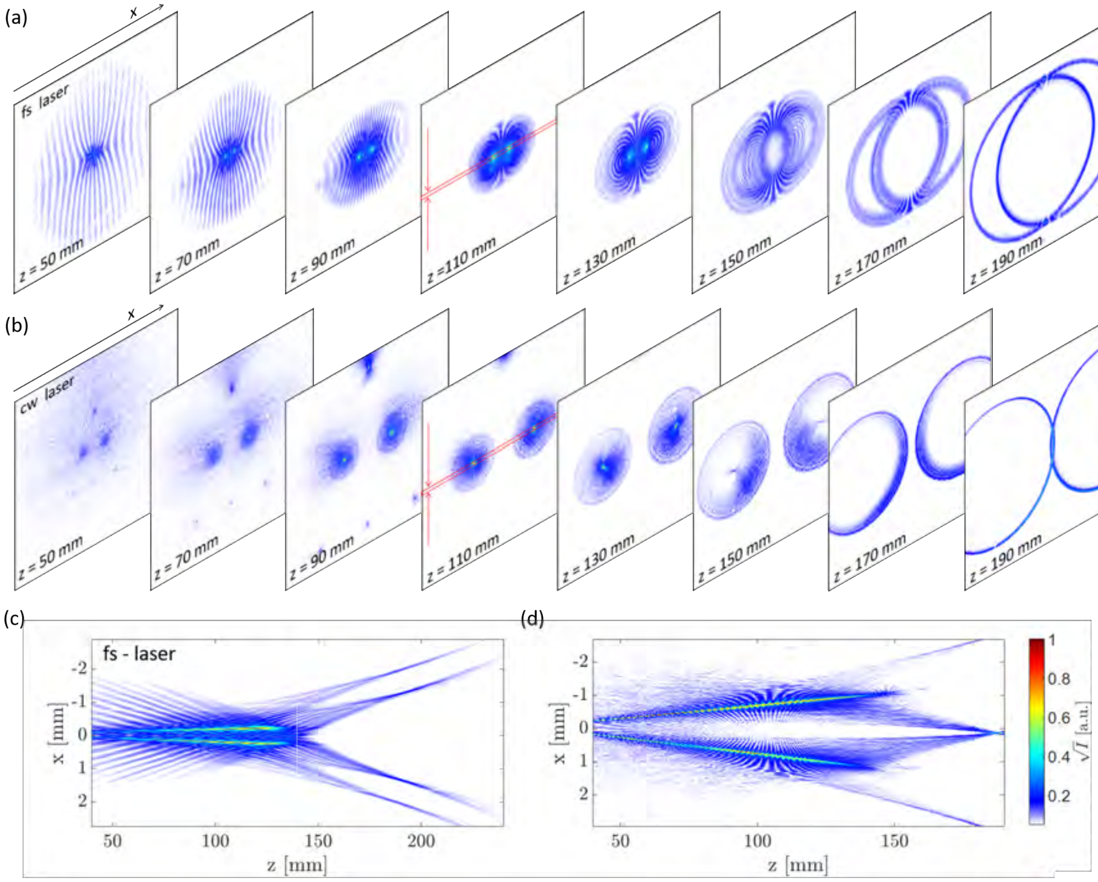

Figure 3: a) Generation of two Bessel-like beams with a combination of lens, axicon and an SLM that provides two tilted wavefronts to the incoming beam. Laser light is centered at 800 nm and 30fs in duration. There are two prominent regions in the spatial profile evolution. From z=50 to 130 mm there are two well defined foci that produce high intensity beams, and at z¿130mm the beams evolve into two large field-free regions. b) same as a) but for a HeNe laser. Figures c) and d) are linetous of the beam profiles as indicated by the red arrows in the panels a) and b) respectively. For transient absorption spectroscopy the sample would be placed in the field free region where only the XUV generated through HHG is phase matched in the forward direction.

One of the main results of this study is to show that the field-free region remains unchanged when the optical or relative CEP phase between the two Bessel beams is changed. Thus, multiple Bessel beams can be used for interferometric XUV spectroscopy.

Future work

We will continue our development of transient absorption spectroscopy methods with Bessel beams applied to the study of aligned molecules an inner shell dynamics. Currently we are working on several excitation schemes, some of which involve field-free alignment of molecular targets. For this, we have already purchased and tested an Even-Lavie valve. Thanks to the high power of our laser we can have several schemes in which multiple pulses can be used for alignment/excitation.

In the Summer of 2020, we will install our new laser source that will open many new possibilities. One of such is to build an XUV/attosecond beam line that will be attached to ions and/or electron detectors. Thanks to an AFOSR grant we are building a high energy velocity map imaging detector that can also be used for molecular dynamic studies.

Peer-Reviewed Publications Resulting from this Project (Project start date August 16th 2018)

- Self referencing attosecond interferometer with zeptosecond precision, Jan Troß, Georgios Kolliopoulos, and Carlos A. Trallero-Herrero, Optics Express, **27**, 22960, (2019)

- High harmonic generation spectroscopy via orbital angular momentum, Jan Troßand Carlos A Trallero-Herrero, The Journal of Chemical Physics, **151**, 084308 (2019)

Laser-Produced Coherent X-Ray Sources

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Program Scope

Using a high-peak-power laser system at the Extreme Light Laboratory of the University of Nebraska-Lincoln, we develop novel femtosecond radiation sources and use them to investigate ultrafast photo-induced processes. Pulses of high energy electrons and x-rays are generated when an optical pulse is focused to ultra-high intensity. The radiation is used to probe the evolution of matter under highly non-equilibrium conditions with atomic-scale temporal and spatial resolution. Moreover, the facility is small enough to fit in a university laboratory, and is operated by graduate students and postdocs.

Recent Progress

The femtosecond electron bunches generated by means of laser-wakefield acceleration (LWFA) are energetic, highly charged, and have excellent beam quality. They can thus be used for ultrafast electron diffraction or to drive femtosecond bunches of x-rays via any of several mechanisms: inverse-Compton scattering, betatron oscillation, or bremsstrahlung. The synchronized pulses of tunable electrons and photons (optical or x-ray) produced in this manner [1] can be used for time-resolved pump-probe studies [2]. We report two important advances: (1) vortex x-rays carrying orbital angular momentum were produced, and (2) plasma waves structures were probed with femtosecond pulses.

Vortex x-rays carrying orbital angular momentum

Research with photons carrying orbital angular momentum (OAM)—associated with the rotation of helically polarized beams—has recently attracted much attention from the scientific community. In the range of extreme ultraviolet (EUV) and x-ray wavelengths, such twisted light can be used to violate the dipolar selection rules to excite new effects in photoionization experiments [3], to unfold quadrupolar and higher-order transitions in x-ray magnetic circular dichroism [4], and to provide information on the structure and properties of many materials in resonant inelastic x-ray scattering [5]. Furthermore, there is a strong expectation that OAM gamma rays could permit the population of nuclear states with angular momentum [6].

The traditional methods for generating twisted beams are based on the use of fork holograms or spiral phase masks. In those methods, both the low damage threshold of the optical masks and difficulties in fabricating high-quality optical surfaces limit the energy of twisted light beams to the EUV and soft x-ray spectral ranges, which consequently limits their applications to the atomic and molecular scales. It was theoretically proposed that Inverse-Compton Scattering can be used to generate twisted x-ray beams, which would allow to alleviate the above limitations, and thus enable application of the twisted hard x-ray beams.

We were able to achieve the first experimental observation of MeV-energy twisted x-rays generated via ICS. A single laser system was used to produce the light used for both scattering and laser-wakefield electron acceleration. A novel technique was developed to add OAM to a high-energy infrared light and focus it to the highest intensity required to achieve high x-ray conversion efficiency. Experimental measurements of the generated x-ray beam were found to be consistent with the properties of twisted light predicted by theory and numerical simulation (see Figure 1).

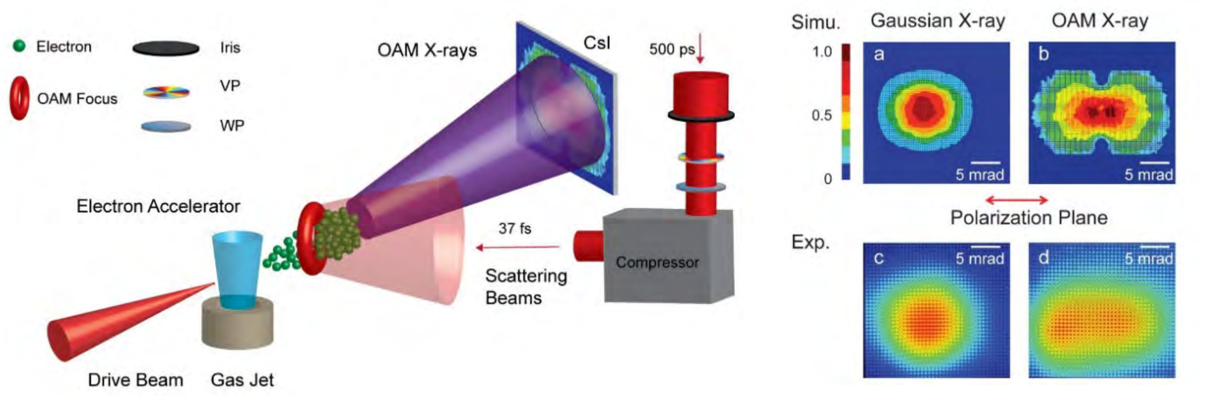

Figure 1. Left: experiment setup for generation of twisted x-rays through ICS. The electron beam was generated by LWFA when the drive beam was focused into the gas jet. The vortex scattering beam was produced by first passing a laser beam through a serrated aperture, to truncate its size, and then through a vortex phase plate. Right: X-ray beam spatial profiles. Left-side column: linearly-polarized scattering laser pulse without OAM focused to Gaussian-shaped spot; right-side column: helically-polarized laser pulse with OAM focused to annular-shaped spot. (a, b) Simulated results based on experimentally measured laser parameters. (c-j) Experimental results.

Plasma wave structure probed with femtosecond pulses

We developed a novel probe of the structure of a plasma wave. Two high-intensity laser pulses were launched into a laser-produced plasma, and made to overlap each other in time and space. Both pulses were strong enough to drive their own wakes. The interaction between the pulses and their wakes results in the injection of the free plasma electrons into the drive wakefield plasma wave [7], and also measures the wave structure of the acceleration buckets. The accelerated electron beam has a quasi-monoenergetic multi-peaked spectra. Particle-in-Cell (PIC) numerical simulations show that multiple buckets of the drive wake are loaded with electrons in each bucket, forming individual bunches, which are separated from each other by a plasma wavelength.

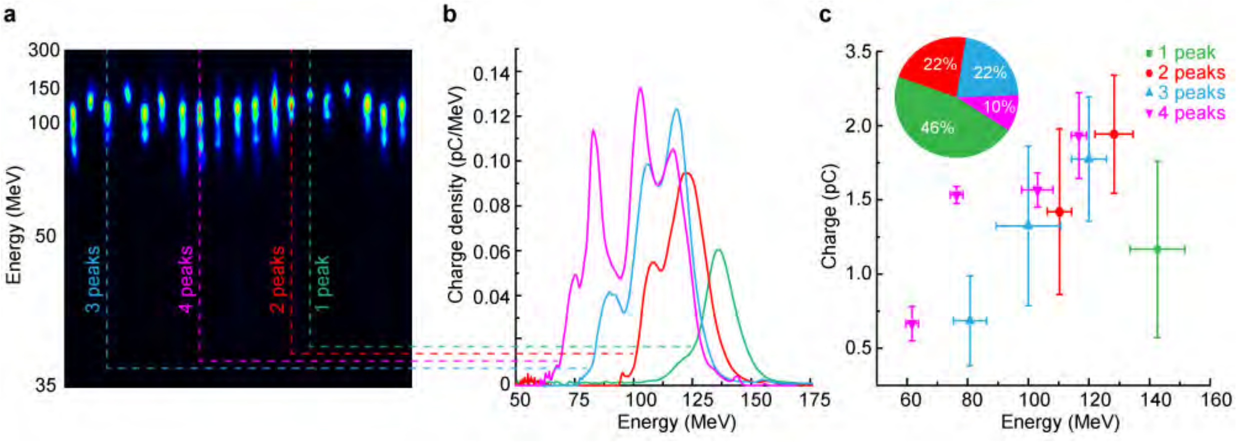

Figure 2. Magnetically dispersed Lanex images of a series of electron beams measured in 19 consecutive laser shots. b) Representative spectra of the beams with 1,2,3, and 4 energy peaks from the series. c) Charge and central energy of individual spectral peaks of single- and multi-peaked electron beams for a larger, but non-consecutive series of 50 laser shots. The inset shows proportions of shots with electron beams with a different number of spectral peaks. For all shown shots the plasma density is 0.76x10^{19} *cm*$^{-3}$*, drive and injector laser pulses normalized vector potentials are* a_0*=1.4 and* a_1*=9 (in vacuum).*

Electron spectra of experimentally measured bunch trains are shown in Figure 2. Evolution of the drive wake after its collision with the injector wake, simulated in 2D geometry with the PIC code EPOCH, is shown in Figure 3, where one can see a train structure of the electron beams.

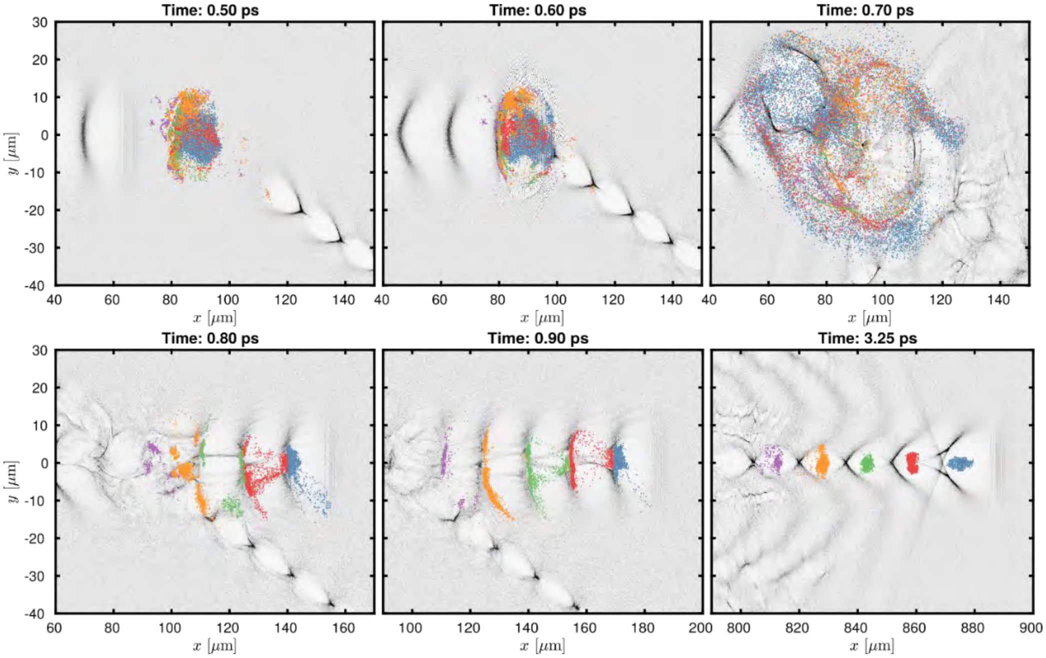

Figure 3. Density snapshots from PIC-simulations showing the evolution of the injection process, $a_1 = 2$*. Color points show the positions of electrons captured in the first five buckets.*

Future Plans

- Model and experimentally study the transfer of orbital angular momentum from a laser photons to x-rays.
- Compare focusing profiles of OAM and non-OAM x-rays.
- Compare photo-processes with OAM and non-OAM x-rays.

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Peer-Reviewed Publications Resulting from this Project (2017-2019)

G. Golovin, W. Yan, J. Luo, C. Fruhling, D. Haden, B. Zhao, C. Liu, M. Chen, S. Chen, P. Zhang, S. Banerjee and D. Umstadter, “Electron Trapping from Interactions between Laser-Driven Relativistic Plasma Waves,” Physical Review Letters **121**, 104801 (2018). doi: 10.1103/PhysRevLett.121.104801.

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

R. Rakowski, G. Golovin, J. O’Neal, J. Zhang, P. Zhang, B. Zhao, M. D. Wilson, M. C. 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,” Sci. Rep. **7**, (2017). doi: 10.1038/s41598-017-16477-0.

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 related molecular sciences. 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 experiments are complemented by time-resolved Rydberg fingerprint spectroscopy experiments, which are conducted at Brown University. Both methods are sensitive to 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, N,N-dimethylpiperazine, 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 advances our knowledge of molecules in excited electronic states and their chemical reaction dynamics. This aids numerous applications and provides benchmark data that support the continued development of computational methods.

II. Recent Progress

Based on exceptionally successful beam times at LCLS, especially LR83 in March 2018, we have achieved important milestones in the determination of time-dependent, excited state molecular structures and chemical reaction dynamics using X-ray scattering off gas phase molecules. In the experiment, an ultrashort laser pulse initiates the dynamic motions by exciting the target molecules to an excited electronic state. The time-delayed X-ray pulse intersects the sample and is scattered off the excited-state molecules, Figure 1. Analysis of the scattering patterns gives a molecular structure, for each moment in time. Stitching the time-sequenced molecular structures together results in a ‘molecular movie’ of atomic motions in molecules during reactive and non-reactive processes.

Several technical advances were implemented in the recent beam runs. The most important one was a separate, shot-to-shot intensity measurement of the X-ray pulse intensity. Even though the intensity of the X-ray pulses fluctuates widely, with the normalization using the diode signals we are able to measure changes in the scattering signals of less than 0.1%. Further, we have now optimized the shielding of the detector from stray X-ray radiation, resulting in a background signal that is more than two orders of magnitude weaker than the scattering from the gas. For reference, our sample length is about 2 mm and the gas pressure is around 4 Torr. All our LR83 experiments were done using 200 nm optical pump pulses.

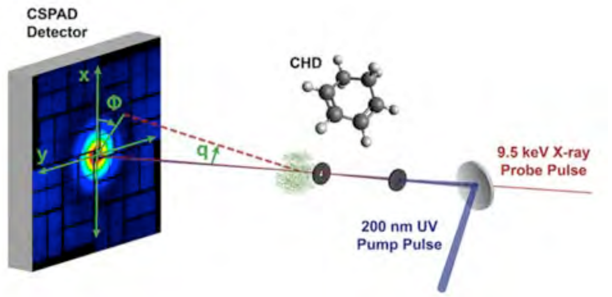

Figure 1: Experimental scheme: The molecules in the interaction region are intercepted by a linearly polarized UV laser (blue) and, at some time delay, by the X-ray pulse (red). Absorption of the UV pump pulse launches the structural molecular response. The X-ray probe is variably delayed with respect to the UV pump pulse to image the time dependent dynamics. Scattering signals are captured by the CSPAD detector.

The beam runs resulted in 100's of TB of data on multiple molecular systems. The analysis of this data requires extracting the molecular motions from this large amount of information. Since no standard way to analyze such data exists, we have developed new algorithms for capturing molecular motions from the scattering data. A selection of results is described in the following.

Orientation of molecular transition dipole moments

A great deal of information is contained in the pump-probe scattering signals. Interestingly, the signals are anisotropic because the linearly polarized laser pulse preferentially selects those molecules whose transition dipole moment is aligned with the laser polarization. The scattering signal therefore shows the structural image of the molecules in the laboratory frame, with the transition dipole moments aligned with the laser polarization. This allows us to measure the orientation of the transition dipole moment with respect to the molecular frame and thereby identify the excited state.[2]

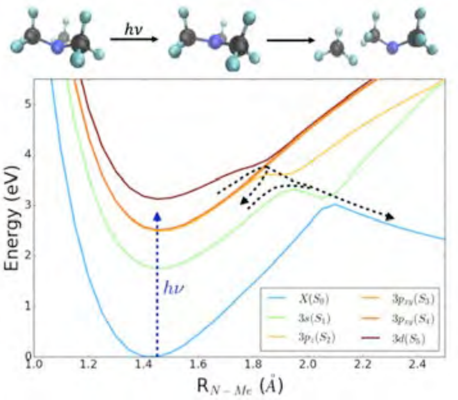

Figure 2: In trimethyl amine, optical excitation leads predominantly via the 3s state to dissociation to the dimethyl amine reaction product. Using small-angle scattering we discovered a minor reaction path that cleaves the N-C bond as the system passes through a conical intersection.

Interestingly, the anisotropy reappears after initial dephasing and persists for a long time. Because in many systems the structure changes as time passes, the long-time anisotropy can be stronger than the signal before dephasing. This helps to extract both the final state of the reacting system and the direction of the transition dipole moment of the original optical excitation.[9]

Bond cleavage as a result of a conical intersection

Tertiary amines are known to undergo internal conversion when excited to the 3p electronic state. From there, predissociation may take place via a repulsive σ* surface. We discovered that in trimethyl amine, there is additionally a minor reaction pathway that cleaves the bond directly as the system passes through a conical intersection. The time-resolved X-ray scattering experiment turns out to be particularly sensitive to dissociation reactions because the signal at small scattering angles is directly proportional to the square of the number of electrons in a molecule. The loss of coherence in the scattering signal resulting from dissociation causes a significant decrease in the small *q* signal, which is readily detected.[4]

Ab initio calculations of the total x-ray scattering signal

The results from X-ray scattering experiments are directly comparable to computational modeling. However, it is important to calculate the total scattering signal, not only the elastic scattering. The total scattering signal relates to electron correlation in the molecule and thus requires the construction of the two-electron density. We have developed tools to do so and found that in small model systems, H_2 and CO_2, the inelastic component of the total scattering varies notably with molecular geometry.[3]

Scattering off molecules far from equilibrium

In many systems, the excitation energy embedded in the molecules upon optical excitation ultimately thermalizes, resulting in systems that encompass structures far from the ground state geometry. For polyatomic molecular systems, large amplitude vibrational motions are associated with anharmonicity and shifts of interatomic distances, making analytical scattering equations using harmonic approximations inapplicable. More generally, the interatomic distances in a polyatomic molecule are not independent of each other, so that the traditional equations commonly used to interpret scattering data may give unphysical results. This correlation between structural displacements during large amplitude vibrations must be considered to correctly interpret scattering patterns.[8]

In 1,3-cyclohexadiene excited at 200 nm, the energy thermalizes quite quickly, leading to structure distributions that deviate significantly from their vibrationless equilibrium.[9] An analysis of the scattering signals shows that a significant contribution to the scattering signal arises from transition state structures near the inversion barrier of CHD. In the hexatriene product, our analysis clarifies that previously inconsistent structural parameters determined [by other groups] using electron diffraction were artifacts that might have resulted from the neglect of the structure correlations.[8]

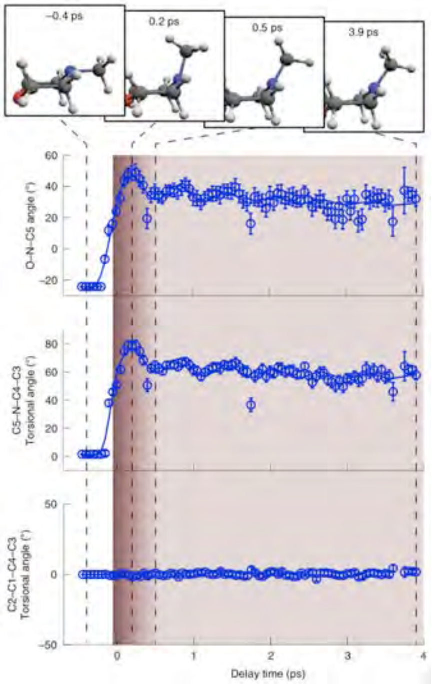

Figure 3: The time-dependent structure of N-methyl morpholine upon excitation to the 3p state with 200 nm pulses.

Complete, time-dependent excited state structures

N-methyl morpholine (NMM) is an interesting model system because it displays a transition from coherent to incoherent dynamics, and because structural coherence survives the transition through a conical intersection that leads from the initially excited 3p to the lower 3s state. The molecules are prepared in the 3p electronic state by a 200 nm laser pulse. Rapid internal conversion on the 100 fs time scale leads to 3s. This leads to a vibrational motion in the umbrella inversion coordinate, which we mapped in time and space using X-ray scattering (Figure 3).

To correctly interpret the scattering patterns, we found it necessary to include the contribution to the scattering signal that arises from electronic excitation. Further, the inelastic scattering needs to be taken into consideration. With that, we have developed an analysis method that uses a large number of structures created by simulations, and that picks the best fitting structure for each time step. The method is robust and yields reproducible bond parameters. Importantly, the method inherently includes the hydrogen atoms and gives the complete molecular structure: all bond distances, bond angles and dihedral angles. The end result of the analysis is the excited state structure with mÅ resolution, as a function of time with 50 fs time steps.

III. Future Plans

We continue to refine the data analysis method with a focus to determine nuclear probability density distributions from the scattering pattern. Additionally, we are developing the tools to extract the electron density distributions. This will be done using existing data sets.

Looking forward, we are implementing a new upconversion scheme to generate shorter UV pulses at the CXI endstation. Shorter pulses will enable us to better resolve the reaction dynamics. Our goal is to image the molecules as they transition conical intersections, something that we hope to be able to do with LCLS-II.

Finally, we are systematically exploring the relative advantages of X-ray scattering versus electron scattering. This will be done using model simulations, and, hopefully, by doing comparable X-ray and MeV-UED experiments at SLAC.

IV. Peer-Reviewed Publications resulting from this Project (Project start date: 08/2017)

1. "Putting the Disulfide Bridge at Risk - How UVC Radiation Leads to Ultrafast Rupture of the S-S bond" M. A.B. Larsen et al., *ChemPhysChem* **2018** *19*, DOI: 10.1002/cphc.201800610.
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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. In the past year we have made significant progress along the following fronts:

2.1 Excited state dynamics in conjugated systems

One of the questions that we want to address in this project is how the structure of conjugated systems affects their excited state dynamics. How does the number and position of double bonds, and the remaining system affect the isomerization products and the lifetimes of excited states? In order to start addressing these questions we have been exploring the dynamics of two conjugated cyclic systems, 1,3-cyclohexadiene (CHD) and 1,3-cyclooctadiene (COD). In both systems there are two alternating double bonds, but the remaining cyclic system imposes different constraints on the dynamics. In CHD, the dynamics are controlled by conical intersections with the ground state that can either lead to radiationless relaxation, or photochemistry to produce hexatriene. On the other hand, in COD there can be cis-trans isomerization in addition to relaxation or photochemistry to a bi-cyclic system or methylenecycloheptane (MCP). We are performing trajectory surface hopping calculations to look at the non-adiabatic dynamics of COD in more detail, exploring the competition between photophysics (i.e. relaxation back to the ground state), isomerization, and photochemistry. The surface hopping calculations reveal that both CHD and COD have very short excited state lifetimes. Figure 1 shows results of the surface hopping calculations which demonstrates the short lifetime and different pathways. Furthermore, there are different conformers of COD which exhibit different dynamics. We plan to further explore the conformer dependent dynamics.

In the past year, we worked on implementing three important experimental upgrades to our UV pump VUV probe apparatus for studying excited state dynamics. First, we worked to decrease scatter of UV and VUV light in the chamber, since the scattered photons led to an overwhelming number of stray electrons which prevented us from measuring time resolved photoelectron spectra. We did this mostly with a series of baffles in the vacuum chamber.

We also recently upgraded our measurement apparatus to improve the time resolution of our measurements. This was important because VUV absorption from the ground state can be stronger than UV absorption in many of the systems we are studying. This leads to dynamics on both sides of timezero, and for an impulse response function of the apparatus similar to the dynamic timescales, there is some mixing of VUV driven dynamics in the measured signal even when the center of the UV pulse precedes the center of the VUV pulse.

Finally, we implemented the Timepix camera into our measurements of excited state dynamics after having used it for the double ionization measurements. This allows us to carry out UV

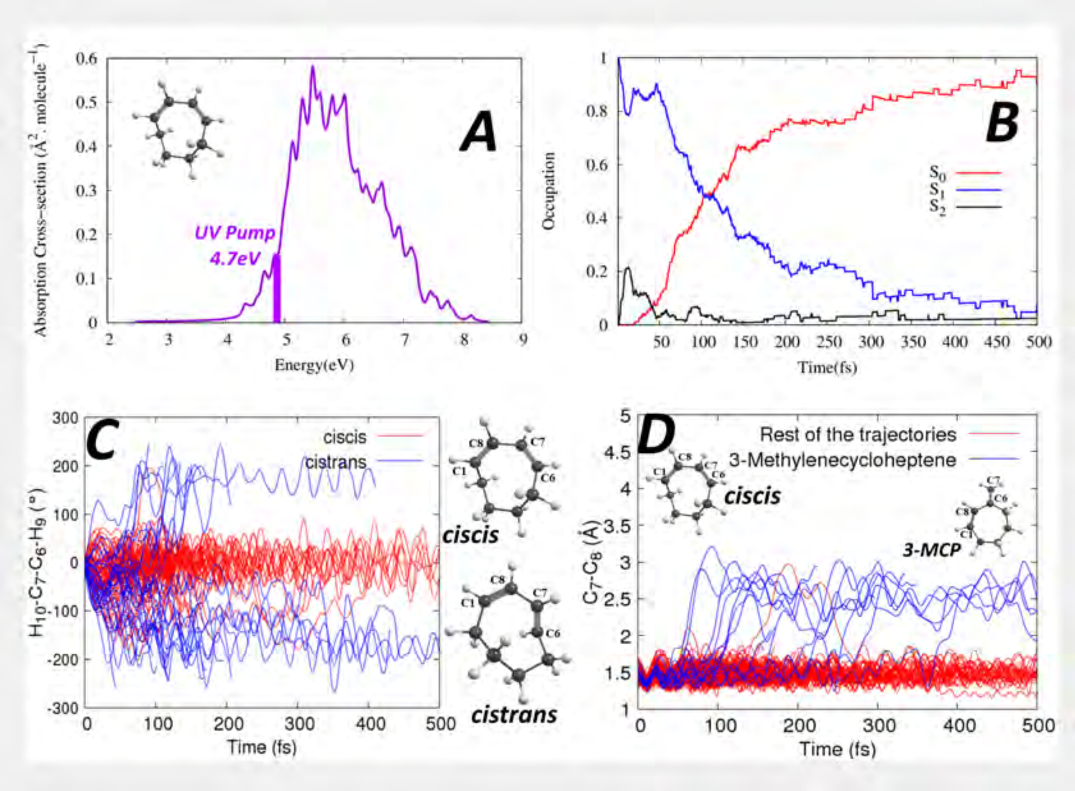

Figure 1: **UV absorption spectrum and trajectory surface hopping calculations for 1,3-cyclooctadiene (COD).** **A**: Calculated UV absorption spectrum. The experimental UV pump wavelength is indicated by the vertical bar. **B**: State populations as a function of time after UV excitation. **C**: Time dependent dihedral angle (H_{10}-C_7-C_6-H_9) for different trajectories. **D**: Time dependent bond lengths (C_7-H_8) for different trajectories.

pump VUV probe measurements of excited state dynamics, with velocity map imaging of both the electrons and ions produced in the interaction. Given the time resolution available with the camera, we do not need to perform an Abel inversion on the ion measurements, as the time information can be used to directly measure the three dimensional velocity distribution. The measurements can also be made in coincidence, measuring ions in coincidence with the electrons for every laser shot. We are not yet taking advantage of the coincidence capabilities at every pump probe delay given the 1 KHz repetition of our laser source, but we can use coincidence measurements to identify features in the photoelectron and photoion spectra that we can follow with non-coincidence measurements. We are now carrying out a series of measurements that we will compare with the trajectory surface hopping calculations described above. Figure 2 shows new measurements that take advantage of the developments described above to make velocity map imaged measurements of the fragment ion yields for COD as a function of VUV pump UV probe delay.

2.2 Strong and Weak-Field Ionization in Pump-Probe Spectroscopy

Another very important area that we have focused on is a comparison between strong and weak field ionization as a probe of excited state dynamics in polyatomic molecules. In previous work we developed and made use of both weak and strong field ionization as a probe of these dynamics. The availability of both approaches gives us the opportunity to compare the results, and determine whether the different probes provide similar or complementary information about the excited state dynamics. Theoretical studies using electronic structure and non-adiabatic dynamics have inter-

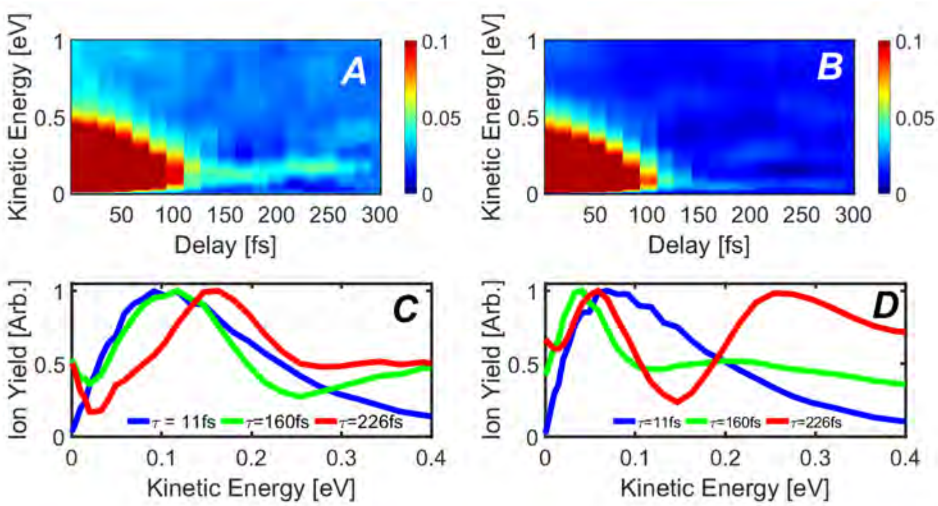

Figure 2: **Time-resolved photo-ion kinetic energy (KE) distribution for COD fragments .** **A**: Kinetic energy distribution of $C_7H_9{}^+$. **B**: Kinetic energy distribution of $C_5H_7{}^+$. **C**: $C_7H_9{}^+$ KE spectra for 3 different pump-probe delays. **D**: $C_5H_7{}^+$ KE spectra at three different pump-probe delays.

preted these results. Strong field ionization is advantageous because it uses wavelengths that are relatively easy to generate, and one can always ionize the molecule with sufficient intensity. However, for strong field ionization it is difficult to calculate observables, such as the time-dependent ion yield, since the calculation of the ionization dynamics including multi-photon processes is computationally expensive, and difficult to carry out for many molecular geometries. Weak field ionization has the advantage that calculations of observables are tractable. However, the generation and implementation of the appropriate wavelengths (photon energies) can be challenging, and the fixed energy of the probe can lead to technical complications in following the dynamics from excited states back down to the ground state. We performed a quantitative comparison of the two approaches for following the excited state dynamics of two molecules, CH_2I_2 and uracil. Our work indicates that while strong and weak field ionization provide qualitatively similar information about the excited state dynamics, only weak field results can be compared quantitatively with calculations.

2.3 Electron correlation in channel resolved strong field molecular double ionization

Strong field ionization plays a fundamental role in attosecond science as the source of electron wave packets which ultimately provide attosecond bursts of radiation as they are driven back to the atom or molecule of origin. Double ionization is an important probe of electron correlation (correlated electron dynamics), which lies at the core of attosecond science. While double ionization of atoms has been studied extensively, the double ionization of molecules is relatively unexplored - particularly for the case of polyatomic systems. Following earlier work on the double ionization of CHD, we performed coincidence (three and four particle) velocity map imaging measurements of molecular double ionization in 1,3-cyclohexadiene (1,3-CHD) and 1,4-cyclohexadiene (1,4-CHD) using our few cycle ($\sim$ 10 fs) laser pulses. The measurements allow us to distinguish between dissociative and non-dissociative double ionization, and we find a difference in the correlation of electrons that come from the different channels. Our calculations of the energy levels of the cations helped us interpret the experimental findings in terms of different inelastic rescattering mechanisms.

3 Future Plans

We have several goals for the immediate future:

1. We plan on carrying out a series of time resolved measurements on COD. These include time resolved ionization spectroscopy measurements, with full momentum resolution for electrons and fragment ions, as well as ultrafast electron diffraction (UED) experiments, which we intend to carry out at the relativistic UED facility at SLAC. Recent measurements on CH_2I_2 illustrated the power of combining theory and these two experimental techniques. We will perform similar experiments on COD, for which we have now interesting calculation results as described above.

2. We plan on extending our measurements of strong field double ionization of conjugated systems. We will make use of our coincidence velocity map imaging system to compare the electrons and ions measured in coincidence for benzene (C_6H_6), and cyclohexane (C_6H_{12}).

3. We plan on extending our excited state dynamics calculations in conjugated systems in order to establish systematic trends in the dynamics and associate features in the photoelectron spectra with specific trajectories.

4 Peer-Reviewed Publications Resulting from this Project (2017-2019)

- "Ultrafast Internal Conversion Dynamics of Highly Excited Pyrrole Studied with VUV/UV Pump Probe Spectroscopy", Spencer L. Horton, Yusong Liu, Pratip Chakraborty, Spiridoula Matsika, and Thomas Weinacht, *J. Chem. Phys.*, **146**, 064306 (2017)

- "Controlling Photorelaxation in Uracil with Shaped Laser Pulses: A Theoretical Assessment", Daniel Keefer, Sebastian Thallmair, Spiridoula Matsika, Regina de Vivie-Riedle, *J.Am. Chem. Soc.*, **139**, 5061 - 5066, (2017)

- "Vibrationally Assisted Below Threshold Ionization", Spencer L. Horton, Yusong Liu, Pratip Chakraborty, Spiridoula Matsika, and Thomas Weinacht, *Phys. Rev. A*, **95**, 063413, (2017)

- "Coincidence velocity map imaging using Tpx3Cam, a time stamping optical camera with 1.5 ns time resolution", Arthur Zhao, Martin van Beuzekom, Bram Bouwens, Dmitry Byelov, Irakli Chakaberia, Chuan Cheng, Erik Maddox, Andrei Nomerotski, Peter Svihra, Jan Visser, Vaclav Vrba, and Thomas Weinacht, *Review of Scientific Instruments*, **88**, 113104 (2017)

- "Quadruple coincidence measurement of electron correlation in strong-field molecular double ionization", Arthur Zhao, Chuan Cheng, Spiridoula Matsika and Thomas Weinacht, *Phys. Rev. A*, **97**,043412, (2018)

- "Strong-Field vs Weak-Field Ionization Pump-Probe Spectroscopy", Spencer Horton, Yusong Liu, Pratip Chakraborty, Philipp Marquetand,Tamas Rozgonyi, Spiridoula Matsika, and Thomas Weinacht, *Phys. Rev. A*, in press (2018)

- "Real-Time Adjustable, 11 Microsecond FWHM, > 5 KHz Piezo Electric Actuated Pulsed Atomic Beam Source", Anthony Catanese, Spencer Horton, Yusong Liu and Thomas Weinacht, *Review of Scientific Instruments*, in press (2018)

- "Strong and Weak-Field Ionization in Pump-Probe Spectroscopy", Spencer L. Horton, Yusong Liu, Pratip Chakraborty, Philipp Marquetand, Tamas Rozgonyi, Spiridoula Matsika, and Thomas Weinacht, *Phys. Rev. A*, 98, 053416, (2018)

- "Electron correlation in channel resolved strong field molecular double ionization", Chuan Cheng, Patricia Vindel Zandbergen, Spiridoula Matsika, and Thomas Weinacht, *Phys. Rev. A*, submitted (2019)

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October 28-30, 2019

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