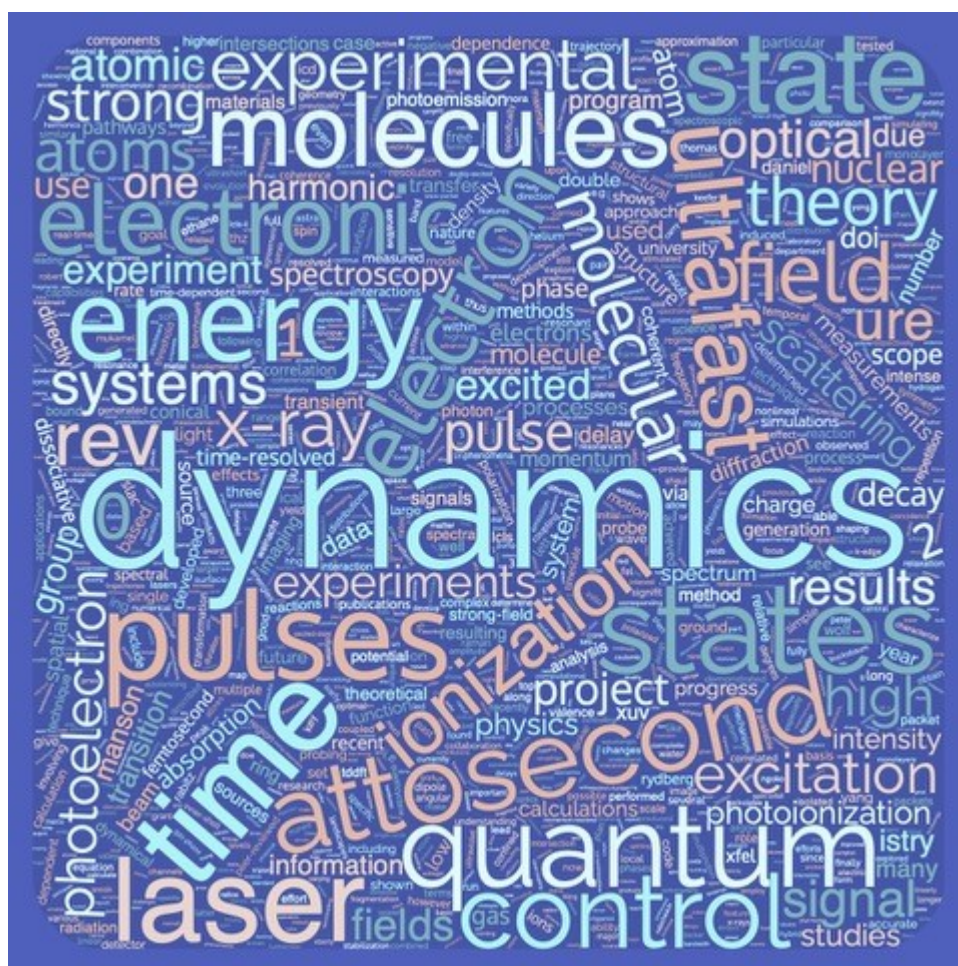# 2021
Atomic, Molecular, and Optical Sciences Research PI Meeting

Virtual Meeting
October 25-27, 2021

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

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Program and Abstracts

2021
Atomic, Molecular, and Optical Sciences
Research PI Meeting

Virtual Meeting
October 25–27, 2021

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

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FOREWORD

This volume summarizes the 41st 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 of the annual PI meeting is to facilitate scientific interchange among the PIs and to promote a sense of program identity.

The AMOS program continues to advance fundamental, hypothesis-driven research in ultrafast chemical sciences, with emphasis on strong-field and x-ray physics and chemical dynamics. The program supports basic experimental and theoretical research aimed at understanding the structural and dynamical properties of atomic and molecular systems. The research targets fundamental interactions of photons and electrons with atomic and molecular systems to characterize and control their behavior. The foundational knowledge and techniques produced by this research portfolio constitute crucial contributions in support of the BES mission.

The 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 DOE missions 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 and virtual 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), Linda Severs, Deneise Terry, and Connie Lansdon, for their help in planning and executing this *virtual* meeting. We also thank Teresa Crocket and Gwen Johnson in BES for their indispensable behind-the-scenes efforts in support of the BES/AMOS program.

L. Paul Parazzoli
Thomas B. Settersten
Gregory Fiechtner
Chemical Sciences, Geosciences, and Biosciences Division
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2021 Atomic, Molecular and Optical Sciences Research PI Meeting

Office of Basic Energy Sciences
U.S. Department of Energy
October 25 to 27, 2021 (Times are EDT)

Monday, Oct 25	
11:45 AM	Zoom Sign On (Zoom details to follow)
OPENING REMARKS	
12:00 PM	*BES/CSGB Update and Outlook* **Bruce C. Garrett,** CSGB Division Director
12:30 PM	*Welcome and Introductory Remarks* **Thomas B. Settersten**, AMOS Program Manager **Paul Parazzoli**, AMOS Program Manager
NEW PROJECTS	*3-minutes, 1 slide Summary*
12:45 PM	**Loren Greenman** Kansas State University
12:48 PM	**Alexandra Landsman** Ohio State University
12:51 PM	**Shaul Mukamel** UC Urvine
12:54 PM	**Tom Allison** Stony Brook University
12:57 PM	BREAK, 18 MINUTES
SESSION 1	*20-minute presentation, 10-minute Q&A*
1:15 PM	*Controlling Excited State Dynamics of First Row Transition Metal Complexes* **Amy Cordones-Hahn,** Stanford University
1:45 PM	*Imaging Photo-Induced Molecular Dynamics* **Daniel Rolles,** Kansas State University
2:15 PM	*Attosecond, Imaging and X-Ray Science* **Louis DiMauro,** Ohio State University
2:45 PM	*Machine-Learning Routes to Getting (Much) More Out of Data* **Abbas Ourmazd,** University of Wisconsin, Milwaukee
3:15 PM	BREAK, 30 MINUTES
SESSION 2	*20-minute presentation, 10-minute Q&A*
3:45 PM	*Strong-Field Molecular Dynamics* **Brett Esry,** Kansas State University
4:15 PM	*Transient Absorption and Reshaping of Ultrafast Radiation* **Mette Gaarde,** Louisiana State University
4:45 PM	*Multiphoton Ionization, Correlations, and Quantum Beat Phenomena* **Chris Greene,** Purdue University
5:15 PM	*Astra, A New Approach to Molecular Close-Coupling Ionization* **Luca Argenti,** University of Central Florida
5:45 PM	ADJOURN

Tuesday, Oct 26	
11:45 AM	Zoom Sign On
SESSION 3	*20-minute presentation, 10-minute Q&A*
12:00 PM	*Applications of Attosecond Wave-Mixing Spectroscopy to Atoms and Molecules* **Daniel Neumark,** UC Berkeley
12:30 PM	*Progress Towards Attosecond Experiments Using Industrial-Grade Lasers* **Michael Chini,** University of Central Florida
1:00 PM	*Attosecond Electron Dynamics Probed by X-Ray Free Electron Laser Pulses* **James Cryan,** SLAC
1:30 PM	BREAK, 30 MINUTES
SPECIAL LCLS SESSION	*Opportunities for AMOS at LCLS-II—*A discussion of the next generation of ultrafast experiments at LCLS-II. This session will explore opportunities to exploit the unique capabilities to study AMO science.
2:00 PM	*Introduction* **Philip Bucksbaum,** SLAC
2:05 PM	*Campaigns at LCLS (e.g., Attosecond Campaign)* **James Cryan,** SLAC
2:15 PM	*Outcome of Multidimensional Workshop* **Nora Berrah,** University of Connecticut
2:20 PM	*Discussion*
2:35 PM	*Attosecond Capabilities at LCLS-II* **Agostino Marinelli, SLAC**
2:45 PM	*Coincidence Spectroscopy End Station at LCLS (DREAM) and Science Applications* **Peter Walter** (SLAC) and **Thorsten Weber** (LBNL)
3:00 PM	*Tender X-ray Imaging Instrument at LCLS* **Andy Aquilla,** SLAC
3:10 PM	*Laser Capabilities at LCLS-II* **Franz Tavella,** SLAC
3:20 PM	*Discussion*
4:00 PM	*Break, 30 minutes*
Session 4	20-MINUTE PRESENTATION, 10-MINUTE Q&A
4:30 PM	*Imaging Electron Dynamics with Time-Resolved Momentum Microscopy* **Tom Allison, Stony Brook University**
5:00 PM	*Conformer-Specific Photochemistry Imaged in Real Space and Time* **Thomas Wolf**, Stanford University
5:30 PM	*Atomic Photoionization by Multiple Temporal Pairs of Slits* **Marcel Ngoko Djiokap**, University of Nebraska, Lincoln
6:00 PM	Adjourn

Wednesday, Oct 27	
11:45 AM	Zoom Sign On
SESSION 5	*20-minute presentation, 10-minute Q&A*
12:00 PM	*Self-Imaging with Slow and Fast Recolliding Photoelectron Wavepackets* **Cosmin Blaga,** Kansas State University
12:30 PM	*Simultaneously Tracking the Multiple Reaction Pathways of Strong-Field Ionized Polyatomic Molecules* **Marcos Dantus**, Michigan State University
1:00 PM	*Femtosecond Dynamics and Spectroscopy from First Principles* **Todd Martinez,** Stanford University
1:30 PM	BREAK, 30 MINUTES
SESSION 6	*20-minute presentation, 10-minute Q&A*
2:00 PM	*High-Resolution Fourier Spectroscopy of Post-Alignment Dynamics in Molecular Cations* **Vinod Kumarappan,** Kansas State University
2:30 PM	*Exploring Nonadiabatic Dynamics Using Theoretical and Experimental Time Resolved Photoelectron Spectra* **Spiridoula Matsika,** Temple University
3:00 PM	*Orbital Optimized Density Functional Theory for Core Excited States* **Martin Head-Gordon,** UC Berkeley
3:30 PM	BREAK, 30 MINUTES
SESSION 7	*20-minute presentation, 10-minute Q&A*
4:00 PM	*X-Ray Propagation Through Strongly Absorbing Media* **Linda Young,** Argonne National Laboratory**,** University of Chicago
4:30 PM	*Imaging Structural Dynamics in Isolated Molecules with Ultrafast Electron Diffraction* **Martin Centurion,** University of Nebraska, Lincoln
5:00 PM	*Timing Dissociative Dynamics of Small Molecules and Dimers with Internal Clocks* **Thorsten Weber,** LBNL
5:30 PM	*Nonlinear X-ray Spectroscopy of Elementary Molecular Events* **Shaul Mukamel,** UC Irvine
CLOSING REMARKS AND ADJOURN	
6:00 PM	**Thomas B. Settersten** **Paul Parazzoli**

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Laboratory Research Summaries (Alphabetical by Institution)

ARGONNE NATIONAL LABORATORY

J. R. MACDONALD LABORATORY

University Research Summaries (Alphabetical by PI)

AMO Physics at Argonne National Laboratory

Gilles Doumy, Phay Ho, Anne Marie March, Stephen Southworth,
Linda Young

Chemical Sciences and Engineering Division
Argonne National Laboratory, Lemont, IL 60439
gdoumy@anl.gov, pho@anl.gov, amarch@anl.gov,
southworth@anl.gov, young@anl.gov

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 and THETA supercomputer at the Argonne Leadership Computing Facility (ALCF). Our expertise in fundamental interactions has generated collaborations across the DOE complex from the Isotope Program to the EFRC on Interfacial Dynamics in Radioactive Environments and Materials, IDREAM.

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 computationally explore new atomistic imaging approaches enabled by the most intense femtosecond and attosecond x-ray pulses using massively parallel code developments built upon a knowledge base of the response of atoms and molecules. We have uncovered the importance of transient resonant excitation, and, have shown the applicability of fluorescence correlation imaging to catalytic nanoparticles. A new ALCC award to explore single particle imaging modalities aims to provide guidance for optimal conditions for x-ray imaging. We have extended our studies beyond non-linear x-ray interactions with isolated atomic and molecular samples to include propagation in optically thick samples where substantial energy exchange between the sample and field exists.

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 inner-shell phenomena in the energy domain and use ultrashort x-ray pulses from free-electron laser sources to explore inner-shell dynamics in the time domain via two-color x-ray pump/x-ray probe photoelectron spectroscopy. We have observed time-evolving chemical shifts and used stimulated x-ray Raman scattering to create localized electronic excitations. We are developing theoretical tools for high-precision predictions of time-evolving photoelectron and photoabsorption spectra in small molecules generated by tunable, intense, two-color attosecond pulses from XLEAP. We have developed and commissioned a new high-electron photoelectron spectroscopy instrument at the APS to study multielectron processes in the deepest inner shells of high-Z elements.

The third subtask focuses on understanding photo- or x-ray-initiated dynamics in condensed

phases at the atomic, molecular and electronic level. The APS is used for timescales picoseconds and longer while XFELs focus on femtosecond phenomena. In anticipation of the new timing structure of the upgraded APS (APS-U), we are developing new high-repetition-rate-optical pump/x-ray multiprobe methods that access timescales from few picoseconds to microseconds. Extensive planning is underway for the new sector at the APS-U with rapidly interchangable monochromatic/broadband capabilities, as well as complementary high-repetition rate optical transient absorption spectroscopy. Finally, studies of radiolysis in aqueous systems, building upon our earlier work, uses the new ChemRIXS beamline at LCLS and optical pump/infrared probe capabilities at the Argonne Center for Nanoscale Materials (CNM).

2 X-ray Physics at the Intensity Frontier

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

L. Young, K. Li[1], M. Gaarde[2], M. Labeye[3], P. J. Ho, G. Doumy, D. Koulentianos, S. H. Southworth, M. Meyer[4], T. Mazza[4], J. Laksman[4], T. Pfeifer[5], Ch. Ott[5], J.-E. Rubensson[6], Z.-H. Loh[7], A. Marinelli[8], J. Cryan[8], S. Li[8] and other collaborators

Project Scope: Understanding how x-rays propagate through optically thick media as a function of intensity. i.e. from the weak- to strong-field regimes as encountered at XFELs, is foundational for a complete understanding of nonlinear x-ray processes. Here we focus on a quantitative understanding of deviations from a linear absorption model for propagation through optically dense media. Using our 3D propagation model we devise experimental plans for validation. Such understanding may allow to tailor the temporal and spectral properties of a transmitted x-ray pulse, inform design of oscillator-based XFELs and serve as a stepping stone to nonlinear x-ray Raman spectroscopies.

Recent Progress: Understanding fundamental x-ray/matter interactions at high intensity is a vibrant frontier enabled by the continued development of x-ray free-electron lasers. Many experiments have now provided an understanding of x-ray–atom/molecule interactions in the single particle regime [13, 14, 43–51]. However, nonlinear propagation through resonant absorbing media where the back-action of the media alters the propagating field, basic for studies in the solid state, solution and gas phases via transmission-based x-ray transient absorption, has been much less studied. XFELs now deliver nearly transform-limited pulses with sub-femtosecond duration with the potential for MHz repetition rates [52] 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 achievable power density produces effects such as stimulated Raman scattering [53, 54], amplified spontaneous emission, pulse compression [55] which are relevant to proposed nonlinear x-ray spectroscopies [56, 57].

This year we published a theoretical study of temporal, spectral, and spatial reshaping of intense, ultrafast x-ray pulses propagating through a resonant medium [10]. Our calculations used a 3D time-dependent Schrödinger equation-Maxwell wave equation approach. While fully generalizable, we studied the case of incident x-ray photon energy on resonance with the core-level $1s \rightarrow 3p$ transition in neon. We studied the evolution of the combined incident and medium-generated field, including the effects of stimulated emission, absorption, ionization and Auger decay, as a function of the input pulse energy and duration. We found that stimulated Raman scattering between core-excited states $1s^{-1}3p$ and $2p^{-1}3p$ occurs at high x-ray intensity, and that the emission around this frequency is strongly enhanced when also including the response of the ion. At ultrahigh intensities, complicated transmitted spectra suggest x-ray dressed structure, self-induced transparency (SIT) and self-focusing.

We resubmitted our proposal to study resonant propagation and transient absorption from the weak- to strong-field regimes in the spectral domain, including results from the new theoretical paper. This is now awaiting scheduling at the EuXFEL SQS endstation for 2022 after COVID cancelled the original June 2020 beamtime. This experiment requires characterization of the incident SASE spectrum using, e.g. a "cookie-box" (an angular array of 16 photoelectron spectrometers perpendicular to the x-ray propagation axis) in the undulator hall [58], replacement of the standard AQS chamber with a target cell chamber designed and fabricated by the MPIK group, and installation of a transmission spectrometer from the Uppsala group. In May 2021, we studied the feasibility of high-resolution characterization of the incident SASE spectrum with the cookie-box in coordination with the EuXFEL staff - see Fig. 1. Using ghost-imaging algorithms [59, 60] we

achieved a resolving power of $\Delta E/E \sim 2000 \sim 0.50$ eV. A paper will be submitted reporting these results [61].

We also submitted a new proposal to LCLS to study propagation-induced reshaping of attosecond pulses in the temporal domain [10] using angular streaking techniques [52,62] in collaboration with SLAC staff (S. Li, J. Cryan, A. Marinelli). This proposal included a series of end-to-end simulations to establish feasibility: a collection of XLEAP attosecond pulses were propagated through the absorbing medium, subsequently streaked with a 4.0 μm laser and detected via co-axial velocity map imaging. Beyond informing applications such as transient absorption and wave-mixing the pulse structures contain multiple peaks and intricate interference fringes, which can be used to test the limitations of the angular streaking as a pulse diagnostic tool. It also provides valuable data for more sophisticated pulse reconstruction algorithm development that can be used to improve resolution and speed of current pulse diagnostics.
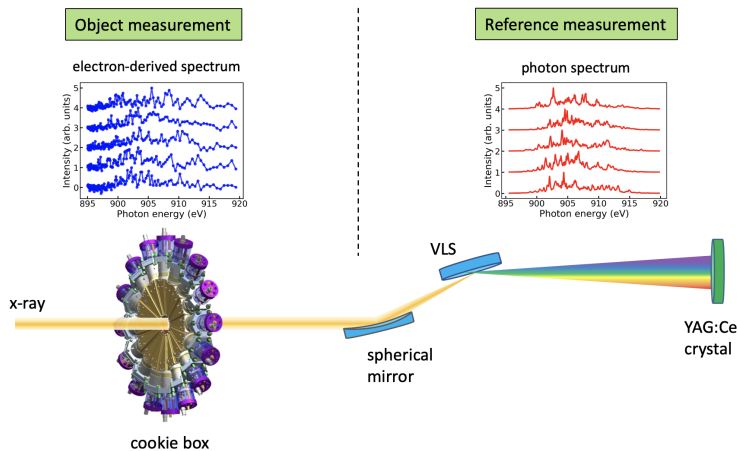
Figure 1: High-resolution single-shot SASE pulse spectral characterization. SASE XFEL pulses interact with dilute Ne gas in the cookie-box chamber where the kinetic energy of 1s photoelectrons are measured by an array of eTofs. The transmitted x-ray pulse is dispersed by a grating and the photon spectrum is imaged on a Ce;YAG screen and recorded on a shot-by-shot basis.

Future Plans: With beamtime at the EuXFEL, we plan to characterize the weak- to strong-field behavior for propagation through dense resonant media and test our theoretical model in the frequency domain. Depending on the outcome of the proposal at LCLS, we would be able to explore propagation-based temporal reshaping of attosecond pulses. We also anticipate potential theoretical extensions to the 3D code include propagation of arbitrarily polarized pulses. Collaborative studies using the code to predict small-gain XFEL oscillator behavior are planned.

2.2 X-ray Imaging Applications with Femtosecond and Attosecond Pulses

P. J. Ho, L. Young, S. H. Southworth, C. Knight[9], T. Gorkhover[10], S. Kuchel[10], C. Bostedt[11], D. Rupp[12], A. Niozu[13,14], Y. Kumagai[15], K. Ueda[14,16] 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 [63], radiation induced damage has been an important topic. Over the past years, our group has contributed to single particle imaging methods [1–6], including virtually contaminant-free sample delivery with an improved

electrospray injector [1], imaging structural dynamics in laser heated nanoparticles [2] and ultra-cold rotating superfluid droplets [6], characterizing crystalline defects in the scattering images [3, 5] and dynamics [13] in the scattering images and coincidence imaging combining single-shot X-ray scattering with fluorescence and ion time-of-flight (TOF) spectroscopy [4].

We continue to develop theoretical tools to explore high-resolution imaging applications with few-fs and sub-fs XFEL pulses. Last year, we submitted a successful ALCC proposal and were awarded 0.3-million node-hours to explore single-particle imaging modalities with resonant scatter-ing and fluorescence intensity correlation for achieving gains in signal and resolution on THETA, a pre-exascale machine at ALCF. We are currently porting our Monte-Carlo/Molecular-Dynamics (MC/MD) codes [64, 65] to the new GPU-based supercomputers at ALCF, THETAGPU and PO-LARIS. On the experimental side, we are continuing our collaboration with Tais Gorkhover and Christoph Bostedt. This year, we finished analyzing the scattering data of Xe clusters obtained with few-fs and sub-fs XFEL pulses at LCLS in soft x-ray regime. We found that transient ionic resonances [8, 45, 48] can be exploited for gains in scattering signals. A manuscript describing these results is being prepared for submission.

In addition to the soft x-ray regime, this year, we started resonant scattering investigations in the hard x-ray regime, which are important for achieving atomic spatial resolution. To guide the experimental study, we performed Monte-Carlo simulations [48, 49] to compute the coherent scattering cross section of atomic Fe. We found that scattering from a transient ion resonance around 6.3 keV (below the Fe K-edge) achieved via a 2-photon process can lead to an overall increased scattering signal for the Fe atom. The required pulse parameters used in the calculation are easily achievable with few-fs pulses from LCLS-II.

Future Plans: In collaboration with Gorkhover, we will perform experimental investigation of resonant and non-resonant imaging processes using sub-fs pulses at LCLS using both Xe and Kr clusters in 2022. An experimental proposal to study the effect of resonant scattering in iron oxide NPs in the hard x-ray regime was submitted. To go beyond the prediction from the Fe atomic calculations, we plan to perform a set of resonant scattering calculations for iron oxide NPs on THETA. The calculations will map out the effect of transient resonances on scattering in a complex environment under realistic experimental conditions. In addition, we plan to explore the effects of coherent electron dynamics, including Rabi oscillations, in resonant scattering.

2.3 Ultraintense, ultrashort pulse x-ray interactions in small molecules

P. J. Ho, A. E. A. Fouda, K. Li[1], G. Doumy, L. Young, A. Rudenko[17], D. Rolles[17], S.-K. Son[18], R. Santra[18],

Project Scope: We study intense x-ray field interactions with small molecules from the linear to nonlinear regime. We explore the sensitivity of the coherent scattering channel to electron correlation effects in molecules and examine x-ray pump / x-ray probe methods that can directly probe x-ray induced ultrafast charge transfer and dissociation.

Recent Progress:

The dream of performing single molecule imaging [63] via coherent x-ray scattering using "diffract-before-destroy" methodology with XFEL pulses has inspired many studies of x-ray-matter interactions at high intensities in free atoms [43–46, 48], molecules [50], and small clusters [65, 66]. In collaboration with researchers at KSU and CFEL, we performed a combined experimental and theoretical study of the ionization and fragmentation of iodomethane resulting from nonlinear x-ray interaction in the hard x-ray regime [14]. The experiment was performed at the CXI beamline of the LCLS. Femtosecond, 8.3-keV XFEL pulses were focused to a focal area of about 0.1 μm^2 in the center of the CXI vacuum chamber hosting an ion momentum imaging spectrometer. To

understand the experimental data, XMOLECULE calculations were performed to follow ionization and charge transfer dynamics. Here the timing of ionization steps leading to a particular reaction product and, thus, the product's final kinetic energy, was determined by the pulse duration rather than the pulse energy or intensity.

In addition to probing the intense-field dynamics via the ion spectra, we continue to explore the coherent (elastic) scattering channel, which has been the workhorse technique for studying larger targets in both the biological community [67,68] and the AMO physics community [8,69,70]. This year we published a theory paper [11] that investigates the x-ray scattering in 1,3-cyclohexadiene (CHD) and CH_3I in the hard x-ray regime from 5 to 24 keV. This work included progress in developing a molecular scattering code [11] that goes beyond the independent atom model (IAM) and employs *ab-initio* molecular wave functions for both ground state and excited states.

Future Plans: We plan to extend our molecular scattering code by combining it with the rate equation and time-dependent Schrödinger equation approach to study the dynamical scattering response of molecules in intense x-ray pulses. We plan to explore the feasibility of using CDI to study molecular bonding and electron correlation effects in small molecules.

2.4   X-ray imaging using higher-order correlations

P. J. Ho, L. Young, A. E. A. Fouda, C. Knight[9], and other collaborators

Project Scope: Coherent diffractive imaging (CDI) with XFEL pulses holds the promise to probe structure and follow the dynamics of non-periodic entities with atomic resolution. However, this approach remains challenging due to sample damage during the pulse [8,65]. 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:

This year we investigated the effectiveness of the fluorescence intensity correlation (FIC) approach [71] for achieving high spatial resolution and elemental contrast in Ar clusters and Mo-doped iron oxide nanoparticles with intense, fs and sub-fs XFEL pulses. We showed that the temporal emission profiles and the number of fluorescence photons, as well as the FICs, depend strongly on the XFEL pulse duration, suggesting that the pulse duration can serve as a control knob to optimize FIC imaging. Also, we showed that, in few-fs or sub-fs pulses, the resulting FICs from $K\alpha^h$ in general reveal a higher contrast than those from $K\alpha$ because of their narrower temporal emission profiles. We found that, while sub-fs pulses will substantially benefit the CDI approach, few-fs pulses may be sufficient for achieving high-resolution information with FIC.

More interestingly, we studied the FIC of heterogeneous nanoparticles, iron oxide structures with three different Mo dopant distributions, in an intense x-ray pulse. We showed that, while the scattering signals in the non-resonant regime are dominated by the Fe and O atoms and possess only small differences between the three structures, the FICs from $L\alpha$ of Mo illuminates the distribution of the Mo dopant. Our work suggested that FIC can be exploited for imaging the distribution of trace elements in non-resonant regime. These results are detailed in a published paper [12].

Future Plans: We plan to investigate the different excitation schemes and fluorescence channels in Mo that are currently accessible at LCLS-II and EuXFEL. This year, we received an ALCC award to exploit the full volumetric data (more than 10^{12} 2-point correlation functions) from a fixed sample orientation for structure analysis. Also, we plan to explore full spatial and temporal coherence, as well as higher-order coherence, $G^{(N)}(\vec{k}_1,...,\vec{k}_N)$ derived from the x-ray fluorescence of a collection of atoms exposed to intense XFEL pulses.

3 Ultrafast X-ray Induced Phenomena

3.1 Time-resolved chemical shifts

G. Doumy, S. H. Southworth, D. Koulentianos, P. J. Ho, A. E. A. Fouda, K. Li, L. Young, L. Cheng[19], A. Al Haddad[11], C. Bostedt[11], A Picon[20], S. Oberli[11], J. Marangos[21], T. Driver[8], J. Cryan[8], C. E. Liekhus-Schmaltz[22], R. B. Weakly[22], M. Khalil[22], N. Govind[23] and other collaborators

Project Scope: The interaction of x-ray photons with inner shell electrons in molecules creates localized excitations that evolve rapidly, leading to charge redistribution, decay cascades involving emission of electrons and photons, nuclear motion and eventually bond breaking. Using two-pulse, two-color modes at XFELs [72], we aim use site-sensitvity to follow both the first steps of electron dynamics in the core-excited states and the evolution of the molecule after the first decay processes take place. This knowledge is crucial in understanding the photochemical behavior of these molecules upon x-ray absorption.

Recent Progress: Our group has pioneered x-ray pump/x-ray probe experiments at LCLS, first looking at the final products of the interaction [73]. To identify the transient species created during the interaction and the ensuing evolution of the molecule, we brought to LCLS our hemispherical electron analyzer. Using x-ray photoemission spectroscopy (XPS), we followed the molecule CO after resonant x-ray excitation of the Oxygen $1s \to \pi^*$ transition. Advanced modeling involving a large number of decay pathways is needed to account for the data [74]. An x-ray absorption spectroscopy (XAS) experiment, led by colleagues from Imperial College, studied the dynamics of inner-valence hole states created by sudden photoionization in the isopropanol molecule through resonant interactions. This measurement paves the way to observe charge migration and charge transfer phenomena with space and time resolution inside a molecule [27].

Both experiments had been performed before the upgrade to LCLS-II and the new TMO endstation with the new soft x-ray undulators allowing for much larger photon energy difference between the two x-ray pulses. Our Nov 2020 experiment aimed at following the electronic and nuclear dynamics in small fluoroalkane molecules following an initial photoionization event at a carbon site. Running the beam in an $\omega/2\omega$ mode, with the first pulse centered at 370 eV (above the carbon K-edge, but below the fluorine K-edge) and the second pulse centered at 740 eV (above the F K-edge), we were able to measure pump/probe x-ray photoemission spectra using the VMI instrument in TMO. Immediately after removal of a C 1s electron, the second pulse probes core-excited molecules, inducing the formation of double core-hole states that were calculated by our collaborator Lan Cheng's group [16]. Analysis of the data collected during the experiment is ongoing.

Finally, two-pulse capabilities are also accessible in the hard x-ray region, and can be used to interrogate transition metal elements in solvated systems. Complex orbital relaxations and electron motions can be initiated by specifically ionizing the transition metal with the first pulse, probed via transmissive X-ray Absorption Near Edge Spectroscopy (XANES) with a second pulse. To model the expected signal, we have combined electron cascade calculations [48,49] and excited-state time-dependent density functional theory calculations (run by collaborators at PNNL) to predict the initial states prepared by the x-ray pump and their absorption spectra [24]. An experiment on the model complex $[Fe^{II}(CN)_6]^{4-}$ was performed at LCLS, and analysis is underway.

Future Plans: On the soft x-ray side, we aim to follow this theme by expanding in two directions. First, obtaining better temporal resolution through the use of attosecond pulses, with 2-pulse, 2-color available for users starting next year. Second, we will take advantage of the high repetition rate of LCLS-II to perform measurements in coincidence to ascertain the location of the first ionization step. Regarding transition metal complexes, we plan to develop an advanced

model to extend our electron cascade calculations to include the impact of the ligand-field splitting.

3.2 Resonant inner-shell excitations with intense attosecond x-ray pulses

G. Doumy, A. E. A. Fouda, D. Koulentianos, P. J. Ho, and others

Project Scope: Resonant interaction of x-rays with matter has been studied in depth, for the practical advantages of increased cross-section, to the ability to selectively excite atoms and molecules into specific electronic or vibrational states (e.g. in our x-ray pump /x-ray probe experiment on CO). On the other hand, intense attosecond x-ray pulses can be used to produce localized valence excitation through x-ray Raman scattering [17, 25] or are seen as necessary tools to image single particles without significant x-ray damage. We aim to study both theoretically and experimentally the unexplored regime of resonant interaction with intense attosecond pulses, identifying and quantifying the new processes that can occur.

Recent Progress: We propose to investigate the response of nitrous oxide N_2O to resonant excitation at the nitrogen K-edge under intense attosecond soft x-ray pulses such as those produced at LCLS. Through their bandwidth, pulse energy and ultrashort duration, these pulses provide unique interaction conditions expected to produce neutral, two-site excited double-core-hole states by promoting two core electrons to the same unoccupied molecular orbital, as shown in Fig.2.
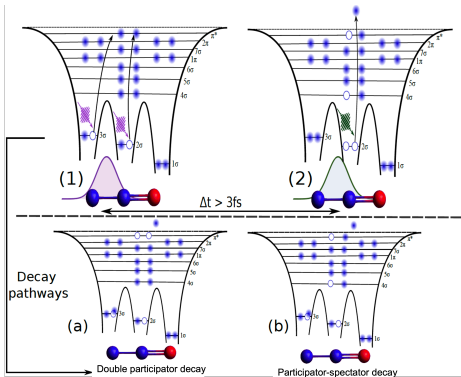
Figure 2: **Double-core excitation in nitrous oxide, and following decays** While the binding energy of core electrons increases significantly when a molecule is core ionized once, our calculations predict that following core-excitation, subsequent core-excitations from a different site occur at photon energies slightly lower than in the ground state. Qualitatively, this can be understood as the result of the stabilization of valence shells due to a higher charged core, while the core electrons binding energy remains essentially the same in the still neutral molecule.

Nitrous oxide is a convenient model system as a small molecule with two distinct atomic centers of the same element (N) with a significant chemical shift of about 4 eV. Advanced modelling techniques can be applied, and experimental observables can separate contributions from the two sites. Experimentally we can collect the deexcitation electron spectrum (i.e. resonant Auger spectrum) using the new, high-resolution, multi time-of-flight electron spectrometer developed for the TMO endstation (MRCO), since it will include additional channels e.g. a double-participator process where the two excited electrons are also involved in the decay process. Second, we will use the attosecond pump-probe capabilities to follow the decay pathways of these exotic states through the first and second decays by measuring evolving chemical shifts using a photon energy above core-electron binding energies following methods described in section 3.1.

Future Plans: A proposal was submitted at LCLS to perform this experiment, and our calculation results will be summarized in an independent paper. Further calculations will explore advanced calculations of the Auger de-excitation spectrum and the effect of the nuclear dynamics in the core-excited states.

3.3 High resolution electron spectroscopy of inner-shell resonance, threshold, and multiple core-hole processes

S. H. Southworth, D. Koulentianos, G. Doumy, S. Li, A. E. A. Fouda, P. J. Ho, L. Young, L. Cheng[19], M. N. Piancastelli,[24] M. Simon,[24] S. L. Sorensen[25] R. Puttner[26], and other collaborators

Project scope: Electron spectroscopies using tunable synchrotron radiation are sensitive to electronic structure, photoionization dynamics, and core-hole decay mechanisms, topics that pose an enduring challenge for theorists. The APS is ideal for Hard X-ray Photoelectron Spectroscopy (HAXPES) of high-Z elements. Heavy atom systems are distinguished by sub-femtosecond inner-shell lifetimes, large 1s-hole fluorescence yields, and multiple electronic shells that participate in core-hole decay pathways leading to highly charged final states and molecular ion fragmentation.

Recent Progress:

We have now implemented at the APS our EW4000 hemispherical analyzer that had previously been used for experiments at LCLS. First measurements were made around the K-edge of Kr (14327 eV) and the Br K-edge of CF_3Br ($\sim$13480 eV). The dominant radiative transfer of the 1s hole to the 2p shell is followed by L-MM Auger electron emission while K-LL emission is followed by LL-LMM Auger emission. The two decay pathways can be distinguished in the L-shell Auger electron spectra as shown in [75]. At APS, the Kr and Br L-MM Auger spectra were recorded across the pre-edge resonances and ionization thresholds to identify transitions resulting from different excitation and vacancy cascade pathways. The Kr L-MM measurements will be correlated with variations of ion charge states across the K-edge reported in [15]. The Br L-MM measurements will be correlated with ion fragmentation measurements following Br 1s ionization of CF_3Br.

Our APS efforts pursue our collaboration initiated with experiments at the SOLEIL synchrotron. From these earlier measurements, the C1s near-edge absorption of the molecule ethyl trifuoroacetate [76] was explained by comparison with coupled-cluster calculations [19], and the analysis of the resonant Auger electron spectra is progressing. In addition, in a project led by our collaborators, O $K^{-2}V$ electron spectrum of CO was recorded and compared with theory [23], helping to disentangle the pathways contributing to the formation of these excited states.

Our expertise in theory and experimental methods of x-ray and inner-shell processes is contributing to a new project lead by collaborators from Argonne's Physics Division. An instrument to capture electrons, ions and x-ray photons in coincidence (Argonne Auger Radioisotope Microscope, AARM) is under development, to be tested at the APS. One goal is to measure Auger electron multiplicities from medical radioisotopes, which use these low-energy Auger electrons to target tumors. Our calculations of x-ray induced vacancy cascades are supporting this development.

Future Plans: Our analyser is now installed in a more compact chamber with the necessary motions to adapt to multiple APS beamlines. Theoretical calculations in support of the first experiments are in progress. We are also analyzing x-ray/ion coincidence data of IBr, CH_2IBr, and CF_3Br recorded previously at APS, while also developing in-house theoretical support.

3.4 Attosecond science at LCLS

G. Doumy, P. J. Ho, S. H. Southworth, L. Young, D. Koulentianos, K. Li, J. Cryan[8], P. Walter[8], A. Marinelli[8] and other collaborators

Project Scope: The unique availability at LCLS of intense, sub-femtosecond pulses in the soft x-ray regime [52] is opening new areas of investigation. The ability to study electronic processes before decay processes or nuclear motion take place, coupled with the site-selectivity afforded by

x-ray interaction is opening a new window on observing electronic motion and electronic coherences.
Recent Progress: A multi-year scientific campaign to establish the basis of attosecond science at XFELs has been launched at LCLS. The effort is led by SLAC scientists, on the accelerator, beamline and photon science sides, and joined by multiple experimental and theoretical teams around the world. The effort focuses on using 2-pulse 2-color modes of operation with attosecond pulses in the soft x-ray regime. The first pulse aims at creating localized electronic coherences, while the second pulse attempts to probe processes such as charge migration.

Our group's involvement stems from years of experience as XFEL users, experience in attophysics using high harmonic sources and theoretical support. For the campaign, the main model molecule identified was para-amino-phenol. This rigid molecule exhibits several atomic centers (including unique O and N sites) that can be selectively excited and/or probed using soft x-ray radiation. Two experimental runs have already been performed to probe electronic coherences initiated by impulsive ionization of several inner-valence orbitals. Two observables were measured as a function of delay following the initial ionization event: transient x-ray absorption (XAS) detected through resonant Auger decay in the cations produced by the initial step, and transient x-ray photoemission spectroscopy (XPS) to detect possible chemical shifts induced by the charge migration process. The XAS measurement uses the same experimental method demonstrated with femtosecond pulses in the isopropanol molecule using our Scienta hemispherical electron analyzer [27], while the XPS also builds on our previous beamtimes.
Future Plans: Extension of the XLEAP project to the high repetition rate capabilities of LCLS-II will happen in late 2022, so the campaign will continue at 120 HZ with further studies on the para-amino-phenol molecule, including extending previous success in producing localized valence excitation using stimulated x-ray Raman scattering in the smaller NO molecule [17].

3.5 First-principles calculations of molecular non-linear x-ray spectroscopies

P. J. Ho, A. E. A. Fouda, G. Grell[20], S. Bokarev[27] and others

Project scope: The goal of this project is to understand the fundamentals of non-linear x-ray interactions with molecules, starting from a first-principles approach. This holistic method allows investigating the effects of competing x-ray induced intramolecular processes on non-linear phenomena such as stimulated x-ray Raman excitations, and paves the way to improved understanding and execution of experiments using attosecond pulses.
Recent Progress: Coherent superpositions of valence-excited states through two-photon Raman transitions can be achieved using the broad-bandwidth, high-field nature of attosecond pulses [17]. However, a multitude of accessible excited states combine to produce a very complex picture. This year, we developed a theoretical method based on a combined multiconfigurational quantum chemistry methods with the time-dependent Schrödinger equation to examine population transfer dynamics in stimulated x-ray Raman scattering (SXRS) in nitric oxide, at both the oxygen and nitrogen K-edges. The population transfer to valence-excited states was found to be quite sensitive to the pulse conditions, including effects due to Rabi oscillations between excited states. Two pulse schemes were also explored to possibly improve the transfer efficiency and selectivity [25].
Future Plans: We plan to include a multiconfigurational quantum chemistry method to calculate continuum molecular wave functions, to be able to calculate electron observables (photoelectron and Auger spectra) of XFEL measurements and investigate the role of continuum and AC Stark shift on the stimulated x-ray Raman processes. Collaboration with Gilbert Grell and Sergey Bokarev to incorporate their molecular continuum wave functions and Auger codes [77] into our x-ray code has started.

4 X-ray Probes of Optical and X-ray Induced Dynamics in Solution

4.1 Dynamics in ionized aqueous systems

L. Young, G. Doumy, S. Li, S.H. Southworth, K. Li, C. Otolski, A. M. March, P.J. Ho, Z.-H. Loh[7], J. E. Rubensson[6], L. Kjellsson[6], Y. Kumagai[15], R. Santra[10,18], L. Inhester[18], A. Krylov[28], K. Nanda[28], K. Kunnus[8], G. Dakovski[8], D. DePonte[8], C. Pearce[29], E. Nienhuis[29], J. LaVerne[30], T. Orlando[31] and other collaborators

Project Scope: Time-resolved x-ray spectroscopies in the water window provide a powerful and unique probe for understanding valence and inner-shell hole dynamics, electronic coherence and proton transfer in ionized aqueous systems. These elementary processes are of fundamental importance as the initiators of radiation damage in condensed phases [78, 79]. Newly developed XFEL x-ray pump/probe techniques enable one to monitor the initial events following inner-valence and core-ionization, and, in combination with laser-ionization of valence orbitals, a means to dissect the full range of ionization phenomena on the ultrafast timescale.

Recent Progress: Last year we reported our studies of hole dynamics in valence-ionized liquid water in two publications [35, 36]. The methodologies associated with these studies, pump-probe x-ray transient absorption (tr-XAS) [35] and resonant inelastic x-ray scattering (tr-RIXS) [36] in the water-window, enable probes of transient radicals produced during water radiolysis (H_2O^+, OH, H_3O^+, H_2O) and are readily generalizable to other situations. This has led to new collaborations aimed at understanding radiolysis on the physico-chemical timescale (a first!) and in the extreme environments associated with legacy waste management at PNNL.

This year, we submitted a successful proposal entitled "The origin of reactive species in radiolysis" to use the ChemRIXS beamline at the LCLS. This proposal pioneers x-ray pump/x-ray probe methods in liquids, building upon our experience in gases (Section 3.1), to track local vs nonlocal decay mechanisms following inner-valence ionization. Using the $\omega/2\omega$ XFEL-operation mode, delay times from $\approx 1 - 100$ fs may be obtained. Here, ω induces non-resonant inner-valence ionization and 2ω provides a tunable resonant probe of valence and inner-valence hole dynamics in the water window. The hole dynamics can be observed directly via transmission through a thin liquid sheet jet for ionization fractions of 1%, as previously demonstrated [35]. Here the new-to-LCLS experimental scheme is to use direct undulator output (i.e. broadband) for the ω pump pulse and dispersed transmission for the 2ω probe. We plan to investigate highly concentrated alkaline aqueous solutions where the presence of other species in the first coordination shell can perturb the ultrafast dynamics. A review perspective has been published on x-ray photon-in/photon-out methods to study radiolysis on the physico-chemical timescale [39]. This paper was the subject of a highlight to DOE. We also submitted a "Scientific Campaign Proposal" for radiolysis studies in solution, interfacial and bulk solid phases of aluminum (oxy)hydroxides prominent in legacy waste.

This year, we have analyzed data obtained at the Argonne Center for Nanoscale Materials (CNM)in 2019 using an infrared probe to understand the response of the hydrogen-bonding network to an ionization pulse in liquid water. Data taken on H_2O and D_2O in the OH stretching region reveal a transient red-shifted spectral feature that is consistent with Raman measurements [80]. We attribute this feature to weakening of O–H bonds adjacent to the hydrated electron. Ultrafast spectral shifting may provide information on structure near the aqueous pre-hydrated electron.

Finally, we are preparing for a followup experiment at the LCLS on the dynamics following strong-field ionization in liquid water. We have devised a simple apparatus to characterize the geometry of prototype $4\times$ thinner converging jet nozzles [81] provided by Dan DePonte which provide larger-area leaf windows with thicknesses ~ 500 nm. At the Argonne CNM we are studying the ionization fraction and IR-signature of the OH radical in these new jets.

Future Plans: Our Dec 2021 experiment extending our studies [35, 36] to shorter timescales to

capture H_2O^+ and the pre-solvated/solvated electron signature is expected to shed light on their electronic structures [82, 83]. Our proposed studies of local and non-local dynamics initiated by inner-valence and core excitation will be scheduled in Run 20 (CY2022) at the LCLS. We plan to complete analysis and publication of the ultrafast infrared probe experiments.

4.2 Pump-probe studies and developments for the upcoming APS advanced spectroscopy beamline

A. M. March, C. Otolski, G. Doumy, S. H. Southworth, L. Young, X. Zhang[32], E. Kinigstein[32], S. Heald[32], S. Kelly[32] and other collaborators

Project Scope: We are preparing to take full advantage of the higher brightness x-rays and finer fill patterns that will be provided by the APS Upgrade as well as the advanced spectroscopy capabilities that will be provided at the new ASL beamline under construction at Sector 25. Our pump-probe x-ray spectroscopy setup at Sector 7 will move to Sector 25 during the upgrade dark period in 2023.
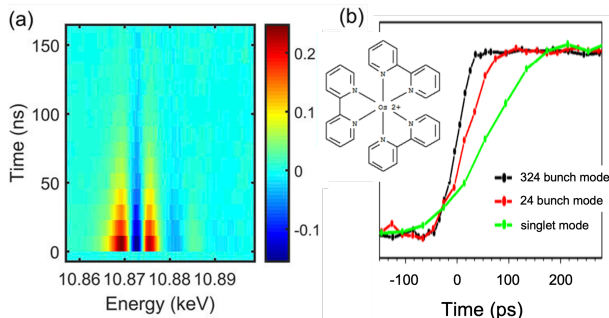
Figure 3: The first x-ray transient absorption measurement using 324 bunch mode at APS where the lowest energy metal to ligand charge transfer triplet state of osmium(II) tris(2,2'-bipyridine was captured by measuring the osmium L_3 edge. Panel (a) shows the 2D plot of XAS spectra at 11.4 ns-spaced delays (324 bunch mode pulse separation). Panel (b) displays the rising edge of kinetic scans taken in the 3 different fill patterns available at APS and shows how the 324 bunch mode provides the best temporal resolution. Figure adapted from Reference [41].

Recent Progress: The high-repetition-rate laser-pump/x-ray-probe spectroscopy endstation we have built at Sector 7 has attracted many collaborators. Results from three collaborative projects were published this past year: a study of polaronic distortions in inorganic lead-halide perovskite nanocrystals [41], a study on bi-molecular electron transfer in an iridium-based photocatalytic system [38], and a study providing supportive experimental data for an LCLS measurement exploring coupled intramolecular electron transfer and solvent reorganization [40]. We are now collaborating with Xiaoyi Zhang, beamline scientist in charge of the pump-probe XAS endstation at Sector 11, to expand the pump-probe x-ray spectroscopy capabilities at APS. We will merge the strengths of our two setups to build a highly flexible, powerful endstation at Sector 25 for spectroscopy studies of liquid phase chemistry across a wide range of relevant timescales. This past year we had three beamtimes to commission a newly developed data acquistion system [42] at high-repetition-rate pump-probe cycling rates. A new asynchronous pumping strategy successfully demonstrated that efficient collection of picosecond, nanosecond, and microsecond data can be achieved in single scans.

Future Plans: We are preparing manuscripts reporting the results from our beamtimes this past year. We plan to design an air-tight sample environment that is compatible with both kHz and MHz pump-probe experiments as well as both XAS and XES studies. This will greatly expand the kinds of chemical systems that can be studied, beyond exclusively air-stable samples.

4.3 Development of few-cycle optical transient absorption at MHz repetition rates for investigations of solution phase molecular dynamics

A. M. March, C. Otolski, G. Doumy, L. Young, J. E. Beetar[33], M. Chini[33]

Project Scope: Optical (UV to IR) transient absorption spectroscopy (OTA) remains an impor-

tant complementary tool to x-ray spectroscopy for studies of solvated transition metal complexes. We are developing a MHz-repetition-rate OTA setup at the APS that can run concurrently with synchrotron x-ray experiments, in an optical-pump/x-ray-probe/optical-probe configuration, or as an independent OTA setup. The nominal laser pulse duration (∼250 fs) limits the temporal resolution, which will be improved using a hollow-core fiber compressor to sub-30 fs while maintaining the high repetition rate [84]. Timescales <100 fs are important for enabling the investigation of structural dynamics, competitive reactive pathways, and controlled reactions of transition metal complexes.

Recent Progress: We have recently relocated the laser system from the 7-ID-D hutch at APS to our laser lab to give us more unrestricted access to the system. Investigations into the generation of white light at various repetition rates as well as detection and chopping schemes have begun. White light generation at 200 kHz has been observed, exceeding traditional setups at ¡10 kHz. We have also ordered the hollow core fiber and compression mirrors for the sub-30 fs pulse generation. These components are expected to arrive within the next few months.

Future Plans: We will decide upon and order the detector that will allow for the most efficient means of collecting pump-probe data. The first experiments using our new OTA setup will be on the iron spin-switch molecule described in Section 4.4. The optical signal will provide valuable information on the timescales involved in the conformational changes of the photochromic ligand, as well as for photodegradation of the samples. We will also explore the dependence of the ferrocyanide aquation reaction on different solvents (see also Section 4.4), using the clear absorption feature at 450 nm of the aquated photoproduct. This will provide valuable insight for subsequent x-ray measurements. After installation of the sub-30 fs pump pulse generation, we will explore these two samples with increased temporal resolution. We envision possibly implementing a multi-pulse excitation of ferrocyanide to interrogate the short-lived singlet species and to control the dissociation reaction mechanism by accessing higher-lying potential energy surfaces.

4.4 Tracking the photochemistry of solvated iron-based coordination complexes

A. M. March, G. Doumy, C. Otolski, S. H. Southworth, L. Young, K. Mulfort[34], Z. Xie[34], W. Gawelda[10], G. Vanko[35], Z. Nemeth[35], D. R. Nascimento[29], A. Andersen[29], N. Govind[29]

Project Scope: Transition metal complexes continue to be of high interest for molecular applications due to the flexible control over their reactivity that can be obtained through synthetic modification of ligands. Iron complexes are particularly interesting to replace the toxic and/or rare metals used presently in many catalysts, and for their magnetic properties that are useful for future molecular electronics applications. We are applying optical-pump/x-ray-probe absorption and emission spectroscopy to understand the complex reactivity of iron-based complexes in solution environments. We aim to understand the initial dynamics that immediately follow photoexcitation and to track the subsequent chemistry that occurs, including unwanted side reactions that may lead to irreversible damage of the molecule. Our studies focus on the wide range of timescales relevant for the photochemistry. We will utilize XFELs, such as the LCLS and the European XFEL, to probe from the picosecond to the femtosecond regime. 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 [28, 29, 31–34, 85–92], allows us to track reactions from about 10 ps to the microsecond regime.

Recent Progress: Our studies this past year have focused on two complexes: aqueous $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and $[\text{Fe}^{II}(\text{H}_2\text{B}(\text{pz})_2)_2\text{L}]$, (where L = novel phenanthroline-based ligands featuring photochromic diarylethene units, pz= 1-pyrazolyl). The first we use as a model system to understand ligand

exchange reactions in water and the second is a spin-crossover complex in which photo-switchable ligands control the iron spin state and that is promising as a practical bistable switch because it can be used at room temperature. Following up on our previous "time-slicing" x-ray absorption studies of $[Fe^{II}(CN)_6]^{4-}$ where we identified a 20 ps-lived intermediate $[Fe^{II}(CN)_5]^{3-}$, that precedes aquation [33], we extended the "time-slicing" technique to x-ray emission spectroscopy to track the spin changes that occur during the reaction. We have measured the complete Fe 1s emission spectrum, including the Kα, Kβ, and valence-to-core regions. Our measurements confirm the triplet state of the pentacoordinated intermediate. Additionally, we have observed small spectral changes, compared to the ground state, for the aquated product $[Fe^{II}(CN)_5H_2O]^{3-}$ that demonstrate the sensitivities of the 1s emission spectrum to influences other than spin state and that provide a challenge for theoretical modelling. We have collected a series of XES spectra for several low-spin iron complexes to compare to the spectral changes we observe for $[Fe^{II}(CN)_5H_2O]^{3-}$ compared to $[Fe^{II}(CN)_6]^{4-}$. A manuscript reporting our observations is presently being prepared. The spin-crossover complex based on phenanthroline ligands with photochromic diarylethene units, was first synthesized and reported by the group of Khusniyarov [93]. Our objective is to use XES and XAS to track the structural evolution of the ligand and spin state at the iron as a function of time to better understand the mechanism by which the switching occurs. Additionally, we hope to understand what underlies switching efficiency and identify side reactions that are detrimental to the switching process. We are collaborating with the group of Karen Mulfort, synthetic chemists at Argonne, and they have successfully synthesized and characterized the compound. We have begun investigations using UV/VIS and XAS/XES to characterize the two bistable states.

Future Plans: The next steps for our work on $[Fe^{II}(CN)_6]^{4-}$ include experimental exploration of the fastest timescales. We have submitted proposals to the European XFEL to do hard x-ray spectroscopy at the Fe K-edge and at the LCLS to do soft x-ray spectroscopy at the Fe L-edge and N K-edge. Additionally, we plan to use the MHz OTA setup (4.3) to explore the aquation reaction in different solvent environments. The MHz OTA will also be used to characterize the switching of the ligand-driven light-induced spin change (LD-LISC) of the iron spin-crossover complex. Our results will aid the pump-probe x-ray spectroscopy study using XES and XAS.

4.5 Photodegradation mechanisms of Mn-based CO$_2$ reduction catalysts followed by transient x-ray absorption

A.M. March, C. Otolski, G. Doumy, C. Elles[36], J. Blakemore[36], W. Henke[36]

Project Scope: This collaborative project with groups at the University of Kansas 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 complexes offer a promising alternative to the toxic and expensive rhenium complexes used for efficient CO2 reduction and other catalytic processes. Unfortunately, they suffer from photodegradation under even mild ambient light, which imposes serious limitations for applications. X-ray spectroscopy provides a powerful probe of the degradation mechanisms, providing insight to guide modification of the complex design.

Recent Progress: This past year we worked to analyze and understand the very rich datasets we obtained during APS beamtimes in June 2018 and December 2019. We had performed transient XANES measurements at both the Mn and Br K-edges. Global kinetic modelling of the data provides insight into the structures of the 5- and 6-coordinate species produced following CO loss and solvent coordination. A structural rearrangement of the Br ligand from an axial to an equatorial position occurs as a solvent molecule coordinates with the penta-coordinated intermediate. A manuscript is being prepared.

Future Plans: These complexes demonstrate the importance of studies spanning multiple time scales. Our ps, ns and μs studies at the APS motivated submission of an LCLS proposal to capture the fs timescale. This was proposed as part of a larger campaign proposal led by Roseanne Sension aimed at studying optical control mechanisms with ultrafast x-rays. Additionally, our APS datasets include the hundreds of ns to microsecon timescale, capturing the diffusion limited, bimolecular chemistry that occurs after the binding of a solvent molecule. We plan to fully analyze this portion of the data and report the results in another publication.

5 Affiliations of collaborators

[1]University of Chicago, Chicago, IL
[2]Louisiana State University, Baton Rouge, LA
[3]École Normale Supérieure, Paris, France
[4]European XFEL, Hamburg, Germany
[5]Max Planck Institute for Nuclear Physics, Heidelberg, Germany
[6]Uppsala University, Sweden
[7]Nanyang Technological University, Singapore
[8]SLAC National Accelerator Laboratory, Menlo Park, CA
[9]Argonne Leadership Computing Facility, Argonne National Laboratory, Lemont, IL
[10]Universität Hamburg, Hamburg, Germany
[11]Paul Scherrer Institute, Villigen, Switzerland
[12]ETH Zurich, Department of Physics, Switzerland
[13]Department of Physics, Kyoto University, Japan
[14]RIKEN SPring-8 Center, Japan
[15]Tokyo University of Agriculture and Technology, Japan
[16]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Japan
[17]Kansas State University, Manhattan, KS
[18]Center for Free-Electron Laser Science, DESY, Hamburg, Germany
[19]Johns Hopkins University, Baltimore, MD
[20]University of Madrid, Spain
[21]Imperial College, London, UK
[22]University of Washington, Seattle, WA
[23]Pacific Northwest National Laboratory, Richland, WA
[24]Université Pierre et Marie Curie, Paris, France
[25]Lund University, Lund, Sweden
[26]Freie Universität, Berlin, Germany
[27]University of Rostock, Germany
[28]University of Southern California, Los Angeles, CA
[29]Pacific Northwest National Laboratory, Richland, WA
[30]University of Notre Dame, South Bend, IN
[31]Georgia Tech University, Atlanta, GA
[32]X-Ray Science Division, Argonne National Laboratory, Lemont, IL
[33]University of Central Florida, Orlando, FL
[34]Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL
[35]Wigner Research Centre for Physics, Hungarian Academy Sciences, Budapest, Hungary
[36]University of Kansas, Lawrence, KS

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Structure and Dynamics of Atoms, Ions, and Molecules

I. Ben-Itzhak, C. Blaga, B.D. Esry, V. Kumarappan,
C.D. Lin, D. Rolles, A. Rudenko, U. Thumm

J.R. Macdonald Laboratory, Kansas State University, Manhattan, Kansas 66506-2601
Award Number: DE-FG02-86ER13491   Email: JRML_Director@phys.ksu.edu

1 Overview

The J.R. Macdonald Laboratory (JRML) focuses on the interaction of intense laser pulses with atoms and molecules for the purpose of understanding and ultimately 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. 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.

A significant fraction of our research is done in collaboration with others, both at JRML and elsewhere, including many within the DOE-AMOS program. 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, and we actively seek new collaborations.

Our newest laser system, nicknamed FLAME, arrived within the last year and is already making an impact on our science. It is a robust, 3-kHz, 5-mJ system that enables pump-probe coincidence measurements with wavelength conversion and serves several different experiments. Many of our coincidence measurements will get an even bigger boost from the high-power 100-kHz, 200-W system that we recently received funding for. These systems currently have a long lead time, however, such that it likely will not be in the Lab for another year or more.

Our research projects are organized around the themes "Strong-field and attosecond science" and "Correlated dynamics". These themes serve as broad categories 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 the improvements enable. The following progress summaries provide brief updates on a select subset of our ongoing projects.

2 Recent Progress Summaries

2.1 Strong-field and attosecond science

To reach the ultimate goal of controlling the flow of energy in a molecule, we must understand its dynamics—i.e., its time-evolving response to external perturbation. The projects in this section present a broad range of approaches to this issue, from characterizing and using soft-X-ray attosecond pulses to probing with intense long-wavelength infrared pulses. Such pulses, and many variations in between, will be used in increasingly complex systems matched by increasingly differential measurements and theory, all in order to gain a quantum-level understanding of the dynamics.

2.1.1 Strong-field excitation and ionization: Low-energy laser-induced electron diffraction — Blaga, Lin

Project scope

This project seeks to develop ultrafast photoelectron metrologies as tools for molecular dynamics studies. During the last decade, our research interests have been focused on developing high-energy laser-induced electron diffraction (LIED) as an imaging probe of ultrafast molecular dynamics. While high-energy LIED "sees" the location of the atoms inside a molecule, it is insensitive to any chemical information. In this project, our recent efforts have been aimed at extending LIED into the low-energy regime such that the returning electron wavepacket "images" not core electrons, but the chemically active valence electrons. If successful, LIED could be used not only to image on a femtosecond timescale the location of the atoms inside molecules, but to "image" the valence electronic distribution, allowing us to observe charge transfer and charge migration in molecular targets as well as the formation of so-called compound states (or transitory states) when the returning electron is temporarily trapped by the parent [71].

Recent progress

Leveraging the λ^2 scaling law and the rescattering mechanism of strong-field physics, we pursued the development of mid-infrared (MIR) ultrafast lasers that allowed us to generate high-energy (>100 eV) returning electron wavepackets that possess the necessary resolving power to determine the location of atomic centers inside the parent molecular ion. These efforts allowed us to observe molecular transformations from bond relaxations in diatomic molecules [72] and cage deformations of fullerenes [7].

This high-energy LIED is a viable ultrafast imaging method because the measured rescattering yields $Y(p, \theta)$ in the photoelectron angular distribution (PAD) occurring at large angles θ and high momenta p can be factorized as a product of the elastic electron-ion differential cross section (DCS) and the returning electron wavepacket $W(kr)$, where kr is the momentum at return [73]. In LIED, structural information is contained only in the DCS term, and not $W(kr)$. In essence, in the strong-field, non-resonant limit (*i.e.*, tunneling), the returning wavepacket is a "good light bulb" that only depends on laser field parameters, similar to the external electron beam in a conventional gas-phase electron diffraction experiment. Furthermore, at large rescattering angles, the DCS can be approximated as the field-free DCS, since the signal is provided predominantly by core electrons, not the valence ones.

Our primary objective during the last year was to demonstrate that the key ingredients that facilitate high-energy LIED, namely the factorization approximation and the "good light bulb", can be realized in the low-energy (5–15 eV) recollision regime. The field-free DCS approximation, on the other hand, is not expected to hold in the low-energy LIED regime. However, this does not affect the feasibility of the approach. Instead, just as in low-energy conventional gas-phase electron scattering, DCS modeling will gain in complexity, and we are working on this issue theoretically as well.

A few years ago, while still at Ohio State (DiMauro-Agostini Group) in collaboration with Louisiana State (Schafer Group), we revisited the high-energy plateau (rescattering) enhancements reported in 1994 by Paulus in the photoelectron spectra of noble gases when irradiated with intense visible and near-infrared (NIR) femtosecond pulses [74]. Our experimental and theoretical investigations — continuing in part at JRML under this project — revealed that the

observed enhancements possess all the necessary features needed for low-energy LIED. The first characteristic is ubiquitousness. Upon exploring a wide range of laser parameters and targets, we found yield enhancements in atoms and molecular targets (all noble gases, methane, ethane) and have developed an empirical formula to predict for a given target what laser parameters are needed. Recently, several groups reported similar findings, identifying enhancements in targets as complex as formic acid [75]. A second characteristic we discovered was a universal rescattering plateau shape when scaled in ponderomotive units, indicating a "good light bulb" characteristic. The results of these extensive investigations will be disseminated soon (manuscript in preparation).

During the last year, we have conducted a series of experiments aiming to demonstrate that the enhancements are spectroscopic features that facilitate low-energy LIED and answer the question: "How good of a light bulb is the returning wavepacket in the low-energy, resonant regime?" Using single-color 800-nm and bichromatic 800+400-nm laser fields, we recorded PADs in argon, methane, and molecular nitrogen as a function of laser intensity and the relative phase of the bichromatic field. For argon, in collaboration with OSU, we have also performed time-dependent Schrödinger equation (TDSE) calculations to complement the experiment. We have also begun the analysis of the extracted DCS from the experimental data and the theoretical calculations. The findings of these investigations will be presented in detail at AMOS2021.

Future plans

In the immediate future, we will focus our efforts on finalizing and publishing our low-energy LIED investigations in argon. The experimental data collection is complete, and we are now concentrating on data analysis and DCS modeling. These investigations will be paired with comprehensive TDSE numerical simulations. In the next phase, we will broaden our experimental investigations to include small molecular targets like methane, ethane and aligned diatomics. One molecule of interest is CH_2I_2, a compound for which we aim to perform UV-pump–MIR-probe high-energy LIED to investigate I_2 elimination in collaboration with the Rudenko/Rolles groups. We also aim to continue our high-energy LIED and ultrafast molecular imaging of field-induced cage deformations in fullerenes, focusing on mapping the dependence of the cage deformation on pulse duration and pulse chirp, both sensitive knobs to control the energy deposition into the cage via the impulsive Raman scattering mechanism at play.

2.1.2 Attoscond correlated electron dynamics — Lin, Thumm

Project scope

Ultrafast electron dynamics in molecules is the progenitor of all chemical reactions and occurs on the few hundreds of attoseconds timescale. This project aims to theoretically understand this attosecond dynamics and the role of correlation. It has been proposed, for instance, that high-harmonic spectroscopy can be used to probe charge migration with attosecond temporal and sub-angstrom spatial resolution. Since experimental harmonic spectra are generated from an ensemble of molecules coherently while charge migration occurs at the individual molecule level, a rigorous retrieval algorithm is needed to make it possible to film attosecond charge migration. This has been achieved for harmonic spectra in CO_2 and N_2. Other probes will be investigated as well for their utility in revealing attosecond electron dynamics.

Recent progress

Filming attosecond charge migration with high-order harmonic spectroscopy High-harmonic generation (HHG) in molecules can be qualitatively understood using the three-step model. To understand how ultrafast charge migration is encoded in the molecular HHG signals, we note that after strong field tunnel ionization at time t_i, the molecule in general is left in the ground and a few excited states of the ion. Once the electron is ejected, the occupation amplitudes of these ionic states should change under the influence of the external laser field, creating a time-dependent many-electron, or equivalently, a hole wavepacket. Such hole dynamics is encoded in the harmonic spectra of each single molecule. Since the sub-cycle return time t_r depends on the harmonic order, the time-dependence of the hole wavepacket is embedded in the harmonic spectra. Using an 800-nm driving laser, harmonic orders 15 to 27 will span a duration of 0.96 to 1.45 fs from ionization to recombination, with time steps of 100 as between odd harmonics, or 50 as if both even and odd harmonics are generated. These are readily understood from the three-step model.

Experimental harmonic spectra and single-molecule complex dipole amplitudes from impulsive partially aligned molecules are related by

$$S(\omega, \tau) = \left| \int_0^\pi D(\omega, \theta) \rho(\theta, \tau) \sin \theta d\theta \right|^2.$$

Thus, the first step is to retrieve the complex-valued $D(\omega, \theta)$ from the experiment. The time-dependent hole wavepacket is governed by the hole hopping coefficients $C_{ij}(t_n, \theta)$ where t_n is the return time of the n-th harmonic. To obtain these coefficients, additional HHG data are needed. This is achieved experimentally by adding a weak second harmonic with varying relative phase to the 800-nm laser to generate even and odd harmonics. Using modern machine learning algorithms, $C_{ij}(t_n, \theta)$ are retrieved for all the measured harmonics and all orientation angles θ simultaneously. Combining with the molecular orbitals of the holes calculated from time-dependent density functional theory (TDDFT), the hole wavepacket is obtained, while the modulus square is the hole migration. Our results (the movies are not shown) reveal that the hole density swirls between the two oxygen centers, instead of bouncing between them, on the timescale of about 10 as. This work gives the first attosecond charge migration movies produced rigorously using experimentally measured spectra, and it has been submitted for publication.

Interferometric signatures of correlated electron dynamics We extended our finite-element discrete-variable representation (FEDVR) code for solving *ab initio* the TDSE for helium atoms in time-dependent external electric fields [76–78] to track electronic correlation in attosecond time- and angle-resolved photoelectron spectra. Our *ab initio* calculated NIR-streaked XUV photoelectron spectra and relative time delays of 18 as between direct (n=1) and shakeup ionization to He$^+$ (n=2) [79] agree well with recent experiments [80] and assess the effect of the residual excited He$^+$(n=2,3) ion's transient induced dipole on the photoemission dynamics [80, 81] (Fig. 1).

Investigating photoelectron interactions with the residual ion on laser-driven continuum-continuum transitions [3] [81], we calculated *ab initio* multi-sideband (SB) interferometric (RABITT) spectra [82, 83] of helium. To reveal the role of correlation during photoemission, we are analyzing relative SB phase shifts obtained from FEDVR *ab initio* and single-active electron calculations [79].
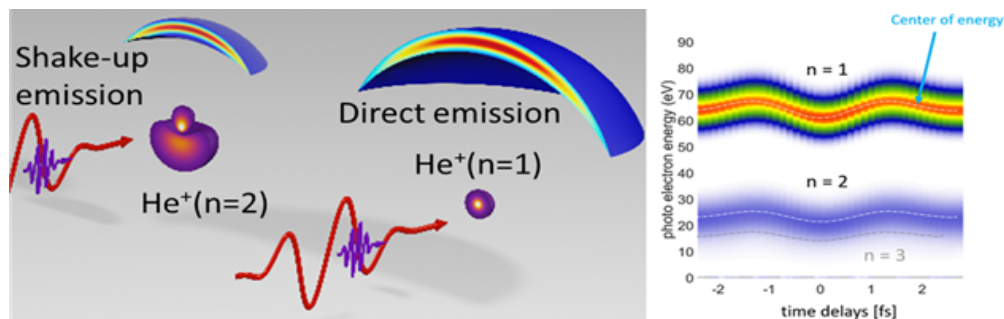
Figure 1: The comparison of direct and $n=2$ shake-up photoemission from He reveals photoelectron–residual-ion entanglement in streaked electron spectra and relative time delays.

Future plans

The charge migration work is closely coupled with experiment through our collaboration with a group in China. Therefore, future progress will depend on new harmonic spectra for other molecules. The immediate plan is to work on C_6H_6 to explore how charge migration behaves around the ring for different directions of the driving laser. Our *ab initio* tools will be applied to angular streaking and RABITT calculations for H^- [84] and H_2 to see how induced residual multipole moments [85,86] affect spectra and photoemission delays. Calculations for H_2 with fixed internuclear distance R will enable us to characterize the residual molecular cation's coherently excited state from the entangled streaked photoelectron spectrum.

2.1.3 Enhancing high-order harmonic generation using two-color driving fields — Ben-Itzhak

Project scope

We experimentally explored the enhancement of high-order harmonic generation by two-color driving fields — inspired by the theoretical predictions by C.D. Lin's group suggesting one to two orders of magnitude enhancement [87].

Recent progress

We demonstrated substantial enhancement of the vacuum-ultraviolet photon flux using HHG driven by two-color, ω–3ω, laser pulses compared to the fundamental ω driving pulse (see Pub. [66]). Specifically, we achieved over an order-of-magnitude enhancement for 20- to 40-eV photons and up to three-orders of magnitude at lower energies.

In addition, we realized control over the mechanism that dominates the HHG enhancement, whether it is the ionization rate or the electron wavepacket's diffusion (also known as "dispersion"). More importantly, we demonstrated that the ω–3ω driving field can be used to control the diffusion of the electron wavepacket. Furthermore, the two-color phase controls the electron excursion time over a factor of two range (see Fig. 2), enabling one to probe the remaining target at different times — a key capability for imaging techniques that use the returning electron wavepacket to probe the remaining ion.

Finally, we also show that the divergence angle of the harmonics is reduced by a factor of two compared to their single-color counterpart, suggesting that the "short" electron trajectories
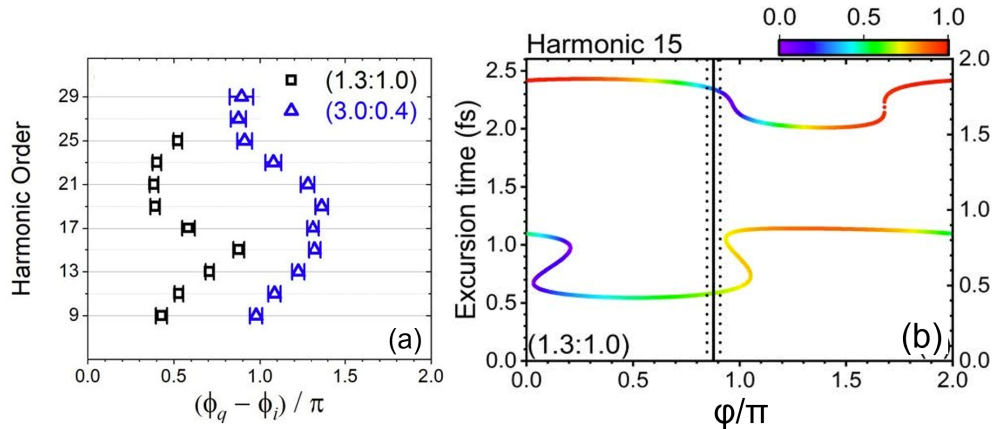
Figure 2: (a) Extracted phase shifts for each harmonic order (q) with respect to the peak ionization yield (i) for both intensity ratios of the ω–3ω field. (b) Excursion times of the classical electron trajectories contributing to the 15th harmonic, as a function of relative phase between the 800- and 266-nm laser fields for the nearly equal intensity ratio of 1.3:1.0. (Adapted from Pub. [66].)

play a more prominent role compared to their "long" trajectory counterparts, thus improving the wavefront of the emerging harmonic beam. These findings indicate that bichromatic driving fields improve HHG's capability as a light source.

On the technical side, it is worth mentioning that these measurements were made possible by the development of an interferometer having a measured 50-as RMSE stability over 3 minutes without any external optical feedback.

Future plans

We have also measured the HHG enhancement by an ω–2ω laser field, and compared it to the ω–3ω, and each single color — all produced with the same input laser power. The results of these measurements are in the final stages of analysis and a manuscript is nearing completion.

2.1.4 Strong-field driven dynamics in small molecules — Kumarappan, Rudenko, Thumm

Project scope

This project aims at experimental and theoretical study of strong-field ionization and dissociation of small molecules. Experimentally, one of the main goals has been to further develop methods for extracting orientation-resolved information from strong-field-induced rotational wavepacket dynamics. In the past year, we have studied the ground and excited states of cations of linear molecules, using high-resolution Fourier spectroscopy of momentum distributions measured with a velocity map imaging (VMI) spectrometer. These experiments allow us to study the cationic wavepacket created by strong-field ionization (SFI) in great detail. On the theory side, our efforts focused on the development of conceptual, analytical, and numerical tools to image and control the effects of intense pulses of NIR to SXR light on the electronic and nuclear dynamics in small molecules, and to extend our investigations from diatomics to larger small molecules.
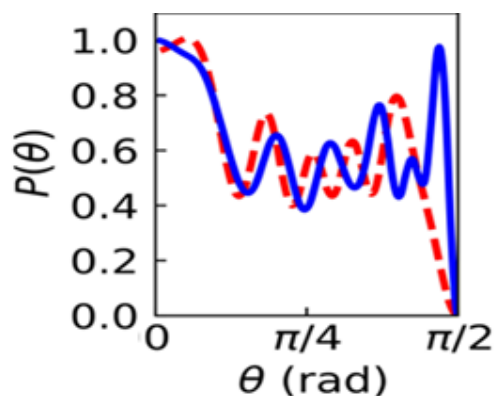
Figure 3: Normalized $O_2^+ \longrightarrow O(^3P) + O^+(^4S^0)$ dissociation yields for 40-fs, 1×10^{14}-W/cm^2 NIR probe pulses and fragment KERs between 0.2 and 0.3 eV. Calculations including rotational excitation (blue curve) and for fixed orientation angle θ (red dashed curve) reveal dynamical rotational motion most prominently near the LICI ($\theta \sim \pi/2$). The θ-dependent modulation frequency and amplitude of the O^+ fragment angular distribution $P(\theta)$ are attributed to bond hardening and nuclear diffraction effects [29] [93].

Recent progress

Light-induced conical intersection dynamics   Addressing open questions in the interpretation of in-house dissociative ionization (DI) experiments [88–92], we studied the DI of O_2. Focusing on the light-driven ro-vibrational nuclear dynamics in O_2^+, we theoretically examined bond-softening and -hardening mechanisms in the time and frequency domains, predicted the probe-pulse-duration-dependent stabilization of excited molecular ions [28], and revealed energy- and angle-dependent fringes in kinetic-energy release (KER) spectra [29]. We found these fringes to be sensitive to the ro-vibrational dynamics near the lowest light-induced conical intersection (LICI) in O_2^+, suggesting a means for examining LICIs in fragment KER spectra (Fig. 3).

Our results cooperate with recently reported diffraction effects in the light-induced dissociation of H_2^+ [94, 95]. Our first tentative results suggest the angle-dependent oscillations are robust against the added effects of focal-volume and initial O_2^+ rotational-state averages. We are currently investigating the controllability of the light-induced dynamics in O_2^+ by modifying the probe-pulse profile, exploring the (i) feasibility of verifiably stopping a pump-pulse-generated O_2^+ nuclear wavepacket into stationary ro-vibrational cationic states [96, 97] and (ii) controlled coherent steering of the nuclear motion in the excited cation towards the LICI.

Dissociation dynamics of triatomic molecules   Extending our work on the DI of O_2 [28, 52], we started to model DI of triatomic molecules. Motivated by recent pump-probe experiments with CO_2 at JRML [98] and the observation of core-hole density oscillations as a result of pump-pulse induced nuclear wavepackets moving across two intersecting CO_2^+ states [99], we are starting wavepacket-propagation calculations for the DI of CO_2 molecules (Fig. 4).

Figure 4: Intersecting CO_2^+A) and CO_2^+B) adiabatic potential surfaces as functions of R_1 and R_2, disregarding O-C-O bending. We obtained adiabatic CO_2(X) and CO_2^+A,B,C) potentials and dipole couplings from MCSCF cc-pVTZ calculations with the quantum chemistry code GAMESS [100].
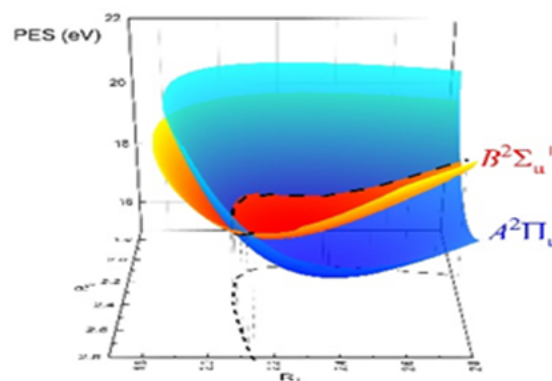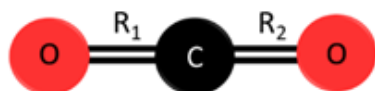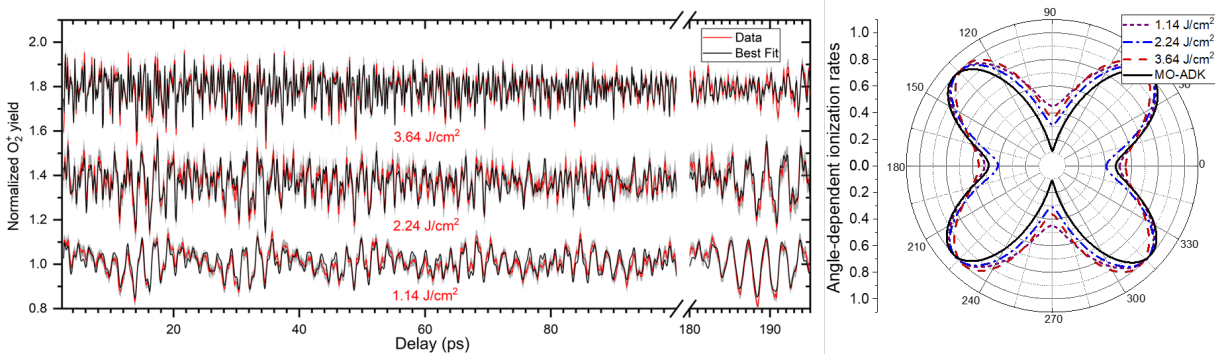
Figure 5: Left: Data and fits for delay-dependent yield of O_2^+ aligned and then ionized by 40-fs, 800-nm pulses. Right: Angle-dependent ionization rates obtained from the fits and calculated using MO-ADK theory. (Adapted from Pub. [69].)

Strong-field ionization and fragmentation of triplet oxygen   By using a jet-cooled ($\sim$2 K) oxygen beam, and weak pulses for impulsive alignment, we were able to observe non-periodic behavior in the rotational wavepacket dynamics in ground-state oxygen molecules [69]. This unusual behavior for a linear molecule is a consequence of the triplet nature of the ground state of oxygen. Fourier spectra of the molecular ion yield as a function of pump-probe delay confirm the source of the non-periodicity, as the measured frequencies match very well with spectroscopic data.

We modeled the angle-dependent ionization rate using an expansion in Legendre polynomials. The expansion coefficients are then determined by fitting the delay-dependent yield data to the molecular axis distribution calculated using an effective Hamiltonian that includes spin-spin and spin-orbit couplings and the polarizability interaction for the alignment dynamics. The fits agree well with the data (see Fig. 5), although not quite as well as other linear molecule fits typically do. The extracted angle-dependence of SFI agrees with calculations using MO-ADK.

We followed up the ionization measurement with a pump-probe measurement of the ionic wavepacket left behind after SFI by the pump pulse. The probe pulse then dissociates these cations and the O^+ fragments are measured using a VMI spectrometer. Fourier transforms of the kinetic energy spectra and the moments of the angular distribution reveal a broad rotational wavepacket in the $b\,^4\Sigma_g^-$ state. This wavepacket is likely populated by a resonant dipole coupling with the $a\,^4\Pi_u$ state [91]. The FFT-KER plots show signatures of both rotational and vibration excitation by the probe pulse, followed by predissociation to the $f\,^4\Pi_g$. Surprisingly, we found no lines corresponding to the lower-lying $a\,^4\Pi_u$, which had been assigned as the state from which most of the low-energy dissociation products originate [101].

High-resolution FFT spectroscopy of strong-field ionized nitrogen   We ionized jet-cooled N_2 with a 40-fs, 800-nm pulse, and then dissociated the bound cations with a 120-fs, 264 nm third-harmonic pulse in a 100-ps-long delay scan with 50-fs step size. The momentum distribution of N^+ ions was measured with a VMI spectrometer and Abel-inverted using the pBasex algorithm. The delay-dependent fit coefficients were Fourier transformed to obtain quantum beat spectra.

An advantage of such measurements is that the spectra have sufficient resolution — limited only by the duration of the scan — to unambiguously identify the pump-excited states that contribute to the dissociation yield. Wavepackets in individual vibrational levels in the X, A, B, and C states of the cation can clearly be identified in the data. For instance, in the $A\,^2\Pi_g$
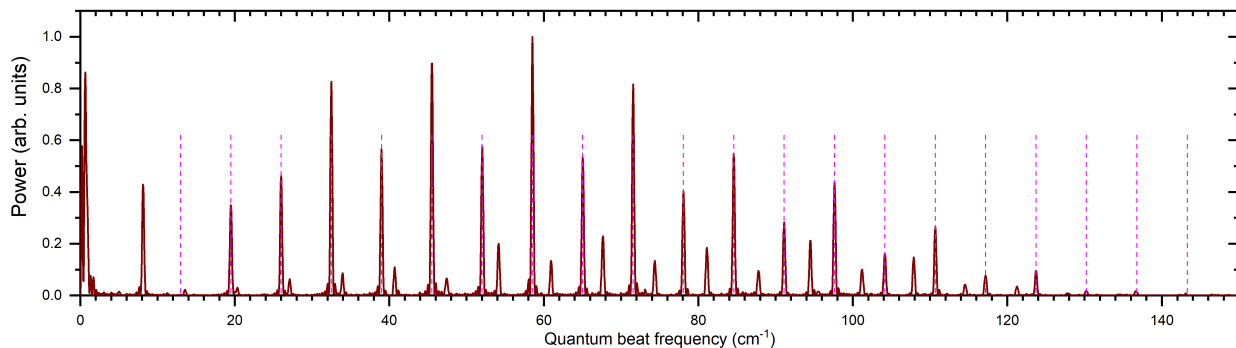
Figure 6: Fourier transform spectrum of the yield of N^+ ions produced by dissociating N_2^+ ions produced by SFI by 800-nm pulses with 264-nm pulses. A single KER channel was selected. Vertical dashed lines in magenta show the expected positions for $\Delta N=2$ coherences in the F_1 level of the $A\,^2\Pi_g\,(v=4)$ state. The second series of weaker lines corresponds to coherences in the F_2 level.

state, rotational coherences in both the F_1 and F_2 fine-structure levels can be identified (see Fig. 6). Delay-dependent momentum distributions from each rotational coherence can also be reconstructed using a filtered inverse FFT.

Future Plans

We plan to work to bring the theory and experiment closer together for more detailed, direct comparisons. For instance, measurements of the momentum distributions of photofragment momenta offer an opportunity to investigate the effect of initial state preparation on wavepacket propagation around LICIs. Since FFT spectroscopy enables the study of the momentum distributions from unambiguously-identified rotational coherences in specific vibronic states, these experiments provide very detailed maps between initial states and asymptotic momentum distributions of fragments. We plan to do these experiments in D_2 to facilitate the comparisons with theory.

Theoretically, we also plan to investigate field-induced molecular orientation, stabilization, and LICI effects in the DI of O_2 for finite initial rotational temperatures and assess the achievable coherent control for steering the nuclei in O_2^+ towards the LICI. In addition, to examine the light-induced nuclear dynamics in $CO_2^{(o,+)}$, we will propagate nuclear wavepackets to quantify ro-vibrational and light-induced couplings between two [99] (later all three) normal modes in KER spectra.

Another direction we plan for the experiments in the near future is to use deep UV from the TOPAS to access the vibrational states most relevant to ion lasing. The phenomenon of ion lasing in nitrogen ions has attracted a lot of theoretical and experimental attention lately. Our current data was taken with a 264-nm probe, which does not efficiently dissociate low vibrational levels on the A and B states. We have found that the KER spectrum is sensitive to small changes in the probe wavelength. The FFT measurements of VMI spectra may shed some light on the mechanism driving ion lasing by characterizing the wavepacket in the cation.

2.2 Correlated dynamics

As the systems we study become more complex, the correlated motion of the electrons and nuclei play an ever larger role. When their time and energy scales — so distinct in the traditional thinking of the Born-Oppenheimer approximation — approach one another as at a conical intersection, the wave functions cease to be well approximated as a simple product, becoming instead a complicated commingling of their degrees of freedom. To complicate matters further, the correlations only among the electrons or only among the nuclei induce similar commingling essentially everywhere. The projects proposed here tackle these inherently multidimensional problems through more differential measurements, more sophisticated analyses of those measurements, and advances in the theoretical treatment.

2.2.1 UV-induced isomerization and dissociation dynamics in gas-phase molecules — Rolles, Rudenko, Ben-Itzhak, Esry

Project scope

This project 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 third-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. In parallel, we are developing the theoretical tools to help understand the experiments.

Recent progress

In order to investigate ultrafast UV-induced isomerization and dissociation in gas-phase molecules, we have performed pump-probe experiments on a variety of halogenated hydrocarbons with our laboratory laser sources at the JRML and at free-electron laser facilities around the world [1,33,58]. Many of our efforts at JRML concentrated on using our newest 3-kHz laser, FLAME, which is equipped with a deep-UV TOPAS that enables experiments at variable pump wavelengths from 190 nm into the visible and beyond. We complement those efforts with pump-probe experiments at our 10-kHz laser, PULSAR, where we have a third and fourth harmonic generation setup that can produce shorter UV pulses than those currently available from the TOPAS. In addition, we have, for the first time, employed ultrafast electron diffraction at the new MeV-UED user facility at SLAC. Some examples of recent and yet unpublished results are presented in the following.

Wavelength dependence and fragment rotation in the UV-induced dissociation of halomethanes In di-halomethanes containing two halogen atoms, varying the wavelength of the pump pulse that is used to excite the molecule via single-photon absorption leads to significant changes in the dissociation dynamics. This can drastically alter branching ratios between different channels, in some cases switching between almost exclusive cleavage of one of the carbon-halogen bonds to the other, or can significantly change the timescale of the dissociation since different electronic excited states are involved.

We have studied these wavelength-dependent effects by comparing the UV-induced dissociation of CH_2IBr, CH_2ICl, and CH_2I_2 at 266 nm and 200 nm via coincident fragment ion momentum
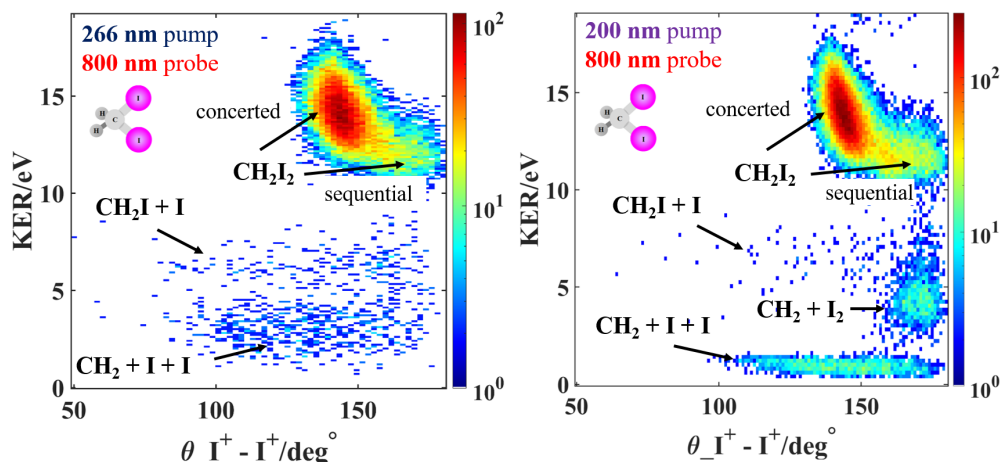
Figure 7: KER of the $CH_2^++I^++I^+$ triple coincidence channel produced by strong-field ionization of UV-exvited CH_2I_2 as a function of the angle between the two momentum vectors of I^+ ions for two different UV wavelengths. In both cases, the intense 800 nm probe pulse arrives 20 ps after the UV pump. While the events with high KER result from triple ionization and subsequent breakup (concerted or sequential) of the bound CH_2I_2 molecule, the events below 10 eV originate from different UV-induced dissociation channels, as indicated in the figure.

imaging. As illustrated in Fig. 7 for CH_2I_2, such coincident measurements enable us to distinguish the different reaction pathways that are triggered by UV absorption since they have different signatures in the fragment ion momentum correlations. At 266 nm, the single-photon dissociation is dominated by a single C-I bond cleavage (CH_2I+I channel), while the strong contribution from the three-body dissociation at low KER mainly results from the two-photon absorption (evidenced by its non-linear dependence on the UV pulse power). In contrast, at 200 nm, the dominant single-photon channels are the three-body dissociation and molecular iodine elimination, whereas the contribution from the CH_2I+I channel is relatively weak.

The C-I bond cleavage at 266 nm results in significant rotation of the remaining molecular radical. When probed via strong-field induced Coulomb explosion imaging, this rotation can be directly visualized, in particular, leading to periodic oscillations in the measured kinetic energies of the fragments. This effect is especially pronounced in CH_2IBr, as illustrated in Fig. 8, where the
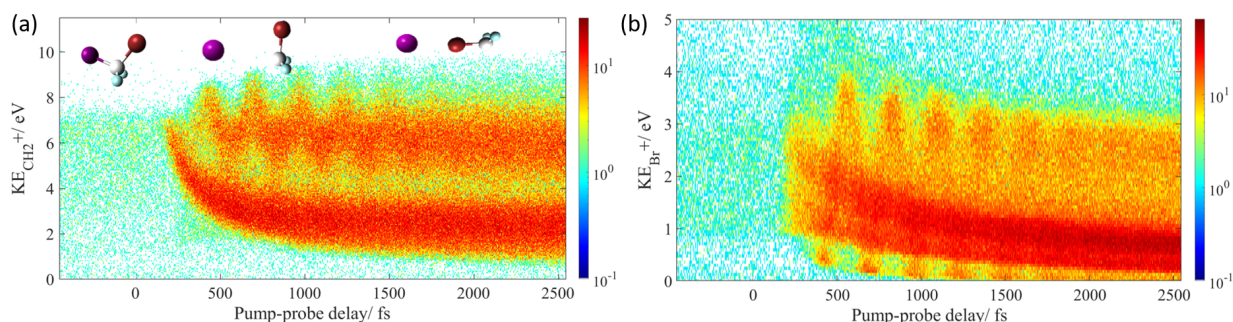
Figure 8: Delay-dependent kinetic energies of (a) CH_2^+ and (b) Br^+ fragments from the $CH_2^++Br^++I^+$ triple coincidence channel produced by strong-field ionization of UV-dissociated CH_2IBr. The oscillatory structure is due to rotation of the CH_2Br radical after the UV-induced C-I bond cleavage [see sketch in panel (a)]. The bands with strongly decreasing kinetic energy are due to competing channels produced by the UV-pump pulse, such as C-Br cleavage and three-body dissociation (F. Ziaee *et al.*, in preparation).
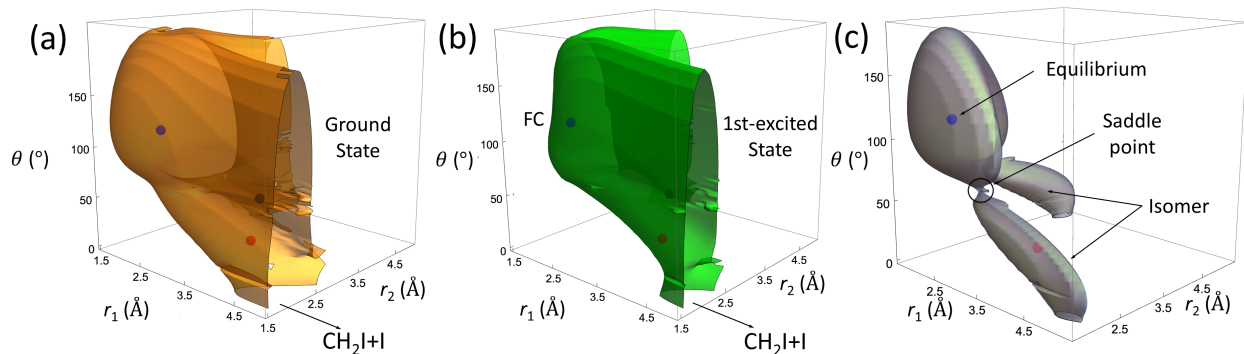
Figure 9: The iso-energy potential surfaces for the ground and first-excited states of CH_2I_2 with all degrees of freedom frozen save for those of the iodine atoms — *i.e.*, two bond lengths and their bond angle. (a) and (b) The energy of these surfaces is 4.6 eV, corresponding to the 266-nm pump of the experiment. (c) The ground-state iso-energy surface at 2.83 eV, corresponding to the top of the saddle point separating the isomer from equilibrium, thus defining the isomer configurations. The blue dot marks the equilibrium in (a) and (c) and the Franck-Condon point in (b). The red dot marks the isomer equilibrium; and the black dot, a conical intersection between the two surfaces.

kinetic energies of CH_2^+ (a) and Br^+ (b) fragments from the $CH_2^+ + Br^+ + I^+$ triple coincidence channel are plotted as a function of UV-NIR delay. According to our preliminary analysis, this rotational excitation seems to be much less pronounced for excitation at 200 nm for all three di-halomethanes studied.

Modeling   To help understand our past, current, and future experiments on the di-halomethanes, we have started to develop the theoretical tools to model the dynamics in collaboration with Loren Greenman. Our strategy is to map out the potential energy surfaces then do any dynamical calculations desired. This approach facilitates exploration and visualization of the surface itself, which can already provide insights.

For example, we consider the first step of the experiment described above with a 266-nm UV pump of CH_2I_2 from its ground state and follow the subsequent dynamics in the neutral before Coulomb explosion. We are interested in modeling the elimination of I and I_2 which suggests treating CH_2 as a rigid body, leaving the C-I bond lengths r_1 and r_2 and the I-C-I bond angle θ as the dynamical degrees of freedom. With these restrictions, the ground and first-excited state iso-energy potential surfaces, calculated at the CCSD level, are shown in Figs. 9(a) and 9(b) at an energy of 4.6 eV corresponding to the energy of the system after the 266-nm pump pulse.

Therefore, the surfaces in the figure represent the classical turning points for all motion following the pump, so that only the volume within the surface is accessible. One sees that the bending motion can explore a large range of angles and that the CH_2I+I channel is readily accessible on both surfaces. The pathways to I_2 elimination are harder to see from the viewpoint used for these surfaces — and the calculations are not complete for large r_i near $r_1 = r_2$ where this must occur — but it does appear possible on both surfaces for relatively small bond angles. Access to this region appears quite restricted, however, which is consistent with the experimental findings that I_2 elimination is relatively weak at 266 nm.

Having the full surface also makes visualizing the space of isomer configurations easier. In particular, Fig. 9(c) shows the ground state iso-energy surface at 2.83 eV. This energy lies at the top of the saddle point that separates the potential well near equilibrium from the isomer well. The saddle point is visible in the figure as the bottleneck between the two regions. One can

therefore define the isomer configurations as those that lie within this surface in the isomer well.

Such a definition is critical for defining an "isomerization" timescale — which, in reality, will just be the time that the system takes to travel through this isomer volume since the pumped system lies 1.77 eV above the saddle point in energy. So, not only will the system not stop in the isomer well, it will speed up as it travels over it. All of these configurations are thus simply passed through on the way to dissociation. We are in the process of carrying out dynamical calculations, which at this point are simply classical trajectories on these surfaces. These trajectories will already be sufficient to provide timescales that we can compare with experiment.

UV-induced dissociation and isomerization and strong-field induced ionization and fragmentation of bromoform (CHBr$_3$) After absorption of a UV photon, bromoform is known to undergo C-Br bond cleavage and possibly an isomerization as a result of hydrogen and bromine migration. The latter process has been elusive to pin down experimentally. In order to address this challenge, we have performed pump-probe experiments employing different pump wavelengths (200 nm, 266 nm, and 800 nm) and strong-field ionization as a probe, along with an extensive characterization of the strong-field induced fragmentation process to better understand the results of those experiments. A particular emphasis was placed on detecting 4 or 5 fragment ions in coincidence since such (almost) complete fragmentation channels are promising candidates to reveal the molecular structure prior to the strong-field ionization. An example of the resulting Coulomb explosion image for 5-fold ionic fragmentation, which strongly resembles the molecular geometry, is shown in Fig. 10. Analysis of the corresponding time-resolved data is in progress.

Future plans

In the next few months, we will have experimental campaigns at the LCLS, ALS, SACLA, and the European XFEL to further pursue our investigations of ultrafast electronic and nuclear dynamics with X-ray based techniques. At JRML, we plan to take advantage of our recent breakthroughs in Coulomb explosion imaging to study a variety of light-induced isomerization reactions triggered by different wavelengths. We are currently building a prism compressor for the TOPAS output, modeled after the UV compressor we have in operation at PULSAR, in order to compress the TOPAS pulses to 50-fs duration or less and thus improve our temporal resolution for experiments at wavelengths other than 200 and 266 nm, which we are planning to do next.
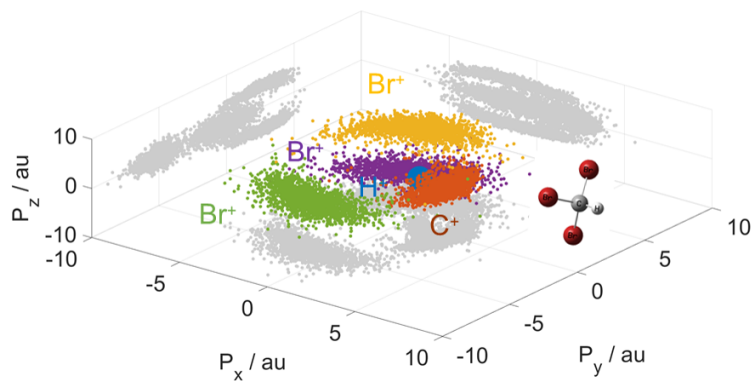
Figure 10: Three-dimensional representation of the molecular-frame ion momentum distribution for the C$^+$+H$^+$+Br$^+$+Br$^+$+Br$^+$ fragmentation channel after ionization by an intense 25-fs, 800-nm pulse. The momentum of the reference ion, H$^+$, is plotted along the x-axis, and all other momenta are normalized to the magnitude of the H$^+$ momentum (S. Bhattacharyya *et al.*, in preparation).

2.2.2 Separating sequential and concerted fragmentation processes using native-frames analysis — Ben-Itzhak, Carnes, Esry, Rolles, Rudenko

Project scope

We are developing the native-frames analysis method [102] and implementing it in studies of multibody photoinduced fragmentation of polyatomic molecules in order to improve the understanding of concerted and sequential fragmentation dynamics.

Recent progress

During the fragmentation of polyatomic molecules, two or more bonds may break in a concerted manner (simultaneously) or sequentially (stepwise). Separating them and following their time evolution is key to better understanding fragmentation dynamics. To achieve this separation, we employ the native-frames analysis method introduced in Ref. [102] and detailed in a recent "tutorial" Ref. [103]. We successfully implemented this method in studies of NH_3 (Pub. [44]), $C_2H_2Br_2$ (Pub. [53]), and D_2O (Ref. [104]) fragmentation, as well as other studies that are still underway.

In the following, we present one example (Ref. [104]) focused on double ionization of heavy water by a single 61-eV photon, followed by sequential breakup via a $D^+ + OD^+$ intermediate into $D^+ + D^+ + O(^3P)$ — a project conducted in collaboration with Weber, Lucchese, McCurdy, and others. Employing the native-frames method [102, 103], we identify, separate, and follow step-by-step two state-specific sequential pathways of the intermediate OD^+.

The signature of this sequential breakup is a uniform $N(\theta_{OD,D})$ distribution and $KER_{OD} < 2.25$ eV, where $\theta_{OD,D}$ is the angle between the relative momenta associated with each breakup step, and KER_{OD} is the second step KER — *i.e.*, the expected KER for predissociation of OD^+ via the metastable $a^1\Delta$ and $b^1\Sigma^+$ states [105]. Some of the OD^+ ions undergo predissociation to the $D^+ + O(^3P)$ limit. Furthermore, we identify two pathways and the associated electronic states in the energy-correlation map shown in Figs. 11(a) and 11(b). Specifically, we separate the fragmentation
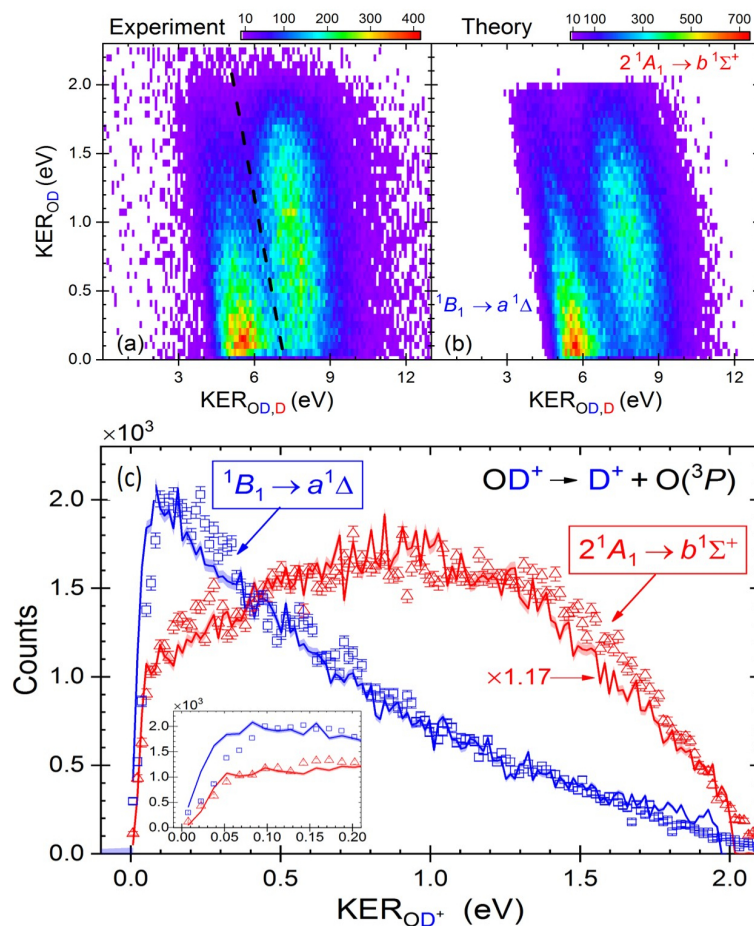
Figure 11: D_2O^{2+} fragmentation: The (a) measured and (b) calculated KER-correlation maps of the first and second breakup steps, and (c) second step KER.

of the $1\,^1B_1$ and $2\,^1A_1$ states of D_2O^{2+} into the $a\,^1\Delta$ and $b\,^1\Sigma^+$ states of the OD^+ molecule, respectively.

Our classical trajectory calculations on the relevant *ab initio* potential energy surfaces verify the sequential fragmentation pathways and enable the determination of the internal-energy and angular-momentum distributions of the OD^+ molecule. Moreover, the calculated and measured KER distribution in each of these pathways match very well, as shown in Fig. 11(c), where the inset shows the suppression at low KER due to the centrifugal barrier predicted by our theory.

Future plans

We plan to continue studying three-body breakup of polyatomic molecules, like CH_2IBr discussed briefly in Sec. 2.2.1, comparing CO_2 and CO_2^+ targets, while improving the native-frames analysis.

2.2.3 Probing ultrafast dynamics of molecules by probing fragmentation branching ratios with strong laser fields — Lin

Project scope

Probing and controlling dynamics of molecules on the femtosecond timescale is at the heart of modern ultrafast chemistry. Since only a small fraction of molecules are excited by the pump or the controlling pulse, intense laser fields are favorable probes for their high efficiency, but their utility is limited so far by the lack of reliable theory. In this project, we develop a simple computation method that can readily calculate the branching ratios of molecular ion fragments that are expected to be strongly dependent on the excited molecules, thus serving as a useful tool for probing ultrafast dynamics of molecules.

Recent progress

Intense lasers have been used to study ionization and breakup of molecules since the early days. While numerous experiments have been carried out, theoretical predictions of the fragmentation have been lacking. Double ionization of molecules is of particular interest since dications would often result in two or more fragments that can be measured in coincidence. Recently, intense lasers have been employed as a probe pulse in a number of pump-probe experiments to monitor the temporal evolution of a dynamic system after the pump pulse, by measuring the energy or momentum of ionic fragments versus the time delay, but the detailed data can only be interpreted qualitatively due to the lack of reliable theory. Typical quantum calculations for such reactions are extremely difficult since the breakup results in at least two free electrons and two free ions. While covariant momentum spectra involving electrons, ions, or electrons and ions, have been reported, the collection of such data and analysis are too tedious, deeming covariant momentum spectra not suitable for probing the temporal behavior of a molecule that has been excited by a pump pulse.

The most elementary information on the fragmentation of a molecule by an intense laser field is the branching ratios of the charged fragments, which are readily available from Coulomb explosion experiments. The branching ratios are expected to depend on laser intensity, pulse duration, wavelength and chirp of the laser. Since only charge states are needed, the target can be probed in many different measurements. To realize this goal, an efficient theoretical method for calculating the branching ratios of the fragments is needed.

In the last eight months, we have developed a theoretical model for calculating the branching ratios for a molecule ionized by strong laser fields using the Octopus quantum chemistry package by imposing many simplifications based on the structure of the molecules. Truncations are made by calculating only channels that would result in the fragments. Using D_2O as an example, the branching ratios for D^+/OD^+, D^++D+O^+ and D^++D^++O are calculated for a number of different laser parameters. The preliminary results are in good agreement with the few experimental data available, showing the great promise of our new approach.

Future plans

For D_2O, our next goal is to prepare molecules initially in a vibrational excited state, or a vibrational wave packet, and calculate how the fragmentation branching ratios will evolve in time. The calculation can be done for different intensity or wavelength to provide guidance for future experiments. Clearly, extension of the calculations to other molecules will be determined in collaboration with experimental groups.

2.2.4 Electron-ion coincidence measurements of di-hydrogen and tri-hydrogen cation formation in photoionized alcohol molecules — Rudenko, Rolles, Ben-Itzhak

Project scope

Intramolecular hydrogen or proton motion plays a vital role for many processes in physics, chemistry, and biology. The main goal of this project is to study ultrafast hydrogen dynamics in several examplary photoinduced reactions utilizing electron-ion coincidence measurements. We focus on di-hydrogen and tri-hydrogen cation elimination from photoionized alcohol molecules, the process that requires breaking and consecutive formation of two or three molecular bonds. Trigerring these reactions by absobing a single XUV photon and detecting the emitted photoelectron in coincidence, we can directly characterize electronic states involved in the formation of a specific ionic fragment.

Recent progress

We have recently studied the elimination of tri-hydrogen cations from various hydrocarbon molecules driven by intense NIR laser field [34, 67] [106, 107]. All of these studies addressed the tri-hydrogen formation in dicationic molecular states. Following up on this work, over the last year we focused on di-hydrogen and tri-hydrogen cation formation triggered by a single XUV photon from a femtosecond high-harmonic source. Choosing the photon energy below, close to, or above the double ionization threshold, we restrict the relevant potential surfaces involved in the reaction. This is illustrated in Fig. 12(a) for the case of deuterated methanol (CD_3OH). Similar to our previous work [34] [106, 107], the use of a deuterated sample allowed us to unambiguously determine whether the formation of a particular fragment proceeds via an "extended" or a "local" pathway — *i.e.*, whether it involves a mixture of hydrogen atoms from the methyl and hydroxyl groups or not.

Remarkably, the ion TOF spectra clearly show that the formation of tri-hydrogen via the extended pathway (D_2H^+) is more probable than for the local one (D_3^+) at the photon energies below the double ionization threshold. For molecular hydrogen formation, the extended pathway
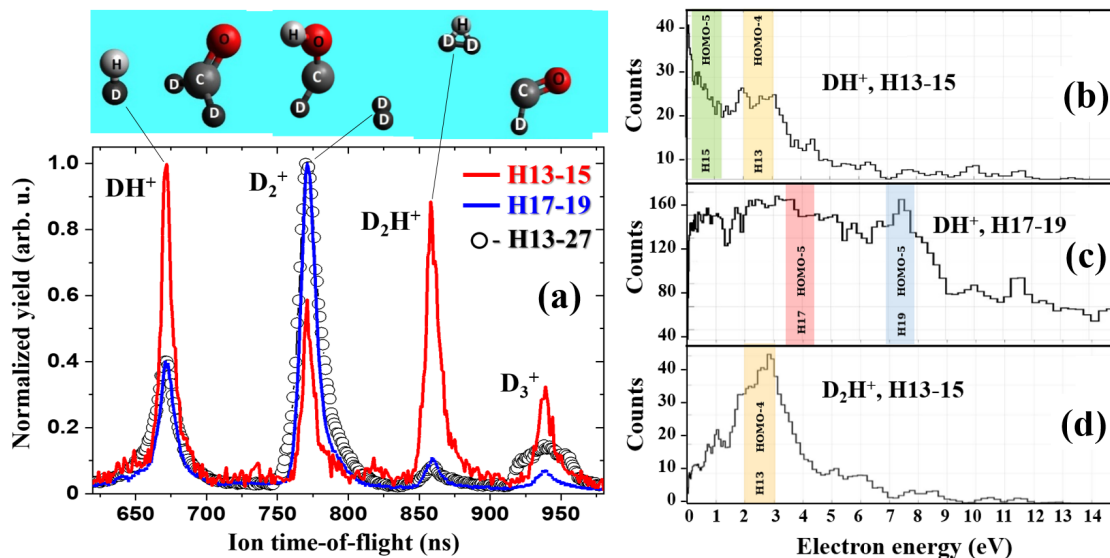
Figure 12: (a) TOF spectra of light ionic fragment emitted from CD_3OH, ionized by various harmonic orders. The double ionization threshold of 32.1 eV lies just above H21, so only the spectrum produced by the harmonic train (open circles) contains the events from double ionization. (b) Photoelectron energy spectrum measured in coincidence with DH^+ ions produced by H13–H15. (c) Same for H17-H19. (d) Photoelectron energy spectrum coincident with D_2H^+ ions produced by H13–H15. The shaded areas in panels (b)–(d) mark photoelectrons resulting from the ionization of the indicated molecular orbital by the harmonic given.

(DH^+) is the dominant channel at the lowest photon energy, whereas at the higher photon energies, the local pathway (D_2^+) becomes the stronger of the two.

This behavior can be rationalized based on the results of our recent calculation, which determines a set of possible electronic states allowing for a particular tri-hydrogen and molecular hydrogen elimination pathway [98]. According to the calculation, the D_2H^+ production mainly results from the ionization out of the HOMO–4 molecular orbital (binding energy 17.5 eV), the local D_2^+ channel is due to the ionization from the HOMO–5 orbital (binding energy 23 eV, not accessible with H13), and DH^+ formation can result from the ionization out of either of these two orbitals. The calculation is benchmarked by the coincident photoelectron spectra shown in Fig. 12(b)–(d), which confirm the assignments of particular channels to certain molecular orbitals.

Future plans

We plan to apply a similar electron-ion-coincidence approach to study other reactions involving hydrogen motion. These experiments are planned for two different modes: addressing the reactions in ionic and in neutral states. For ionic states, we plan to study several elimination and hydrogen migration reactions using a configuration similar to the one discussed above, where the ionization is performed by a single high-harmonic photon. For neutral molecules, we will use UV photons to trigger dynamics involving hydrogen motion in excited states. Here, we will exploit the ability of the FLAME TOPAS to tune the wavelength of the pump pulse to the state of interest, and probe the dynamics with a second UV pulse that can ionize this state.

Peer-Reviewed Publications Resulting from this Project (2019–2021)

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

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

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
OGessner@lbl.gov, MHead-Gordon@lbl.gov, SRLeone@lbl.gov, RLucchese@lbl.gov,
CWMcCurdy@lbl.gov, DMNeumark@lbl.gov, TNRescigno@lbl.gov, DSSlaughter@lbl.gov,
TWeber@lbl.gov

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 the flow of charge, energy, and coherence in atoms and molecules in the gas phase, in the condensed phase, and at interfaces. Studies apply a broad span of existing and emerging tools based on combinations of laboratory- and facility-scale pulsed XUV and X-ray light sources and electron beams with state-of-the-art experimental techniques. Table-top femtosecond and attosecond XUV and X-ray light sources, X-ray free electron lasers, synchrotron radiation, and low-energy electron beams are employed in combination with transient XUV and X-ray absorption and photoemission spectroscopy, XUV nonlinear and four-wave mixing spectroscopy, electron and ion momentum imaging, coincidence techniques, ultrafast X-ray scattering and coherent diffractive imaging, as well as ultrafast electron diffraction. 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-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, and Th. Weber

Attosecond Dynamics *(Leone, Neumark)*

The attosecond dynamics subgroup develops new nonlinear spectroscopies with attosecond extreme ultraviolet (as-XUV) pulses produced by high harmonic generation (HHG) for time-domain measurements of ultrafast electron dynamics in atoms and molecules. These experiments probe electronic wavepacket propagation excited by an as-XUV pulse using two independently controlled few-cycle near-infrared (NIR) pulses via background-free, attosecond four-wave mixing (FWM). The attosecond subgroup developed this new method to overcome the challenges of the many overlapping and interfering signals in attosecond transient absorption spectroscopy (ATAS). The FWM technique exploits the phase-matching condition for generating nonlinear wave mixing signals using a noncollinear beam geometry in which each pulse has a unique wavevector. Thus, FWM signals emit spatially according to specific combinations of the incident wavevectors, enabling background-free characterization of electronic, vibrational, and vibronic dynamics in atoms and molecules (Cao *et al*. **2018**, *Phys. Rev. A* 97, 023401; Warrick *et al*. **2018**, *Faraday Discuss.* 212, 157). Comparing ATAS and FWM signals of $^2P_{1/2}$ *ns/d* autoionizing states in Kr showed the superior sensitivity of FWM to obtain accurate measurements of ultrafast decaying states (Fidler *et al*. **2019**, *J. Chem. Phys.* 151, 114305). A refined understanding of the signal generation, achieved in collaboration with theorists Mette Gaarde and Kenneth Schafer at Louisiana State University, shows a time-dependent accumulation of an AC Stark phase grating (Fidler *et al*. **2019**, *Nat. Comm.* 10, 1384). These developments enabled the first demonstration of as-XUV multidimensional spectroscopy (Marroux *et al*. **2018**, *Sci. Adv.* 4, eaau3783).

Recent Progress: Recent work has used the enhanced signal specificity of FWM to understand short lived, complex electronic dynamics. Angularly diffuse XUV beams were successfully used in a self-heterodyned noncollinear wave-mixing experiment on helium, enhancing the 1*snp* states to reveal seven previously undetectable light-induced states (Fidler *et al*. **2020**, *J. Phys. Photonics* 2, 034003). ATAS measurements at the iodine $N_{4,5}$ pre-edge of ICl show orbital alignment-dependent core-excited state lifetimes, indicating that non-local decay channels involving chlorine electrons enhance the decay rates of core-hole states aligned parallel with the molecular axis (Marroux *et al*. **2020**, *Nat. Comm.* 11, 5810). Currently, FWM experiments and simulations have investigated excited electronic wavepackets in autoionizing Rydberg states of Ar from 3*s*→n*p* excitation (Gaynor *et al*. **2021**, *in preparation*). Spectral line widths for the 3*s* → 4*p*, 5*p*, and 6*p* states in the literature suggest that the autoionizing lifetimes should be 8.2 fs, 23.3 fs, and 52.2 fs, respectively. However, strong coherences with nontrivial dynamics are observed in the FWM emission (Fig. 1-1a). Modelling the emissions as a propagating electronic wavepacket fits the data exceedingly well and intuitively explains the measured signals (Fig. 1-1b). We find that the FWM signals observed at the n*p* state emission frequencies are significantly influenced by the (n+1)*p* state dynamics (inset Fig. 1-1b), which explains the observed coherences and decay times. Mechanistically, this is explained by transition dipole moments that connect the n*p* and (n+1)*p* states, which are driven non-resonantly by the NIR pulses. Using the dipole moments and the NIR pulses to simulate the experimental spectrum by solving the time-dependent Schrödinger equation confirms this interpretation. Fourier transforming the experimental FWM spectrum (Fig. 1-1c) and the simulated spectrum (Fig. 1-1d) reproduces the coherences involving the n*p* and (n+1)*p* states.
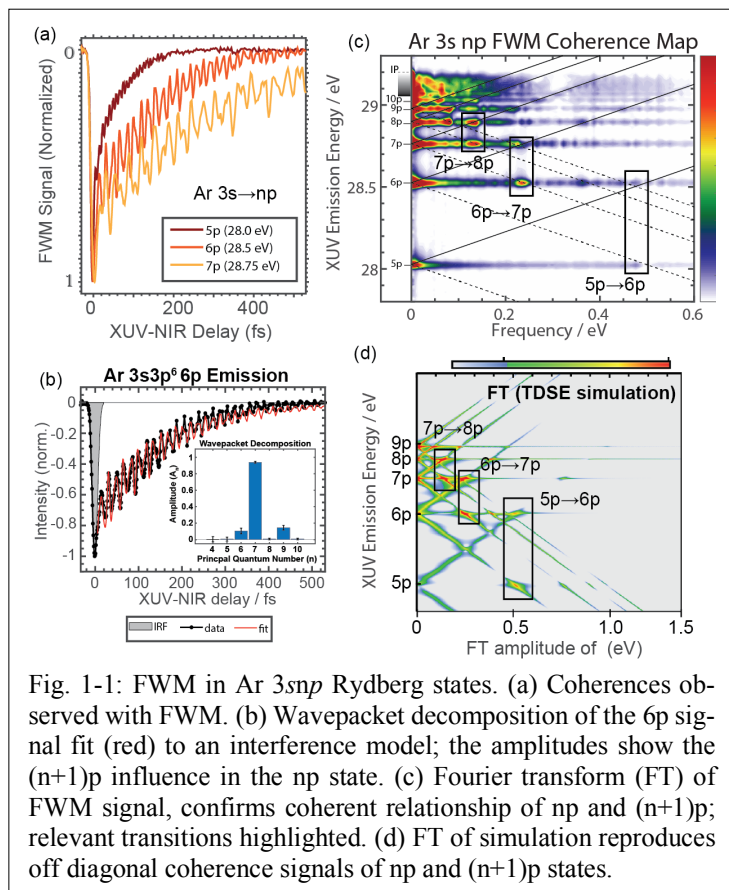
Fig. 1-1: FWM in Ar 3snp Rydberg states. (a) Coherences observed with FWM. (b) Wavepacket decomposition of the 6p signal fit (red) to an interference model; the amplitudes show the (n+1)p influence in the np state. (c) Fourier transform (FT) of FWM signal, confirms coherent relationship of np and (n+1)p; relevant transitions highlighted. (d) FT of simulation reproduces off diagonal coherence signals of np and (n+1)p states.

We also showed FWM spectroscopy can be used to study few-fs complex electronic dynamics of atom-like excitations in solids (Gaynor *et al.* **2021**, *Phys. Rev. B* 103, 245140). Here, the Na^+ $L_{2,3}$ edge (Na $2p \rightarrow 3s$) is studied in NaCl crystalline thin films. Core-excitons are bound electron core-hole pairs, which, in this case, are highly localized to the Na^+ ion of NaCl. Using FWM, we measure many more core-excitons than previously observed, which have 6-8 fs decay times, driven by many-electron correlations.

Recently, we achieved the first precise FWM time-domain measurement of an excited state lifetime in a molecule (Lin *et al.* **2021**, *Faraday Discuss.* 228, 537). This study showed that coupled electronic-nuclear dynamics in gaseous O_2 dictates the relaxation of the 3s Rydberg state in the ionic c $^4\Sigma_u^-$ state series. The 3s Rydberg state supports v=0 and 1 vibrational levels at 20.85 eV and 21.05 eV, respectively, and includes competing autoionization and dissociation decay channels. These decay channels are isolated experimentally from other FWM signals by adjusting the overlap angles of the two noncollinear NIR beams, revealing 5.8 ± 0.5 fs and 4.3 ± 0.7 fs lifetimes for the v=0 and v=1 states, respectively. Collaboration with Program PIs McCurdy and Lucchese provided theoretical support (see Subtask 3). Calculated results of 5.6 fs and 4.8 fs, respectively, match the experimental values very well and provide deeper insight into the dominant decay mechanisms. While predissociation might appear to explain the different lifetimes, theory suggests autoionization dominates the decay for both vibrational states and that nuclear motion can affect this autoionization rate.

Future Directions: Facilities renovations were completed in the laboratory by the end of 2020 to allow for the installation of a new high-powered laser system; a completely rebuilt wave-mixing apparatus has been under construction since January. We are currently working towards generating high harmonics with greater flux above 50 eV and utilizing a hollow core fiber broadened 1.3 μm output from a high-power optical parametric amplifier to enable attosecond pulses at the carbon K-edge (~300 eV). New small molecule dynamics studies with elemental specificity of carbon will be achieved with these capabilities. For example, FWM experiments on alkyl iodide molecules will be possible by studying both the 4d^{-1}6p core-excited states of I and the 1s core excitations of the carbon chain. Bond-length dependent core-hole lifetime measurements in CH_3I will use a 266 nm pulse to trigger iodine dissociation followed by an XUV-UV-UV pulse sequence. The bond-length dependence of non-local decay mechanisms will be directly measured and will serve as a benchmark for future theoretical models. These developments will provide an incisive picture

of the otherwise inaccessible electronic and nuclear motions governing chemical reaction dynamics.

Ultrafast Excited State Dynamics Probed by Multidimensional Momentum Imaging

Particle angle- and energy-resolved molecular photoionization measurements are sensitive to the coupled motion of electrons and nuclei as well as their ionization and fragmentation mechanisms. In particular, Molecular and Recoil Frame Photoelectron Angular Distributions (M/RFPADs), i.e., the body-fixed frame electron emission patterns in molecules, sensitively interrogate the molecule from within. This technique sheds light on fundamental properties such as symmetry, particle correlation and entanglement, energy transfer between electrons and nuclei as well as vibrational dynamics such as bending and stretching of the molecular backbone, which are at the core of many photochemical reactions and the focus of our studies. We investigate these phenomena in great detail via electron-ion coincidence measurements in momentum space, which, at this point, we are able to pursue in single to quadruple ionization experiments of small quantum systems with reaction microscopy a.k.a. COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS). The investigations are realized using XUV synchrotron radiation, 2-VUV photon absorption schemes with our tabletop intense high harmonic generation laser system, and two or more soft X-ray photons from single free electron laser pulses. Our studies focus on fundamentally important systems ranging from small molecules and dimers (N_2, O_2, D_2O, HeHe and NeKr) to more complex systems (CH_3OH) that are within reach of both complete experimental characterization and accurate theoretical treatment and interpretation, enabling tight coupling of the experiment and the theory thrusts, which directly complement, inspire, and inform each other.

The Role of Dipole-Forbidden Autoionizing Resonances in Non-Resonant One-Color Two-Photon Single Ionization of N_2 *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: In photoionization, continuum states that decay via autoionization can provide an indirect channel to final target states that can interfere with the direct ionization channel to those very same final states. This so called Fano effect can be sensitively observed in the photoelectron angular distributions (PADs), where the amplitudes and phases of the angular momentum components of the photoelectron scattering wave functions from direct ionization interfere with those of the electrons originating from autoionization. Such information is challenging to obtain by either experiments or calculations alone. In a collaborative effort, however, energy- and angle-resolved experimental and theoretical insight on the photoionization dynamics of N_2 enabled us to advance in this direction and analyze ionic-state-selective valence PADs, following non-resonant one-color two-photon single ionization (NOTPSI) of neutral nitrogen molecules. We applied coincidence electron-ion 3D momentum imaging and intense 9.3eV femtosecond pulses, produced via 400 nm driven HHG of short (~ 50 fs) laser pulses.

Two-photon single ionization by two 9.3 eV photons populates the first three ionic states $X^2\Sigma_g^+$, $A^2\Pi_u$, and $B^2\Sigma_u^+$ of the molecular nitrogen cation, where we found that the PADs associated with the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states varied notably with changes in photoelectron kinetic energy E_e of only a few hundred meV (see Fig. 1-2 for e.g. the $A^2\Pi_u$ state). We attributed this rapid evolution in the PADs with minor changes in the photoelectron kinetic energy to the excitation and decay of dipole-forbidden autoionizing resonances of the Hopfield series, each having different total symmetry (Larsen *et al.* **2020**, *Phys. Rev. A* 102, 03118). In addition to the direct two-photon, single ionization channel, these continuum-embedded discrete states provided an indirect pathway to the $X^2\Sigma_g^+$
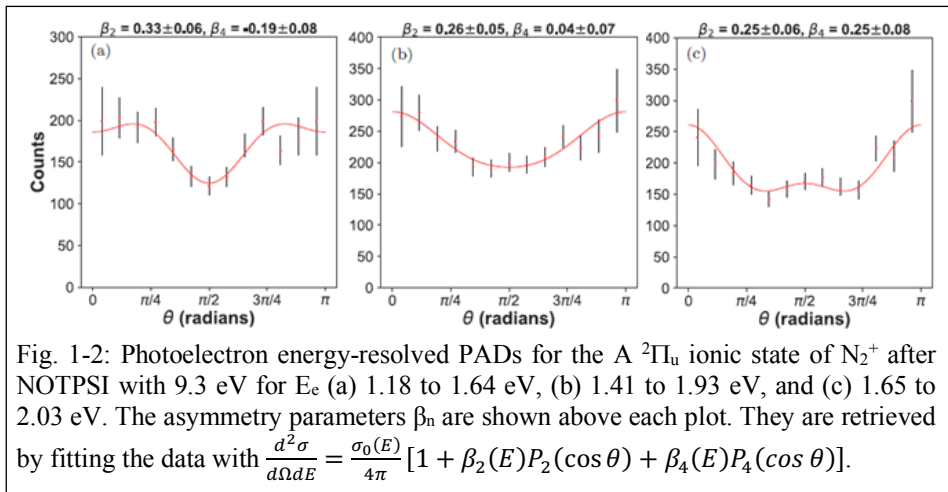
Fig. 1-2: Photoelectron energy-resolved PADs for the A $^2\Pi_u$ ionic state of N_2^+ after NOTPSI with 9.3 eV for E_e (a) 1.18 to 1.64 eV, (b) 1.41 to 1.93 eV, and (c) 1.65 to 2.03 eV. The asymmetry parameters β_n are shown above each plot. They are retrieved by fitting the data with $\frac{d^2\sigma}{d\Omega dE} = \frac{\sigma_0(E)}{4\pi}[1 + \beta_2(E)P_2(\cos\theta) + \beta_4(E)P_4(\cos\theta)]$.

and A$^2\Pi_u$ final states of the N_2 cation. With a limited theoretical treatment, only invoking a single virtual intermediate state and, hence, treating the two-photon ionization as quasi-resonant, our calculations provided insight into the non-resonant two-photon ionization dynamics, highlighting the important role of the dipole-forbidden autoionizing states in shaping the PADs and resulting β parameters. The calculated np and nf Rydberg series contributed differently depending on the respective kinetic energy region, which resulted in completely different PADs as depicted in Fig. 1-2 (a)-(c) for the A$^2\Pi_u$ final state. The computed energies of the dipole-forbidden autoionizing states were insensitive to the particular intermediate state, which suggests that the theory, while quasi-resonant, adequately captures the importance of autoionizing resonances for the experimentally studied non-resonant case.

The two competing pathways of autoionization and direct ionization, leading to the same final state, can produce interference in the photoelectron momenta. In the present work, the target N_2 molecules were randomly oriented, and, hence, we were not able to isolate the small subset of events that would sensitively exhibit interference effects in the MFPADs. However, follow-up experiments could employ impulsive alignment of the neutral molecule with respect to the polarization vector of the intense VUV pulse prior to photoionization by 2 VUV photons to gain deeper insight.

Future Plans: We are in the process of complementing our NOTPSI investigations with energy- and angle-resolved *resonant* one-color two-photon single ionization (ROTPSI) experiments of molecular oxygen, using coincidence electron-ion 3-D momentum imaging. Although the resonantly populated intermediate electronic states are dissociative, and the VUV pulse duration is a few tens of femtoseconds, we found in our preliminary analysis that the motion of the nuclei is not a critical factor in the two-photon ionization dynamics; using the fixed equilibrium geometry of the molecule appears to yield a very good approximation to the photoionization dynamics. In this ongoing collaborative project with our in-house theory team (see Subtask 3), we are currently analyzing the apparently accurate description of the photoionization dynamics when neglecting wavepacket motion on the intermediate states. These excited states reside in an energy range of an avoided crossing and may involve non-adiabatic couplings and resonance effects.

Time-Resolved Dynamics of Interatomic Coulombic Decay in Single NeKr Dimers *(Weber)*
Recent Progress: We gained detailed experimental and theoretical insight into the contraction of $Ne^+(2s^{-1})Kr$ dimer ions upon single photoionization of NeKr dimers followed by interatomic Coulombic decay (ICD), which happens on a femtosecond (fs) timescale. By applying our coincidence

electron-ion 3D momentum imaging scheme at the Advanced Light Source, we were able to perform a kinematically complete experiment on single, isolated NeKr dimers. While exploiting the post-collision interaction (PCI) of the electrons in this photo double ionization (PDI) process, we were able to set up an internal clock, which has been successfully tested for timing dynamics of HeHe dimers on picosecond (ps) timescales. In our experiment, the NeKr dimer absorbed a single photon expelling a very slow photoelectron that started to leave the singly ionized dimer behind. However, as the ICD happened, the photoelectron is "overtaken" by the faster ICD electron and pulled back by the Coulomb force of the newly created doubly charged dimer ion. This results in a decrease of the kinetic energy of the emerging photoelectron, whereas the kinetic energy of the ICD electron increases. As demonstrated in previous work (Trinter *et al.* **2013**, *Phys. Rev. Lett.* 111, 093401), the amount of deceleration of the photoelectron depends on the emission time of the ICD electron, which emerges from the ion and "overtakes" the slower photoelectron, changing the attractive cation potential to a dication one. Thus, by measuring the energy shift of the photoelectron, information on the time delay between the excitation and decay can be retrieved.

Without the need for a pump-probe interrogation scheme, we were able to resolve the nuclear dynamics on a femtosecond timescale even though single synchrotron light pulses with 80 ps duration were used to photoionize the dimer. The results provide insight into the ultrafast time evolution of the vibrational wave packet dynamics of the $Ne^+(2s^{-1})Kr$ dimer cation undergoing ICD, and we obtained snapshots of a "molecular movie" (summarized in Fig. 1-3). We found that ICD in the $Ne^+(2s^{-1})Kr$ ion evolves within the first 250 fs after photoionization. Hence, using the internal clock technique, we successfully tracked dynamics that are >100 times faster than the nuclear motion in e.g. contract-
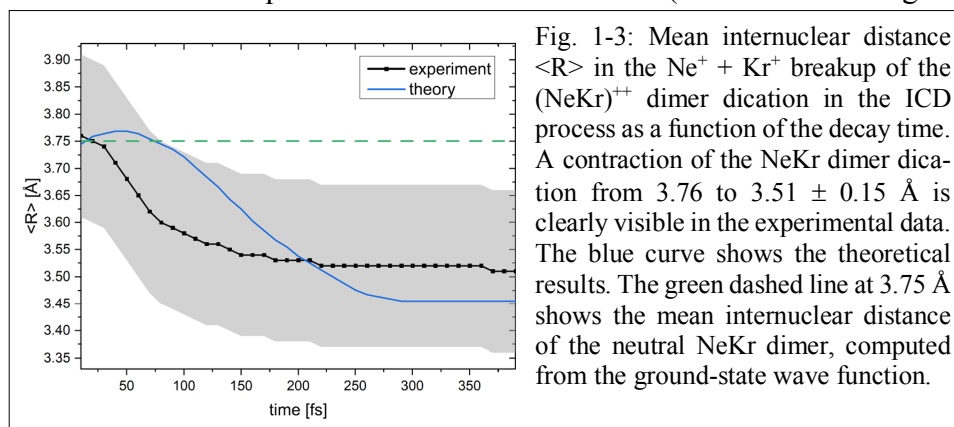
Fig. 1-3: Mean internuclear distance <R> in the $Ne^+ + Kr^+$ breakup of the $(NeKr)^{++}$ dimer dication in the ICD process as a function of the decay time. A contraction of the NeKr dimer dication from 3.76 to 3.51 ± 0.15 Å is clearly visible in the experimental data. The blue curve shows the theoretical results. The green dashed line at 3.75 Å shows the mean internuclear distance of the neutral NeKr dimer, computed from the ground-state wave function.

ing HeHe dimer cations. An average time resolution of ~10 fs was achieved, while changes in the internuclear distance as small as 0.3 Å have been resolved. During this time, the NeKr dimer cation contracted from 3.76 Å (±0.15 Å) towards the classical turning point of the $Ne^+(2s^{-1})Kr$ cation potential energy curve, reaching a minimum internuclear distance of 3.51 Å (±0.15 Å), before the ICD electron was released (Trinter *et al.* **2021**, *submitted to J. Chem. Phys.*).

Future Plans: Internal clocks can be set up in different ways in highly differential measurements of small quantum systems. While the above timing scheme in dimers exploited the energy shift of the photoelectron due to the PCI effect, electron and ion angular distributions can be used as well to time dissociation dynamics. For instance, in earlier PDI experiments on H_2O we took advantage of the anisotropy in the autoionization electron angular distribution to probe the distance between a fragment proton and the autoionizing co-fragment (OH^*) during the dissociative PDI process $H_2O + h\nu \rightarrow H_2O^+ + e^- \rightarrow H^+ + OH^* + e^- \rightarrow H^+ + OH^+ + 2e^-$ (Sann *et al.* **2011**, *Phys. Rev. Lett.* 106, 133001). The autoionization electron angular distribution exhibited a diffraction pattern that enabled us to track the departing proton and estimate the internuclear distance when the autoioni-

zation took place and, hence, the decay time. This approach shall be applied to the PDI of deuterated methanol to study the competition between dissociation and autoionization and to follow the dynamics of these processes along various potential energy surfaces.

Investigating Charge-Up and Fragmentation Dynamics of Oxygen Molecules after Interaction with Strong Free-Electron Laser X-ray Pulses *(Weber)*

Recent Progress: In Photoelectron-Auger (PA), Photoelectron-Photoelectron-Auger-Auger (PAPA), or Photoelectron-Shakeup-Auger (PSA) ionization sequences, multiphoton absorption from intense X-ray free electron laser (XFEL) pulses initiates intricate nuclear dynamics as a molecule starts to fragment during the charge-up process. From our COLTRIMS experiment, performed in a large international collaboration at the EuXFEL, we obtained the kinetic energy of the photoelectrons E_e, their emission directions with respect to the molecular axis (MFPADs), the kinetic energy of the fragment ions (KER), as well as their charge states (z) and their emission directions. We used this information to follow the route of the charge-up and fragmentation dynamics of O_2. For the creation of an O_2^{5+} ion via a short soft X-ray pulse we identified and isolated two pathways, i.e. the "main": $O_2 \xrightarrow{PSA} O^{1+} + O^{2+} \xrightarrow{PA} O^{3+} + O^{2+}$ and the "satellite" route: $O_2 \xrightarrow{PA} O^{1+} + O^{1+} \xrightarrow{PSA} O^{3+} + O^{2+}$, where each right arrow indicates the absorption of an X-ray photon. The nuclear dynamics during the charge-up, initiated by the intense XFEL pulse ($\sim$ 25fs, 670 eV, 30 μJ), was governed by the fragmentation steps of the molecule. Information on the internuclear separation R of the two ionic fragments at the instant of the secondary O(1s) photoionization was imprinted on the KER of the ions. In order to interconnect R and KER, a classical Coulomb explosion model, based on our previous work (Kastirke *et al*. **2020**, *Phys. Rev. X* 10, 021052), was applied. It assumed a sequence of steps: First, the primary O(1s) ionization sequence takes place at the equilibrium separation R_{eq}, which forms the $O^{z(l)+} + O^{z(r)+}$ charge-states at the two atomic sites ("left" and "right") of the O_2 molecule. Thereafter, the O-O bond elongates on the repulsive potential $[z(l)z(r)]/R$ until R, where the secondary O(1s) ionization sequence takes place forming the final $O^{z'(l)+} + O^{z'(r)+}$ charge-states, which then fragments on the repulsive potential $[z'(l)z'(r)]/R$. The resulting KER and internuclear distance R are then related via the Coulomb potential curves as:

Fig. 1-4: Comparison between the experimental backward to forward ratios (symbols with error bars), measured for the O^{3+} + O^{2+} final charge state and the photoelectron kinetic energy ranges of: (a) E_e = 55 to 80 eV and (b) E_e = 80 to 110 eV. The ratios fitted with our analytical model (broken curves) and the *ab initio* theoretical results (solid curves with symbols) represent individual contributions from the main channel O^{1+} + $O^{2+} \rightarrow O^{3+}$ + O^{2+} in panel (b) and from the satellite channel O^{1+} + $O^{1+} \rightarrow O^{3+}$ + O^{2+} in panel (a).

$$\text{KER} = \frac{z(l)z(r)}{R_{\text{eq}}} + \frac{z'(l)z'(r) - z(l)z(r)}{R}. \qquad \text{Eq.} \,(1-1)$$

MFPADs of the secondary photoelectron (MF2$^{\text{nd}}$PADs) depend strongly on the internuclear distance R. The photoelectron flux towards the singly-charged oxygen ion, which after photoionization and Auger decay becomes triply-charged, exhibits an oscillatory trend with respect to R. The

oscillation of the backward to forward photoelectron emission intensities in the molecular frame corresponds to the interference between the direct and scattered waves, and we are able to analyze the backward/forward ratio of the MF2ndPADs as a function of KER for electron energies E_e(low) = 55 to 80 eV and E_e(high) = 80 to 110 eV, which we attributed to the "satellite" and "main" pathways, respectively, as seen in Fig. 1-4(a) and (b). Both, *ab initio* theoretical results (provided by Ph. Demekhin *et al.*) and the results employing our analytical model fitted to the data points, reproduced the experimentally observed forward/backward emission ratios.
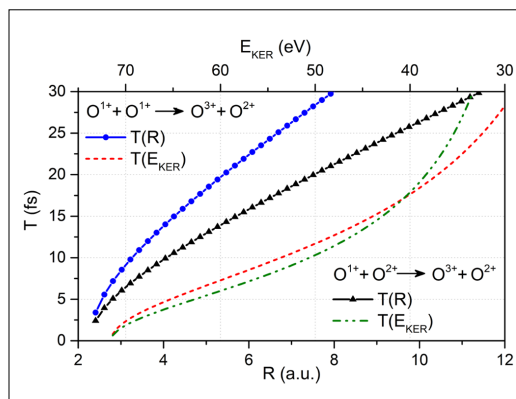
Fig. 1-5: The relation between the O-O bond length R and the second ionization time T given by our classical model (solid curves with symbols, refer to the lower horizontal scale) together with the relation between the KER and the second ionization time T with the O-O bond length R given as a function of KER via Eq. (1-1) (broken curves, refer to the upper horizontal scale) for the main $O^{1+} + O^{2+} \rightarrow O^{3+} + O^{2+}$ and satellite channel $O^{1+} + O^{1+} \rightarrow O^{3+} + O^{2+}$ (see legends).

Using the same Coulomb explosion model, the temporal variation of the internuclear distances in the intermediate states $O^{1+} + O^{1+}$ and $O^{1+} + O^{2+}$ during the XFEL pulse are examined and visualized as shown in Fig. 1-5. According to this model, it takes, for example, ~18 fs to yield a KER as low as 40 eV for the main and satellite dissociation path. During that time, the O-O bond length increased to about 7 a.u. for the $O^{1+} + O^{2+}$ and 5 a.u. for the $O^{1+} + O^{1+}$ channels (Kastirke *et al.* **2021**, *submitted to Phys. Rev. Lett.*).

Future Plans: The international COLTRIMS collaboration at EuXFEL now focuses on the PDI of water molecules via the absorption of two soft X-ray photons from single short and intense FEL pulses. The absorption of the two X-ray photons will initiate asymmetric deformation and bond-angle opening of the water dication and lead to 2- and 3-body fragmentation on an ultrafast time-scale. Employing a similar approach, as used in the analysis of O_2, which exploited the mostly pure Coulomb repulsion of the ionic fragments, we are in the process of investigating and timing the molecular structural dynamics of the H_2O^{2+} dications.

Investigations of Dynamics in Transient Anions Formed by Electron Attachment

Transient anions formed by electron attachment to polyatomic molecules can exhibit highly-coupled electronic and nuclear motion, which is often rooted in conical intersections between meta-stable electronic states. Dissociative Electron Attachment (DEA) is an electron-molecule reaction in which free electron energy is efficiently converted into nuclear degrees of freedom such as dissociation and vibrational excitation. The flow of energy and charge within the molecular anion provides rich information on fundamental chemistry beyond the Born-Oppenheimer approximation and has relevance to applications involving reactive anionic and radical species that are often produced by dissociation.

Electron Attachment and Dissociation Dynamics in Polyatomic Molecules *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: The rich electron-driven chemistry observed in ices containing methanol draws recent attention to the fundamental importance of Feshbach resonances in methanol molecules upon DEA. An incident electron promotes any of the three outermost valence electrons into the now doubly-occupied Rydberg orbital. These resonances are electronically stabilized by strong

electronic correlation, allowing dissociation to compete with autodetachment. In collaboration with Joshua Williams (University of Nevada, Reno), we have measured and analyzed H^-, O^-, and CH_3O^- fragment momentum distributions to seek potential signatures of isomerization reactions such as CH_4 and H_2 formation. Of particular interest are the mechanisms producing O^- fragments following DEA to methanol at the higher two Feshbach resonances (Fig. 1-6). The 8 eV resonance produces O^- with low momentum < 10 atomic units (a.u.), yet electron attachment energies only 2 eV
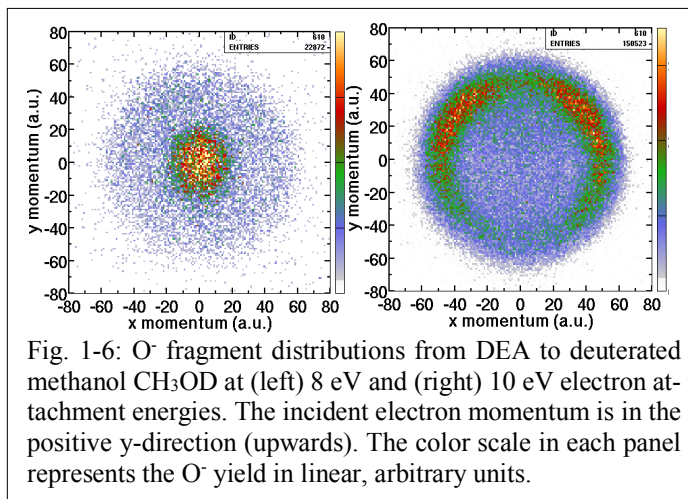
Fig. 1-6: O^- fragment distributions from DEA to deuterated methanol CH_3OD at (left) 8 eV and (right) 10 eV electron attachment energies. The incident electron momentum is in the positive y-direction (upwards). The color scale in each panel represents the O^- yield in linear, arbitrary units.

higher produce a much more energetic O^- fragment having 40 to 50 a.u. of momentum and a pronounced preference for dissociation in the forward hemisphere relative to the incident electron direction! The reason for this drastic change in the O^- fragment kinematics is yet unknown and presents new challenges for future investigations by the AMOS theory team.

Future Plans: In work reported recently (Panelli *et al.* **2021**, *Phys. Rev. Res.* 3, 013082), we investigated the possible role of Feshbach and shape resonances in the breaking of a model peptide bond by low energy (~6 eV) electrons. Next, we will explore the effect of substitutions, specifically methylation of model systems including formamide and nitroimidazole, on their DEA dynamics. The high site-specificity in DEA, i.e., the strong dependence of the number of bonds that break upon small changes in electron attachment energy, offers the possibility of exquisite control of the chemistry involving low energy electrons generated by ionizing radiation. Examples can be found in molecular radio-sensitizers such as 5-bromouracil. We aim to reveal key mechanisms and dynamics behind the different isomerization and dissociation channels in these model molecules, and their nitro-, methyl-, or halogen-substituted derivatives.

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

O. Gessner, M. Head-Gordon, S. R. Leone, D. M. Neumark, D. S. Slaughter, Th. Weber

Ultrafast Core-to-Valence Transient Absorption Spectroscopy *(Gessner, Head-Gordon, Leone, Neumark)*

Excited-state molecular dynamics are probed from the perspectives of well-defined reporter atoms using femtosecond time-resolved transient XUV absorption (TXA) spectroscopy. Experiments using laboratory-based HHG are complemented by high-level *ab initio* calculations of XUV spectroscopic fingerprints of possible reaction intermediates and products.

Recent Progress: Photoinitiated heterocyclic ring-opening reactions and molecular dissociation along potential energy surfaces (PES) involving antibonding σ* orbitals determine the photophysical properties of a broad range of molecules. In particular, sulfur-containing compounds have recently attracted considerable attention due to the potential impact of triplet states and intersystem

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crossings (ISC) on their intramolecular relaxation pathways, adding to the complexity of nonadiabatic molecular dynamics. We have probed electronic and structural changes during the 268 nm-induced dissociation of 2-iodothiophene using iodine 4d core-to-valence TXA spectroscopy. Complementary transient signals from parent molecule depletion and delayed neutral iodine fragment emergence indicate the involvement of a multi-step dissociation mechanism that appears to extend up to ~1 ps. The TXA experiments are currently interpreted with the aid of *ab initio* molecular dynamics (MD) simulations in combination with simulated XUV absorption spectra of transient configurations derived with the recently developed restricted open-shell Kohn-Sham (ROKS) approach for high-precision *ab initio* predictions of inner-shell excitation energies (Hait and Head-Gordon **2020**, *J. Phys. Chem. Lett.* 11, 775–786 and Hait *et al*. **2020**, *J. Chem. Phys.* 153, 134108, also see Subtask 3). Preliminary results indicate involvement of both $\pi\pi^*$ as well as $\pi\sigma^*$ excited states in the relaxation cascade.

A major improvement in the sensitivity of the TXA technique has been achieved by exploiting correlations between signal variations across the HHG energy spectrum. By carefully characterizing and suppressing these correlated fluctuations using an adaptive iteratively reweighted principal component regression (airPCR) technique, a 40-fold mean noise power reduction has been demonstrated. This enabled a TXA study of NIR modulated autoionizing $2snp\ ^1P^o$ ($n \geq 2$) Rydberg states of helium with sub-mOD sensitivity (Faccialà *et al.* **2021**, *Opt. Express*, *in press*).

Future Plans: We are working toward gaining a complementary viewpoint of the dynamics from the perspective of the sulfur and carbon atoms by expanding the photon energy range of the high-harmonics setup using a combination of a high-power optical parametric amplifier (OPA) and a high-pressure HHG setup.

UV-induced Dissociation Dynamics of Bromoform Probed by Ultrafast Electron Diffraction *(Gessner, Leone, Neumark)*

This is a new activity in the program, designed to complement ultrafast spectroscopy studies of excited-state molecular dynamics by femtosecond time-resolved electron diffraction. The UV photochemistry of bromoform is investigated by using mega-electron-volt ultrafast electron diffraction (MeV-UED) to study excited-state dissociation dynamics on femtosecond to picosecond timescales. Bromoform is a main contributor to ozone depletion, as it produces bromine radicals. Other possible photoproducts are Br_2 and HBr. In previous work using femtosecond TXA spectroscopy, it was concluded that, following excitation with 268 nm, the dominant pathway is direct dissociation into $CHBr_2$ and a bromine atom along an approximately C_s symmetrical trajectory (B. W. Toulson *et al.* **2019**, *Struct. Dyn.* 6, 054304). The same dissociation had previously been proposed to have a roaming-like dissociation pathway through iso-$CHBr_3$. The quantum yield of the Br-producing reaction channel was measured to be 76±3 %.

Recent Progress: To get further insight into the dissociation mechanism and to identify possible candidates for the remaining 24 % of photoproducts, we performed a UED experiment at SLAC National Accelerator Laboratory. Similar to the TXA experiment, bromoform was excited by a 267 nm pump pulse. A pulsed 3.7 MeV electron beam with typical pulse lengths of ~100 fs was used to probe the excited state dynamics by UED. Diffraction pattern differences between excited state configurations at positive pump-probe delays and ground state bromoform at negative delays are shown as false-color plots in Fig. 2-1. Blue and red bands indicate loss and gain of signal, respectively, in excited state compared to ground state structures. Comparison with the false-color map from a TDDFT-based molecular dynamics simulation of an approximately C_s symmetrical trajectory shows qualitative agreement in some features.
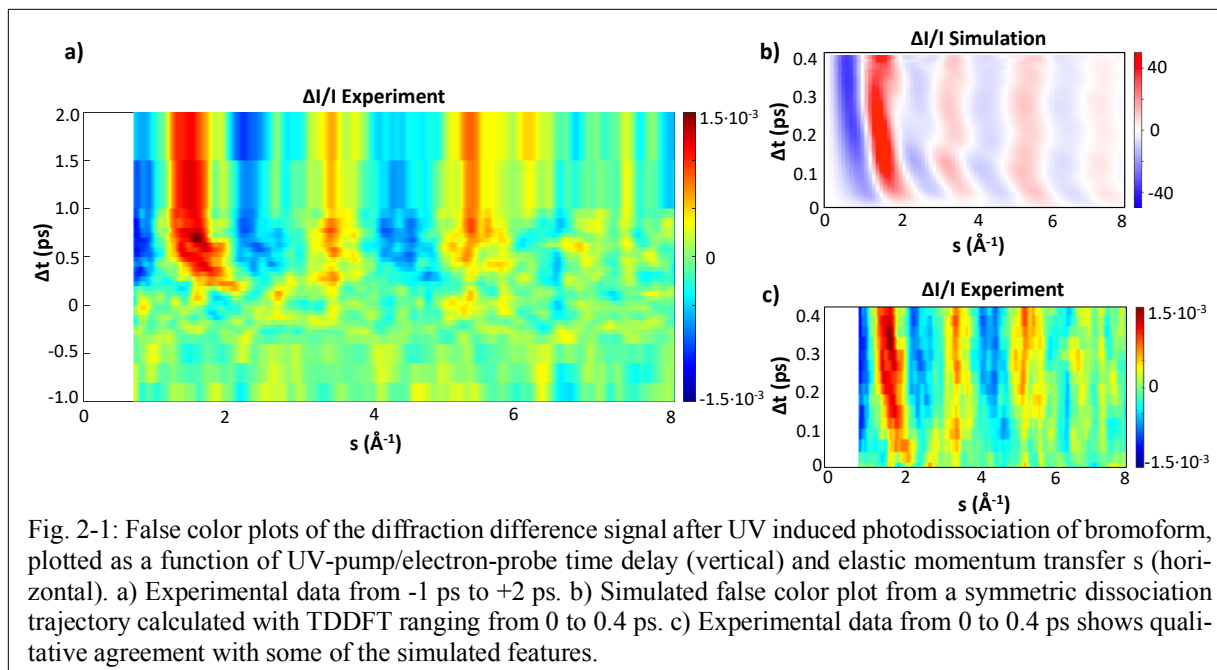
Fig. 2-1: False color plots of the diffraction difference signal after UV induced photodissociation of bromoform, plotted as a function of UV-pump/electron-probe time delay (vertical) and elastic momentum transfer s (horizontal). a) Experimental data from -1 ps to +2 ps. b) Simulated false color plot from a symmetric dissociation trajectory calculated with TDDFT ranging from 0 to 0.4 ps. c) Experimental data from 0 to 0.4 ps shows qualitative agreement with some of the simulated features.

Future Plans: The analysis of the UED data will be expanded to pair-distribution functions (PDFs) to identify the observed photoproducts with branching ratios and dynamic timescales. We plan to complement the experimental data with *ab initio* theory to gain deeper understanding of the underlying reaction dynamics. We also plan to extend the UED activities to include UV-induced dynamics in 2-iodothiophene. These will complement the TXA studies described above and further aid in identifying possible reaction pathways such as the involvement of ring-opening during the photodissociation. Strong scattering signals from iodine, sulfur, and carbon atoms are expected to enable high sensitivity in the experiment.

Time-Resolved X-ray Photoelectron Spectroscopy Studies of Interfacial Energy- and Charge-Transfer Processes in Heterogeneous Light-Harvesting Systems *(Gessner)*

In this effort, time-resolved X-ray photoemission spectroscopy (TRXPS) techniques are developed and applied to unravel fundamental processes underlying the conversion of photon energy into mobile charges and chemical transformations using heterogeneous light harvesting systems. Studies encompass photoinduced charge dynamics at molecule-semiconductor interfaces, energy- and charge-transfer in organic heterojunctions, as well as photodynamics in nanoplasmonic light harvesters. Synchrotron-based picosecond TRXPS studies are complemented by campaigns at XFELs to access the femtosecond regime.

Recent Progress: Organic Heterojunctions. Interfacial charge-transfer (ICT) configurations play a particularly important role for solar light harvesting, as they are considered gateways between the light absorption and the charge separation steps of the photovoltaic/photocatalytic cycle. For the copper phthalocyanine(CuPc)-C60 system, it was long believed that only ICT configurations with substantial energy surplus compared to their lowest energy states are able to overcome the Coulomb barrier for charge separation and, consequently, only photons in the visible range of the spectrum are able to generate charges. However, using femtosecond time-resolved X-ray photoelectron spectroscopy at the FLASH Free Electron Laser in Hamburg, we revealed that even when using near-infrared photons to excite some of the lowest-lying ICT states, these configurations are

able to dissociate into separate charges with an efficiency of ~22%, despite strong competition from exciton recombination on a timescale of ~1 ps. Key enabling factors for this insight are the interfacial site-specificity of X-ray transitions and the capability to characterize the emergence of both ICT states and charge-separated configurations on femtosecond timescales (Fig. 2-2, Roth *et al.* **2021**, *Nat. Commun.*12, 1196).

Expanding upon our work with CuPc-C_{60} systems, we have recently turned to studying interfacial dynamics involving manganese phthalocyanines (MnPc) as light absorbers, which will provide additional insight as to how particular material properties such as electronic and chemical structure affect their dynamic function. Photoin-

Fig. 2-2: Unravelling a new path for light-to-charge conversion in a metal-organic heterojunction: a) CuPc-donor/C_{60}-acceptor configuration, b) femtosecond time-resolved $C1s^{-1}$ XPS spectra with dominant C_{60} (left) and CuPc (right) contributions, c) schematic illustration of newly detected channel for charge generation from interfacial charge-transfer exciton, *Nat. Commun.* 2021, 12, 1196.

duced interfacial charge transfer dynamics across Si-C_{60} and Si-MnPc-C_{60} interfaces has been probed by femtosecond TRXPS at FLASH. Preliminary analysis indicates that transient core-level shifts have been detected that appear consistent with photoinduced ICT.

Dye-Sensitized Nanoporous Semiconductors. An alternative heterogeneous light harvesting system, consisting of a nanocrystalline ZnO electrode sensitized for visible absorption by adsorbed N3 dye molecules, has been studied with picosecond TRXPS, in combination with UV-photoemission spectroscopy, and optical absorption spectroscopy. We have derived a self-consistent model that describes all available steady-state and time-resolved data based on a multi-step electron injection process in combination with a self-trapping-like mechanism for injected electrons near the molecule-semiconductor interface (Neppl *et al.* **2021**, *J. Phys. Chem. Lett.*, *submitted*).

Nanoplasmonic Light Harvesting Systems. Based on our recent picosecond TRXPS study of charge injection efficiencies and carrier lifetimes in nanoporous TiO_2 electrodes sensitized with gold nanoparticles (Borgwardt *et al.* **2020**, *J. Phys. Chem. Lett.* 11, 5476), we are expanding the work on nanoplasmonic light harvesting systems in two major directions. One aims at a better understanding of the earliest electron dynamics in the femtosecond regime, the other at the impact of liquid environments, which are typical for application-like settings, on the charge dynamics. During a recent FLASH beamtime, we recorded preliminary data that support the feasibility of femtosecond TRXPS experiments on gold nanosphere decorated TiO_2. Preliminary picosecond TRXPS experiments at the Advanced Light Source indicate a drastically increased lifetime of separate charge carriers for a wet compared to a dry gold nanoparticle (AuNP) - TiO_2 system.

Future Plans*:* Ongoing efforts focus on the analysis of the FLASH data of CT in Si-C60 and Si-MnPc-C60 interfaces, in particular how different layering orders affect the direction and/or efficiency of CT. We will also delve into the role that layer thickness has on the CT process. A proposal to study the AuNP-TiO_2 system at the ALS while varying the ambient H_2O pressure and

AuNP diameter was highly rated. With user operations expanding again at the ALS after the COVID shutdown, we intend to use the allocated beamtime to reproduce our initial findings, as well as investigate how changing the system parameters will affect the interfacial CT dynamics. Physical interpretations of the system's dynamics are being investigated. To this end, collaborations with the groups of Jin Qian (LBNL) and Tod Pascal (UCSD) have been established. They will perform theoretical calculations regarding the impact of the aqueous environment on the fundamental dynamics underlying the observed trends. Based on the preliminary FLASH results for the AuNP-TiO$_2$ system, a revised proposal for a full beamtime is in preparation. In this context, a new collaboration with the group of Yvonne Joseph (TU Freiberg, Germany) has been initiated to provide high-quality, tailored samples on demand and in close geographic proximity to FLASH.

Dynamics in Helium Nanodroplets *(Gessner, Neumark)*
This effort uses XFEL-based ultrafast X-ray scattering, coherent diffractive imaging (CDI), and ion mass spectroscopy techniques to gain deeper insight into ground- and excited-state dynamics in pure and doped helium nanodroplets. The relatively simple electronic structure of He atoms makes pure droplets particularly well suited to test models of collective electronic properties and associated dynamics in complex systems. Strong-field and intense X-ray-induced charging and disintegration dynamics are studied by single-pulse X-ray coherent scattering and ion spectroscopy. The same XFEL based techniques are also used to study quantum-enabled ground-state phenomena.

Recent Progress: Results from an LCLS experiment enable the study of charging and ion ejection dynamics of helium droplets exposed to intense, short X-ray pulses. The inherent X-ray intensity fluctuations of the experiment on target allow us to study the transition from the Coulomb explosion (CE) regime to the hydrodynamic expansion/nanoplasma regime. The key enabling factor of the study is a combination of ion time-of-flight spectra measured in coincidence with small angle X-ray scattering images, all detected on a pulse-by-pulse basis. From the information contained in each scattering image, the droplet size, X-ray flux on target and, using well-established He ionization cross sections, the absolute degree of ionization frustration, α, is determined for each hit. The parameter α is defined as the ratio of the number of ions generated by photoionization and the number of ions required to generate a Coulomb potential deep enough to stop any photoelectrons from leaving the droplet. Complementary to the droplet ionization conditions, we retrieve the maximum ion kinetic energy from the ion TOF spectra. Correlating the degree of frustration with the maximum ion kinetic energy reveals a continuous relationship, with ion kinetic energy increasing with the degree of frustration, as seen in Fig. 2-3a. Results reveal that the maximum ion kinetic energy is governed by Coulomb repulsion of unscreened ions across the weakly frustrated into deeply frustrated regime. Further, we find that the results are consistent with the emergence of a spherical shell of unscreened ions surrounding a quasineutral plasma core, as the degree of frustration increases. In Fig. 2-3b, the distribution of unscreened ions is visualized and correlated with the degree of frustration by plotting the shell thickness of unscreened ions, normalized to the droplet radius, as a function of α. At small α, the droplet is weakly ionized and unscreened ions are homogeneously distributed. As α increases, with the onset of frustration and electron trapping, trapped electrons move to the center of the droplet to screen ions, resulting in the emergence of a quasineutral core. At large α, the majority of the droplet is comprised of the quasineutral core, with unscreened ions occupying less than 1% of the droplet radius (Saladrigas *et al*. **2021**, *EPJ-ST*, *in press*).

In a recent experiment at the European XFEL (EuXFEL) facility, highly charged helium droplets were used to study equilibrium distributions of surface charges, which serve as an experimental
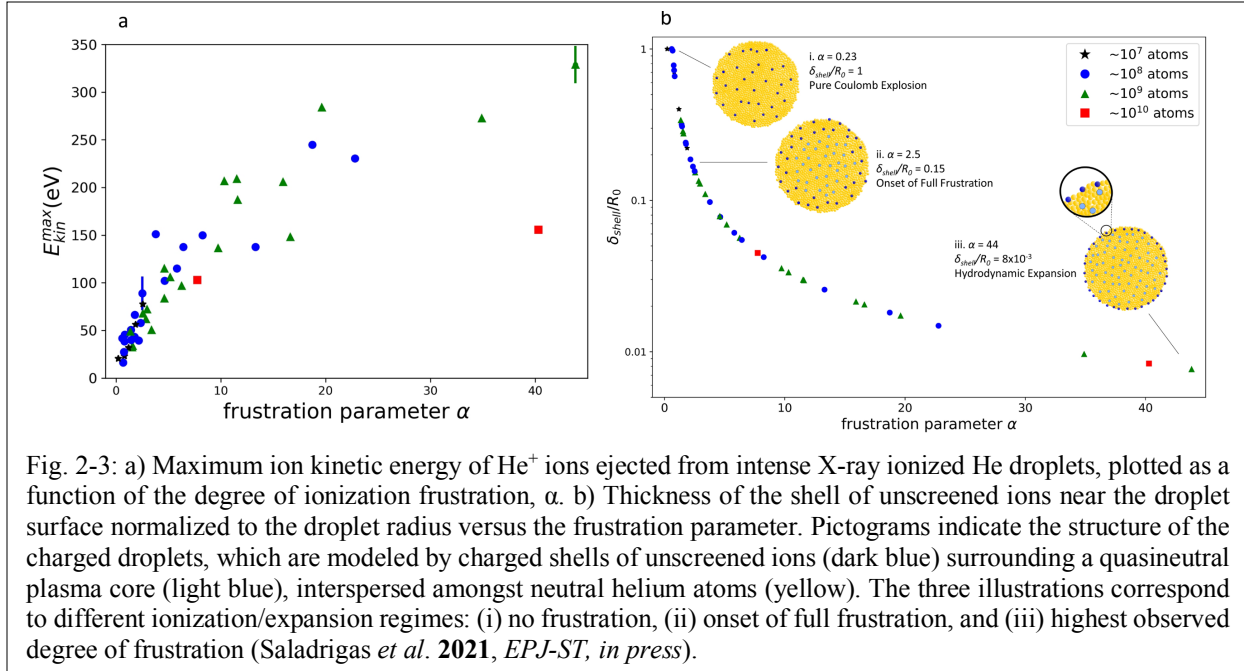
Fig. 2-3: a) Maximum ion kinetic energy of He$^+$ ions ejected from intense X-ray ionized He droplets, plotted as a function of the degree of ionization frustration, α. b) Thickness of the shell of unscreened ions near the droplet surface normalized to the droplet radius versus the frustration parameter. Pictograms indicate the structure of the charged droplets, which are modeled by charged shells of unscreened ions (dark blue) surrounding a quasineutral plasma core (light blue), interspersed amongst neutral helium atoms (yellow). The three illustrations correspond to different ionization/expansion regimes: (i) no frustration, (ii) onset of full frustration, and (iii) highest observed degree of frustration (Saladrigas *et al.* **2021**, *EPJ-ST, in press*).

implementation of the Thomson problem (i.e., the optimal configuration of charges on a sphere to minimize the Coulombic energy). The charged droplets were studied using single shot CDI at the SQS endstation. After formation, the droplets were heavily doped with either electrons or holes using an electron beam ionizer. The charged droplets were then doped with Xe, which is used as an X-ray contrast agent to track the charges. From the X-ray scattering images, charged, doped droplet configurations are reconstructed revealing the distribution of charges. The analysis of this experiment is ongoing.

Future Plans: Following the success of our previous LCLS experiment to monitor both surface and bulk evolution dynamics in strong-field ionized He nanodroplets (Bacellar *et al.* **2021**, *Phys. Rev. Lett. submitted*), a proposal has been submitted for beamtime at EuXFEL with an expanded collaboration that will enable detailed studies of the impact of electron seeding on the strong-field - droplet interactions.

XUV Ultrafast Transient Polarization Spectroscopy (X-UTPS) *(Slaughter, Weber)*
The aim of this thrust is to establish a new multidimensional, polarization-based nonlinear XUV and X-ray spectroscopy method to monitor ultrafast gas- and condensed-phase chemical dynamics with high detail. Ultrafast Transient Polarization Spectroscopy (UTPS) (Thurston *et al.* **2020**, *Rev. Sci. Instrum.* 91, 053101) employs a FWM scheme to probe both the real and imaginary parts of the 3rd-order nonlinear response of excited electronic states in molecules by exploiting the Optical Kerr Effect (OKE) in the time domain. The unique sensitivity of the intensity-dependent refractive index (χ^3) to electronic structure, electronic and vibrational coherences, and the correlated motion of electrons and holes provides access, for example, to dynamics near conical intersections, even if there is no change in the electronic binding energies. The central goal of this effort is to push the unique strengths of nonlinear techniques based on 3rd-order optical responses into the XUV and X-ray regime, labeled X-UTPS. Both UTPS and X-UTPS probe the nonlinear response of a system using one excitation pulse and only two FWM probe pulses, instead of the three or more probe pulses in other FWM techniques. This reduces the number of beam splitters, delay stages and mirrors required for FWM experiments, enabling higher fluence, higher phase stability and higher

wavefront uniformity at the sample. These properties enable us to extend UTPS to XUV or X-ray wavelengths with relatively low technical complexity.

The inclusion of inner-shell electronic resonances and absorption edges in X-UTPS is expected to provide access to atomic site-specific information including local electronic dynamics within a molecule under conditions where other inner-shell techniques are less sensitive. Thus, X-UTPS will complement both linear and other nonlinear XUV- and X-ray spectroscopy techniques, with a particular emphasis on larger molecules and liquids.

Recent Progress: X-UTPS is an extension of UTPS, recently demonstrated using near-infrared pulses (Thurston *et al.* **2020**, *J. Phys. Chem. A* 124, 2573–2579), to the XUV regime. A new experimental setup has been designed and the assembly and alignment is progressing. We already produce XUV by HHG using a long 6 m focus of intense (15 mJ) ultrashort (40 fs) NIR (780 nm) pulses at a repetition rate of 1 kHz. With a new grazing-incidence XUV-reflective NIR-transparent beamsplitter (Fig. 2-4), currently under construction, we will separate the initially-colinear NIR and XUV pulses in vacuum. Additionally, a waveplate and polarizer will control the NIR
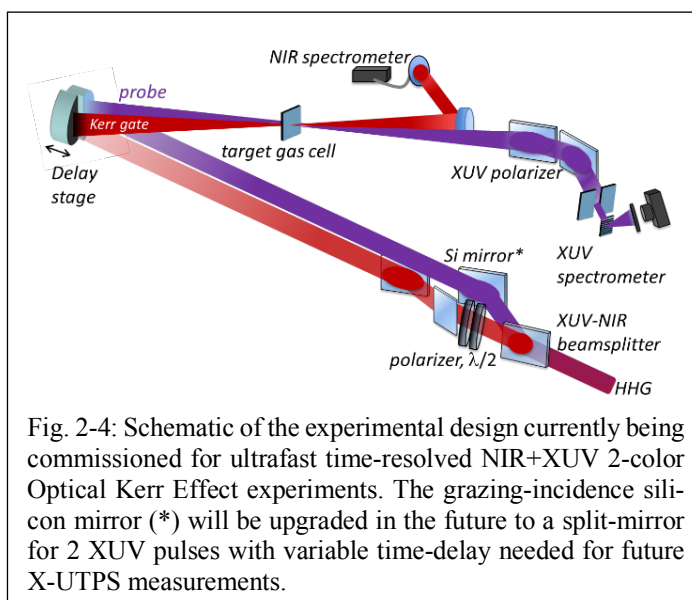
Fig. 2-4: Schematic of the experimental design currently being commissioned for ultrafast time-resolved NIR+XUV 2-color Optical Kerr Effect experiments. The grazing-incidence silicon mirror (*) will be upgraded in the future to a split-mirror for 2 XUV pulses with variable time-delay needed for future X-UTPS measurements.

intensity and polarization after the beamsplitter, before the XUV and NIR beams are focused using curved split mirrors on an existing optical delay stage to control the NIR delay relative to the XUV pulse. For a relative NIR-XUV polarization of 45°, XUV signals due to the optical Kerr effect will pass through a gas cell to a newly designed reflective XUV polarizer (calculated extinction ratio 750:1 and transmission 5%, at 88 nm) and an existing XUV spectrometer, currently being optimized. To effectively read out the XUV spectrometer, we have developed a technique to process amplitude-modulated data arrays for lock-in amplified XUV spectra. This work was recently accepted for publication in *Measurement Science and Technology*.

Detailed interpretation of UTPS and X-UTPS experiments demands the development of new methods to model and predict the 3rd-order polarization response of molecules in excited electronic states. In collaboration with Liang Tan (Molecular Foundry, LBNL), we have employed multi-configurational self-consistent field (MCSCF) calculations in nitrobenzene to model the electronic structure using Dalton (Aidas *et al.* **2014**, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 4, 269-284). In this approach we simulate the time evolution of the target system in Liouville space, using electronic state energies and the relevant transition dipole moments from *ab initio* MCSCF electronic structure calculations, as well as electronic population decay rates and dephasing rates determined from experimental measurements. We have validated this numerical method with the analytical solution (Boyd **2008**, *Nonlinear Optics*) for the steady-state 1st- and 3rd-order optical susceptibility of a 2-level atom (Fig. 2-5). The numerical solution does not yet provide χ^3 on an absolute scale, nevertheless the qualitative agreement between the numerical 3rd order polarization

and the analytical χ^3 is good for both resonant and near-resonant photon energies, and a range of population decay rates and dephasing rates.

Future Plans: With the new NIR + XUV setup offering independent delay and polarization control, we will investigate the ultrafast transient 2-color OKE response in N_2 with a femtosecond FWM experiment. This will allow us to develop and test the essential instrumentation on previously-investigated dynamics (Warrick *et al.* **2018**, *Faraday Discuss.* 212, 157–174) of excited bright ungerade and dark gerade electronic states in N_2, by 2-color NIR + XUV FWM, while working towards future X-UTPS experiments. X-UTPS experiments will be enabled by upgrading our XUV beamline - primarily by implementing a grazing-incidence split mirror (Sturm *et al.* **2016**, *Rev. Sci. Instrum.* 87, 063110) at the position of the Si mirror in Fig. 2-4, and spectral filters (not shown) to isolate specific XUV harmon-

Fig. 2-5: Optical frequency dependence of the steady-state 3rd-order polarization signal (crosses, left axis), which is proportional to the 3rd order susceptibility χ^3, from the present time-dependent numerical simulation. Curves (normalized to the peak signal at frequency 5 atomic units, a.u.) show the exact analytical solution for the same two-level system with energy levels separated by 5 a.u.. Blue, orange, and green correspond to decay rates of 0.1, 0.2, and 0.3 a.u., respectively.

ics in the XUV pump and probe arms, each arriving with a controlled delay relative to the NIR pulse. OKE signals will carry information on the dynamical resonant coupling between the ground electronic state, the b $^1\Pi_u$, b′ $^1\Sigma_u^+$, c $^1\Pi_u$, as well as the c′ $^1\Sigma_u^+$ XUV-excited electronic states, and the a″ $^1\Sigma_g^+$ dark state, in 2-NIR-photon down-up transitions. Time-resolved dynamics involving higher lying Rydberg states may also be observed due to up-down 2-NIR-photon transitions from the XUV excited state.

Our computational efforts are now directed at making direct comparisons between the simulation and our recent experiments on nitrobenzene with NIR pulses (Thurston *et al.* **2020**, *J. Phys. Chem. A* 124, 2573-2579). Depending on the success of the numerical model of nitrobenzene to describe purely electronic dynamics on the low-lying electronic states, the model will be extended to include nuclear motion along one or a few relevant degrees of freedom. In parallel, we will apply a similar approach to model N_2 and other small molecules to simulate the dynamics investigated by the X-UTPS experiments.

Subtask 3: First-Principles Theory of Dynamics and Electronic Structure
M. Head-Gordon, R. R. Lucchese, C. W. McCurdy, T. N. Rescigno

Time Delay in Molecular Photoionization (*Lucchese, McCurdy, Rescigno*)
Recent Progress: We have previously explored the degree to which hole localization can be detected in RFPADs of core ionization of molecules with chemically equivalent atoms, as in our study of CCl_4 ionization discussed below. A new tool that may be able to probe core-hole dynamics is the measurement of photoionization time delays. In collaboration with H. J. Wörner (ETH Zurich), who was the PI on a recent experiment performed on the TMO instrument at the LCLS, such time delays have been measured using angular streaking with a combination of the FEL provided

by the LCLS and a coincident circularly polarized infrared pulse with VMI detection of the photoelectrons. The target molecules were a series of azabenzenes where both N 1s and C 1s core holes can be created. Comparing the VMI image from these two different types of holes can yield the relative time delay in the two processes. In Fig. 3-1 we present the total cross sections for the N 1s ionization of pyrimidine, which is one of the systems that was studied. These calculations show that the incoherent
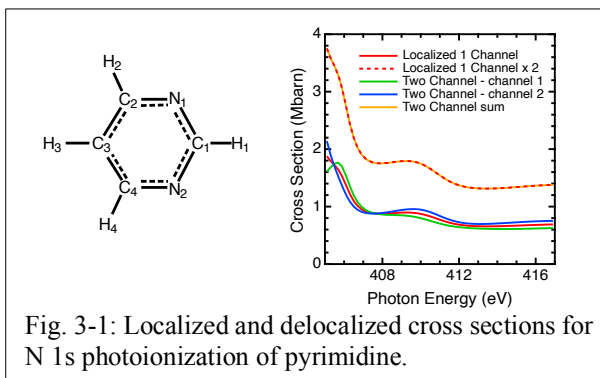
Fig. 3-1: Localized and delocalized cross sections for N 1s photoionization of pyrimidine.

sum of the cross sections of two localized one-channel calculations gives the same cross section as the coupled two-channel calculation with delocalized holes. Thus, at the level of the total cross section, one cannot detect the effects of localization. This work was done in collaboration with Prof. Cynthia Trevisan of Cal State Maritime, who has participated in the Berkeley Lab Undergraduate Faculty Fellowship (BLUFF) in recent summers.

Future Plans: We will compute MFPAD amplitudes and the corresponding photoionization time delays, which are the energy derivatives of the phases of the amplitudes, for pyrimidine and the other azabenzenes that were studied at the LCLS: pyridazine and S-triazine. In each system, we will examine signatures of hole localization in both the MFPADs and photoionization time delays in comparison to the case of pyridine which contains only one N atom. We will also explore the dependence of the time delays on emission direction in the molecular frame to explore possible qualitative models for time delays dependence on the electron-ion scattering processes.

Treatment of Short Pulse Ionization with Nuclear Motion *(Lucchese, McCurdy)*

Recent Progress: We have published (Bello *et al.* **2021**, *Phys. Rev. Res.* 3, 013228) a comprehensive study probing the details of the dynamics on the first excited state of the LiH molecule with an ultrafast pump and ionizing probe pulse. Nuclear motion is treated simultaneously with correlated electronic motion including transitions to the ionization continuum. The essence of our approach is to calculate ionization amplitudes using the multichannel Schwinger variational method for photoionization, developed by Lucchese and coworkers, on a grid of internuclear distances visited by the wave packet. We use those amplitudes and dipole transition amplitudes in the time

propagation of the nuclear wave packet on multiple potential surfaces that includes dissociation of the LiH$^+$ cation produced by the probe pulse. Fig. 3-2 shows how the wave packet dynamics and changes in the character of the excited LiH state from ionic to covalent character are visible in the experimental measurables.

Future Plans: This capability was developed for application to other diatomic and linear systems accessible to laser-based
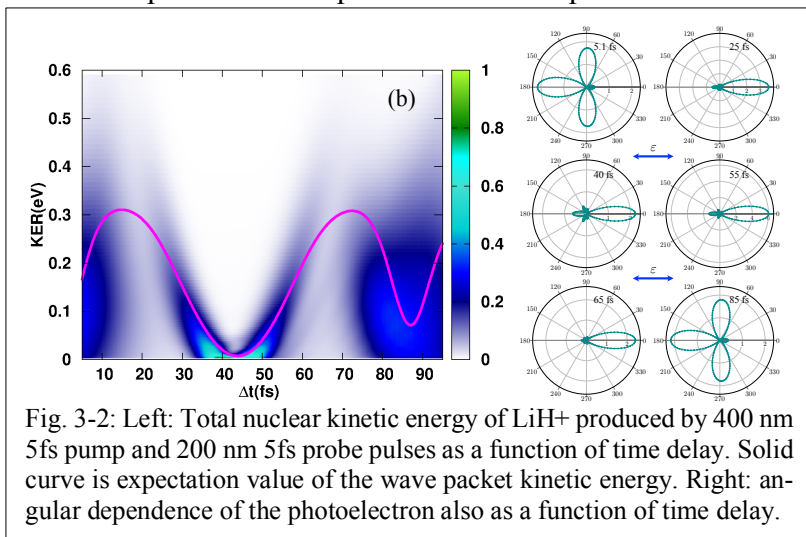
Fig. 3-2: Left: Total nuclear kinetic energy of LiH+ produced by 400 nm 5fs pump and 200 nm 5fs probe pulses as a function of time delay. Solid curve is expectation value of the wave packet kinetic energy. Right: angular dependence of the photoelectron also as a function of time delay.

momentum-imaging experiments at LBNL. We will explore new pump/probe experiments with N_2, O_2, CO and CO_2, which can be accurately described by the numerical Schwinger method, and predict the signatures of their nonadiabatically coupled excited state dynamics in photoionization and dissociative photoionization in preparation for joint experimental and theoretical ultrafast studies at LBNL.

Double Photoionization of Molecules by One Photon *(Lucchese, McCurdy, Rescigno)*

Recent Progress: To analyze the ALS experiments on one-photon double ionization of water using the COLTRIMS method, we are continuing our major project to calculate full body-frame triple differential cross sections (TDCS) for double ionization as a function of the directions of both electrons for a polyatomic molecule for the first time. We published two studies on the dissociation of the H_2O^{++} dication that is produced in its ground and eight excited states in late 2018. Now data from a second experiment on D_2O has been analyzed by the Kansas State group led by Itzik Ben-Itzhak using the "native frames" method, which detects the presence of sequential processes in a COLTRIMS experiment. As seen in Fig. 3-3, the agreement with our *ab initio* classical trajectory simulation is nearly perfect and reveals the distributions of rotational states of the OD^+ fragments after double ionization from sequential dissociation through two different electronic states. A manuscript has been submitted by the collaboration.
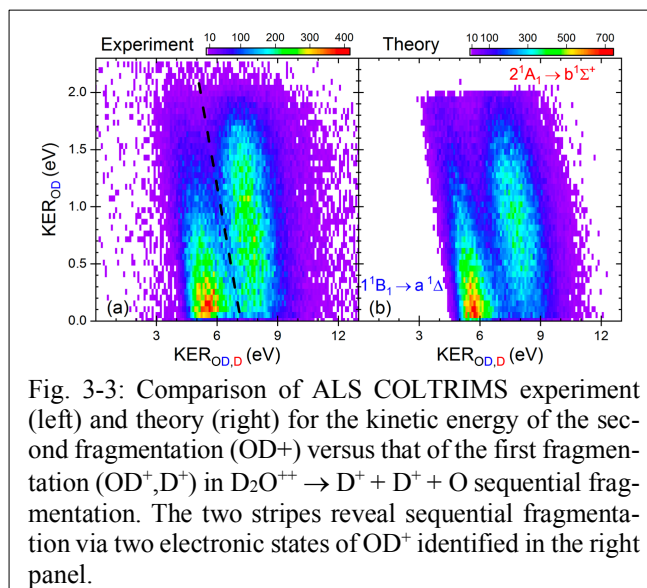
Fig. 3-3: Comparison of ALS COLTRIMS experiment (left) and theory (right) for the kinetic energy of the second fragmentation (OD+) versus that of the first fragmentation (OD+,D+) in $D_2O^{++} \rightarrow D^+ + D^+ + O$ sequential fragmentation. The two stripes reveal sequential fragmentation via two electronic states of OD^+ identified in the right panel.

As we work on multiple improvements to the computational algorithms that we previously applied to double photoionization of H_2 in order to make it possible to solve this challenging problem in water, we have performed calculations on the double ionization of Li_2 and LiH to explore the role of correlation in the bonding orbitals from which two electrons are ejected in one-photon double ionization. In H_2 the TDCS for double ionization is exquisitely sensitive in both magnitude and shape to the details of electron correlation, as we expect to be the case in water and LiH. Li_2 however has little sensitivity to correlation. This work is being done in collaboration with Prof. Frank Yip (California State University, Maritime), who has participated in the visiting faculty programs (VFP and BLUFF) at LBNL in recent summers.

Future Plans: In collaboration with Roger Bello, a postdoc in our group until last May and now at the Autonomous University of Madrid, we will complete the TDCS calculations for double ionization of water to produce the three states in which two electrons are removed from one valence orbital. In collaboration with Prof. Frank Yip we will complete the Li_2 and LiH double photoionization calculations and analyze the role of electron correlation in the initial state of the neutral molecule in those two examples and publish them in preparation for the same analysis in the case of water.

Intense Field Double Ionization in Molecules *(Lucchese, McCurdy)*

Recent Progress: In a collaboration begun two years ago at the DOE BES AMOS PI meeting with the groups of Profs. Tom Weinacht and Phil Bucksbaum, we have completed an analysis of the

three body dissociation of the D_2O^{++} dication after intense field ionization by laser pulses as short as 10 fs. The experiment employs velocity map imaging with coincidence detection of the ionic fragments ($D^+ + D^+$ in this case). The gross features of the dynamics of dissociation of the dication in strong field ionization are strongly reminiscent of the dynamics of its dissociation following double ionization by one photon. However, by comparing our detailed classical trajectory studies with experiments, we and our collaborators were able to reveal the details of the non-vertical double ionization that occurs in intense fields. A simple model for the differences involving modification of the nuclear wave packet due to a coordinate-dependent Keldysh ionization rate was explored. The results of this collaboration between three groups in the AMOS program was published this year (Cheng *et al.* **2021**, *Phys. Rev. A* 104, 023108).

Future Plans: The collaboration has proposed an experiment at FERMI that would combine laser and FEL ionization in a time-dependent investigation of the mechanisms of both direct and sequential breakup of D_2O^{++}. That experiment and associated theory would for the first time directly probe the breakdown of the axial recoil approximation that we have predicted and used to analyze the ALS experiments.

O^+ from One-Photon Double Ionization of Water (*Lucchese. McCurdy, Rescigno*)

Recent Progress*: O^+ ions are observed as a minor channel (0.6% of total DPI signal) in the double ionization of water by single photon absorption at 61.0 eV in the ALS experiment led by Weber. Of this small yield, overlapping low- (~5.7 eV) and high- (~7.7) KER subchannels can be distinguished. Since dissociative states of the water dication leading directly to $O^+ + H + H^+$ are inaccessible at this energy, the pathway leading to this channel must necessarily be sequential and must involve a spin-orbit induced charge transfer. We have, on the basis of *ab initio* calculations, identified three distinct dissociation mechanisms. The dissociative triplet states (Fig. 3-4 (left)) cross the lower singlet states near 5.5 bohr, but an isolated crossing between singlets and triplets is unlikely to result in a charge exchange unless some trapping mechanism is involved. Cursory examination of Fig. 3-4 (left) shows that the $^1B_1$ state has a shallow well; non-vertical transitions within the Franck-Condon region can access geometries where the well is deeper and lead to a trapping of dications which increases the probability of a spin-orbit induced charge-exchange. Classical trajectory calculations on the $^1B_1$ surface were carried out to estimate the fraction of the trajectories that pass through the small energy window between the top of the $^1B_1$ barrier and the point where it crosses the triplet dication. Of the 100,000 trajectories sampled, roughly 0.3% met these criteria, which is consistent with observations for the low-KER subchannel.

Fig. 3-4: (left) Excited states of H_2O^{++}, relevant to present discussion, at 104.5º and equal O-H bond distances; (right) Calculated PECs of the 1^1A_2, 1^1B_1, and 2^3A_2 dication states at HOH bond angles of 85º for a range of asymmetric geometries with one ($OH_{(2)}$) stretch fixed while the other ($OH_{(1)}$) stretch is varied. The electron transfer is happening between the neutral O and the more distant singly charged H_1, while H_2 remains singly charged.

Our calculations point to the $^1A_2$ dication as the major contributor to high-KER O^+ production. In this case, trapping at intermediate O-H separations is not possible. However, we found, by examining asymmetric $O-H_1/O-H_2$ geometries, seams of energetically decreasing near degeneracy between the $^1A_2$ and $^3A_2$ surfaces that extend over several Bohr, providing an enhanced probability

for spin-orbit induced charge-exchange (see Fig. 3-4 (right)). Another possible high-KER O^+ mechanism involves an internal $H^+ - O \rightarrow H - O^+$ charge exchange when the OH^+ and H^+ fragments are well separated. The charge-exchange would involve a transition between $^1\Pi$ and $^5\Sigma^-$ OH+ states, with the distant H^+ ion acting as a spectator. Since this mechanism can be neither confirmed nor disproved solely on the basis of the measured data, it must be treated as speculative.

Future Plans: There is evidence that autoionization processes, i.e. indirect DPI, can also lead to $O^+ + H + H^+$ fragmentation. This will be the subject of a future study.

Global Fit of RFPAD Data in the 2p Ionization of CCl_4 (*Lucchese, McCurdy, Rescigno*)

Recent Progress: As mentioned above, we are studying core hole localization dynamics in the one-photon ionization of CCl_4 to form Cl $(2p)^{-1}$ holes. This study is also a collaboration with Prof. Trevisan. This system has been studied at the ALS by AMOS PIs Weber and Slaughter and coworkers. In this process, when the spin-orbit coupling is neglected, there are twelve different hole states possible. We have shown how one can compute very accurate MFPADs and the corresponding RFPADs in a three-channel calculation, including only the localized hole states on one Cl atom. Then an incoherent sum of these cross sections from the holes formed on the four different Cl atoms can give a good representation of a full twelve channel calculation due to the very weak coupling between the localized holes on the different Cl atoms. Additionally, we have shown that the spin-orbital coupling will not substantially change the predicted RFPADs for a given photoelectron kinetic energy. Unlike the case of the F (1s) ionization of CF_4, where we could identify clear evidence of localization of the 1s hole states by the dissociation process, in CCl_4 the measured RFPADs do not indicate a strong connection between the location of the initial hole state and the identity of the Cl^+ atom, which eventually is emitted in the fragmentation process. Taking a linear combination of computed RFPADS we obtained the best fit to the experiment, shown in Fig. 3-5, when the hole is assumed to be 75% delocalized and 25% localized.

Fig. 3-5: Comparison of experimental (black dots) and computed RFPADs (red lines) for CCl_4 $(2p)^{-1}$ ionization. Values of θ_n and the photoelectron kinetic energy (and energy in the computation) are indicated in each panel. I_{ave} is the average over all polarization directions. The Cl+ fragment is emitted at 0°.
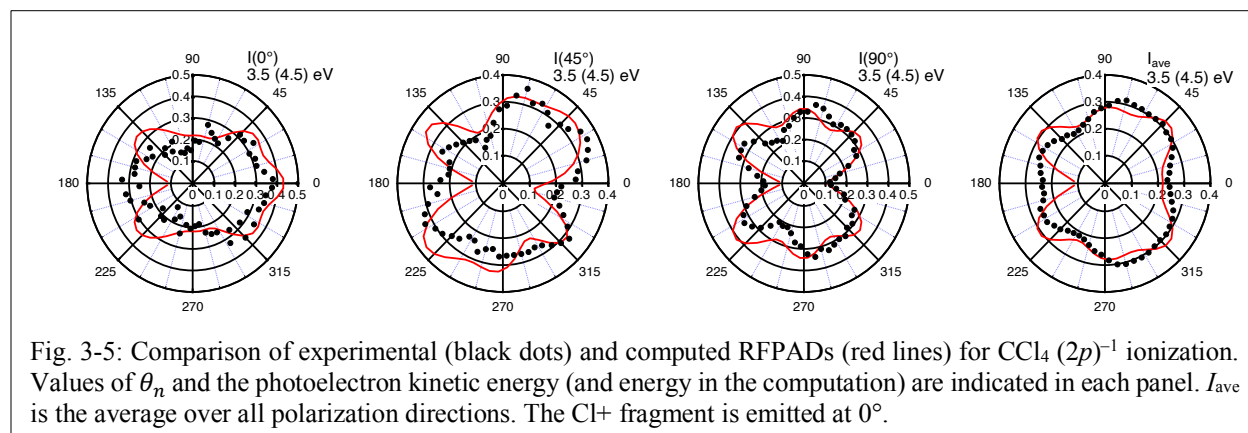
Two-Photon One Color Ionization (*Lucchese, McCurdy*)

Recent Progress: In support of the experimental efforts of Slaughter and Weber described in Subtask 1, we have continued the development of the capability to compute two-photon ionization of molecules using the lowest order of perturbation theory. These calculations use the weak-field one-photon transition matrix elements computational capabilities of our multichannel Schwinger code to provide all the matrix elements needed to evaluate the two-photon amplitude. In the one-color two-photon single ionization experiment on the O_2 molecule with a photon energy of ~9.3 eV,

there are two intermediate states $B\ ^3\Sigma_u^-$ and $E\ ^3\Sigma_u^-$, which are nearly resonant with the excitation by the first photon and thus dominate the two-photon transition amplitude. With just these two intermediate states included, the computed photoelectron angular distributions, shown in Fig. 3-6, are in good agreement with the experiments, leading to the conclusion that the nuclear dynamics on the intermediate state during the light pulse are not important.

Future Plans: This new capability for the computation of two-photon processes will be applied to cases where there are no nearly-resonant states, thus requiring a sum over many intermediate states. Systems to be considered are the two-photon ionization of Ar and N_2 for which Slaughter and Weber have published data, but for which there is not satisfactory agreement with earlier theory.

Fig. 3-6: Computed and measured 2-photon photoelectron angular distributions of the ionization of O_2 by 9.3 eV photons. Computed angular distributions correspond to β_2=0.54 and β_4= 0.43.

These studies will be useful to verify our approach for computing such processes as well as to provide understanding of the types of electron correlation to which these processes are sensitive. An additional application will be to two-photon processes at FELs, which have been proposed for study. In particular, we are working with K. Ueda (Tohoku University) on a proposed experiment to measure photoionization time delays through the interference between a two-photon $2 \times \hbar\omega$ ionization with a one doubled photon $1 \times (2\hbar\omega)$ ionization process. Due to the different symmetries of these processes in the molecular frame, it should be possible to measure the time delay in a resonant process which is accessible by only one of these paths relative to the time delay in the other path. Such an experiment would be possible at the LCLS using the planned DREAM coincidence spectrometer.

State-Targeting DFT for Excited States, Including Core Excitations *(Head-Gordon)*

Recent Progress: Many *excited* states of molecules can be quite well described using *ground* state DFT with a restricted open-shell Kohn-Sham (ROKS) framework. This model optimizes the Kohn-Sham orbitals specifically for each individual excited state, which are conceptually described as a single spin-adapted configuration state function. Hence the ROKS approach corresponds to state-specific orbital optimized DFT (Hait *et al.* **2021**, *J. Phys. Chem. Lett.* 12, 4517−4529). ROKS can work effectively for states where TDDFT fails to give reasonable results, like charge-transfer excited states, as illustrated in Fig. 3-7 and, as discussed below, core excitations. The ROKS energy is a minimum only for the lowest excited state; higher excited states are saddle points. We therefore developed a new algorithm (Hait *et al.* **2020**, *J. Chem. Theory Comput.* 16, 1699−1710), that performs square gradient minimization (SGM) to reliably find the higher saddle points. SGM is robust and efficient (only 3 times the cost of a standard DFT calculation). This algorithm has enabled our recent breakthrough on accurately computing DFT core-excited states.
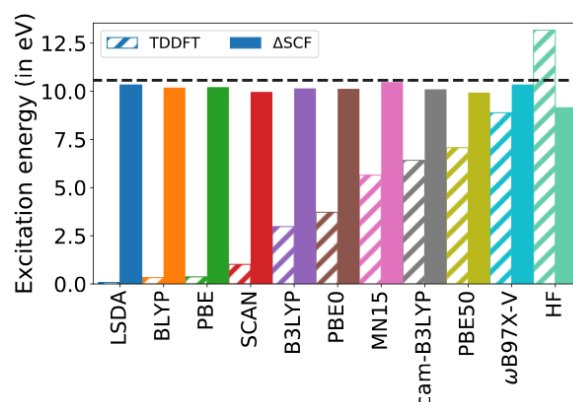
Fig. 3-7: Orbital-optimized DFT (OO-DFT, or ΔSCF) out-performs time-dependent DFT (TDDFT) for challenging problems such as charge-transfer excited states. The results shown are for the singlet CT state of a complex between ammonia and fluorine at long range. Note how functional-insensitive ΔSCF is.

Using SGM, we have achieved a breakthrough in the accuracy that we can achieve for core excitation energies at low computational cost (Hait *et al*. **2020**, *J. Phys. Chem. Lett.* 11, 775–786). We have shown that core excitations can be very accurately computed using ground state density functionals by finding saddle points, rather than minima, of the restricted open shell DFT energy functional in orbital space. The modern SCAN and ωB97X-V functionals predict the K-edge of C, N, O, and F to an RMS error of ∼0.3 eV. Equally good results are obtained for L-edge spectra of third row elements, when a perturbative spin-orbit correction is used. A sample calculated versus experimental spectrum is shown in Fig. 3-8. This high accuracy can be contrasted with normal TDDFT, which typically has > 10 eV absolute error and requires translation of computed spectra to align with experiment. To go beyond core excitations in molecules with singlet ground states, we have recently been able to extend the theory to recouple more than two determinants together, as necessary to treat core excitations in open shell molecules via ROKS (Hait *et al*. **2020**, *J. Chem. Phys*. 153, 134108). For both singlet molecules and radicals, the new approach is computationally tractable (same scaling as ground-state DFT) and can be applied to geometry optimizations or even *ab initio* molecular dynamics of core-excited states. *It is hard to overstate the potential significance of this development for routine calculations of core-excited states*. The main limitation of the method is cases where there is essential configuration interaction between more than two determinants in the core excitation, which appears to be rare for species with singlet ground states.
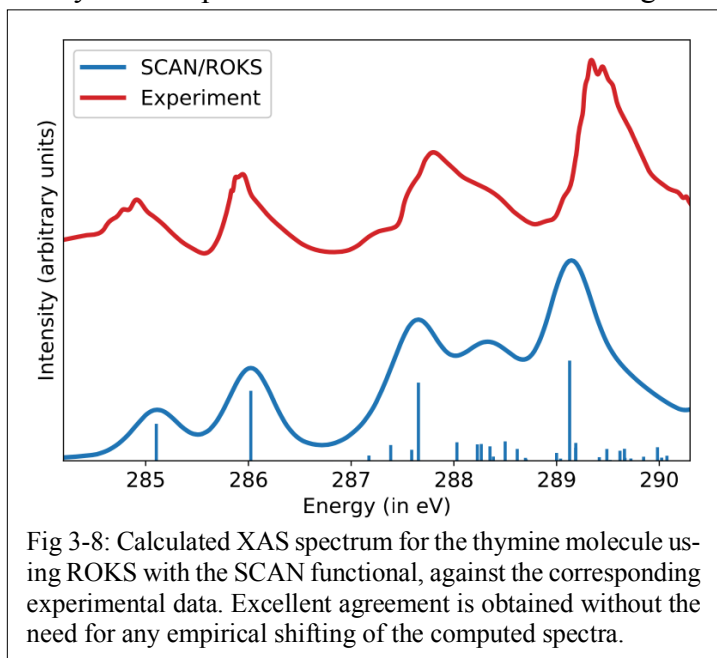
Fig 3-8: Calculated XAS spectrum for the thymine molecule using ROKS with the SCAN functional, against the corresponding experimental data. Excellent agreement is obtained without the need for any empirical shifting of the computed spectra.

Future Plans: A number of collaborations using the ROKS approach are underway with other members of the LBL AMOS program (Gessner and Leone), which will hopefully yield useful results on a range of problems of experimental interest. Since core excitations can be a reporter on chemical dynamics, computational modeling on predicted products of photon-initiated reactions can play a role in enabling the assignment of experimental signals. There are also some limitations in our implementation, and the associated theory. To date, we have included spin-orbit and relativistic corrections separate from our calculations, using atomic values. We are starting to think about direct inclusion of the spin-orbit terms, as well as the possibility of properly including scalar relativistic corrections. Albeit a non-trivial extension of our code, this would enable us to confidently move towards heavier elements including transition metals.

State-Targeting Coupled Cluster Theory for Doubly Excited States, Including Double Core Hole States *(Head-Gordon)*

Recent Progress: We have revisited the idea of using the coupled-cluster (CC) ground state formalism to target excited states (Lee *et al*. **2019**, *J. Chem. Phys*. 151, 214103). Our main focus was targeting doubly excited states and double core hole states. Typical equation-of-motion (EOM) approaches for obtaining these states struggle without higher-order excitations than doubles. We showed that by using a non-Aufbau determinant optimized via the maximum overlap method, the

CC ground state solver can target higher energy states. Furthermore, just with singles and doubles (i.e., CCSD), we demonstrated that the accuracy of ΔCCSD and ΔCCSD(T) (triples) far surpasses that of EOM-CCSD for doubly excited states. The accuracy of ΔCCSD(T) is nearly exact for doubly excited states considered in this work. For double core hole states, we used an improved ansatz for greater numerical stability by freezing core hole orbitals. The improved methods, core valence separation (CVS)-ΔCCSD and CVS-ΔCCSD(T), were applied to the calculation of the double ionization potential of small molecules. Even without relativistic corrections, we observed qualitatively accurate results with CVS-ΔCCSD and CVS-ΔCCSD(T). The tools and intuition developed in this work may serve as a stepping stone toward directly targeting arbitrary excited states using ground state CC methods.

Future Plans: Inspired by our success for double excitations, we are actively working on a generalization of the method to describe open shell singlet excited states, which is being piloted at the level of second order many-body perturbation theory (MP2). We have so far established that core correlation is absolutely essential to achieve useful accuracy, as well as numerical stability against variational collapse, and have implemented an algorithm that performs well for this purpose.

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. While OO-DFT is perhaps the most promising approach in the short term, it is also important to build an extensible wavefunction-based framework. To pursue this objective, one first needs a reference wavefunction (akin to mean field for the ground state). For this purpose, we defined and implemented the non-orthogonal configuration interaction singles (NOCIS) method for core-excited states. NOCIS is a black-box variant of NOCI (that in itself makes NOCIS a very rare variant of NOCI), which uses a set of core-ionized determinants followed by electron reattachment 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, size-consistent, and delivers multiple states. We have extended the NOCIS theory to doublet radicals, yielding promising results with an accuracy comparable to those obtained for closed shell ground states (Oosterbaan *et al.* **2019**, *J. Chem. Theory Comput.* 15, 2966–2973). We observed that CI between determinants on a single atomic center is much stronger than CI between determinants on different centers, which motivated the development of a single center (1C) approximation to NOCIS that neglects the off-diagonal elements of the Hamiltonian (Oosterbaan *et al.* **2020**, *Phys. Chem. Chem. Phys.* 22, 8182–8192). Interestingly, 1C-NOCIS for closed shell molecules reduces to the venerable static exchange approximation (STEX), while it is a natural generalization to core excitations of molecules in open shell states. With greatly improved computational efficiency, and the same accuracy, 1C-NOCIS is our preferred form of the theory for most purposes. Available for both closed and open shell molecules, it can capture the essential configuration interaction that so far eludes OO-DFT, and is a potentially useful starting point for describing electron correlation effects.

Future Plans: The main factor limiting the accuracy of 1C-NOCIS (and NOCIS itself) is its neglect of dynamical electron correlation (NOCIS includes only essential electron correlations). We have designed a potentially tractable approach to include dynamic electron correlation, and are beginning to work on its implementation.

Predicting Twisted Intramolecular Charge-Transfer Excited States *via* Optimal Tuning *(Head-Gordon)*

Recent Progress: Electronically excited states characterized by intramolecular charge transfer play an essential role in many biological processes and optical devices. The ability to make quantitative *ab initio* predictions of the relative energetics involved is a challenging yet desirable goal, especially for large molecules in solution. We (Shee *et al*. **2020**, *J. Chem. Theory Comput. 16,* 6244–6255) assembled a data set of 61 experimental measurements of absorption and emission processes, both in the gas phase and in solvents representing a broad range of polarities, which involve intramolecular charge transfer mediated by a nonzero, "twisted" dihedral angle between one or more donor and acceptor subunits, as

Fig. 3-9: Illustration of the charge migration associated with a twisted intramolecular charge transfer (TICT) excited state in PXZ-TRZ dye molecule. At right is a schematic summary of the optimally tuned TDDFT approach that avoids the usual TDDFT failures for CT states by molecule-specific tuning of the range separation parameter so that the HOMO and LUMO orbital energies recover the IP and EA.

illustrated in Fig. 3-9. Among a variety of density functionals investigated within the framework of linear-response theory, the "optimally tuned" LRC-ωPBE functional, which utilizes a system-specific yet nonempirical procedure to specify the range-separation parameter, emerges as the preferred choice. For the entire set of excitation energies, involving changes in dipole moment ranging from 4 to >20 Debye, the mean signed and absolute errors are 0.02 and 0.18 eV, respectively (compared, e.g., to −0.30 and 0.30 for PBE0, 0.44 and 0.47 for LRC-ωPBEh, 0.83 and 0.83 for ωB97X-V). We present empirical evidence implicating the outsized importance for small donor−acceptor systems of relaxation effects that cannot be accounted for by the linear-response time-dependent density functional theory within the adiabatic approximation. We also demonstrate the utility of the optimally tuned density functionals by targeting the charge-transfer states of a large biomimetic model system for light-harvesting structures in Photosystem II.

Modeling Strong-Field Ionization *(Head-Gordon, McCurdy)*

Recent Progress: As an initial step of a collaboration between McCurdy and Head-Gordon on time-dependent approaches to describing strong molecule-field interactions, we have established the existence of generalized Coulson-Fischer points associated with strong-(static) field ionization of atoms and molecules. Such points arise as a consequence of Löwdin's symmetry dilemma, which is a ubiquitous issue in approximate quantum chemistry. In the context of Hartree-Fock (HF) theory, the use of Slater determinants with some imposed constraints to preserve symmetries of the exact problem may lead to physically unreasonable potential energy surfaces. On the other hand, lifting these constraints leads to the so-called broken symmetry solutions that usually provide better energetics, at the cost of losing information about good quantum numbers that describe the state of the system. This behavior is very well characterized in the context of bond dissociation. We characterize the behavior of different classes of HF spin polarized solutions (restricted, unrestricted, and generalized) in the context of ionization by strong static electric fields. For simple

Fig. 3-10. The electrostatically embedded energy of the He atom as a function of static field strength (in atomic units) evaluated by restricted Hartree-Fock (RHF) and unrestricted HF (UHF). UHF correctly captures information about both the first and second ionization potentials, whereas RHF, which forces the electrons to pair, cannot properly describe the first ionization event. A lower total energy is obtained for UHF in that regime, and the unpairing of the electron pair is the generalized Coulson-Fischer point.

two electron systems, unrestricted Hartree-Fock (UHF) is able to provide a qualitatively good description of states involved during the ionization process (neutral, singly ionized, and doubly ionized states), whereas RHF fails to describe the singly ionized state, as shown in Fig. 3-10. For more complex systems, even though UHF is able to capture some of the expected characteristics of the ionized states, it is constrained to a single M_s (diabatic) manifold in the energy surface as a function of field intensity. In this case, a better qualitative picture can be painted by using generalized Hartree-Fock as it is able to explore different spin manifolds and follow the lowest solution due to lack of collinearity constraints on the spin quantization axis.

Future Plans: We are currently working on implementing methods based on time-dependent coupled cluster (CC) theory to describe the response of the electrons in molecules to strong time-dependent electric fields.

Peer Reviewed Publications Resulting from this Program (2019–2021)

1.	Bello, R. Y.; Yip, F. L.; Rescigno, T. N.; Lucchese, R. R.; McCurdy, C. W., Role of Initial-State Electron Correlation in One-Photon Double Ionization of Atoms and Molecules. *Phys. Rev. A* **2019**, *99*, 013403, DOI 10.1103/PhysRevA.99.013403.

2.	Boll, D. I. R.; Fojón, O. A.; McCurdy, C. W.; Palacios, A., Angularly Resolved Two-Photon Above-Threshold Ionization of Helium. *Phys. Rev. A* **2019**, *99* (2), 023416, DOI 10.1103/PhysRevA.99.023416.

3.	Champenois, E. G.; Greenman, L.; Shivaram, N.; Cryan, J. P.; Larsen, K. A.; Rescigno, T. N.; McCurdy, C. W.; Belkacem, A.; Slaughter, D. S., Ultrafast Photodissociation Dynamics and Nonadiabatic Coupling between Excited Electronic States of Methanol Probed by Time-Resolved Photoelectron Spectroscopy. *J. Chem. Phys.* **2019**, *150* (11), 114301, DOI 10.1063/1.5079549.

4.	Fidler, A. P.; Camp, S. J.; Warrick, E. R.; Bloch, E.; Marroux, H. J. B.; Neumark, D. M.; Schafer, K. J.; Gaarde, M. B.; Leone, S. R., Nonlinear XUV Signal Generation Probed by Transient Grating Spectroscopy with Attosecond Pulses. *Nat. Commun.* **2019**, *10* (1), 1384, DOI 10.1038/s41467-019-09317-4.

5.	Fidler, A. P.; Marroux, H. B. J.; Warrick, E. R.; Bloch, E.; Cao, W.; Leone, S. R.; Neumark, D. M., Autoionizing Dynamics of (^{2}P$_{1/2}$)*ns/d* States in Krypton Probed by Noncollinear

Wave Mixing with Attosecond Extreme Ultraviolet and Few-Cycle Near Infrared Pulses. *J. Chem. Phys.* **2019**, *151* (11), 114305, DOI 10.1063/1.5113912.

6.   Fukuzawa, H.; Lucchese, R. R.; Liu, X.-J.; Sakai, K.; Iwayama, H.; Nagaya, K.; Kreidi, K.; Schöffler, M. S.; Harries, J. R.; Tamenori, Y.; Morishita, Y.; Suzuki, I. H.; Saito, N.; Ueda, K., Probing Molecular Bond-Length Using Molecular-Frame Photoelectron Angular Distributions. *J. Chem. Phys.* **2019**, *150* (17), 174306, DOI 10.1063/1.5091946.

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PULSE Ultrafast Chemical Science

P.H. Bucksbaum, D.A. Reis, K. Gaffney, T. Heinz, T. Martinez, T. Wolf, A. Natan, J. Cryan, S. Ghimire, A. Cordones-Hahn, E.G. Hohenstein, SLAC National Accelerator Laboratory, 2575 Sand Hill Rd. MS 59, Menlo Park, CA 94025. Email phb@slac.stanford.edu

Project Scope:

The PULSE Ultrafast Chemical Science program at SLAC investigates ultrafast chemical physics using SLAC's x-ray and high energy electron facilities, including LCLS-II, SSRL, and Ultrafast Electron Diffraction (UED). Our goal is to advance chemical science within the ultrafast AMOS mission that makes optimal use of these unique tools for fundamental discoveries and new insights.

Recent Progress:

Our recent research continues to emphasize this close connection between the advanced facilities at SLAC and advanced research in PULSE. Here are some recent examples:

- Attoscience: We are opening up attosecond x-ray research to the AMO community by leading the LCLS Attosecond campaign and by collaborating on new user beamtimes that use the attosecond mode.
- Collective Electron Dynamics on the Nanoscale: We have viewed the wavefunction of an exciton in a two-dimensional system through momentum-space imaging, via time-and angle-resolved photoemission spectroscopy.
- Excited States in isolated Molecules: We performed successful soft X-ray spectroscopy and hard X-ray and electron scattering experiments at LCLS and the UED facility investigating excited state proton transfer and electrocyclic reactions.
- High Harmonics in Optical Media: We have explored how disorder in the external environment of 2D layers can led to readily observable changes and fluctuations of energies of electronic excitations.
- Nonlinear X-ray Science: We furthered efforts to image the low order nonlinear optical response of materials with atomic-scale resolution, also image nonperturbative currents associated with solid-state high-harmonic generation.
- Nonperiodic X-ray Imaging: We demonstrated ultra-wide-angle X-ray Scattering spanning a scattering angle range of more than 100 degrees, and we developed a new method for real-space inversion and super-resolution in ultrafast x-ray scattering.
- Solution Phase Chemistry: Our X-ray spectroscopy study identified covalency as an important parameter in the design of Fe-based photosensitizers. We demonstrated liquid ultrafast electron diffraction as a viable new method to probe solution-phase reaction dynamics.
- Strong Field AMO Physics: We have demonstrated direct imaging of photoemission features associated with multiple pathways of sub-cycle field ionization, providing stringent tests of holographic theories of strong-field ionization.
- Ultrafast Theory and Simulation: We demonstration that quantum effects of the nuclei are critically important to describing ultrafast dynamics of vibrationally excited OH bonds.

More summaries of our work are 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.

Management Structure: This Ultrafast Chemical Science program is directed by Phil Bucksbaum from within the SLAC Chemical Sciences Division directed by Kelly Gaffney, within the SLAC Energy Sciences Directorate directed by Tony Heinz. The intellectual vitality of the 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;
> Research Scientist Dr. Ed. Hohenstein, Theoretical Chemistry

The program is organized into nine subtasks:

1. UTS: Ultrafast Theory and Simulation (Martinez, Hohenstein)
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:

Todd Martinez: Woodward Lecturer, Harvard University; Remsen Award, Maryland Section of the ACS
James Cryan: Elected APS Fellow
Tony Heinz: 2021 *Medard Welch Award* of the American Vacuum Society.

Personnel changes in the past 12 months: None.

PULSE Ultrafast Chemical Science Major themes: Ultrafast science has emerged as a primary arena for scientific progress across all areas of BES, and it has also been established as a primary mission focus for SLAC.[1] PULSE has been advancing this area for more than a decade, starting with this AMOS program, and so we are in leadership positions now in selected broad areas of

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

the field. We have a growing list of research accomplishments in sub-femtosecond or femtosecond-resolved investigations that capture the motion of electrons within molecules, using methods that require the improved characteristic of the LCLS-II linac and x-ray laser. We also have developed methods with Angstrom resolution to record chemistry at the level of the intramolecular bonds. And we also have investigated a range of multiphoton x-ray interactions using x-ray nonlinear spectroscopy.

The AMO research that is especially pushed forward by the capabilities of LCLS-II and at UED can be grouped into three main *research themes*:

Three Research Themes

• 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.

Linked to these themes are three *science frontiers*, which encompass the activities of our FWP:

The Science Frontiers

• The frontier of attosecond electronic motion

• The frontier atomic field strengths

• The frontier of collective electron dynamics

The scientific case for these advances was highlighted in a recent BES workshop on LCLS-II science opportunities, "*Virtual Workshop: Non-Linear Multidimensional Methodologies for Studying Chemical Sciences,*" that was organized by a collaboration including LCLS, Nora Berrah, and five of the PIs from this FWP (Reis, Cryan, Cordone-Hahn, Wolf, and Bucksbaum) in December 2020. In addition, these science areas are 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 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.

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. Additional space exists in the new SLAC Arriaga Science Center for future opportunities.

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

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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

Michigan, Kansas State University, Stony Brook University, the Ohio State University, the University of Connecticut, Louisiana State University, 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.

- Several PULSE scientists now have staff positions at LCLS. This year Dr. James Cryan has taken on a the role of AMOS Department Head at LCLS.

- We connect LCLS to the Stanford PULSE Institute by assisting 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. This is done jointly with CFEL in Hamburg. This year the UXSS was completely on line for the second time and directed from Hamburg. These remote UXSS sessions have attracted a large number of students and other attendees. Next year we expect UXSS to be in person on the SLAC campus.

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

Project Scope

This project 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 in Gas and Condensed Phases: We continue extensive collaborations with the ultrafast electron diffraction team centered at SLAC. In a recent study, we have explored the femtosecond electron diffraction of photoexcited phellandrene (Champenois, et al. Science 2021). The phellandrene molecule is a form of substituted cyclohexadiene, where the methyl and isopropyl substituents provide the ability to better track the details of the excited state reaction mechanism such as the conrotatory/disrotatory sense of ring opening. Additionally, the substituents give rise to a number of ground state conformers – a contrast to cyclohexadiene which has only a single ring-closed conformation. Theory and simulation

Figure 1. Comparison of experimental and simulated pair distribution functions for phellandrene after photoexcitation.

results almost entirely preceded the experiments, yet the agreement is nearly quantitative as shown in Figure 1. We have also simulated terpinene, which exhibits a different substitution pattern. Experiments for this molecule have been recently completed. We plan to compare all of these different but closely related molecules to determine how substitution patterns can change the excited state dynamics.

We also contributed to a UED study of the dynamics of liquid water after vibrational excitation of the O-H stretch (Yang, et al. Nature 2021). Here, we showed that the quantum mechanics of the initial conditions are critical to reproduce the experimental signals. Purely classical dynamics was unable to describe the experimentally-observed contraction of the hydrogen bond after vibrational excitation, but sampling the initial conditions from a quantum Wigner distribution was able to provide nearly quantitative agreement with experiment. This demonstrates the critical role of quantum mechanical effects of the nuclei even in condensed phase systems (when protons are involved).

Improved approaches for electronic excited state dynamics. The ab initio multiple spawning (AIMS) approach has been our core method for simulating nonadiabatic dynamics (which was used for the excited state UED simulations described above). AIMS provides a basis set description of the nuclear wavepacket in terms of travelling Gaussian trajectory basis functions (TBFs), with new TBFs being created adaptively in order to model wavepacket splitting at conical intersections. As more TBFs are created, the calculation becomes more costly. More importantly, the probability of a failure (for example, nonconvergence in the electronic structure method) increases linearly with the number of TBFs. We have dealt with that in the past by improving convergence procedures to make the failure probability small. Nevertheless, this difficulty limits the length of time which one can simulate. We realized that a simulation of many coupled TBFs may be identical in certain instances to many simulations of independent groups of TBFs. Specifically, if a TBF is very far from all other TBFs in the simulation, such that the Hamiltonian matrix element connecting it to other TBFs is negligible, then there is no advantage to including all the TBFs in the same simulation. We

Figure 2. Comparison between full AIMS, AIMS with splitting, and SSAIMS with repetition. Diagram follows Figures 1 and 2, with simulation time flowing vertically from top to bottom and the x axis denoting schematic position. Ellipses indicate that multiple runs are carried out for SSAIMS with repetition.

developed a "stochastic selection" approach (SSAIMS) to recognize and exploit this fact (Curchod, 2020 J. Chem. Phys.). The idea is to divide the simulation at any point in time into sets of coupled TBFs. The probability of each of these sets (computed as their contribution to the wavepacket norm) is then used to select a single set to continue. One needs to repeat the simulation many times and average the results, but we showed that this procedure can reproduce an AIMS simulation. The benefit is that each of the AIMS simulations now contains a smaller number of TBFs (generally this fluctuates between one and three in the test cases we investigated). This will be especially important in cases where there are many electronic states, such as transition metal complexes.

Future Plans

Over the next year, we plan to continue to investigate excited state dynamics of molecules which can be studied with ultrafast electron or x-ray diffraction. We have reported predicted UED signals for azobenzene and are working to prepare these for stilbene. Azobenzene has yet to be studied with UED, but should be feasible. What is more, it involves nπ* and ππ* states, so one should be able to use inelastic scattering signal to track electronic state changes, as we did previously for pyridine (Yang, et al. 2020 Science). Stilbene has been the subject of a few attempted experiments and we will work to combine this experimental data with our simulated results. We will simulate femtosecond diffraction for a number of other molecules in advance of the experiments in order to establish the predictiveness of the current tools. We also intend to incorporate SSAIMS into our simulation workflow, which will enable simulations of inorganic photochemistry and highly excited states, e.g. organic molecules excited to S_3 or higher states.

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ATO: Attosecond Science

PIs: James Cryan and Phil Bucksbaum
jcryan@slac.stanford.edu, phb@slac.stanford.edu
Stanford PULSE Institute, SLAC National Accelerator Laboratory
2575 Sand Hill Rd. Menlo Park, CA 94025
Participants: Taran Driver, Siqi Li, Agostino Marinelli,
Jordan O'Neal, Anna Wang, Jun 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 couples 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. What role does coherent electron motion (on the attosecond scale) play in the chemistry (longer timescale nuclear motion) of a molecule? What can attosecond scale measurements tell us about electron correlation interactions?

Recent Progress

Creating and Probing Electronic coherences in molecules: In FY2019 we demonstrated the generation of isolated, GW-scale, soft x-ray (SXR) attosecond pulses with an X-ray free electron laser [Duris2020]. These pulses are intense enough to drive nonlinearities in molecular systems. A simple nonlinear technique for driving 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 [O'Neal2020]. The impulsive excitation is resonantly enhanced by the oxygen $1s\text{-}>2p\pi^*$ resonance and can be exploited to drive ultrafast charge motion.

ISXRS is not the only method for preparing non-stationary electronic states: impulsive ionization of inner valence electrons has been proposed as a method for creating a coherent superposition of ionic excited states. In comparison to ISXRS, impulsive ionization is more easily realized, but provides less control of the non-stationary state and lacks site-specificity of the excitation. Never-the-less, in a collaboration led by Jon
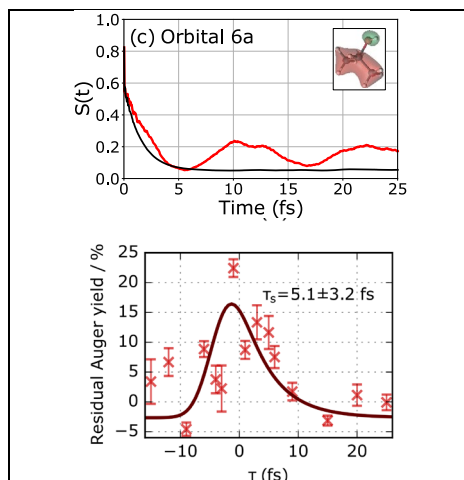
Figure 1 – Decay of Inner Valence Vacancy in Isopropanol - The upper panel shows the hole survival probability for ionization of the 6a inner valence orbital following sudden ionization. The colored curve corresponds to a mixture (1:1) of the two lowest conformers of the molecule. The black curves correspond to the averaged dynamics over geometries sampled over the spread of zero-point energy. The lower panel shows the time-dependent yield of Auger electrons detected when an x-ray probe pulse is resonantly tuned to the 1s->6a transition in the cation. The decay of the Auger signal is a signature of the dynamics of the inner valence hole and decays on a similar timescale.

Marangos (Imperial College) we have used an x-ray pump/x-ray probe scheme to investigate ultrafast hole dynamics in isopropanol [Barillot2021]. Combining the measurements with *ab intio* calculations of the ionization dynamics we can develop a complete picture of the electron dynamics following ionization of an inner valence hole and make the first tentative observation of dynamics driven by frustrated Auger-Meitner transitions, as shown in Figure 1. The site- and state-specific measurement scheme we present paves the way to observations of transient hole dynamics in molecular systems, localized in space and time. Hopefully elucidating the charge transfer phenomena that are fundamental in chemical and material physics.

Time-Resolving Molecular Auger Decay: Resonant excitation with broad bandwidth x-ray pulses provides another route toward creating electronic wavepackets. When tuned to the vicinity of a near-edge resonance, these broadband pulses will coherently populate multiple core-excited resonances. As the core-excitation decays, the Auger-Meitner emission from the different states in the

Figure 2 – Angular Streaking of X-ray Photoemission. The left panel shows the measured Auger emission in the presence of a 2.3 μm streaking laser field (black dots). Looking as a function of angle between the streaking laser direction and Auger emission direction we can map out the temporal profile of the Auger emission. Comparing to a simple model with (dark lines) and without (transparent lines) interference between core-excited states, we clearly resolve the quantum beat in the Auger emission resulting from the coherent superposition of core-excited states.

wavepacket will interfere producing a beat in the Auger emission rate. Using the angular streaking technique [Hartmann2018, Li2018], we have successfully resolved this quantum beat. This is the first demonstration of time-resolved Auger emission that goes beyond extracting an exponential decay lifetime for the emission process. By tuning the central frequency, we can alter the core-excited wavepacket and thus alter the beat in the Auger emission as shown in Fig. 2. In follow-up experiments we hope to further resolve the electronic coherence and study the coupling of the coherence to nuclear motion on timescales shorter than the Auger lifetime.

Channel Coupling in Photoemission: 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 (CO_2) [Kamalov2020]. 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.

We have also explored the coupling of electronic and nuclear degrees of freedom in photoemission experiments. Recent measurements of time- and vibrationally-resolved ionization of H_2, shows a distinct breakdown of the adiabatic approximation typically used in describing photoionization of small molecular systems.

Figure 3 – Time-Resolved X-ray Absorption Spectrum of Para-aminophenol (pAp). The left panel shows the resonant Auger-Meitner of ground state pAp. Using 260 eV attosecond x-ray pulse to drive inner-valence ionization we observe a transient signal in the x-ray absorption below the ground state absorption features (lower right panel). The integrated absorption signal (upper left) shows a sub-femtosecond transient with a revival feature near 4 fs.

Future Plans

Probing Electronic coherences: We have just begun our attosecond campaign at the Linac Coherent Light Source. This is a multi-beamtime experiment with the goal of performing real-time measurements of attosecond electron dynamics and subsequent coupling to nuclear motion using the soft X-ray attosecond capabilities described above. In the first experiment we have measured the time-dependent x-ray absorption spectrum of para-aminophenol (pAp) following soft x-ray ionization below the carbon *K*-edge (at 250 eV). This signal, shown in Figure 3, consists of a sub-femtosecond transient with a revival feature near ~ 4 fs. The strongest modulation in the x-ray absorption is red shifted from the neutral absorption features implying that we are probing a transient ionic state. We are still working on theoretical modeling of the spectroscopic observable to fully interpret the absorption spectrum.

Attosecond X-ray Photoemission: In order to diagnose the isolated attosecond pulses described above, we adapted the angular streaking (or atto-clock) method developed by Hartmann *et al.* [Hartmann2018] to work with isolated attosecond pulses. In addition to diagnosing the x-ray temporal waveform, this streaking technique can be used to study the temporal dynamics of x-ray 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). The nitrogen *1s* electrons provide a reference wavepacket to remove features induced by the phase of the ionizing x-ray pulse. Scanning near threshold we observe many features in the relative photoemission delay, likely related to the *2pπ** shape resonance. We are currently collaborating with Sasha Landsman (OSU) to model the two-color photoemission process in NO

Electron Correlation in Attosecond Photoemission: We will also continue our efforts in using angular streaking to explore attosecond photoemission delays in X-ray ionization. We will study the complicated many-body problem of correlated electron dynamics using the model process of photoemission.

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1. T. Barillot, O. Alexander, B. Cooper, T. Driver *et int.* J. P. Cryan and J. P. Marangos "Correlation-Driven Transient Hole Dynamics Resolved in Space and Time in the Isopropanol Molecule." Physical Review X **11**, 031048 (2021).

2. Siqi Li, Taran Driver, *et int.* Agostino Marinelli, Jon P Marangos, and James P. Cryan "Two-dimensional correlation analysis for x-ray photoelectron spectroscopy." Journal of Physics B: Atomic, Molecular and Optical Physics **54**, 144005 (2021).

3. Daniel Ratner, F. Christie, J. P. Cryan, A. Edelen, A. Lutman, X. Zhang "Recovering the phase and amplitude of X-ray FEL pulses using neural networks and differentiable models." Optics Express **29**, 20336-20352 (2021).

4. Siqi Li, Taran Driver, Oliver Alexander, Bridgette Cooper, Douglas Garratt, Agostino Marinelli, James P Cryan, Jonathan P Marangos "Time-resolved pump–probe spectroscopy with spectral domain ghost imaging." Faraday Discussions **228**, 488-501 (2021).

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8. Andrei Kamalov, Anna L. Wang, Philip H. Bucksbaum, Daniel J. Haxton, James P Cryan "Electron correlation effects in attosecond photoionization of CO_2." Physical Review A **102**, 023118 (2020)

9. Jordan T. O'Neal, Elio G. Champenois, *et int.* James P. Cryan "Electronic Population Transfer via Impulsive Stimulated X-Ray Raman Scattering with Attosecond Soft-X-Ray Pulses." Physical Review Letters **125**, 073203 (2020)

10. Taran Driver, Siqi Li, Elio G. Champenois, Joseph Duris, Daniel Ratner, Thomas J. Lane, *et int.* Agostino Marinelli and James P. Cryan "Attosecond transient absorption spooktroscopy: a ghost imaging approach to ultrafast absorption spectroscopy." Physical Chemistry Chemical Physics **22**, 2704-2712 (2020)

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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
Email: gaffney@slac.stanford.edu, acordon@slac.stanford.edu

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 and electron methods. Our previous research has emphasized the development of simultaneous hard x-ray solution scattering (XSS) and x-ray emission spectroscopy (XES) as probes of charge, spin, and metal-ligand bonding dynamics in electronic excited states (Gaffney 2021). 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 hard x-ray scattering as a probe of site-specific solvation dynamics and catalyst-reactant complex formation.

Recent Progress

Controlling MLCT lifetimes of 3d transition metal complexes through ligand modification (Kjaer 2019; Kunnus 2020a; Kunnus 2020b; Ledbetter 2020b; Tatsuno 2020; Vacher 2020; Cordones 2021; Gaffney 2021; Reinhard 2021): Our long standing goal of controlling charge transfer excited states of 3d complexes continues to broaden the scope of ligands investigated. Mechanistic studies of excited state relaxation in Fe model photosensitizers focused on the mixed ligand complex $[Fe(pp)(CN)_4]^{-4}$, where pp is a polypyridyl ligand and the incorporation of CN ligands is known to destabilize MC states and extend the MLCT lifetime. Our most recent work

has focused on ligand control of MLCT lifetimes, using polypyridyl ligand modifications as a pathway to controlling excited state relaxation processes (Kunnus 2020a). These studies have used a novel combination of ultrafast optical spectroscopy and Fe L-edge resonant inelastic x-ray scattering (RIXS) to demonstrate that the MLCT relaxation mechanism transitions from one mediated by metal-centered excited states at large chemical driving force to one driven by vibrational tunneling in the Marcus inverted region at lower chemical driving force. These findings strongly indicate that successful design of ligands for long MLCT lifetimes requires both reducing the chemical driving force and minimizing the charge transfer induced distortions of the electron accepting ligand. These finding are directing the next steps of this research project.

We have also begun a project focused on understanding the impact of metal-ligand covalency on charge transfer excited state lifetimes by investigating highly covalent iron carbene and iron amido complexes. The Fe-C bond of organometallic Fe carbene complexes generates a strong ligand field that destabilizes MC excited states, resulting in MLCT lifetimes ≥ 100 ps. We applied simultaneous hard x-ray WAXS and Fe Kα and Kβ XES to investigate the dynamics of an Fe carbene photosensitizer, $[Fe(bmip)_2]^{2+}$ where bmip = 2,6-bis(3-methyl-imidazole-1-ylidine)-pyridine, induced by MLCT excitation (Kunnus 2020b). This measurement shows temporal oscillations in the XES and XSS difference signals with the same 278 fs period oscillation. These oscillations originate from an Fe-ligand stretching vibrational wavepacket on a ^{3}MC excited state surface. Our observations demonstrate that MC excited states remain a viable relaxation challenge, even for the large ligand field carbenes. From a methodological perspective, this study demonstrates an unexpected sensitivity of the Kα XES to molecular structure, which originates from a small change in the average Fe-ligand bond length in the initial (1s) and final (2p) core-ionized states of the Kα emission process (Vacher 2020). In our prior studies we have assumed the x-ray emission signal is insensitive to the details of the molecular structure. Clearly, this assumption does not apply to the strongly covalent Fe carbenes and we are working to determine the prevalence of vibronic effects in hard x-ray emission spectroscopy.

Ultrafast x-ray and electron liquid-phase scattering studies of solvation **(Haldrup 2019; Kong 2019; Ledbetter 2020a; Nunes 2020; Biasin 2021; Yang 2021a; Yang 2021b)**: The SPC subtask has led the development and commissioning of a new liquid-jet endstation for the first solution-phase experiments at SLAC's ultrafast electron diffraction (UED) facility, in collaboration with Thomas Wolf, Jie Yang, and Xijie Wang (Nunes 2020; Yang 2021b). Using the new liquid-phase UED capabilities, we probed the photo-induced structural changes of liquid water under conditions ranging from vibrational to strong field excitation. In collaboration with Jie Yang, following vibrational excitation of water we observed a transient hydrogen bond contraction occurring on the ~80 fs timescale, followed by thermalization. This result captures the intermolecular structural response of water that precedes vibrational relaxation for the first time and demonstrates the spatial distribution of the proton in the H-bond must be treated quantum mechanically to accurately model the magnitude of the contraction (Yang 2021a). In collaboration with Ming-Fu Lin, following the strong field ionization of water we characterized the structure of the short-lived $OH \cdot (H_3O^+)$ radical-cation complex formed via ultrafast proton transfer within 140 fs of water ionization for the first time. Looking beyond neat water solutions, we investigated the ability of liquid-phase UED to interrogate photochemical structural dynamics of solute molecules dissolved in solution. We probed the photodissociation reaction of aqueous I_3^- to form I_2^- and I.

By comparison with molecular dynamics simulations, we were able to extract an average dissociation speed for the reaction, and observe geminate recombination of the fragment molecules on the few ps timescale (Ledbetter 2020a).

In collaboration with Adi Natan and the NPI sub-task, we are utilizing the extended high energy x-ray range of LCLS-II to expand the capabilities of ultrafast x-ray solution scattering (XSS). We completed a successful beamtime in FY21 and preliminary analysis demonstrates the increased momentum transfer range will (1) allow the shape of a vibrational wavepacket to be extracted and (2) enable solute and solvation dynamics to be disentangled.

Future Plans

Identifying Design Principles for the Covalent Control of Electronic Excited State Reactivity in Transition Metal Complexes: Ultrafast optical spectroscopy has clearly demonstrated that changes in metal center, ligand field strength, and oxidation state can lead to large variations in electronic excited state properties and reactivity, but a predictive understanding of the interplay between metal-ligand bonding and non-equilibrium dynamics remains elusive. Through a synergistic combination of synthesis and ultrafast x-ray spectroscopy, we will address two critical aspects of metal-ligand bonding:

- We will investigate the primogenic effect, which highlights the importance of the spatial extent of the nd orbitals associated with the metal center, by comparing isoelectronic 3d, 4d, and 5d (Ni, Pd, Pt) complexes and investigating $3d^6$ molecular complexes with metals in distinct oxidation states (Co(III), Fe(II), Mn(I)) where moving down a period leads to expansion of the d orbitals and moving rightward along the 3d row leads to contraction of the 3d orbitals.
- We will investigate the relative impact of σ- and π-bonding covalency by (1) comparing the excited state electronic structure of metal bis(dithiolene) and bis(dithiolate) complexes and (2) comparing the impact of strongly σ-bonding carbenes and strongly π-bonding amido complexes, as well as heteroleptic ligand complexes targeting ligands with distinct bonding character.

These objectives will be pursued by developing and applying ultrafast RIXS as a probe of photo-induced non-equilibrium electronic structure. We aim to demonstrate that ultrafast RIXS provides the ideal probe of electronic excited state metal-ligand covalency because (1) transition metal L-edge RIXS enables photo-induced changes in the ligand field strength and nephelauxetic reduction of the inter-electron repulsion to be measured and (2) both metal L-edge and ligand K-edge RIXS enable the covalency associated metal-ligand σ- and π-bonding to be separated and quantified via the strength and symmetry of RIXS generated charge transfer excited states. This fundamental understanding will then be applied to the design of transition metal complexes for light driven applications.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

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Kunnus, K., M. Vacher, T. C. B. Harlang, et al. (2020b). Vibrational wavepacket dynamics in Fe carbene photosensitizer determined with femtosecond X-ray emission and scattering. *Nature Comm.* **11**: 634.

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NPI: Non-Periodic Ultrafast X-ray Imaging

Adi Natan

SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025

natan@slac.stanford.edu

Project Scope: The NPI subtask goal is to image atomic motion and transient structure dynamics of molecules in the gas and condensed phase using ultrafast hard x-ray scattering. We develop experimental and computational methods to measure, analyze and understand how to image dynamics in molecular systems of various complexities, help LCLS develop effective science protocols for x-ray scattering experiments, demonstrate important new capabilities as soon as they become feasible at LCLS, and leverage development of new modalities and detection schemes.

Recent Progress: In March 2021 we led an LCLS beamtime titled "Disentangling Ultrafast Solute and Solvation Dynamics with high-energy X-ray Scattering" that demonstrated the new high-energy (18 keV) hard X-ray capability in solution. The experiment was a collaboration with the SPC and EIM subtasks, and with researchers from DTU. We have obtained high fidelity time-resolved scattering data of the model photocatalysts PtPOP ($[Pt_2(POP)_4]^{4-}$, and IrDimen ($[Ir_2(dimen)_4]^{2+}$ in several solvents. These complexes provide ideal systems for demonstrating the ability of high-Q ultrafast scattering and QM/MM simulations to decompose ultrafast solvation dynamics into specific changes in the solute-solvent pair distribution function with a particular focus on how electronically excited states change the interaction between the solvent and photo-catalytically active metal sites. We also introduced an approach to further utilize the high-energy capability and demonstrated a new ultra-wide-angle X-ray Scattering modality using two perpendicular detectors, spanning a scattering angle range of more than 100 degrees. We developed a procedure to calibrate the 3D positions and tilts of the detectors using powder diffraction conic sections fitting procedure and obtained a range of Q<14 A^{-1}. This significant increase will be transformative for ultrafast diffuse x-ray scattering measurements, enabling to disentangle the solute scattering difference signal, that persists to higher Q from the bulk solvent and solute-solvent cross-terms difference signals, enhance QM/MM modeling prediction ability and make analysis less dependent on simulation. The extended range also opens the way to resolve in real-space details regarding coherent wavepackets motions beyond their center-of-mass positions. Data analysis is ongoing. In December 2020 we had an LCLS beam time collaborating
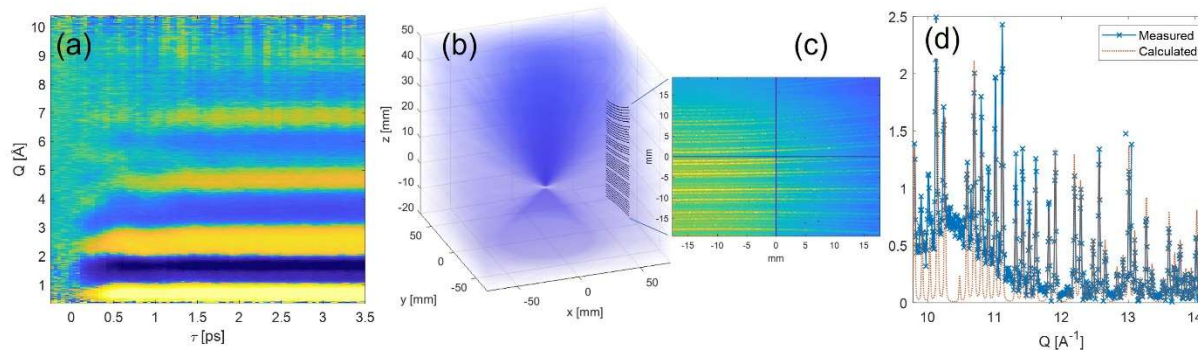
Figure 1: (a) First high-energy (18 keV) ultrafast difference scattering signal of IrDimen in MeCN (preliminary analysis). (b) Full 3D calculation of LaB6 powder diffraction (PD) was used to calibrate (c) the measured PD signal on additional perpendicular detector, (d) extending the measured scattering angles and Q-range to 14 A^{-1} for the photon energy used.

with Prof P. Bucksbaum, Prof. R. Sension, Prof. A. Kirannder, and Prof G. Dixit, titled: "Multidimensional Multimodal Molecular Motion Viewed with Hard X-Rays" aiming to extend our efforts to map the interactions involving multiple degrees of freedom in small polyatomic systems CS_2 and CH_2IBr to excite and trace the polyatomic motions. Data analysis is ongoing.

High-Order Anisotropy X-ray Scattering: We have presented the first results on ultrafast X-ray scattering of strongly driven molecular systems and analysis of high-order anisotropic components of the scattering signal, up to four-photon absorption. We discussed the technical details of retrieving high fidelity high-order anisotropy components and outlined a method to analyze the scattering signal connecting the high-order anisotropy measured by the detector and the theoretical anisotropy scattering curves. We use simulated anisotropic scattering signals and Fourier analysis to map how anisotropic dissociation motions can be extracted from various Legendre orders. We experimentally observed a multitude of dissociation and vibration motions simultaneously arising from various multiphoton transitions and used the anisotropy information of the scattering signal to disentangle the different processes and assign their dissociation velocities on the Angstrom and femtosecond scales de-novo. The approach we demonstrated opens the way to image strong-field-induced motions directly.
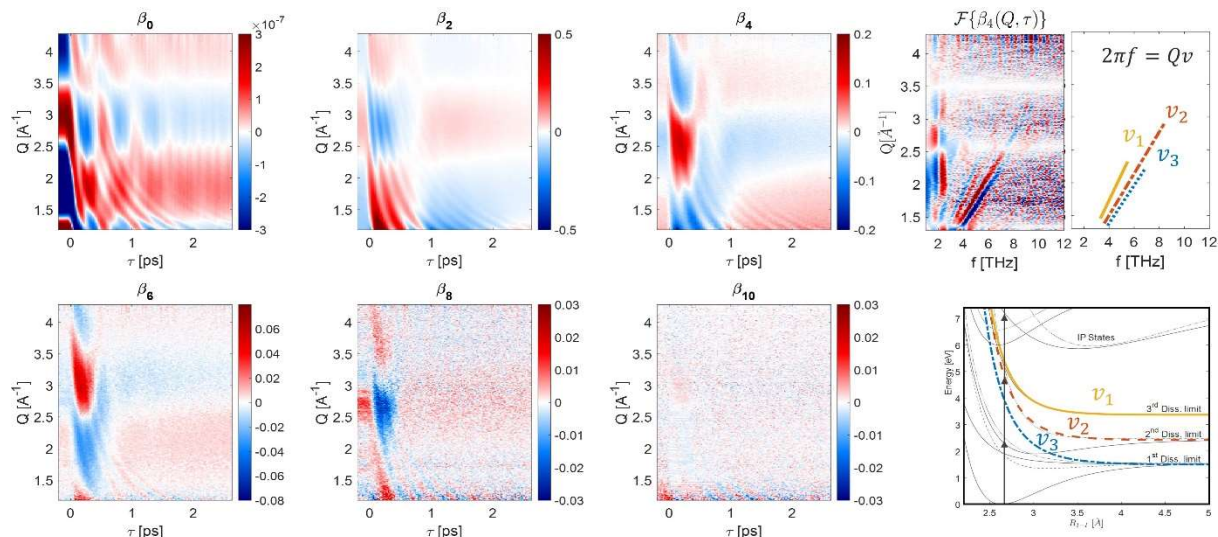
Figure 2: First results on time-resolved high-order anisotropy X-ray scattering. The anisotropy coefficients (mean-subtracted) obtained using Legendre decomposition capture up to 4-photon processes in strongly driven Iodine. For example, Fourier analysis of β_4 is used to disentangle and resolve 3 dissociation pathways that stem from the related 2-photon absorption.

Computational analysis methods development: The inversion of ultrafast x-ray scattering signals to obtain the real-space pair distribution function is generally limited by the available range of the scattering vector for the photon energies used in XFEL experiments. As a result, the methods that were developed to interpret typical scattering signals were mostly model-based and relied on calculating and attaining trajectory statistics for the specific system under study, where retrieval of the transient structure was usually limited to a single reaction pathway. Complex atomic motions that take place simultaneously and involve multiple pathways were often not resolved or discussed. The inversion of the total measured signal entails an additional degree of complexity, as it may be composed of different pairs of atomic species, where each pair contribution has to be disentangled from the overall signal to account for its respective form factors.

To address this, we leverage inverse problems theory and describe a way to realize an adaptive signal representation formalism that is used to create a dictionary of parameterized real-space waveforms or kernels, that naturally arise from the experimental parameters, the measurement process, and the way it is analyzed, including for cases where several motions and several types of atom pairs contribute. We show how we can use a natural scattering kernels based dictionary in a deconvolution scheme to super-resolve the real-space distorted signals using signal priors, such as smoothness and sparsity, with regularization and convex optimization, overcoming the limitations that are imposed by an inversion procedure with limited Q-range.

We validate this approach using ground truth TDSE and trajectory calculations of different complexity to generate synthetic scattering signals with measurements constraints similar to XFEL experiments. We show that we can super-resolve simultaneous motions de-novo and discuss the resolution limit as a function of fidelity. We introduce an effective form factor approximation to demonstrate the approach for a polyatomic system with more than one type of atomic pair. This approach may help to bridge the successful pair-distribution function analysis that requires much higher Q ranges ($>30A^{-1}$) with time-resolved high-energy 15-25 keV scattering experiments that became operational in LCLS. A manuscript describing the method is currently under review.

<u>Energy Resolved Scattering</u>**:** We are continuing our efforts to develop methods to resolve x-ray scattering in energy, a modality that will be a significant step forward in uncovering electronic motions in photo-excited systems. In July 2021 we have led beamtime in SSRL, collaborating with H. Yavas (LCLS), to characterize the energy resolution and fidelity trade-offs of a novel non-uniformly segmented spherical crystal analyzer that we have designed and fabricated. The measurement mapped energy response as a function of various properties of the analyzer segments, such as their area and aspect ratios.

Future Plans: We will continue to develop the high-energy scattering modality and plan experiments to resolve the shape of wavepackets in photoexcited systems. We collaborated on several LCLS campaign proposals that involve condensed phase chemistry. These proposals were submitted in 2021 and with the expectation that these collaborations will fruit to beamtimes in 2022. We are also interested in extending the imaging approach to include condensed phase non-periodic systems in different environments that include geometrical constraints. Building on the results of the SSRL beamtimes, we will iterate and improve the design of the spherical analyzer and prepare to use it for energy-resolved scattering studies. In addition, collaborating with H. Yavas have submitted a proposal to APS to validate the imaging configuration modality when using bent spherical crystal analyzer, titled "Novel use of spherical crystal analyzers to enhance speckle contrast ". This proposal has received the highest-ranking score, however, due to Covid-19 restrictions, it has not been allocated time in 2021. We are hopeful that by 2022 we will be able to run the experiment. We will be continuing to collaborate with the ATO task as part of their campaign proposal, and plan to collaborate on the extension of the XLEAP capability and the angular streaking technique to characterize attosecond pulses in the hard X-ray regime.

Peer-Reviewed Publications Resulting from this Project (2019-2021):

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- T. Driver, S. Li, E. G. Champenois, J. Duris, D. Ratner, TJ Lane, P. Rosenberger, A. Al-Haddad, V. Averbukh, T. Barnard, N. Berrah, C. Bostedt, P. H. Bucksbaum, R. Coffee, L. F. DiMauro, L. Fang, D. Garratt, A. Gatton, Z. Guo, G. Hartmann, D. Haxton, W. Helml, Z. Huang, A. LaForge, A. Kamalov, M. F. Kling, J. Knurr, M. Lin, A. A Lutman, J. P. MacArthur, J. P. Marangos, M. Nantel, A. Natan, R. Obaid, N. H. Shivaram, A. Schori, P. Walter, A. Wang, T. J. A. Wolf, A. Marinelli, J. P. Crya,n **Attosecond Transient Absorption Spooktroscopy: a ghost imaging approach to ultrafast absorption spectroscopy,** *Physical Chemistry Chemical Physics* (2020).

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- Natan, A,, Schori A., Owolabi G., Cryan J. P., Glownia, J. M., and Bucksbaum, P. H **"Resolving multiphoton processes with high-order anisotropy ultrafast X-ray scattering"**, Faraday Discuss, 228, 123-138 (2021) doi: 10.1039/D0FD00126K

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- Werby, N., Natan, A. Forbes, R., and P. H. Bucksbaum. **"Disentangling the subcycle electron momentum spectrum in strong-field ionization."** *Physical Review Research* 3, no. 2 023065 (2021) doi:10.1103/PhysRevResearch.3.023065

SFA: Strong Field AMO Physics

PI: Philip H. Bucksbaum

Stanford PULSE Institute, SLAC National Accelerator Laboratory

2575 Sand Hill Rd. Menlo Park, CA 94025

phb@slac.stanford.edu

Participants: Phil Bucksbaum (PI), Adi Natan (co-PI), James Cryan (co-PI), Nick Werby, Ian Gabalski. Collaborators: Ruaridh Forbes, David Reis, Mike Glownia, Mike Minitti, Matt Ware, Thomas Wolf, Nanna Holmgaard, Todd Martinez (PULSE); Robert Luccese (LBNL); Peter Weber (Brown); Carla Faria (UCL), Andrew Maxwell (Copenhagen).

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 is particularly relevant for focused beams from 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.

Recent Progress: ***Strong-field attosecond electronics:*** Here we explore the motion of electrons inside strong coherently driven molecules by direct detection of the electron momenta. Notable recent progress has been made in studying sub-cycle strongly driven photoionization usng methods of coherent pulse shaping together with velocity-map imaging. Much of the information these patterns could reveal about sub-cycle attosecond dynamics within the molecules is still not understood. Our immediate goal is to understand as much as possible from experimental methods about the origins of so-called holographic interference patterns in the momentum distributions of field-ionized electrons. Theory simulations suggest that these arise from the convergence in momentum space of distinct trajectory classes in strong-field ionization.

For example, the interference between two different types of coulomb-steered returning trajectories gives rise to the well-known spider legs that dominate the intensity distribution in the region below eA_0 in nearly all atomic or small molecule strong-field ionization momentum maps. Still more subtle interference patterns with names like "the fan" and "the carpet" that emerge in calculations have proved to be more difficult to reproduce in experiments until this year, when we reported on our success in observing most of these patterns in experiments that employing new time-filtering methods (See Fig. 1).

Details of time-filtering were reported in last year's AMOS meeting. Briefly, the VMI momentum maps are projected onto a Legendre basis and then transformed into radial energy maps, where the distance of each point to the origin is linear in electron energy. Then a radial Fourier Transform converts the radial axis into a time correlation coordinate, showing how periodic features are related to time differences. A low-pass filter then preserves the sub-cycle features, which are transformed back to produce the time-filtered image.

Now we are using these time filtering methods to measure the electron trajectories that cause the interference. That is, we want to localize the individual trajectory classes in both momentum and time, to see how the different patterns are created. To do this, we need to combine three experimental methods that we have developed in this PULSE program: High fidelity ve-

locity map imaging for electrons; time-filtering to reveal sub-femtosecond features of these patterns; and coherent pulse shaping of strong fields and their harmonics. This last area draws on experience with the RABBITT method, which has been employed successfully in the ATO subtask to measure attosecond delays in HHG photoemission. When we employ this method in time-filtered field ionization, we take advantage of the exponential field amplitude dependence of the field-ionized electron current.
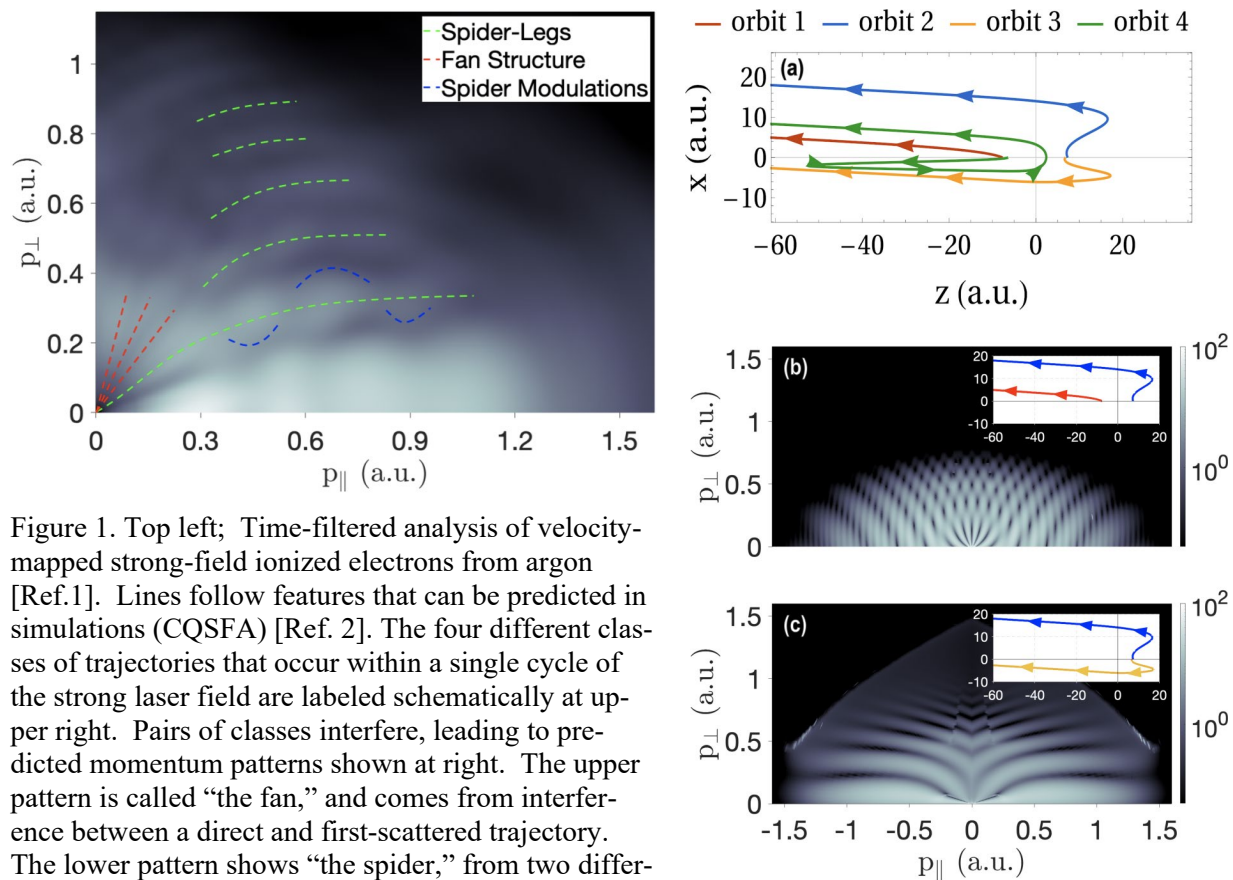
Figure 1. Top left; Time-filtered analysis of velocity-mapped strong-field ionized electrons from argon [Ref.1]. Lines follow features that can be predicted in simulations (CQSFA) [Ref. 2]. The four different classes of trajectories that occur within a single cycle of the strong laser field are labeled schematically at upper right. Pairs of classes interfere, leading to predicted momentum patterns shown at right. The upper pattern is called "the fan," and comes from interference between a direct and first-scattered trajectory. The lower pattern shows "the spider," from two different returning trajectories.

We collect 2-color ($800nm$ with a $400nm$ phase-controlled perturbation) VMI spectra of argon, from which we extract two quantities of interest: the relative phase contrast (RPC) and the phase for peak ionization (PP) (Figure 2). PP encodes the ionizing field phase, since ionization probability scales exponentially with field amplitude, so trajectories ending at that pixel in the data are enhanced when the peak of the $400nm$ pulse overlaps that ionization phase. RPC encodes the range of ionization times. Rescattering features are particularly distinct, providing strong clues to the origins of electrons responsible.

Femtosecond X-ray Diffraction. In this program we study atomic motion in strongly driven systems, revealed by femtosecond hard x-ray scattering at LCLS and other hard x-ray FELs worldwide. Laser-driven polyatomic molecules exhibit many competing modes of atomic motion, including rotation, bending, stretching, and fragmentation. Many reaction pathways couple more than one of these modes, and the results are not easy to predict. Time-resolved X-ray

scattering (TRXS) can spatially and temporally resolve the complex atomic motion of such photoexcited molecules.
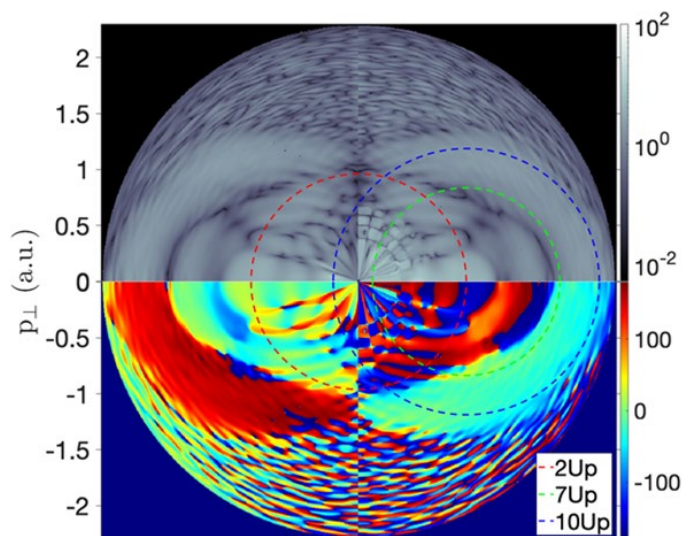
Figure 2. 2-ω phase analysis to determine the trajectories in VMI spectra for strong-field ionization in Ar. We collect $800\ nm\ /\ 400nm$ with peak intensity of $105\ TW/cm^2$ and $1\ TW/cm^2$, respectively. Upper half: Normalized contrast of the electron signal modulation as the phase difference is scanned. Lower half: The phase for maximum signal. The dotted circles indicate classical boundaries for rescattered electron momenta according to SFA. The red circle is the boundary for direct field ionization. The blue circle is the boundary for electrons rescattered on their first re-encounter with the atom, and the green circle shows the boundary for rescattering after the second encounter. (unpublished figure)
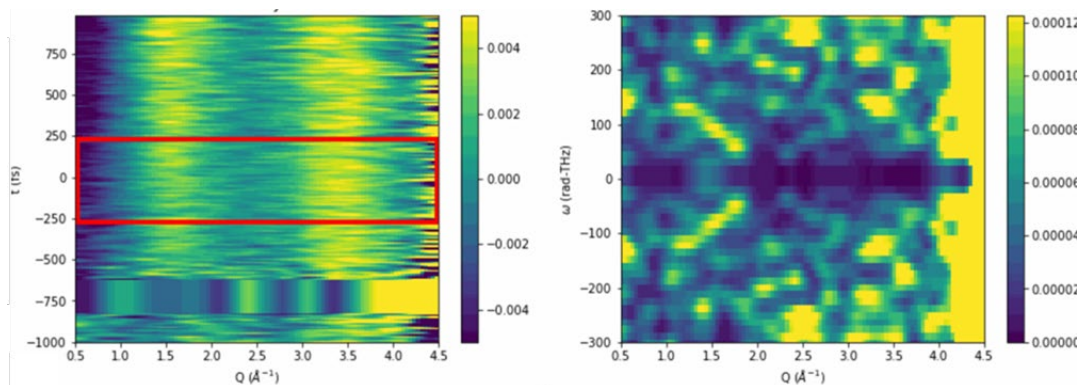
Figure 3. Left: $S(Q,\tau)$ for 200nm pump and 9.8keV probe of CS_2 at CXI LU92. Right: Lomb-Scargle FRXS analysis can reveal dissociation and vibration (unpublished.)

This year we studied the intramolecular motion of CS_2 following photoexcitation at 200 nm using TRXS with 9.8 keV X-rays at LCLS. COVID limitations on participation, as well as some early Run 18 commissioning difficulties limited our ability to collect as much high-quality scattering data as we wanted, but we still have some interesting results, summarized in Fig. 3.

CS_2 excited at 200 nm exhibits both symmetric stretch and bending motion followed by dissociation into multiple exit channels. These types of motion are best viewed in the frequency-resolved basis $S(Q,\omega)$, where they appear as sparse features with simple interpretations. We employ the Lomb-Scargle periodogram to view our noisy, non-uniformly sampled data in this basis, and observe both vibrational and dissociative motion. Sliding the transform window over a subset of the data enables identification of the onset of vibrations and subsequent coupling to dissociation channels.

Future Work: *Strong-field attosecond electronics:* We are building a double-interferometer that will allow us to probe strong-field processes with a weak second and third harmonic beam and two independent relative phases. This will allow us to identify pairs of interfering field-ionized electron trajectories. *Femtosecond X-ray Diffraction.* We have beam time at SACLA in 2022 to use TRXS to map intramolecular motion during and following strong-field ionization in polyatomic molecules. We also have a proposal for Run 20 at LCLS on imaging quantum coherence at conical intersections using FXRS methods.

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NLX: Nonlinear X-ray Science

David A. Reis

Stanford PULSE Institute, SLAC National Accelerator Laboratory,
Menlo Park, CA 94025 dreis@slac.stanford.edu

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. Our recent focus has been on x-ray and optical wave-mixing to image the nonlinear optical responses with atomic-scale resolution, and eventually utilize the method to image strong-field-driven attosecond electronic dynamics responsible for solid-state high-harmonic generation. We have also continue to pursue fundamental x-ray nonlinearities including two-photon scattering and absorption processes. The goal is to develop new methods for understanding correlated and collective electron dynamics. Our program is synergistic with other strong-field investigations in PULSE and makes use of the unprecedented intensities at hard x-ray wavelengths of LCLS and SACLA free-electron lasers. The results could have a profound impact on future light sources such as the LCLS-II.

Recent Progress:

Much of our focus over the past year has been on x-ray optical wavemixing experiments. We designed new x-ray optics to reduce backgrounds and improve resolution. Unfortunately, we had two beamtimes that could not be scheduled (one shortlisted and the other cancelled due to COVID). However, as I am typing this, we are preparing for a new beamtime on the SwissFEL in early October, with an overall goal of measuring the second order local nonlinear response in centrosymmetric materials, although we will also measure linear response. We have also submitted a new manuscript on nonlinear Compton scattering which is currently under review. This manuscript extends our previous studies of anomalous two-photon Compton scattering to higher red-shift as well as lower momentum transfer in beryllium, as well as presenting a limited set of measurements on diamond.   Finally, we continue to work closely with Ghimire and Heinz on strongly driven electron dynamics leading to high-harmonic generation in 2D and other materials. Finally, we had a proposal accepted to the FACET-II user facility at SLAC to study strong-field effects in transition radiation from dense relativistic electron beams.

Future Plans:

We will continue to push or studies of fundamental nonlinear x-ray interactions using x-ray free-electron lasers as well as strong-field studies using laser and electron beam interactions.   In particular, we are interested in ways to simultaneously measure spectroscopic and structural information as well as new ways to look at electron correlation. We plan to continue our efforts on x-ray and optical wavemixing, as well as to understand our observation of multi-photon inelastic x-ray scattering in Fe and Cu which involve multiple electron effect, and eventually push towards soft+hard x-ray scattering when it becomes available on the TXI instrument of LCLS-II.

Submitted

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Peer-Reviewed Publications Resulting from this Project (2019-2021)

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2. Yuki Kobayashi, Christian Heide, Hamed Koochaki Kelardeh, Amalya Johnson, Fang Liu, Tony F Heinz, David A Reis, Shambhu Ghimire, "**Polarization flipping of even-order harmonics in monolayer transition metal dichalcogenides**" Ultrafast Science, AAAS, Special Issue Attosecond Science and Technology, 2021, 2021doi: 10.34133/2021/9820716 (collaborative with HHG)

3. D. Baykusheva, A. Chacón, D. Kim, D. E. Kim, D. A. Reis, and S. Ghimire, **"Strong-field physics in three-dimensional topological insulators"**, Phys Rev A 103, 023101, 023101 (2021). (collaborative with HHG)

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Electron Dynamics on the Nanoscale

Tony F. Heinz, PI

SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025

Email: tony.heinz@stanford.edu

Project Scope

The dynamics of electron motion and electronically excited states in nanostructured systems is the subject of this component of the SLAC ultrafast chemical science research program. In these studies, we examine dynamical processes occurring on the intermediate in scale between small molecules and bulk materials, drawing and linking conceptual foundations from both regies. Our current investigations emphasize the properties of electrons in atomically thin two-dimensional (2D) layers of van-der-Waals crystals and heterostructures formed from them, using transition metal dichalcogenide semiconductors as model systems. We employ 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.

Beyond understanding of the properties of individual 2D monolayers of these materials and their interactions with the environment, we take advantage of the ability to form nearly arbitrary vertical heterostructures of the monolayer building blocks using stacking techniques, including control of the relative crystallographic orientation of these layers. These systems provide a diverse platform in which to examine elementary photochemical processes, such as interfacial charge separation and recombination. In addition to probing behavior in the regime of weak perturbations, in collaboration with other subtasks in this program, we have also made use of these materials for understanding high-field light-matter interactions through studies of non-perturbative high-harmonic generation.

Recent Progress

During the current year, our studies focused primarily on understanding the electronic excited states, their dynamics, and strong-field effects in atomically thin transition metal dichalcogenide (TMDC) layers in the class of MX_2 (M = Mo, W and X = S, Se, Te). Interest in these material systems has generated by their very strong excitonic interactions, their valley optical selection rules, and their ready assembly into heterostructures supporting interlayer excited states and moiré effects. Here we highlight two new and complementary probes, the high-field response seen in the high-harmonic generation process and probing exciting states with time- and angle-resolved photoemission spectroscopy.

High-harmonic generation in 2D semiconductors: probing the strong-field electron response

Building upon our initial report of readily observable high-harmonic generation (HHG) in TMDC monolayers carried out under this award, we performed a detailed investigation of the polarization properties of the HHG process in these systems. The work involved collaboration with FWP co-PIs Ghimire and Reis, as well as Stanford collaborator and Chemistry Professor Fang Liu for sample growth. As presented in a recent publication [1], we obtained a striking result about the

relation between the excitation polarization and the polarization of the high-harmonic radiation for WS₂ and MoSe₂ monolayers. Using ultrafast infrared excitation, we measured HHG spectra consisting of both odd- and even-order harmonics, with a high-energy cutoff extending beyond the 15th order for a laser-field strength around ~1V/nm. In WS_2, we found that the polarization direction of the odd-order harmonics smoothly follows that of the laser excitation, irrespective of the crystal orientation. On the other hand, the direction of the even-order harmonics is fixed by the crystal mirror planes. Furthermore, the polarization of the even-order harmonics shows a flip in the course of crystal rotation when the laser field lies between two of the crystal mirror planes.

By numerically solving the semiconductor Bloch equations for a gapped-graphene model, we were able to reproduce these experimental features and find the polarization flipping to be associated with a significant contribution from interband polarization. In contrast, high-harmonic signals from $MoSe_2$ exhibited deviations from the laser-field following of odd-order harmonics and crystal-mirror-plane following of even-order harmonics. We attribute these differences to the competing roles of the intraband and interband contributions, including the deflection of the electron-hole trajectories by non-parabolic crystal bands. These investigations are deepening our understanding of the mechanism of HHG in solids where, because of the monolayer thickness, there are no complications from propagation effects and the band structure is relatively simple.

<u>Probing the excitonic wavefunction in 2D semiconductors by time-resolved ARPES</u>

Angularly resolved photoemission spectroscopy (ARPES) is a powerful tool to examine the occupied states in 2D materials, providing a direct mapping of the 2D band structure to the photoelectron energy and momentum distribution. When carried out with ultrashort pulses to induce photoemission, the resulting time-resolved ARPES (tr-ARPES) permits the study of excited electronic states of the material following its photoexcitation and the ability to track the ensuing electron dynamics. Through a collaboration with the group of Kashev Dani at the Okinawa Institute of Science and Technology in Japan, initiated during Dani's visit to SLAC, we have successfully applied tr-ARPES to 2D TMDC semiconductors. As published last year and summarized in last year's progress report, our initial investigations focused on signatures of momentum-dark excitons, i.e., excitons where the electron and hole reside in different valleys and where optical emission or excitation is forbidden without the intervention of a phonon or defect. The direct momentum imaging capability of the method allowed us to establish the presence of such momentum dark excitons in the model WSe_2 as a consequence of rapid scattering of the allowed excitons created with the electron and hole both at the K valley.

Here we report on a detailed study of the characteristics of the ARPES signal from excitons in the K valley. We obtained two noteworthy results [2]: One concerning the dispersion for the photoemitted electrons and one concerning their width in momentum space. We discuss each briefly in turn.

Emission from a distribution of uncorrelated electrons in the conduction band of a 2D semiconductor would simply lead to an ARPES signal with a dispersion reflecting that of the band, just as is the case for the occupied conduction band. What we observed experimentally, however, for the ARPES response from a WSe_2 monolayer following creation of excitons by resonant pumping was actually a downward was a dispersion relation that curved downward curving

dispersion relation. While this result may initially seem unintuitive, it actually conforms precisely to theoretical expectations for emission from a cold ensemble of excitons.

To understand this behavior, one must recognize that for cold excitons the photoelectrons are generated by projecting out a component of the excitonic wavefunction with a given momentum. A photoemitted electron with momentum corresponding to the bottom of the band will then have an energy given by that of the photon reduced by the electron affinity and exciton binding energy. If the electron has, however, finite momentum relative to the bottom of the conduction band valley, then a hole must, by conservation of momentum, be left behind after the photoemission process that possesses the same momentum. The energy of the photoemitted electron will be reduced accordingly and lead to the creation of an ARPES dispersion relation reflecting the valence band in which the remaining hole resides. Our experimental result thus provided a direct confirmation of the excitonic nature of the initial state in the tr-ARPES study.

Beyond the observed ARPES dispersion, the width in momentum space of the distribution of the emitted photoelectrons is also very significant. Assuming, as is appropriate in our measurements, that the excitons have little kinetic energy, this width arises entirely from the existence of different momentum components within the correlated electron-hole wavefunction that defines an exciton. Consequently, the width of the distribution of the ARPES signal in momentum space directly maps the excitonic wavefunction and the Fourier transform of the corresponding amplitude reveals the wavefunction in real space. Thus, such measurements can directly map the size of the exciton in real space.

We have obtained such data mapping the excitonic wavefunction for the WSe_2 monolayer [2], revealing an RMS radius in momentum space of 0.72/nm, corresponding to a real-space RMS radius of 1.4 nm. This result compared well with theoretical results from our collaborators based on many-body perturbation theory using the Bethe-Salpeter equation to describe the exciton.

Future Plans

We intend to continue investigations of the excited-states and exciton dynamics in TMDC materials using tr-ARPES. We will apply this approach to examine the properties and dynamics of interlayer excitons in TMDC heterostructures. Initial experimental results have shown the possibility of observing such interlayer excitons and of determining the valley and layer identity of both the corresponding electron and hole.

Investigations of strong-field response will examine the influence of photoexcitation of the material on the HHG process. Such studies can provide access to information about carrier dephasing in the strong-field regime, as well as clarify intra- versus interband mechanisms. Collaborating with other co-PIs in this FWP, we also wish to examine changes in charge distribution under high-field conditions using ultrafast x-ray probes at x-ray free electron lasers.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

1. Y. Kobayashi, C. Heide, H. K. Kelardeh, A. Johnson, F. Liu, T. F. Heinz, D. A. Reis, and S. Ghimire, "Polarization flipping of even-order harmonics in monolayer transition metal dichalcogenides," *Ultrafast Science* **2021,** 9820716 (2021).
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EIM: Excited States in Isolated Molecules

Thomas Wolf

SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025

thomas.wolf@slac.stanford.edu

Project Scope

Our interest is the investigation of elementary chemical processes in the excited states of 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 combine time resolved spectroscopy at wavelengths ranging from the extreme ultraviolet to soft x-rays with electron and X-ray diffraction experiments at the Linac Coherent Light Source (LCLS) and the megaelectronvolt ultrafast electron diffraction facility.

Recent Progress

We have expanded our studies of electrocyclic photochemistry by investigating two derivatives of the prototypical molecule 1,3-cyclohexadiene (CHD), α-phellandrene (aPH) and α-terpinene (aTP). Both molecules exhibit an isopropyl and a methyl substituent on opposite sides of the carbon ring. However, their position with respect to the bond, which is broken during the electrocyclic ring-opening, is different for the two derivatives. In aPH, the isopropyl substituent is bound to one of the sp^3-hybridized carbons directly involved in the bond breaking. In aTP, both substituents are bound to sp^2-hybridized carbons.

The presence of the substituents does not substantially alter the ring-opening dynamics of aTP with respect to CHD. However, the presence of the additional carbon atoms of the substituents generates additional distances and, therefore, additional features in the static and time-dependent atomic pair distribution functions. These "reporter" distances are sensitive to structural dynamics in the excited state and prior to ring-opening, which could not be observed in CHD. We observe the change in hybridization of the sp^3-hybridized carbons towards sp^2-hybridization, which partially happens in the excited state according to *ab initio* multiple spawning (AIMS) simulations of Todd Martinez' UTS subtask.

In contrast to aTP, the position of the substituents has a profound impact of the photochemistry of aPH. It gives rise to two possible conformers in the ground state with the isopropyl group either in quasi-equatorial or quasi-axial orientation to the carbon ring. The fact that we observe only one of the conformers in the gas phase and the high structural sensitivity of ultrafast electron diffraction allows us to directly observe for the first time the evolution of a specific reactant conformer into the specific reaction product, which is predicted by the Woodward-Hoffmann rules. Furthermore, in comparison with AIMS simulations from the UTS subtask, we observe

influences of the rotational orientation on the ring-opening timescale.

Apart from our work on electrocyclic ring-opening reactions, we also investigated excited state intramolecular proton transfer in acetylacetone in a series of beamtimes at LCLS using soft X-ray absorption spectroscopy to follow transient changes in the electronic structure and X-ray diffraction at 15 keV to follow the correlated structural dynamics.

Future Plans

We plan to continue our studies of the interplay between electronic and nuclear degrees of freedom during ultrafast structural dynamics in molecules in the gas phase. In particular, we are planning to work on the analysis of our two recent LCLS beamtimes. Furthermore, we are planning to investigate Norrish-type photochemistry at LCLS and the UED facility.

Peer-Reviewed Publications Resulting from this Project (2019-2021):

- T. J. A. Wolf, D. M. Sanchez, J. Yang, R. M. Parrish, J. P. F. Nunes, M. Centurion, R. Coffee, J. P. Cryan, M. Gühr, K. Hegazy, A. Kirrander, R. K. Li, J. Ruddock, X. Shen, T. Veccione, S. P. Weathersby, P. M. Weber, K. Wilkin, H. Yong, Q. Zheng, X. J. Wang, M. P. Minitti, T. J. Martínez, **The photochemical ring-opening of 1,3-cyclohexadiene imaged by ultrafast electron diffraction,** Nat. Chem. 11, 504 – 509, (2019).
- T. J. A. Wolf, M. Gühr, **Photochemical Pathways in Nucleobases measured with an X-ray FEL**, Philos. Trans. Royal Soc. A, 377, 20170473 (2019).
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HHG: Frontier in High-order Harmonic Generation

Shambhu Ghimire, SLAC National Accelerator Laboratory
2575 Sand Hill Rd, Menlo Park, CA, 94025
shambhu@slac.stanford.edu

Scope of the program

This sub-task focuses on the investigation of solid-state HHG physics with the use of the LCLS and other experimental capabilities at SLAC. This investigation will advance our understanding of intense laser-matter interactions by focusing on the fundamental role of interatomic bonding and periodicity in crystals [Ndabahimiye2016]. Similar to their gas-phase counterparts, solid-state HHG has shown the potential to be a novel ultrafast probe of condensed phase dynamics. However, the solid-state HHG physics is different from its atomic version because of the defining roles of periodic potential to all three steps of the recollision model [Corkum1993], as manifested through a markedly different high-energy cutoff scaling[Ghimire2011]. The main questions we are addressing include: (i) what contributes to the novel HHG mechanism (ii) can HHG become an atomic-scale probe of solid-state dynamics similar to how they probe structure and dynamics of molecules, and (iii) what are time-domain profiles or polarization properties of solid-state harmonics in terms of their suitability to support attosecond light sources.

Recent Progress

Probing electron-hole coherence in strongly-driven solids using HHG: In the quest of using HHG as an atomic-scale probe of the source material, we perform the first all-optical probing of electron-hole dephasing time in strongly driven TMDCs. In experiments, we produce high-order harmonics in atomically thin two-dimensional crystals MoS_2 using intense MIR laser pulses of peak intensity in the range of 10^{10} W/cm^2 (field strength 0.6/nm). The monolayer crystals are prepared using the novel gold-tape exfoliation method, which yields mm-sized flakes, which are then transferred to fused silica substrate. Experiments are performed at normal incidence as shown in figure **1a**. The laser

Figure 1. a) shows the experimental setup, where a strong MIR driving pulse generates high-order harmonics from a monolayer two-dimensional MoS_2 crystal. A weak broadband pump is overlapped with MIR pulse. **b)** shows three steps of the HHG process: 1. Generation of electron-hole (e-h) pairs, 2. Acceleration of e-h in their respective bands, 3. Coherent recombination of e-h. **c)** shows measured high-harmonic spectrum with pump on and off. The integrated and normalized efficiency (pump-on/pump-off) for each harmonic order is shown on the right panel.
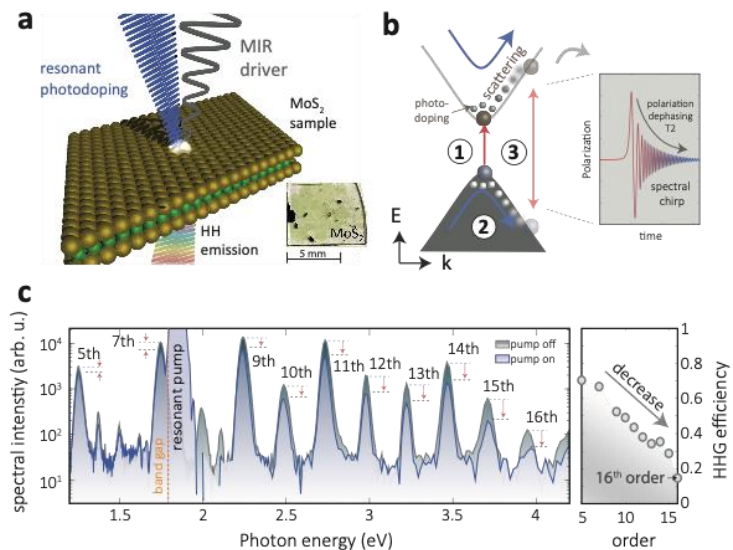
wavelength is centered around 5 micrometers. A representative spectrum of harmonics, as shown, comprises of plateau harmonics with both the even and odd orders extending to beyond the 15th order.

Based on our modeling, for this material and the laser parameters mentioned above, high-harmonics, particularly above the bandgap (1.8 eV), are dominated by inter-band polarization. The semiclassical description of this mechanism consists of three steps: tunneling, which creates e-h pairs in valence and conduction band; acceleration of e and h in their respective bands; and coherent recombination of e-h pairs. In experiments, we disrupt the HHG process, particularly its third step, by introducing photodoped carriers using a broad bandgap relatively weak pump, whose wavelength is centered around 660 nm. We find that an increased carrier concentration reduces the overall efficiency of HHG, with more prominent effects as the high-harmonic order increases.

Within the framework of the semiconductor Bloch equations, we attribute this observation to reduced coherence (smaller dephasing time: T2), likely because of the increased electron-electron or electron-photon scattering processes that become important at high initial carrier densities. Additionally, we find that higher orders are affected more significantly because their corresponding e-h trajectories have longer excursion ranges. The reduction in the HHG signal as a function of harmonic order for various initial carrier concentrations can be reproduced by our theory. Although this analysis does not provide the measurement of absolute coherence time, we can deduce the change in coherence time as a function of the number of initial carrier concentrations. We find that T2 is decreased by 40% as we reach the maximum photocarrier doping around 7×10^{12} cm^{-2}. It means that if the coherence time for pristine samples is around 4.5 fs, which corresponds to the quarter of the optical cycle, our measurements and analysis show that it can reduce to around 2.5 fs[Hiede2021].

Probing topological states using HHG:
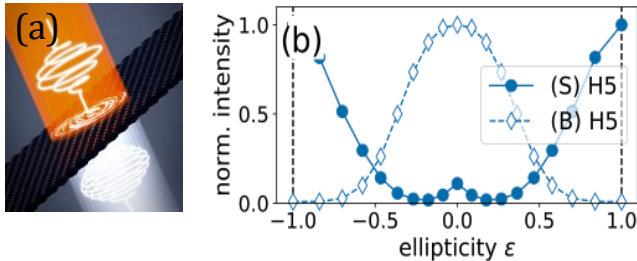
Figure 2. a) shows a proposed experimental setup, where a strong circularly-polarized MIR driving pulse generates high-order harmonics from a thin film Bi$_2$Se$_3$ crystal at normal incidence. **b)** shows calculated harmonic signal as a function of the ellipticity of the MIR driving pulse. The bulk and surface states show contrasting behavior. The surface is most efficient for circular polarization while the bulk is most efficient for the linear polarization.

We study the high-harmonic response of three-dimensional topological insulator Bi$_2$Se$_3$ using circularly-polarized MIR laser pulses. In calculations, we analyze the contributions from the spin-orbit-coupled bulk states and the topological surface bands separately and reveal a major difference in how their harmonic yields depend on the ellipticity of the laser field. Bulk harmonics show a monotonic decrease in their yield as the ellipticity increases, in a manner reminiscent of high harmonic generation in gaseous media. However, the surface contribution exhibits a highly nontrivial dependence, culminating with a maximum for circularly polarized fields. Figure **2a** shows

an artistic representation of the experimental setup and figure **2b** shows the calculated intensity of the 5th harmonic from the bulk and surface bands as a function of laser ellipticity. We attribute the observed anomalous behavior to (i) the enhanced amplitude and the circular pattern of the interband transition dipole and the Berry connections in the vicinity of the Dirac point and (ii) the influence of the higher-order, hexagonal warping terms in the Hamiltonian, which are responsible for the hexagonal deformation of the energy surface at higher momenta. The latter is associated directly with spin-orbit-coupling parameters. The detailed theory has been published [Baykusheva2021].

Use of the LCLS to probe novel HHG physics: We use transient x-ray absorption spectroscopy (XAS) at the LCLS to explore microscopic dynamics relevant to HHG. We use a prototypical strongly correlated electron system NiO as source material. First, we studied crystal-orientation dependence on HHG, where we found that harmonic generation efficiency is much stronger along Ni-O bond directions (cubic direction) than to Ni-Ni or O-O bond directions (diagonal direction). Then, we probed time-resolved absorption using soft-x-rays at the LCLS by tuning their photon energy around Ni and O K-shell absorption edges. We find dynamical changes on O K-edge while Ni K-edge is largely unaffected. Also, the x-ray absorption is higher along the cubic direction compared to the diagonal direction, as the anisotropy in HHG. We note that during this beamtime the x-ray pulses are much longer than the half-cycle of the optical laser field. Even in such conditions, where measurements only provide average effects, we observed robust transient absorption signals around the O K-edge. A full report on this topic is under review [Granas2020]. We plan to extend these measurements to attosecond X-ray pulses that are now available at the LCLS.

Synergistic activities: We continue synergistic activities with other sub-tasks particularly the EDN sub-task, which is led by the *Heinz* group and the NLX sub-task, which is lead by the *Reis* group.

Planned Research

A string of experimental surprises on the fundamental high-harmonic responses is emerging particularly on special classes of materials such as monolayer TMDCs, three-dimensional topological insulator crystals, and strongly-correlated electron systems. To investigate the fundamental strong-field response, in particular, the HHG response we will perform attosecond x-ray absorption spectroscopy on strongly-driven solids. We will capitalize on the newly developed attosecond capabilities of the LCLS. We will also perform multi-dimensional high-harmonic spectroscopy and RABBITT experiments to measure the crystal-orientation-dependent spectral phase of high harmonics from wide bandgap dielectrics.

Peer-reviewed publication resulting from this project (2019-2021)

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Imaging Singlet Fission with Angle-Resolved Photoemission
Award #: DE-SC0022004

Thomas K. Allison
Departments of Chemistry and Physics
Stony Brook University, Stony Brook, NY 11794-3400
email: thomas.allison@stonybrook.edu

Program Scope

In the process of singlet fission, a singlet excited state is converted into two triplet excited states. In a molecular crystal or aggregate, the generated triplets can separate, giving two mobile charge carriers for one absorbed photon, with applications in photovoltaics, optoelectronics, and photocatalysis. Like other forms of internal conversion, singlet fission presents challenges, both conceptual and computational, that impede our fundamental understanding of the process and our ability to harness it for applications.

Much of the difficulty surrounding singlet fission involves describing the intermediate triplet-pair states that are populated during the conversion of the initial photoexcited singlet excitation into separated, independent triplet excitons. We will study these states with high-performance time- and angle-resolved photoemission spectroscopy (ARPES), using an instrument developed at Stony Brook with previous DOE support (DE-SC0016017) and also two user facilities coming online over the next three years. The highly differential nature of full-collection 3D ARPES data recorded at every pump/probe delay will enable us to more cleanly isolate spectral signatures due to correlated triplet pair states than has previously been possible.

Recent Progress

2021 has been a breakthrough year for our long-term time- and angle-resolved photoemission (tr-ARPES) effort implementing a unique combination of cavity-enhanced high harmonic generation (CE-HHG) [1] and time-of-flight momentum microscopy [2]. After tackling many technical challenges over the years (see previous AMOS meeting abstracts for previous award DE-SC0016017), the instrument is finally working as we've always envisioned it could and we now have a wealth of data we are writing up. The competition in this arena is fierce with several well-funded research efforts in Canada, Europe, and Asia, now fielding tr-ARPES machines based on high repetition-rate HHG and time-of-flight momentum microscopy. To our knowledge we are still the only effort in the U.S.. With all of this actvity, it is not an overstatement to say that the field is about explode with new science enabled by the new technology. We summarize both technical breakthroughs and scientific results in the past year at Stony Brook in the items below:

- **Electron high-pass filtering:** After some trial and error, we have now implemented a very effective high-pass filter scheme in the momentum microscope using two repeller grids right before the delay-line detector. Optimizing the grid geometry and voltages, we can achieve a fairly abrupt (dead band ~ 0.3 eV) cutoff to the electron distribution and maintain sharp momentum focusing for passed electrons and even electrons in the deadband. This attenuates unwanted low-energy (well below the Fermi level) and secondary electrons by a factor of more than 5×10^3 and this is critical to using the momentum microscope in pump/probe experiments, such that the dynamic range of the detector is used for excited electrons of interest near the Fermi level and not consumed by the hordes of low-energy electrons. We are

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preparing a paper about this high-pass filter scheme, and overall optimization of momentum microscopy for tr-ARPES, for publication [3].

- **XUV focusing:** Through careful alignment of our XUV beamline and CE-HHG, we have achieved nearly diffraction-limited focusing of our harmonics at the sample, free from aberrations from the toroidal mirrors. Figure 1 shows the focus of the 21st harmonic, measured at the sample position by imaging photoelectrons using our photoemission electron microscope (PEEM) in real-space mode. The 16 μm x 17 μm spot is close to the theoretical spot size expected under 1:1 imaging of the source to the sample [1, 4], and improves our XUV intensity at the sample by a factor of 20 over our previous reported results. This is very helpful for studies of μm-scale samples produced by exfoliation, since photelectrons generated by a larger beam from substrate regions outside the sample only contribute to background and space charge, but not to the signal.

- **Time-resolved ARPES of energetic electron dynamics in graphite and monolayer graphene:** We have done a series of experiments on both graphite and graphene (i.e. monolayer graphite) under 2.4 eV excitation, at absorbed fluences even below 1 μJ/cm^2, using a range of probe photon energies between 17 and 30 eV. Scanning the pump fluence over a wide range, we can disentangle electron-electron scattering dynamics from electron-phonon coupling. Interesting long-lived non-equilibrium momentum distributions are observed to persist in both graphite and graphene, which is different than previous work in the high-fluence regime [5]. Several papers are in preparation [6, 7].

- **Time-resolved ARPES of excitons in bulk and monolayer WS$_2$:** We have done a series of experiments in both bulk and monolayer WS$_2$. Experiments in bulk WS$_2$ excite above the band gap and image inter-valley scattering in the conduction band. Experiments in mono-
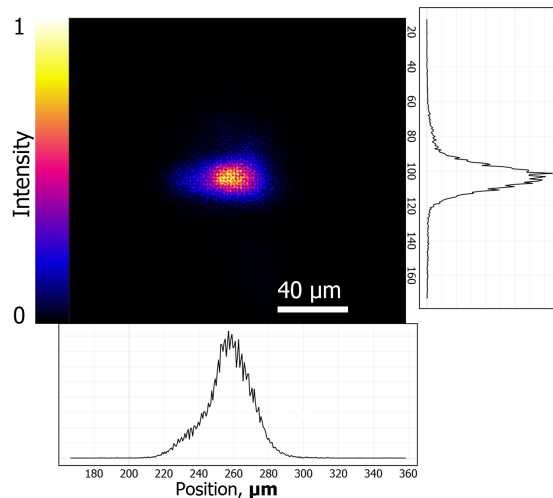
Figure 1: **XUV spot at the sample:** Real space PEEM image of the 21st harmonic (25.2 eV) on the sample. At 45 degree incidence angle on the sample, the beam is 24 μm $\times$ 16 μm wide (FWHM), corresponding to 17 μm $\times$ 16 μm FWHM measured normal to the beam. The high-pass filter grid in front of the delay-line detector is visible in the image.

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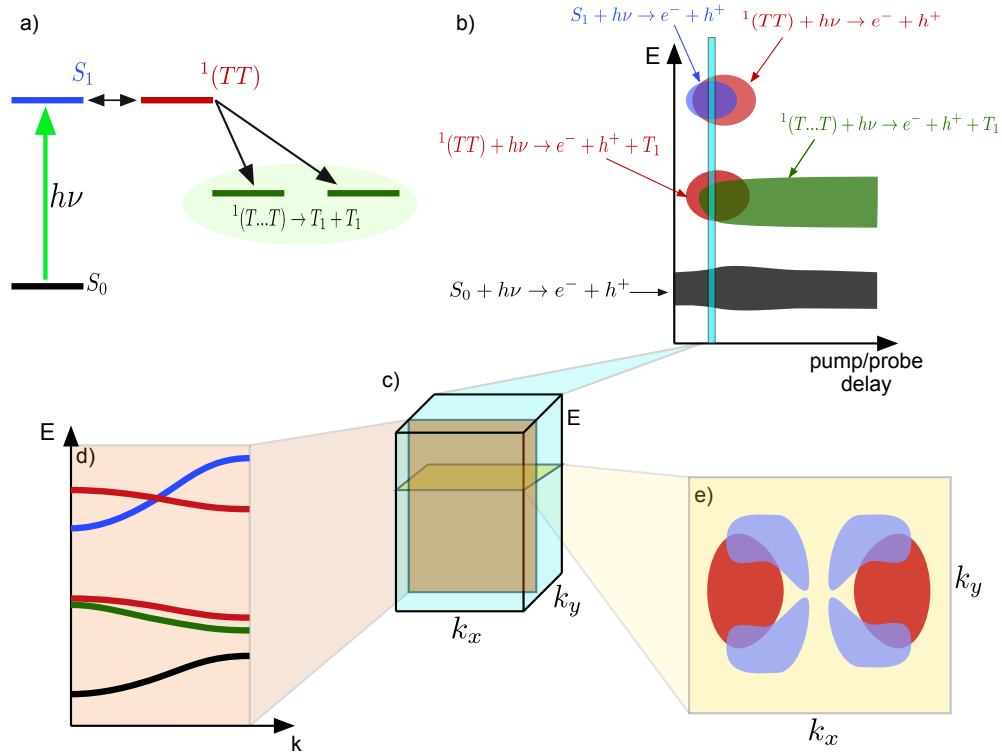
Figure 2: **Overview of planned experiments on singlet fission:** a) Energy level diagram for singlet fission. Photoexcitation initially populates a singlet excited state S_1, which is strongly mixed with triplet pair states $^1(TT)$, in which the two triplets are still electronically coupled. The character of the $S_1/^1(TT)$ state evolves with time and eventually decays (or decoheres) into two electronically independent triplet excitons that maintain spin coherence $^1(T...T)$. Eventually, on much longer timescales spin coherence is lost giving two completely independent ground-state triplets $T_1 + T_1$ [10]. b) A typical time-resolved photoelectron spectrum without resolving momentum, as might be obtained via two-photon photoemission via low-energy photons [11]. E = electron kinetic energy. Signals from $^1(T...T)$ overlap strongly with signals from S_1 and $^1(T...T)$. c) Our proposed experiments will utilize time-of-flight momentum microscopy to record full 3D (E, k_x, k_y) photoelectron distributions spanning multiple Brillouin zones at each pump probe delay. From this data the time-dependent band structure d) and angular intensity distributions e) can be used to separately resolve the $^1(TT)$ signal.

layer WS$_2$ excite the B-exciton just below the band-gap and follow relaxation among exciton states. Several papers are in preparation [8, 9].

Future Plans

In the new project, we will apply the Stony Brook tr-ARPES instrument to crystals of tetracene, pentacene, and eventually hexacene. We will also perform experiments at the LCLS and the NSF NeXUS. An overview of the basic tr-ARPES experiment and the information gained compared to previous work is sketched in figure 2. We will record the full 3D (E, k_x, k_y) photoelectron distribution (illustrated by the rectangular box in figure 2c) across multiple Brillouin zones at every pump/probe delay step. The key advantages of ARPES here are illustrated in figures 2d) and 2e). In the momentum-integrated photoelectron spectrum of figure 2b) (or momentum-limited in the case of 2PPE), the spectral features of $^1(TT)$ strongly overlap with those of S_1 and $^1(T...T)$, but in ARPES they can be separated via their band dispersion (fig. 2d) and angular distributions (fig. 2e) directly related to the orbitals involved [12]. However, the tr-ARPES measurements will pro-

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vide much more information than simply separating the signal of $^1(TT)$; the band dispersion and angular intensity distributions are both quantities of fundamental interest directly reporting on the nature of the wave functions of all the quantum states involved and our experiments will record *all* of this information simultaneously. Furthermore, momentum-resolved tr-ARPES measurements can address the recently proposed hypothesis of momentum-dependent singlet fission rates [13]. The data sets produced from this work will provide important guidance to theory in this area. Indeed, there are already many theoretical predictions for the delocalization of the triplet excitons, and the resulting band dispersion, but this has not been measured. The ultimate improvement in fundamental understanding and modeling can lead to engineering of optoelectronic devices based on singlet fission, just as deep fundamental understanding of conventional semiconductor physics has enabled high-performance silicon-based electronics.

Peer-Reviewed Publications Resulting from this New Project (Project start date: 7/15/2021)

No publications to report yet crediting the new project, but several in preparation as described above.

References

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4

Femtosecond and Attosecond Strong-Fields Processes in Two-Dimensional Finite-Systems: Graphene and Graphene-Like Nanopatches and Polycyclic Molecules

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Vadym Apalkov (PI)

Department of Physics and Astronomy, Georgia State University, Atlanta, GA 30303

E-mail: vapalkov@gsu.edu

1. Program Scope

The program is aimed at theoretical investigation of a wide range of phenomena induced by ultrafast laser-light excitation of nanostructured or nanosize systems. The program is concentrated on finite nanopatches of two-dimensional materials and large polycyclic molecules. The program is specifically focused on theory of ultrafast processes in strong optical fields in finite systems: nanopatches of two-dimensional materials of hexagonal symmetry and hexagonal polycyclic molecules.

2. Resent Progress and Publications

The recent progress covers the period of 2019-2021 and is illustrated by publications [1-14].

2.1 Bilayer graphene in strong ultrafast laser fields [10]

We have shown numerically that, in AB-stacked bilayer graphene, it is possible to generate the valley polarization by using a circularly polarized ultrashort optical pulse that is incident at an oblique angle. Due to the normal component of the optical field, such pulse breaks dynamically the inversion symmetry of bilayer graphene and opens a dynamical band gap, which finally introduces the residual valley polarization of the system. The origin of such ultrafast valley polarization is the topological resonance, which can happen only in topological systems with the finite bandgap. For example, in pristine graphene, which is gapless, the valley polarization cannot be generated by a circularly polarized optical pulse. Thus, in bilayer graphene, the valley polarization can occur only in the field of the optical pulse that has an oblique angle of incidence.

The valley polarization can be tuned by the angle of incidence, the amplitude and the angle of the in-plane polarization of a circularly polarized pulse. For example, we have shown that at the angle of incidence of 80^0, in-plane polarization of 30^0, and the field amplitude of 0.7 V/A the valley polarization can be as large as 36%. Experimentally, such a valley polarization can be measured by time-resolved angle-resolved photoelectron emission spectroscopy.

The valley polarization generated by a chiral optical pulse can be also controlled by a following linearly polarized femtosecond-long optical pulse. Such pulse can be used to tune the valley

polarization and also to probe the valley-polarized residual state of the system through generated anomalous Hall current. Our protocol provides a favorable platform to design ultrafast all-optical valleytronic information processing.

2.2 Ultrafast absorption of graphene quantum dots [11]

We have studied theoretically interaction of graphene quantum dots (GQDs) with ultrashort and strong optical pulses. Such interaction is characterized by three energy scales: (i) the QD's bandgap or the characteristic energy separation between the GQD levels, Δ_g, (ii) the frequency of the pulse, ω_0 and (iii) the characteristic energy of interaction of electrons with the electric field of the pulse, aF_0, where a is the lattice constant of graphene monolayer and F_0 is the field amplitude. The competition between these energy scales determines the specific features of ultrafast electron dynamics in GQDs. One of the important characteristics of such dynamics is the energy absorbed by the system. This energy can be also related to the residual population of the excited GQD levels.

At low field amplitudes, $F_0 \ll 1\ V/A$, the GQD absorbance is well described by the perturbation theory with strong dependence on the GQD bandgap, i.e. the GQD size. For GQDs with zigzag boundaries, due to the existence of zero energy edge states, the bandgap is less than the one for the GQD with the armchair boundary of the same size. As a results in the low field regime, the zigzag GQDs have much larger absorbance compared to the armchair GQDs.

At large field amplitudes, $F_0 > 1\ V/A$, the energetics of the optical pulse is determined by F_0 and the GQD absorbance has weak dependence on the frequency of the pulse. As a function of the GQD size, the absorbance has a maximum for the GQD with the number of atoms ~ 60, for both the armchair and zigzag GQDs. The absorbance can reach the value of up to 4%.

In general, the absorbance of GQDs has nonmonotonic dependence on the field amplitude. It has a maximum at $F_0 \sim 1\ V/A$, while the exact position of the maximum depends on the GQD size. Such behavior is in contrast to the absorption properties of pristine graphene monolayer, for which the absorbance monotonically decreases with the field amplitude. Thus, for GQDs, there are optimal parameters, both for the GQD size and for the amplitude of the pulse, so that the absorbance has the maximum value.

2.3 Transition metal dichalcogenide monolayers interacting with an ultrashort optical pulse [13]

We have developed a theory of interaction of an ultrafast intense linearly polarized optical pulse with monolayers of transition metal dichalcogenides (TMDCs). We have considered the following TMDC materials: MoS_2, WS_2, $MoSe_2$, WSe_2, $MoTe_2$, and WTe_2. These materials cover the bandgap from 0.8 to 2.0 eV and the lattice constant from 3.19 A to 3.56 A. If such monolayers are placed in strong optical pulse, then electrons are excited from the valence to the conduction bands and, within each band, they are also transferred through the whole Brillouin zone, which finally results in generation of femtosecond currents during the pulse. Due to large bandwidth of the incident pulse, this process is completely an off-resonant.

The TMDC monolayers have the symmetry group of D_{3h} and the broken inversion symmetry. With only three axises of symmetry, which are along the armchair directions, the response of

TMDC monolayer to an optical pulse is highly anisotropic. If the optical pulse is polarized along the direction of symmetry of TMDC monolayer then the electric current is generated only along the direction of polarization. But if the polarization of the optical pulse is along a non-symmetric direction, for example, along the zigzag direction, then the electric current has both the longitudinal and transverse components, i.e., components along the direction of polarization and in the perpendicular direction. For all TMDC monolayers the longitudinal electric current shows similar behavior as a function of time. The generated electric current in TMDC monolayers is mainly determined by the interband contribution. As a result, the residual current as a function of time shows oscillations, the frequency of which is determined by the bandgap of the corresponding TMDC monolayer. The generated electric current also transfers the electric charge through the system. For longitudinal currents, the charge is transferred in the direction of the field maximum of the pulse. As a function of the field amplitude, the transferred charge has a maximum, the position of which depends on the lattice constant of TMDC monolayer. Among all TMDC materials, $MoTe_2$ monolayer is the most sensitive to the parameters of the optical pulse. The charge transferred through $MoTe_2$ monolayer shows strong depends on the field amplitude with well pronounced maximum at ≈ 0.3 V/A. Such unique properties of $MoTe_2$ monolayer are related to its lattice parameters, which determine delocalized nature of the interband dipole matrix elements and correspondingly delocalized distribution of the conduction band population distribution in the reciprocal space. For other TMDC monolayers, the conduction band population is mainly concentrated near the K or K' valleys.

The transverse electric current, i.e., Hall current, also results in the charge transfer through the system during the pulse. The magnitude of the transferred charge monotonically increases with the field amplitude, while the direction of the transfer depends on the TMDC material. While for all TMDC monolayers, except $MoTe_2$, the charge is transferred, for example, in positive direction, for $MoTe_2$ monolayer the charge is transferred in the opposite, i.e., negative, direction. Control of an electron transport on a femtosecond time scale pave the way for ultrafast electronic application of TMDCs monolayers.

3. Future Plans

We will develop the comprehensive theory of ultrafast nonlinear optical response of nanoscale topological systems (quantum dots) in the field of ultrashort and strong optical pulse. The examples of such systems are nanopatches of graphene-like materials, both monolayers and multilayers, and transition metal dichalcogenides. The developed theory will cover generation of high harmonics, where we will pay special attention to relaxation effects, which will be described within the density matric approach.

4. Peer-Reviewed Publications Resulting from this Project (2019-2020)

[1] S. Azar Oliaei Motlagh, F. Nematollahi, A. Mitra, A.J. Zafar, V. Apalkov, M.I. Stockman, "*Ultrafast optical currents in gapped graphene*", Journal of Physics: Condensed Matter **32** (6), 065305 (2019).

[2] S. Azar Oliaei Motlagh, F. Nematollahi, V. Apalkov, M.I. Stockman, "*Topological resonance and single-optical-cycle valley polarization in gapped graphene*", Physical Review B **100** (11), 115431 (2019).

[3] S. Azar Oliaei Motlagh, V. Apalkov, M.I. Stockman, "*Laser pulse waveform control of Dirac fermions in graphene*", Quantum Nanophotonic Materials, Devices, and Systems, **11091** (2019).

[4] F. Nematollahi, S. A. Oliaei Motlagh, V Apalkov, M.I. Stockman, "*Weyl semimetals in ultrafast laser fields*", Physical Review B **99** (24), 245409 (2019).

[5] F. Nematollahi, Azar Oliaei Motlagh, J.S. Wu, R Ghimire, V. Apalkov, M.I. Stockman, "*Topological resonance in Weyl semimetals in a circularly polarized optical pulse*", Physical Review B **102** (12), 125413 (2020)

[6] Azar Oliaei Motlagh, A.J. Zafar, A. Mitra, V. Apalkov, M.I. Stockman, "*Ultrafast strong-field absorption in gapped graphene*", Physical Review B **101** (16), 165433 (2020).

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[13] S. A. O. Motlagh, V. Apalkov, and M. I. Stockman, "*Transition metal dichalcogenide monolayers interacting with an ultrashort optical pulse: Femtosecond currents and anisotropic electron dynamics*", Phys. Rev. B **103** (15), 155416 (2021).

[14] R .Ghimire, F. Nematollahi, J.S. Wu, V. Apalkov, M.I. Stockman, "*TMDC-Based Topological Nanospaser: Single and Double Threshold Behavior*", *ACS Photonics* **8**, 3, 907–915 (2021).

New correlated numerical methods for attosecond molecular single and double ionization

Early Career, grant N° DE-SC0020311

Luca Argenti

Department of Physics and CREOL, the College of Optics & Photonics

University of Central Florida, Orlando, FL32816

e-mail: Luca.argenti@ucf.edu

Project Scope

Continuous advances in the XUV and soft-x-ray ultrafast technologies, pursued at large free-electron-laser facilities and in attosecond laboratories worldwide, have reached shorter attosecond-pulse 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 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. Computational tools for molecular single and double ionization are needed to complete the "attosecond revolution".

This project concerns the merge of hybrid-basis close-coupling approaches with numerical techniques for the single- and double-ionization continuum, and for correlated ion bound states, to describe both single- and double-escape processes from poly-electronic molecules. Whereas recent interfaces of quantum-chemistry codes to hybrid Gaussian-B-spline close-coupling (CC) space give promising results, more advanced methods are required to achieve ~1keV energies for single core photoionization, and to describe the multi-photon double-ionization processes targeted by upcoming attosecond experiments. For this reason, we are developing and integrating in the new ASTRA code (AttoSecond TRAnsitions) the numerical tools for the representation of free-electron and 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

Since Sep. 2019 (start of the project), we have made progress in several scheduled directions.

i) Becke's partitioning scheme [Becke1988] is a common way to evaluate electronic integrals for polyatomic molecules, in conjunction with multi-center grids of comparable size. This scheme, however, is inefficient for integrands that do not fall off rapidly at large distances, such as the states in the electronic continuum. To overcome this limitation, we have developed a modified version of Becke's scheme, which applies to molecular photoionization and electron-molecule scattering, where the atomic weights are switched off outside the molecular region. In this way, the atomic integrals are evaluated on grids, centered on each atom, with a radius of the order of few bond lengths. A central master grid covers the complementary smooth weight in the interstitial and long-range region. **[Ref. 1]**

ii) In collaboration with Jeppe Olsen, we have extended the general configuration-interaction code LUCIA, so that it can generate one-, two-, and three-body transition density matrices (TDM) [McWeeny1969] between ionic states with arbitrary (possibly, different) symmetry and multiplicity, using the formalism of string-based determinant expansions of wave functions [Olsen1988]. LUCIA is now able to give in formatted output all TDMs up to second order, as well as subsidiary quantities, such as matrix elements between ionic states augmented with active orbitals, between spin-uncoupled states, and for selected spin magnetic quantum numbers.

iii) We have written the interface programs that converts the TDMs data from LUCIA into the underlying invariant (reduced) TDMs, as well as one that converts the hybrid integrals from the single-file generated by the GPL scatci library of UKRmol+ [Masin2020] into ASTRA database, and complements it with expansion-B-spline integrals.

iv) We have derived and tested the matrix elements formulas for one- and two-body operators between spin-coupled single-ionization states in terms of reduced ionic transition density matrices of first and second order and hybrid integrals.

v) We have completed the single-ionization sector of ASTRA, which implements the formulas of point iv) based on the integrals and TDMs generated in point ii). The code can readily generate all the structural close coupling blocks for overlap, Hamiltonian, and dipole operators. The code, which considers the group symmetry, multiplicity, close-coupling-space composition, is automatized and a major progress: it is an order of magnitude faster than the benchmarks, for simple cases, more for larger CI, and has the capability of scaling the ionic CI and photoelectron energy beyond the benchmark we have tested it against can.

vi) We have written an *ad hoc* prototype code for the calculation of the Rydberg states of the N_2 molecule in a close-coupling basis, using the CIS approximation, to establish a validation chain between 1) UKRmol+, 2) the "elementary" CIS Prototype code, and 3) the general ASTRA code, based on TDM. All these links have been successfully tested.

vii) The XCHEM code, of which the PI is a co-developer, is a benchmark as well as a placeholder for the development of ASTRA modules. In collaboration with V. Borrás, we have entirely rewritten the modules to compute the scattering states, the diagonalization of the Hamiltonian for the confined system with ScaLapack, the projection of arbitrary wave packets on scattering states, the calculation of the molecular-frame photoelectron angular distributions (MFPADs), and the corresponding laboratory-frame observable for randomly oriented molecules. The new changes have been tested on the channel-resolved MFPADs of the CO molecule **[Ref. 2]**.

viii) We have tested the ASTRA CC code to compute bound-states (Rydberg) observables in the N2 molecule, with both uncorrelated and correlated ions, finding a good agreement with XCHEM.

ix) In March 7-12, 2020 (before lockdown), we held our first annual meeting between the internal and external collaborators to this project, to align our efforts. In 2021, a second in-person meeting was impeded by the pandemic, but all the contributors kept meeting online on a weekly basis.

x) We have developed decoherence models for the strong-field N1s core ionization of the N2O molecule, to reproduce the ATAS spectrum measured by the group of Prof. Jiro Itatani **[Ref. 3]**, as a precursor to the *ab initio* calculations we will conduct with ASTRA.
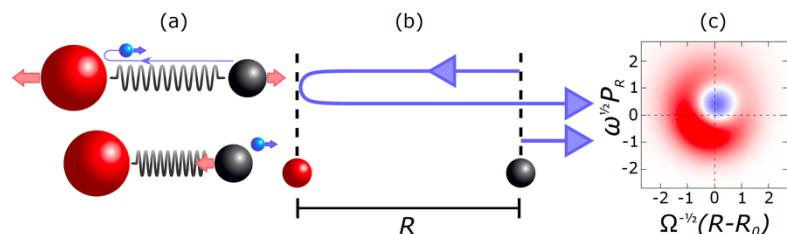
Figure 1(a) Pictorial representation of the nuclear recoil as the photoelectron from the C-1s ionization of CO is emitted towards the other nucleus, possibly reflecting many times (top), or directly out (bottom), resulting in an expansive and compressive boost, respectively. (b) Representation of two interfering pathways of the outgoing photoelectron. (c) The corresponding ionic nuclear Wigner Distribution when the molecule is ionized by an ultrashort pulse, showing that the ion emerges in a non-classical coherent state.

xi) We have developed a model for the direct photoemission recoil and intramolecular photoelectron scattering recoil in the C 1s ionization of the CO molecule to explore the temporal aspects of these two phenomena and the control of the vibrational coherence of the residual ion with ultrashort x-ray pulses **[Ref. 4]**. This is a precursor to *ab initio* study we will do with ASTRA.

xii) Dr. Juan Martín Randazzo, an established and tenured researcher at the Argentinian Research Council (CONICET), has joined the effort as postdoctoral fellow from Jan 2020 to Jan 2021, and contributed to points iii-vi. In July 2021, we hired on a two-year basis two new postdocs, Carlos Marante and Siddhartha Chattopadhyay, who will focus on completing the development of the single- and double-ionization sectors of ASTRA, respectively.

xiii) We have started involving an undergraduate student from the college of Optics to make basic calculations with ASTRA as a user, which will accelerate the development of the user interface, and prepare future group members.

Future Plans

We are currently finalizing all the tests for the energies of and dipolar coupling between a large set of Rydberg molecular states for the N2 molecule using *ad hoc* CI singles and correlated CC calculations with XCHEM as benchmark, as well as CC calculations with significantly more correlated ionic states, which are affordable with ASTRA. These results are used in the preparation of the first methodological paper on the ASTRA approach to single-ionization CC.

We are also incorporating in ASTRA the scattering modules that we have developed and tested with XCHEM in the first year of the project. As soon as those are tested, possibly by early Spring 2022, we will use the program to evaluate the effect of ionic correlation on the valence MFPADs of various molecules, including CO. In particular, we hope to reduce the residual discrepancy between theoretical and experimental partial cross sections still observed with XCHEM. We will also use the program to compute fully *ab initio* the resonant transition amplitudes that we estimated in the for the N1s N2O ionization in our collaboration with the group of Jiro Itatani **[Ref. 3]**, and

those we computed with a simple 1D model in our manuscript on the intramolecular scattering effects on photoemission delay and vibrational coherence **[Ref. 4].**

Siddhartha Chattopadhyay, is developing double ionization capabilities along two fronts. First, he is implementing a virtual sequential two-photon double ionization model [Horner2007] which is known to give, in helium, reliable semi-quantitative predictions even for overlapping pulses below the sequential threshold. After reproducing the known helium results, he'll pass to polyelectronic atoms, and subsequently to molecules. Second, he is deriving the expressions for the matrix elements of spin-coupled double-ionization close-coupling states. Once tested, we will proceed with the extension of ASTRA to compute double-ionization channels *ab initio*.

We plan to hold a second meeting, with Jeppe Olsen traveling from Denmark and Juan Martín Randazzo traveling from Argentina, in January or February 2022, to advance the development of the correlation space (a.k.a. pseudo-channel, Q-space, optical potential, or dynamic correlation).

Now that the pandemic is coming to a close, with UCF metrics, and that ASTRA is delivering results, we will hire a graduate student to apply the code to problems of experimental interest.

In the third year we will add to ASTRA the programs needed to evaluate stationary scattering states, Siegert states, to solve the time-dependent Schrödinger equation in the presence of external fields, and to analyze the photoelectron spectra and optical response. We will also start including perturbatively the vibrational degrees of freedom, within the BO approximation.

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Peer-Reviewed Papers from this Project (Sep2019-2021, 2 published, 2 under review):

1. H. Gharibnejad, N. Douguet, B. I. Schneider, J. Olsen, L. Argenti, Comp. Phys. Commun. **263**, 107889 (2021)
2. V. J. Borràs, J. González-Vázquez, L. Argenti, F. Martín, J. Chem. Th. Comput. *in press* (2021)
3. Nariyuki Saito, N. Douguet, H. Sannohe, N. Ishii, T. Kanai, Y. Wu, A. Chew, S. Han, B. I. Schneider, J. Olsen, L. Argenti, Z. Chang, J. Itatani, Attosecond electronic dynamics of core-excited states of N2O in the soft x-ray regime (*under 1st rev. round at PRR - 2021*)
4. B. Ghomashi, N. Douguet, L. Argenti, Attosecond Intramolecular-Scattering and Vibronic Delays (*under 2nd rev. round at PRL – 2021*).

Attosecond dynamics driven by ultrashort laser pulses
(Award No. DE-SC0001771)

Principal Investigator: Andreas Becker

JILA and Department of Physics, University of Colorado at Boulder,
440 UCB, Boulder, CO 80309-0440

andreas.becker@colorado.edu

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 more than a decade. One of the challenges is the realization of a 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.

We seek to provide theoretical support for 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. Excitation with Bichromatic Circularly Polarized Laser Pulses

Excitation of atoms (and molecules) is known to play an important role in many strong-field processes. Previously within this project we have studied the distributions over the orbital angular momentum number in Rydberg states due to the interaction with a linearly polarized laser pulse [1]. Over the last couple of years, we have extended our analysis on this topic to the superposition of two circularly polarized laser pulses, which recently has seen an upsurge in activity in strong-field experiment and theory. In a recent experiment on strong-field ionization by a bichromatic circularly polarized pulse it has been shown that the probability to ionize an atom is significantly enhanced if the two fields are counter-rotating as compared to co-rotating fields [2].

We have therefore studied the excitation of hydrogen atom by bichromatic $(\omega, 2\omega)$ circularly polarized laser pulses using numerical solutions of the time-dependent Schrodinger equation [DOE3, DOE6]. First, we focused on the identification of the general pathways to excitation and could show that the results agree with the multiphoton selection rules, namely excited states are populated in which orbital angular momentum and magnetic quantum numbers are either both odd or both even, independent of the relative helicity, peak intensity, and pulse duration of the pulses [DOE3]. Furthermore, the results confirmed the conjecture of the experiment [2] that in the case of counter-rotating fields an enhancement of excitation occurs due to the increased density of excited states accessible.

A surprising new insight based on our results is that besides pathways via direct photon absorption a transfer of population among the Rydberg states via three different higher-order Raman transitions occurs. A detailed analysis of the mechanism showed that the redistribution requires at least three photons, two at the longer wavelength and one at the shorter wavelength [DOE6]. We have further shown that the redistributions mechanisms are also present in $(\omega, 3\omega)$ and $(\omega, 4\omega)$ fields. The range of the populated magnetic sub-levels increases as the difference in the central frequencies of the two fields gets larger.

B. Asymmetries in Ionization and Imaging of Electron Dynamics

In another thrust of our work, we focus on few-photon ionization of atoms with ultrashort pulses. The general renewed interest in this topic is driven by the recent rapid technical development in the production of deep-ultraviolet and extreme-ultraviolet pulses using high harmonic generation (HHG) and free-electron lasers (FEL). The ongoing quest in shortening pulses at these wavelengths towards the single-cycle regime in duration are achieved via large spectral bandwidths (e.g., [3]). Such broadband energy pulses give rise to competition between one- and two-photon (as well as three-photon) ionization processes for emission at a given energy.

Previously, we have focused on the analysis of photoelectron angular distributions and related anisotropy parameters for the competition of one- and two-photon ionization of helium atom and other rare gas atoms in an ultrashort EUV laser pulse, using numerical results from the time-dependent Schrodinger equation. Among other aspects, we have explored the competition between the two processes for an atom prepared in the ground state [DOE2].

We then turned our attention to quantum systems in superposition states. First, we extended the toolbox for the identification of competing pathways from photoelectron angular distributions (PADs) by developing a new set of generalized asymmetry parameters [DOE5]. More recently, we showed how the reconstruction of a wave packet and the corresponding electron dynamics in an atom via PADs in a pump-probe scheme as a function of time delay can be achieved [DOE7]. In the reconstruction predictions of first- and second-order perturbation theory are used to determine the unknown phases and amplitudes of the initial state from the PADs, which we simulate via solutions of the time-dependent Schrödinger equation in the single-active-electron approximation. Results of applications show that the reconstruction is highly accurate for probe pulse intensities below 10^{13} W/cm^2 while allowing for CEP (intensity) variations of 10% (20%) from shot to shot. Additionally, a detection accuracy for the PADs of about 1% for a reconstruction with small error is required.

C. Doorway states in ionization with short circularly polarized laser pulses

Over the last year we started a new project in which we study the dependence of the laser induced ionization probability of atoms on the magnitude and sign of the magnetic quantum number of the initial state. The selectivity in ionization to the sense of the electron's rotation in the initial state with respect to the rotation direction of a circularly polarized laser field is a key element towards the generation of ultrashort spin-polarized electron pulses. These can be used to probe chiral systems and magnetic properties of materials on ultrafast timescales. Previously, it has been shown that in the highly nonperturbative intensity and wavelength regime of laser-atom interaction, spin polarization of about 30%–50% can be achieved [4-7].

Results of our calculations revealed a much larger selectivity and a surprisingly large change by a factor of about 100 in the ionization ratio of electrons in initial states counter-rotating with respect to the field over corotating electrons in the previously unexplored intermediate few-photon ionization regime [DOE8]. The physical mechanism behind this observation is related to resonant enhanced ionization via states close in energy to the initial states. These doorway states are accessible exclusively from the initial state for counter-rotating electrons within the respective wavelength regime. The results may open a new route to control the generation of spin-polarized electrons by ultrashort laser pulses.

Future Plans

We plan to continue our studies in the three thrusts and extend our investigations to simple molecules. For the laser-driven excitation and ionization with bicircular (and other structured) laser pulses we will consider the interaction with molecules, taking the hydrogen molecular ion and the hydrogen molecule as the first targets. Determination of the photoelectron angular distributions in these cases will also allow us to seek for an extension of the concept behind the new set of asymmetry parameters to the molecular case. Furthermore, we plan to establish a more general understanding of the selectivity in the electron emission from different atomic magnetic quantum levels in laser fields over a broad range of wavelengths, from single-photon to tunnel ionization, and with

various forms of polarization, as well as consider the potential impact of the insights on other strong-fields processes.

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[DOE2] J. Venzke, A. Jaron-Becker, and A. Becker, *Ionization of Helium with ultrashort laser pulses,* Journal of Physics B: Atomic, Molecular and Optical Physics **53**, 085602 (2020).

[DOE3] J. Venzke, Y. Gebre, A. Becker, and A. Jaron-Becker, *Pathways to excitation of atoms with bicircular laser pulses,* Physical Review A **101**, 053425 (2020).

[DOE4] R. Reiff, T. Joyce, A. Jaron-Becker and A. Becker, *Single-active electron calculations of high-order harmonic generation from valence shells for quantitative comparison with TDDFT calculations,* Journal of Physics Communications **4**, 065011 (2020).

[DOE5] J. Venzke, A. Becker, and A. Jaron-Becker, *Asymmetries in ionization of atomic superposition states by ultrashort laser pulses,* Scientific Reports **10**, 161164 (2020).

[DOE6] Y. Gebre, J. Venzke, A. Jaron-Becker, and A. Becker, *Transitions between Rydberg states in two-color corotating circularly polarized laser pulses,* Physical Review A **103**, 013101 (2021).

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

Nora Berrah**,** Award Number: DE-SC0012376
Physics Department, University of Connecticut, Storrs, CT 06268
e-mail:nora.berrah@uconn.edu

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)** Femtosecond time-resolved molecular dynamics investigations using pump-probe techniques using free electron lasers (FELs), such as the LCLS-II x-ray FEL at SLAC National Laboratory but also at the XUV FERMI FEL in Italy, at the XUV FLASH-II FEL and at the 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 in the soft and hard x-ray regime. **3)** The investigations of electron dynamics in molecules at the attosecond timescale with the new XLEAP capability at LCLS-II.

We use IR/UV table-top lasers with our COLTRIMS at our UConn-based lab and at 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) Time-resolved study of resonant interatomic Coulombic decay in helium nanodroplets

A novel type of energy transfer process known as interatomic Coulombic decay (ICD) [a] has been successfully studied in weakly-bound systems. In cases where local Auger-Meitner decay is energetically forbidden, an excited atom or molecule releases its excitation energy by transferring it to a neighboring atom or molecule. As a result, that atom or molecule is ionized as it receives the energy. This phenomenon is due to electron correlations which we seek to investigate.

With the advent of seeded FELs with intense, tunable radiation, new types of resonant ICD have been observed in vdW clusters [b] where energy is exchanged between neighboring excited atoms. When weakly-bound complexes are multiply excited by intense electromagnetic radiation, resonant interatomic Coulombic decay leads to enhancement of ionization efficiency. This process has been predicted to be relatively slow, typically tens to hundreds of picoseconds. Our work, conducted with an international collaboration led by my UConn postdoc Aaron LaForge, directly measured the ICD timescale in resonantly excited helium droplets using the tunable, extreme

ultraviolet FERMI FEL. Over an extensive range of droplet sizes and FEL intensities, we find the decay to be surprisingly fast, with decay times as low as 300 femtoseconds, and to show only weak dependence on the density of the excited states. Using a combination of time dependent density functional theory and ab initio quantum chemistry calculations, we elucidated the mechanisms of this ultrafast decay process (Pub 1).

2) Time-resolved quantum beats in the fuorescence of helium resonantly excited by XUV radiation

We carried out an experiment at the FERMI FEL to observe the time-resolved quantum beats in the helium fluorescence from the transition 1s3p→1s2s, where the initial state is excited by XUV FEL radiation. The quantum beats we measured originate from the Zeeman splitting of the magnetic sub-states due to an external magnetic field. We performed a systematic study of this effect and we discussed the possibilities of studying this phenomenon in the x-ray regime (Pub 7).

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<u>Future Plans.</u>
The principal areas of investigation planned for the coming year are to: **1)** Conduct the time-resolved experiment with FEL beamtime scheduled in December 2021 at FERMI. The beamtime consists of probing, time-resolved, double interatomic Coulombic (dICD) decay in helium nanodroplets. dICD leads to double ionization. **2)** Plan the time-resolved experiment with FEL beamtime to investigate intermolecular interactions of molecular iodine solvated in small water clusters. The experiment will use the FLASH-II FEL paired with a COLTRIMS to measure ion-ion coincidences with 400 Hz rep rate. This experiment prepares us to use the future high rep rate at LCLS-II. **3)** Finish the analysis and write the publication of our non-linear physics experiment on H_2S carried out at the EU-XFEL. **4)** Continue the analysis and write the publication of the time-resolved ultrafast dynamics experiment, subsequent to the ionization of C_{60} near giant resonances in the XUV regime using the FLASH-II FEL. These resonances consists of strongly correlated electrons. **5)** Analyze the data from the successful time-resolved UED experiment conducted in January 2021 at SLAC National lab regarding the ring opening process of 2-bromothiophene (C_4H_3BrS).

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Imaging Structural Dynamics in Isolated Molecules with Ultrafast Electron and X-ray Diffraction

PI: Martin Centurion

Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588-0299

martin.centurion@unl.edu

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 and X-ray 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 or X-ray pulse. The scattering pattern 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 UED 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 360 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. We are now planning to also carry out X-ray diffraction experiments at the LCLS, which will be complementary to the UED measurements.

Recent Progress

Over the last year we have completed the data analysis on the proton transfer reaction of o-nitrophenol, carried experiments at the SLAC MeV-UED facility and at LCLS and supported multiple experiments during and after the first SLAC gas phase MeV-UED user run.

Analysis and interpretation of proton-transfer UED experimental data:

Intramolecular proton transfer (IPT) is the initial step in many important biological and chemical processes, and amongst the fastest elementary photo triggered reactions in nature. Knowledge of the interplay between electronic and nuclear dynamics leading to IPT and an atomistic understanding of the ensuing motions could provide a pivotal new insight into photobiological processes, and lead to the development of new technologies. O-nitrophenol is a prototypical molecule for the study of such dynamics, as its strong charge transfer character, facilitated by the proximity between electron donating and withdrawing groups, potentiates IPT. Although numerous studies have explored the electronic relaxation of o-nitrophenol following photoexcitation to its first-excited state, the nuclear dynamics leading to IPT and subsequent internal conversion back to the ground state have not been observed experimentally. Using relativistic ultrafast electron diffraction (MeV-UED), we have experimentally observed the structural dynamics leading to IPT, the ensuing motion that enables the wavepacket to reach a conical intersection leading to the ground state, and the vibrational energy distribution of the molecule after the reaction is completed. The three-dimensional molecular structure and thus the key motions are retrieved from the experimental data at each time step using a genetic algorithm (Figure 1). The transient compression of the non-bonded O-O distance, which is the key motion that enables the proton transfer, was retrieved directly from the diffraction signal to pinpointing the moment at which the proton transfer takes place. Directly after the proton transfer, we observed a time-delay in which no major structural changes take place, followed by a sudden out-of-plane torsion of the newly formed nitrous acid motif. This torsion allows the nuclear wavepacket to access the S1/S0 conical intersection. The dynamics are interpreted in terms of changes in the slope of the potential energy surface as the wave packet travels from the Franck-Condon region towards the conical intersection. After traversing the conical intersection the molecule returns to the ground state, where excess internal energy is redistributed into multiple nuclear degrees of freedom leading to ample torsions of the nitrous acid motif and loss of ring planarity. These experimental observations are supported and complemented by ab initio nonadiabatic molecular dynamics calculations performed by the group of Todd Martinez. This is
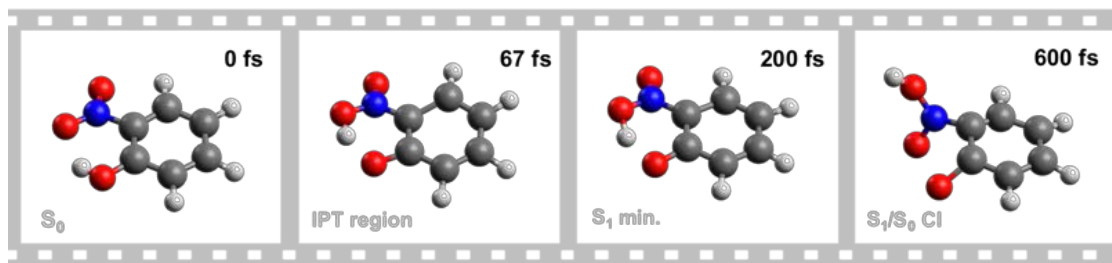
Figure 1. Experimentally retrieved o-nitrophenol structures. From left to right: Ground state structure, at the moment of proton transfer, at the S1 minimum showing a slight distortion of the ring, at the conical intersection showing a rotation HONO group.

the first spatially resolved imaging of a proton transfer reaction.

Data analysis of the isomerization of cis-stilbene: We have investigated the ultrafast cis-trans isomerization of stilbene using the MeV-UED instrument at SLAC. We had tried this experiments twice before but did not succeed due to sample delivery issues. Finally, after installing and testing an improved sample delivery system, we succeeded in acquiring UED data during the commissioning run in the Fall of 2020. We have made significant progress in the data analysis, and are currently working with our collaborators in the group of Todd Martinez to interpret the results with the help of AIMS simulations of the dynamics. In the data, we see the characteristic signals of the isomerization, in particular the appearance of new peaks in the PDF at long distances in the range of 8-9 Å, which are present in the trans but not in the cis form. Additionally, we see a depletion of intermediate distances around 5 Å, which is also consistent with the transformation. We are currently investigating discrepancies between the experiment and theory that appear at shorter distances and checking the data for any artifacts that were not removed by the data cleanup.

Support for first user run at SLAC MeV-UED: My group provided support to more than ten experiments during the first gas phase user run at the MeV-UED instrument in Fall 2020 – Winter 2021. These were remote beam times, and my group provided support in online data acquisition, analysis and interpretation. We continue to support multiple groups in data analysis through regular biweekly meetings, with participants from eight different institutions.

X-ray scattering experiments at LCLS: We carried out an ultrafast X-ray scattering experiment at LCLS (LV11, PI: Thomas Wolf) in 2020. The purpose of this experiment was the investigation of UV-induced structural dynamics in three molecules: pyridine, α-terpinene, and acetylacetone. Our experiment was the first user beamtime to employ the higher photon energies (15 keV) from the new hard X-ray undulators in a gas phase scattering experiment. Due to difficulties with sample delivery and some unforeseen challenges from the higher photon energies, we were only able to obtain a time-dependent dataset on one molecule, acetylacetone. We photoexcited acetylacetone to a $\pi\pi^*$ state, where the population is expected to undergo relaxation to a lower-lying $n\pi^*$ state involving intramolecular proton transfer and a conical intersection within <100 fs. The preliminary data analysis shows a rapid change in the structural signatures within the first 100 fs, which qualitatively fit to simple simulations of the signal based on the expected structural changes in the $\pi\pi^*$ an $n\pi^*$ states. The experiment demonstrated the capability to capture data up to 7 $Å^{-1}$, a significant improvement for X-ray scattering at LCLS.

We have submitted a proposal for an ultrafast X-ray scattering experiment at LCLS run 20 (LX 74 "Imaging roaming mediated dynamics in halogenated alkanes by ultrafast X-ray scattering" PI: Martin Centurion) to investigate a possible roaming channel in the photodissociation of CH_2I_2. If successful, this would be the first time that a roaming reaction is spatially resolved.

Future plans

Continue data analysis of stilbene. Carry out UXRD experiments at LCLS (or submit a new proposal if not accepted). Develop high temperature sample delivery capable of reaching 300 C (first at UNL, then implement a similar system at SLAC MeV-UED) to carry out UED experiments on uracil and thymine. Apply for MeV-UED beam time.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

1. T. J. A. Wolf, D. M. Sanchez, J. Yang, R. M. Parrish, J. P. F. Nunes, M. Centurion, R. Coffee, J. P. Cryan, M. Gühr, K. Hegazy, A. Kirrander, R. K. Li, J. Ruddock, X. Shen, T. Vecchione, S. P. Weathersby, P. M. Weber, K. Wilkin, H. Yong, Q. Zheng, X. J. Wang, M. P. Minitti & T. J. Martínez, "The photochemical ring-opening of 1,3-cyclohexadiene imaged by ultrafast electron diffraction" *Nature Chemistry* 11, 504 (2019).

2. K.J. Wilkin, R. M. Parrish, J. Yang, T. J. A. Wolf, J. P. F. Nunes, M. Guehr, R. Li, X. Shen, Q. Zheng, X. Wang, T. J. Martinez, M. Centurion, "Diffractive imaging of dissociation and ground-state dynamics in a complex molecule" *Phys. Rev. A* 100, 023402(2019).

3. S. Schippers, E. Sokell, F. Aumayr, H. Sadeghpour, K. Ueda, I. Bray, K. Bartschat, A. Murray, J. Tennyson, A. Dorn, M. Yamazaki, M. Takahashi, N. Mason, O. Novotný, A. Wolf, L. Sanche, M. Centurion, Y. Yamazaki, G. Laricchia, C. M Surko, J. Sullivan, G. Gribakin, D. Wolf Savin, Y. Ralchenko, R. Hoekstra,and G. O'Sullivan "Roadmap on photonic, electronic and atomic collision physics: II. Electron and antimatter interactions" *Journal of Physics B*: At. Mol. Opt. Phys. 52 171002 (2019).

4. X. Shen, J. P. F. Nunes, J. Yang, R. K. Jobe, R. K. Li, Ming-Fu Lin, B. Moore, M. Niebuhr, S. P. Weathersby, T. J. A. Wolf, C. Yoneda, M. Guehr, M. Centurion and X. J. Wang, "Femtosecond gas-phase mega-electron-volt ultrafast electron diffraction" *Structural Dynamics* 6, 054305 (2019).

5. 24. J. P. F. Nunes, K. Ledbetter, M. Lin, M. Kozina, D. P. DePonte, E. Biasin, M. Centurion, C. J. Crissman, M. Dunning, S. Guillet, K. Jobe, Y. Liu, M. Mo, X. Shen, R. Sublett, S. Weathersby, C. Yoneda, T. J. A. Wolf, J. Yang, A. A. Cordones, and X. J. Wang "Liquid-phase mega-electron-volt ultrafast electron diffraction" *Structural Dynamics* 7, 024301 (2020).

6. 25. Yusong Liu, Spencer L. Horton, Jie Yang, J. Pedro F. Nunes, Xiaozhe Shen, Thomas J. A. Wolf, Ruaridh Forbes, Chuan Cheng, Bryan Moore, Martin Centurion, Kareem Hegazy, Renkai Li, Ming-Fu Lin, Albert Stolow, Paul Hockett, Tamás Rozgonyi, Philipp Marquetand, Xijie Wang, and Thomas Weinacht, "Spectroscopic and Structural Probing of Excited-State Molecular Dynamics with Time-Resolved Photoelectron Spectroscopy and Ultrafast Electron Diffraction" *Phys. Rev. X* 10, 021016(2020).

7. 16. Jie Yang, Xiaolei Zhu, J. Pedro F. Nunes, Jimmy K. Yu, Robert M. Parrish, Thomas J. A. Wolf, Martin Centurion , Markus Gühr, Renkai Li, Yusong Liu , Bryan Moore, Mario Niebuhr , Suji Park, Xiaozhe Shen , Stephen Weathersby , Thomas Weinacht , Todd J. Martinez, Xijie Wang, "Simultaneous observation of nuclear and electronic dynamics by ultrafast electron diffraction" *Science* 368, 885–889 (2020) .

8. K Ledbetter, E Biasin, JPF Nunes, M Centurion, KJ Gaffney, M Kozina, M-F Lin, X Shen, J Yang, XJ Wang, TJA Wolf, AA Cordones, "Photodissociation of aqueous I3- observed with liquid-phase ultrafast mega-electron-volt electron diffraction" *Structural Dynamics* 7, 064901 (2020).

9. J. Yang, R. Dettori, J.P.F. Nunes, N.H. List, E. Biasin, M. Centurion, Z. Chen, A,A. Cordones, D.P. Deponte, T.F. Heinz, M.E. Kozina, K. Ledbetter, M.F. Lin, A.M. Lindenberg, M. Mo, A. Nilsson, X. Shen, T.J.A. Wolf, D. Donadio, K.J. Gaffney, T.J. Martinez, X. Wang, "Direct observation of ultrafast hydrogen bond strengthening in liquid water" Nature 596, 531 (2021).

Capturing Ultrafast Electron Driven Chemical Reactions in Molecules

PI: Martin Centurion

Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588-0299

martin.centurion@unl.edu

Co-PIs: Daniel S. Slaughter, Robert R. Lucchese and C. William McCurdy

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Program Scope

The goals of this project, 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 and photo-fragment spectroscopy following electron transfer from an iodide anion to a molecule within a mass-selected molecular dimer. Iodide binds only weakly through the dipole interaction with many polar molecules, and such molecules forming a dimer with iodide undergo only small changes from the equilibrium geometry in isolation. When the electron is transferred from the iodide, the iodine atom is no longer bound, so the electron transfer step can be considered analogous to electron attachment and brings the key advantage of ultrafast timing precision. 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, forming a transient anion that dissociates. The metastable transient anion system evolves from the electronic continuum, so dissociation competes with autodetachment. 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 highly challenging to accurately describe the dynamics with existing quantum chemistry methods. It is also very 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 both photoelectrons and neutral fragments 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

We have successfully completed the construction and testing of an experimental apparatus including a mass-selecting anion cluster source, comprising a pulsed nozzle, a time-of-flight spectrometer with mass selector, a reflectron mass spectrometer and ion detector. We have also improved the stability and count rates of each anion species produced by the source, and constructed the laser beam line and timing and synchronization system to temporally and spatially overlap the laser and anion pulses. Figure 1 shows the experimental setup. With this setup, measurements of laser triggered fragmentation of iodide-molecule clusters are ongoing, where we will soon investigate the fragmentation pattern as a function of the wavelength of the excitation laser. We will compare these fragmentation channels with those produced by direct interaction with an electron beam with a narrow energy distribution, using the existing DEA reaction microscope at LBNL. The setup for the time-of-flight experiments is completed, the VMI for the time-resolved photoelectron measurements has been designed but not yet installed.

Anion source: The anion source comprises a pulsed valve through which a mixture of gases is flown, an electron gun with tunable energy to generate a high density of anions (and cations) at the exit of the nozzle. The anions are transferred

a)

A: Electron gun
B: Faraday Cup
C: Even-Lavie valve
D: Cooling assembly for the valve
E: Steering assembly for the valve
F: Skimmer
G: Deflector and Einzel lens sets
H: TOF plates
I : Einzel lens
J: Deflector sets
K: Mass gate
L: Channel Electron Multiplier 1
M: Reflectron Assembly
N: Channel Electron Multiplier 2

b)
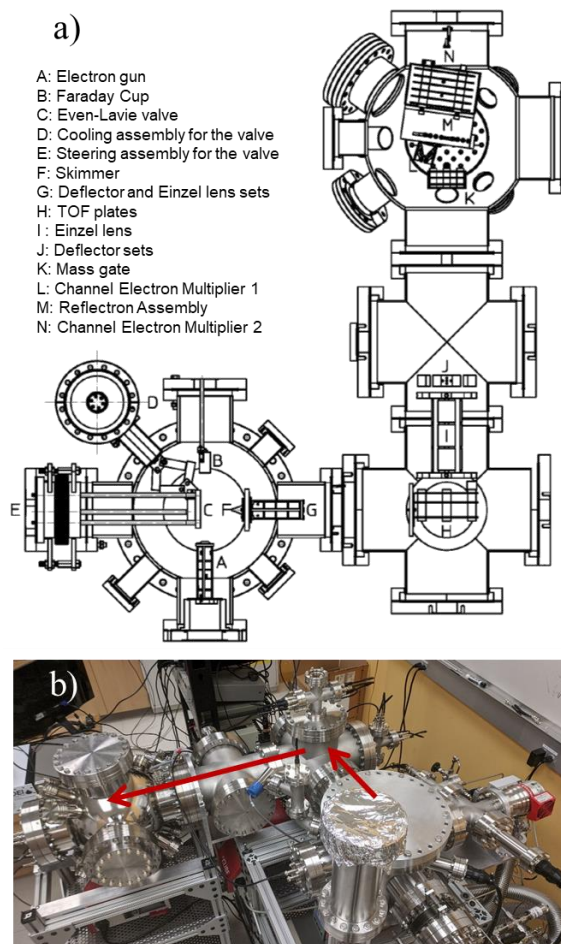
Figure 1. a) CAD design of the source, TOF spectrometer and target chambers. b) Photograph of the constructed setup, the red arrow indicate the path of the anions from the nozzle to the detector.

through a small aperture to a second chamber where they are accelerated by a set of electrodes in a time-of-flight (TOF) configuration, and detected using a channeltron. The source has been tested using a mixture of nitromethane, CF_3I and argon, and we have successfully produced high yields of the nitromethane-iodide dimer, along with atomic iodide and other anions. The relative pressures of the three gases were adjusted to optimize the production of the desired cluster. A recent improvement in the setup was introducing an additional pressure regulator to keep the relative pressure of argon constant during the experiment, which keeps the signal levels steady over several hours. Figure 2a shows a typical TOF spectrum showing I-, and nitromethane anions and the nitromethane-I- clusters.

Mass selection. Experiments will require the selection of a single anion for photoexcitation. We have implemented a mass selector for this purpose. The mass selector is composed of three concentric circular electrodes that are held at a voltage to repel all anions. At the time the anion of interest reaches the vicinity of the first electrode, a voltage pulse is applied to lower the barrier and let only the selected anion pass. The mass selector was successfully installed and tested. Figure 2b shows a TOF spectrum with the mass selector tuned to the nitromethane-iodide cluster. The selected cluster is transmitted with an efficiency of more than 50% and the remaining anions are completed blocked (below the noise floor of the measurement).

Figure 2. a) TOF spectrum measured on the reflectron spectrometer. The species of interest are iodide (I-), the iodide nitromethane cluster (I-NM) and a cluster of iodide with two nitromethane molecules (I-(NM)2). b) The TOF spectrum with the mass selector tuned to pass only the I-NM clusters.

Reflectron spectrometer. In our setup, a laser pulse will be used to transfer an electron from the iodide to the molecule. A reflectron spectrometer will be used to capture the anion fragments produced by the electron attachment. A reflectron was designed using SIMION to optimize the mass separation to the range of interest. The reflectron consists of a set of electrodes with different static voltages, which can be adjusted to target different mass ranges. The potentials can be adjusted to reach a temporal focus on the detector for different target masses. Based on the simulations, we expect that a mass resolution of approximately 5% of the mass of the target

fragment when operated over a large mass range, which will allow us to resolve unit mass (single H atom) changes in small fragments. With this we expect to be able to determine the fragmentation pattern of the parent anion. The reflectron spectrometer can be operated with considerably higher mass resolution for a limited range of masses, which will allow heavier fragments to be precisely identified, even if they are only a single or a few Da different in mass. The detection is done by a pair of rectangular channeltrons, which were chosen based on the spatial distribution of the mass dispersed anions after the laser interaction in the SIMION simulations. The reflectron has been successfully tested and shown to produce similar count rates to the single channeltron at the end of the TOF setup.

Laser beamline. We have constructed a laser beam line to transport the ultraviolet beam from the laser lab (next door) to the target chamber. The laser is transported through a beam tube connecting the two laboratories through the wall, and guided and focused onto the anion beam using a set of mirrors and lens. The laser pulses are monitored at the output of the chamber with a fast photodiode to determine time of arrival and power stability.

Laser timing and synchronization. The arrival of the laser pulses and the anion packets has to be synchronized to better than the duration of the anions packets, which is ~ 500 ns. We use the laser trigger signal to operate the pulsed nozzle in the source, the laser photodiode signal, and a set of delays to ensure the temporal overlap of the laser and anion packets. The synchronization system has been built and will be tested in the immediate future.

Data acquisition. We have completed the data acquisition setup to record interleaved data where the pump laser is ON/OFF for every other shot. This will allow us to accurately subtract background counts and look for small signals. The signal from the channeltron is recorded for each shot, along with the laser trigger signal. The laser is run at a repetition rate of 100 Hz, and the nozzle is run at a repetition of 200 Hz. The 200 Hz signal is created by copying and delaying the 100 Hz signal, such that the laser and the pulsed nozzle are synchronized. This creates an interleaved data stream with shots with and without the pump laser. The recorded trigger signal is used to identify and ON and OFF shots.

We are currently preparing a manuscript tentatively titled "Instrument for generation and mass-selection of anion cluster beams for ultrafast time resolved electron attachement studies."

Future plans

This project ended on Sept/2021

Peer-Reviewed Publications Resulting from this Project (2019-2021)

None.

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

Award number DE-SC0020276

PD/PI: Martin Centurion[1]. PIs: Adam Kirrander[2,3], Kenneth Lopata[4], Daniel Rolles[5], Artem Rudenko[5], Peter Weber[2]

[1]Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588-0299, *martin.centurion@unl.edu*
[2]Department of Chemistry, Brown University, Providence, R.I. 02912
[3]School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ
[4]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803
[5]J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS, 66506

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 and Adam Kirrander at Brown University and Kenneth Lopata at Louisiana State University. A series of ultrafast photo-triggered ring-opening and ring-closing reactions are investigated, 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 and computational models to capture a complete picture of the dynamics. The work over the first two years focuses on the strained multi-ring reaction in the conversion of quadricyclane to norbornadiene and the possible 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 is the combination of multiple state-of-the-art probing methods that provide complementary information along with theoretical models 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 important strategic step is a concerted effort to employ several of the new and complementary techniques on a specific class of photochemical reactions. Application of complementary methods, coupled with a coordinated computational model and data analysis, is expected to yield significant new insights into the reaction dynamics and pathways.

The interconversion between different ring structures is an important theme in organic synthesis. Ring conversion reactions change the number of atoms in organic ring structures, and are therefore essential in the creation of a large number of cyclic molecular motifs. They involve a range of chemical transformations including redistribution of charges, creation or release of ring strain, making or breaking of aromaticity or electron conjugation, and the conversion between simple and complicated multi-ring motives. Ring interconversion reactions are an important theme in organic synthesis, industrial chemistry, chemical biology and pharmacology. Photochemically induced electrocyclic reactions in particular 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 rationalize pericyclic reactions, and play an important role in the photo-induced vision mechanism and the light-induced formation of previtamin D. To date, only a few select model systems have been studied using advanced time-resolved spectroscopic and scattering methods. Consequently, many aspects of the nuclear and electron dynamics of ring interconversion reactions remain unknown.

The experimental portfolio includes ultrafast electron and X-ray diffraction experiments that are directly sensitive to the nuclear and electronic structures of molecules. Ionization-based methods are also sensitive to the electronic and nuclear structures, and additionally to the energies of the orbitals, electronic states and vibrational states of the molecule. The ultrafast ionization-based experiments include ion mass spectrometry, Coulomb explosion imaging, photoelectron spectroscopy, and Rydberg fingerprint spectroscopy. All experiments are carried out in the PIs laboratories and at large-scale facilities such as the XFEL and MeV electron sources at SLAC National Lab, the European XFEL in Hamburg, and the FERMI FEL in Trieste.

Recent Progress

We report our recent experimental and theoretical progress in five sections: I. Interconversion of quadricyclane (QD) to norbornadiene (NB), which includes two complementary experimental measurements and theory; II. Coulomb explosion imaging, which shows clear differences between structural isomers; III. Ring-opening and ring-closing dynamics of cycloocta-1,3-diene (COD), which reports on MeV-UED experiments carried out at two different excitation wavelengths; IV. Simulations of electronic dynamics, scattering and high throughput simulations, which describes recent progress in theory and simulations; V. Determination of excited state structures, which focuses on methods of structural retrieval. The ultrafast electron diffraction experiments are led by M. Centurion, the Rydberg spectroscopy and ultrafast x-ray scattering experiments are led by P. Weber, the photoelectron spectroscopy measurements by D. Rolles, the Coulomb explosion imaging experiments by A. Rudenko, the theory development by K. Lopata and A. Kirrander. All PIs are currently working together on developing new methods and tools for combining multiple measurements and theory to produce a complete picture of the electronic and nuclear motions.

I. Interconversion of quadricyclane (QD) to norbornadiene (NB)

We employ a combination of time-resolved photo-electron spectroscopy (TRPES) measurements, ultrafast electron diffraction (UED) experiments and first-principles simulations to build a comprehensive understanding of the electronic and nuclear dynamics governing the photo-induced ring interconversion of quadricyclane (QD). Previous spectroscopic observations have proposed that QD isomerizes to norbornadiene (NB) upon photo-excitation to its Rydberg manifold by 208 nm light[1]. In the following sections, we present the results TRPES experiments carried out at the seeded free-electron laser facility FERMI, UED experiments performed at the SLAC National Accelerator Laboratory, and quantum dynamics simulations exploring the photo-induced ring interconversion of QD. Electronic wavepacket dynamics captured with TRPES will be combined with spatially resolved nuclear motions from UED to produce a cohesive model of the interconversion reaction. These experimental results will serve as a benchmark for quantum dynamics simulations, which will then be used to elucidate both electronic and nuclear dynamics and in turn augment our experimental findings.

I.1. Time-Resolved Photoelectron Spectroscopy with Free Electron Lasers

Here we discuss the results of an experimental study, where after the UV photoexcitation of QD, extreme ultraviolet (XUV) radiation from a free-electron laser was employed to probe the dynamical electronic structures in the molecule. The FERMI seeded FEL[2] provides sufficient photon energy to ionize both ground- and excited-state molecules, thus making it possible to probe the entire electronic excitation and relaxation pathway all the way to the ground-state photoproducts. In this case, 19-eV XUV photons were selected in order to be below the ionization energy of the helium carrier gas. The narrow bandwidth of 20 meV from this seeded FEL enables one to resolve the electronic structure between the different isomeric products.

Figure 1 shows a schematic of the measurement along with the experimental time-resolved photoelectron data. The latter are represented as a two-dimensional plot of the photoelectron yield as a function of binding energy and UV pump- FEL probe time delay quantified with a saturated color map. The reaction is triggered by absorption of a UV photon, lifting the molecular wavepacket out of the ground state. This is experimentally observed by the strong depletion (shown in blue) in the binding energy region of 7.5 to 8.7 eV, corresponding to ground-state QD[3].

As shown in the schematic in Fig. 1a, the UV pulse excites the molecule by promoting an electron from the outermost valence shell intoa Rydberg state with a binding energy between 1.5 and 2.5 eV.. The integrated photoelectron yield as a function of delay for this and other regions of interest are shown in figure 2. Comparing the temporal characteristics of the yield in the Rydberg region with other work that used 208 nm excitation wavelength, we see significantly shorter decay time constants of 191 fs versus 320 fs, of Rudakov and Weber[1]. The reason for the discrepancy is still under investigation, however we believe that it is due to the different excitation wavelengths that populate a different mix of Rydberg states (see Sec. I.3).

The enhancement in the electron yield shortly after time overlap at binding energies higher that the strong Rydberg peak, i.e. between 3.0 to 6.5 eV. is attributed to a relaxation through a valence state that evolves from the 3p states of QD, as observed upon excitation of norbornadiene[4] and other heterocyclic molecules[5]. At larger delays, the enhanced yield settles in the binding energy region between 6.5 and 7.5 eV, which we attribute to the formation of ground-state QD or NB with significant internal (vibrational) energy although competing depletion and enhancement signals make identification of photoproducts difficult. The latter can be aided with similar experiments of photoexcited dynamics of the norbornadiene system, as well as the structural dependent measurement of MeV-UED, especially at larger time delays.
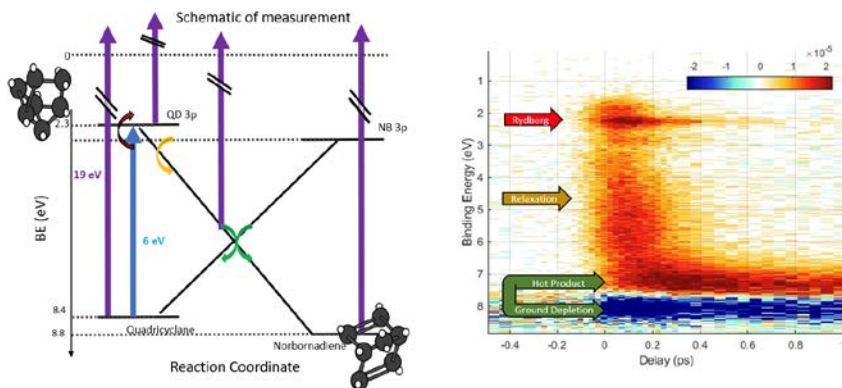
Figure 1: a) Schematic of the XUV ionization probing UV excited, ring reconfiguration isomerization of Quadricyclane. b) Experimental TRPES signal.

I.2. Ultrafast Electron Diffraction

Here we present the results of the UED study of QD and discuss our interpretation of the difference scattering signal. The UED experiment was carried out at the SLAC MeV-UED facility, described in detail in references[6,7]. Briefly, we used 3.7 mega-electron volt electrons pulses to probe a gas jet of QD. Structural changes triggered by optical excitation 200 nm laser light were captured in diffraction patterns recorded as a function of probe-pump delay. Figure 2A shows a false color plot of the difference-diffraction signal of QD generated by taking the difference between radial averaged diffraction patterns at time t and a reference signal recorded at a delay time before t = 0. These data revealed 3 time- dependent features: α, β and γ, centered at 0.75, 2.75 and $5.5 \overset{\circ}{A}^{-1}$ respectively. Feature α appears immediately after time-zero and consists of a fast-transient peak with a full-width-half-maximum of approximately 300 fs. This region of the momentum transfer spectrum does not typically encode structural information for a molecule the size of QD. Therefore, we assign this feature to a change in the electronic structure expressed as an increase in small angle inelastic scattering. A similar signature has been recently captured for the ultrafast internal conversion of the heterocyclic organic pyridine[8]. The lifetime of the transient α peak was found to be in good qualitative agreement with lifetimes reported by Weber and Rudakov for the 3p state of quadricyclane and 3s state of the photoproduct norbornadiene[1]. We, therefore, postulate that feature α may arise from the internal conversion of QD to NB to the ground state. However, our UED results cannot determine which states are involved in this change in electronic structure. For this information we rely on the finding from TRPES and simulations. The time evolution of features β and γ, shown in Figure 2B, revealed two different temporal profiles. Feature β shows a slightly faster rise time than its higher momentum-transfer space counterpart and its onset is delayed by 300 fs with respect to both time-zero and the onset of feature γ. The structural implication of these signatures remains to be assigned.
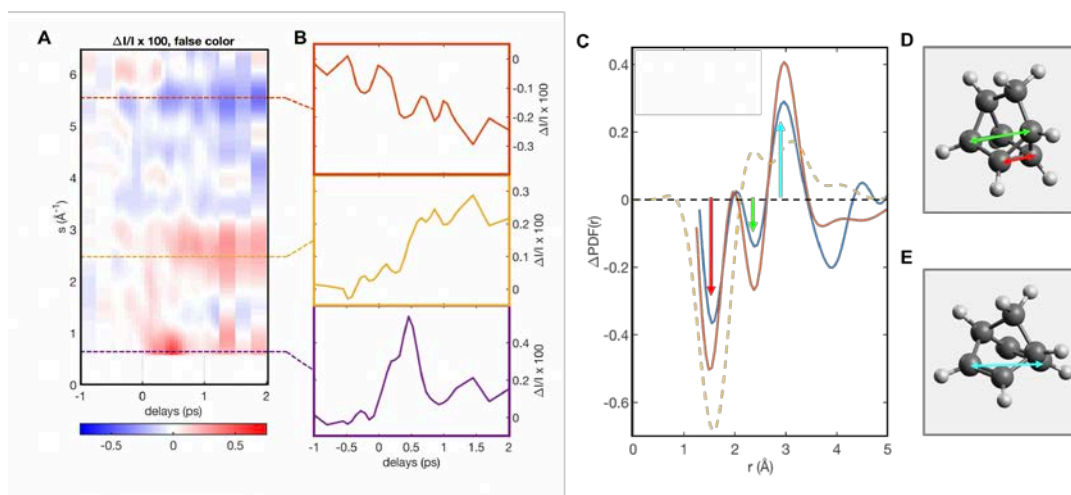
Figure 2: MeV UED reults. Panel A shows false color plot of the difference-diffraction signal of quadricyclane and panel B shows the time evolution of the 3 strongest features, α, β and γ from bottom to top. Panel C shows the simulated (dashed yellow) and experiment difference pair-distribution function of quadricyclane before 1 ps (blue) and after 20 ps (orange). Panels D and E show the geometries of quadricyclane and norbornadiene, respectively, with colored coded arrows illustrating the distances lost and gained upon photo-excitation

Figure 2C shows the difference-pair-distribution function, ΔPDF, calculated from the average difference-diffraction signal before 1 ps and after 20 ps. These data revealed a decrease in interatomic distances around 1.5 and 2.5˚A, which is consistent with the loss of C-C bonds and the nearest-neighbors C—C distances; an increase in distances around 3.5˚A, consistent with the formation of structure of with less ring-strain, such as NB. Although suggestive of the formation of NB, these signals do not match our simulations for the interconversion of QD to NB. These results suggest that

Figure 3: Example trajectory involving Rydberg interconversion, calculated using aug-cc-pVDZ- SCS-ADC(2). At ≈ 130 fs, the trajectory switches from QC to NB, breaking the three- and four- membered rings.

multiple pathways with structurally different products may play an active role in the photo-relaxation of QD. Moreover, the increase in signal amplitude between 1 and 20 ps, implied that some of these pathways may have time-constants in the order of a few picoseconds.

I.3. Electronic structure calculations and molecular dynamics

As the system is simulated after photoabsorption, the dynamics method must include a description of the non-adiabatic effects. The simplest method to perform this is surface hopping, where the nuclei are modelled classically, and propagate on electronic potential energy surfaces. The non-adiabatic effects are simulated by a probability of a trajectory "hopping" from one electronic state to another.

When performing surface hopping, a method to describe the electronic structure is needed. This molecule is challenging to describe, for a variety of reasons. The system displays a large motion from QC to NB, and the description must be consistent across the entirety of it. The Rydberg nature of the excited states necessitates a good description of dynamical correlation to calculate the correct excitation energy, and the Rydberg-valence coupling along the coordinate leads to sharp coupling.

CASSCF is widely used due to its ability to describe excited states on equal footing with the ground state, but its lack of stability and dynamical correlation can make it difficult to use with dynamics simulations. CASSCF necessitates the use of an 'active space', a subset of orbitals which are optimised. No suitable active space has yet been found for this molecule, and as such no attempt at dynamics with CASSCF has been performed. ADC(2) is an alternative electronic structure method to CASSCF which has recently gained popularity in the dynamics community. It can be thought of as an excited-state analogue to Møller-Plesset perturbation theory, relying on a ground-state wavefunction found using Hartree-Fock. ADC(2) scales well, and provides a good treatment of the dynamical correlation.

As the excitation energy of 6.2 eV is different from the 5.96 eV in the original Rudakov and Weber paper, careful simulation of the excitation process was performed to attempt to calculate the correct excitation character. ADC(2) predicts the character to be mostly 3p excitation, but with some 3s and some 3d excitation. Surface hopping trajectories are currently being

performed, and the system shows three broad motions. An ultrafast decay (< 30 fs), a longer decay where the molecule remains on the QC side, and a crossing motion similar to that proposed in Rudakov and Weber, where the wavepacket moves from QC to NB on the Rydberg manifold. An example trajectory of the last example is provided in figure 3. Ground-state calculations will be performed using ab initio molecular dynamics with MP2, which will give a long timescale to the dynamics, allowing for analysis of the fragmentation.

I.4. Multi-modal analysis

The multi-modal experimental study of QD has been extraordinarily beneficial to the development of an adequate theoretical description of its photo-induced dynamics. The size of QD can make reference calculations exceptionally time consuming. and thus, it can be challenging to fully benchmark the methods used without experimental assistance.

Another advantage of our multi-modal approach, has been the diversity of experimental observables highlighting areas which would benefit from further theoretical scrutiny. For example, the presence of time-dependent UED features in the picoseconds timescale, indicate that effort should be put into finding a good theoretical method for the simulation of picosecond dynamics in the ground state. For the case of the experimental TRPES, we clearly see different timescales for population decay for different photoproducts, this is ostensibly in good agreement with the longer timescale observed for maintaining the QD structure, as seen with the surface hopping calculations. Concentrating on this is an exceptionally useful starting point for simulations. The choice of ADC(2)/MP2 dynamics was informed by this data - the ease of the switch to the long term dynamics (and the length of time that can be calculated) should allow a good simulation of fragmentation patterns.

For TRPES, the observed short-term dynamics is crucial for us to look at the possible fast decay pathways. Further close study can be performed on these to see if the trajectories give the same TRPES data. This would immediately give us confidence in the trajectories, which is crucial when performing theoretical studies. Lastly, UED can provide information of additional product formation, including fragmentation of the molecule, beyond the QD-NB reconfiguration within the Rydberg manifold. Implementing this could prove vital for TRPES, as disentangling and identifying so many competing processes in the ground state region of the binding energy spectrum is unlikely to be feasible without some initial conjecture.

II. Coulomb Explosion Imaging

Complementing our work from the previous year, where we studied the strong-field induced fragmentation and isomerization of toluene using a combination of ultrafast electron diffraction and momentum-resolved coincidence ion mass spectroscopy[9], we recently investigated the same process by time-resolved Coulomb explosion imaging (CEI) at the European XFEL (EuXFEL). Conceptually, the experiment consisted of two parts: First, verifying that the XFEL-based CEI method, which we successfully demonstrated for iodopyridine and iodopyrazine molecules in a prior beamtime at EuXFEL[10], is also applicable to molecules without "marker atoms", i.e. consisting only of carbon and hydrogen atoms. And second, recording time-resolved CEI data in a pump-probe arrangement to study the strong-field induced fragmentation and isomerization process.

For the first part, we recorded static Coulomb explosion images for toluene and two of its isomers, cycloheptatriene (a seven-member ring) and heptadiyne (a seven-member chain), which

are possible products of the isomerization of interest. Preliminary Coulomb explosion images for the former two molecules are shown in Fig. 4. Both show a ring-like structure, and in the case of toluene, 6 atoms can be clearly distinguished (the seventh being the "reference" ion, which is not plotted). For cycloheptatriene, the atomic positions are not as clearly resolved in the preliminary data, but we are still working on identifying appropriate cuts through the three-dimensional momentum data.

While the pump-probe data is still being analyzed at the moment, the preliminary analysis during the beamtime showed clear differences in the

Figure 4: Coulomb explosion images of toluene and cycloheptatriene (C_7H_8). The experimental data taken at the European XFEL shows the momentum correlation between three singly charged carbon ions detected in coincidence. It is presented as 3-dimensional Newton scatter plots, where the momentum of one of the carbon ions is along the x-axis and the momenta of the other two fragments are plotted relative to that direction.

3-D Newton plots before and after time zero, suggesting that we are able to capture structural changes induced by the near-infrared pump pulse.

Inspired by the success of our EuXFEL experiment and the progress in the data analysis and visualization, we have recently also performed CEI experiments on various ring molecules with the 10-kHz PULSAR laser at JRML/KSU, which have also yielded similarly striking Newton plots as the one shown in Fig. 4.

III. Ring-opening and ring-closing dynamics of cycloocta-1,3-diene (COD)

The photoexcitation of cycloocta-1,3-diene (COD) can lead to multiple products including: ring-opening and formation of octa-1,3-diene, or ring closing and formation of the four-membered ring bicyclo [4.2.0]oct-7-ene. Using MeV-UED and UXRD, we aim to capture the electronic and nuclear dynamics that take place during the ring conversion, retrieve the structure of photoproducts and determine the abundance of different reaction pathways. The UED experiments were carried out in the Fall of 2020, using an excitation wavelength of 200 nm. During the same UED run, a second experiment let by Thomas Weinacht investigated the dynamics of COD excited at 260 nm. We are now collaborating in a joint analysis of the two data sets, which will allow us to not only determine the dynamics but also learn about the wavelength dependence.

We show here the analysis of the 200 nm data. Based on the signal level, we estimate an excitation percentage of approximately 5%. The data shown here corresponds to 12 hours of data acquisition, during which we have determined that there was a significant timing drift between the laser and electron pulses. We have corrected the relative timing drifts by splitting the whole data sets into 9 smaller subsets and fitting an error function to the most prominent features. The data is then re-binned in time. With this procedure, the overall instrument response function extracted from the data was improved from 160 fs to 120 fs, but most importantly new time-dependent features were revealed in the data, while other features became more prominent. Figure 5 shows the difference diffraction intensity divided by the ground state diffraction intensity $\Delta I/I$, which can be interpreted as a time-dependent percent difference signal in momentum space.
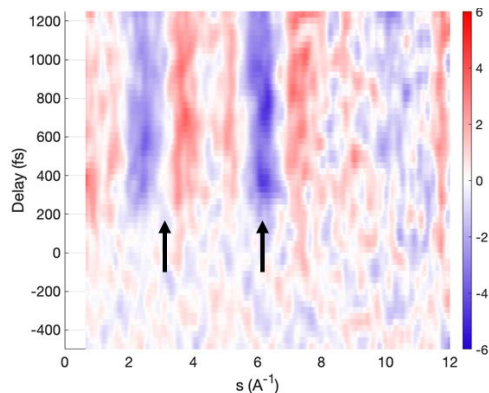
Figure 5. Diffraction difference signal after correcting for timing drifts shows oscillations in signal amplitude and position for up to a picosecond after excitation.

The data over the first few hundred femtoseconds has several features indicating a coherent structural motion, such as the periodic motion of the feature at 3.5 Å^{-1} and the amplitude modulation of the feature at 6.2Å^{-1} (indicated by arrows in the figure). The features observed at long times are qualitatively consistent with the simulated difference signal for many of the expected outcomes of a photoexcited COD, *i.e.* vibrationally hot COD, cis-trans isomerized COD and octa-1,3-diene. We have recently completed a bootstrap analysis of the data to generate error bars, which we will no use to fit the data and quantitatively determine the reaction end products. We have also observed, on both the 200 nm and the 260 nm data, stronger signals at longer time delays of tens of picoseconds. We are in the process of processing these signal to remove artifacts from changes in the electron beam pointing. The next step in the analysis is to analyze the signals in real space and compare with simulations.

IV. Simulations of electronic dynamics, scattering and high throughput simulations

Reconstruction of a reaction pathway from an X-ray/electron scattering experiment is challenging, as it requires a simulated X-ray/electron scattering pattern for a wide range of possible structures. In conjunction with the X-ray scattering experiments, we continued work on simulating scattering signals in molecules from

Figure 6.(a) Calculated percent differences in the X-ray scattering signal from the oxazole molecule upon core-hole ionization at various sites. The greater the localization of the core hole (O > N > C), the greater the change in the scattering. (b) These differences arise primarily from changes in the elastic part of the response.

first-principles. As X-rays scatter exclusively from electrons, these measurements selectively probe density distribution changes during a reaction, including both nuclear rearrangement, as well as changes to arising from charge density dynamics. In general, structures can include both neutral and ionized molecules in both ground and excited electronic states. Given the large number of structures, this necessitates a predictive but efficient means of computing the scattering from a particular structure/state, which can form the basis for a high throughput workflow. Traditional approaches to scattering theory based on atomic densities (e.g. the independent atom model; IAM) are not suitable for ionized molecules and cannot be applied to excited states.

To address this, we developed a method for computing scattering from ionized molecules with core-holes, based on density functional theory (DFT) for the ground state electronic structure[11]. Although typically less accurate than multi-configurational methods like CASSCF, DFT offers a good trade-off between accuracy and computational cost, which is advantageous for planned high-throughput simulations. To compute the differential cross-section, we used DFT to solve for ground state orbitals, and constructed a reduced two-electron density matrix (2RDM) for the corresponding stationary state. Fig. 6(a) shows the computed depletion in scattering for an oxazole molecule upon to core-hole creation at various sites on the molecule. These modulations are primarily due to changes in the elastic part of the scattering (Fig 6(b)). Generalizations to valence ionized and excited molecules is ongoing.

Additionally, we completed work simulating how X-ray scattering is sensitive to electron density dynamics following excitation via a resonant X-ray pump. Using a probability continuity argument, these attosecond X-ray scattering modulations can be viewed as probes of diverging electron current rather than density or holes. As shown in Fig. 7, the curved electron flows in an O 1s excited oxazole molecule (a) manifests as modulations in the X-ray scattering (c), with low Q signals at the times when there are long-range ring currents, and higher Q signals when there is density convergence/divergence on single atoms. These simulations set the stage for possible future scattering measurements at LCLS or similar facilities. To enable rapid computation of these and similar scattering patterns, we have begun implementation of an X-ray scattering module in the free/open source NWChem package based. The electron density (for a purely elastic scattering calculation) or the 2RDM will be computed using the standard DFT code, and the two-electron integrals and Fourier transform integrals can be carried out in a massively parallel fashionusing NWChem's existing architecture. The high-throughput method developments are matched by accurate calculations of elastic, inelastic and total scattering cross sections, both for X-rays and electrons, using high-level ab initio wavefunction methods such as complete active space self-consistent field (CASSCF) and multireference configuration interaction (MRCI), with further developments ongoing such as complete active space second-order perturbation

Figure 7. (top) Simulated attosecond ring currents in oxazole following O core-hole ionization with the corresponding time-dependent X-ray scattering signals (bottom). Long-range currents manifest as low Q signals, and currents flowing to/from single atoms give high Q signals.

theory (CASPT2) requiring the implementation of analytical gradients for CASPT2. An important advance is the implementation of computer codes that exploit analytical Fourier transforms of Gaussian-type primitive functions (GTO's), McMurchie-Davidson expansion coefficients, and the Gaussian product rule to achieve a degree of computational efficiency, as shown in Figure 8[12]. An important aspect is that rotational averaging, which is a computational bottleneck requiring onerous numerical integrations, is handled analytically. Furthermore, we have established a conceptually useful decomposition of the scattering signal into elastic and net inelastic contributions that relate to either molecular distortion (nuclear motion) or changes in
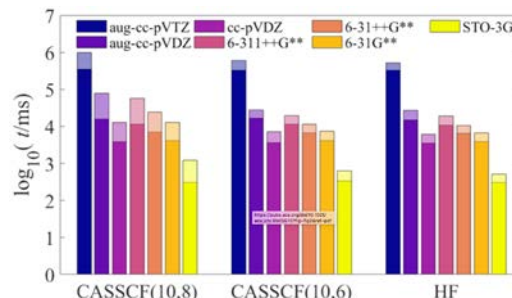
Figure 8.Comparison of the computational time required for the calculation of the isotropic elastic and total X-ray scattering signals in NH3. Different ab initio methods are considered, as well as basis sets. Note that the computational scaling is expressed as a logarithm of the CPU time in milliseconds. The solid part of the bars represents the elastic scattering, whereas the shaded area at the top shows the extra time required to compute the total scattering with the same level of theory and basis set.
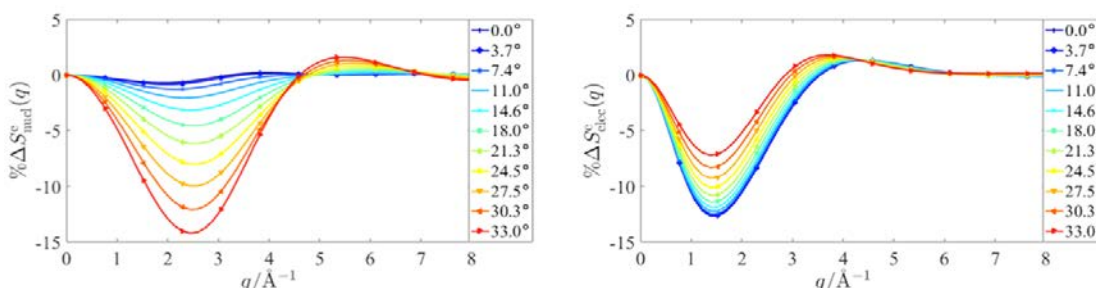
Figure 9. Breakdown of the total percentage fractional intensity change along the umbrella motion in the 3s Rydberg state of ammonia relative the ground state equilibrium geometry. The displacement along the normal mode is labeled in terms of the pyramidalization angle between NH bonds and the plane of the hydrogen atoms. On the left, the nuclear elastic component of the scattering and on the right the electronically elastic component. The electronic component is shifted to small q compared to valence electronic states due to the diffuse nature of the Rydberg state.

electronic structure in the absence of structural changes. This makes it possible to examine the qualitative and quantitative contribution of various scattering cross sections to the net signal, as shown for the molecule ammonia, NH_3, undergoing umbrella motion in the first excited 3p Rydberg electronic state, shown for the nuclear and electronic components in Figure 9.

It is worth noting that in the context of electron dynamics and electron flux, it is necessary to evaluate matrix elements that correspond to the interference of scattering cross-terms, also called coherent mixed scattering (CMS)[13]. These cross-sections will be key when analyzing experiments that probe for instance ring-currents, as discussed above. The capacity to calculate the CMS cross-sections has been included in the highly accurate codes and is being implemented in the DFT code which will greatly improve the accuracy of predicted scattering signals for comparatively large molecules.

Future Plans

Experimental: We will continue to carry out our experimental work both at our local laboratories and at large scale facilities. We have one upcoming beam time at SOLEIL in February 2022 (PI: Rolles) to measure UV and XUV absorption spectra of NB and QD. We have several pending beam time proposal at LCLS, several in which a member of our team is the PI and two where we will participate as collaborators: LX65 (PI: P. M. Weber): Tuning Strained-Ring Cyclization via Conical Intersections; LX87 (PI: D. Rolles): UV-Induced Bidirectional Ring-Interconversion of Quadricyclane and Norbornadiene LX93 (PI: R. Forbes): Competing reaction pathways: ring-opening versus bond cleavage in cyclic molecular systems LY05 (PI: T. Wolf): Structural Insight into Norrish Type-I Reactions of Cyclic Ketones LY78 (PI: A. Rudenko): Imaging femtosecond charge transfer in PENNA cation after site-specific valence photoionization. We have also submitted a proposal to FLASH to study a ring-conversion reaction using TREPS, and are planning to apply for beam time at the SLAC MeV UED facility for the next run in 2022.

A series of experiments is planned at KSU, UNL and Brown with participation of team members from the other labs: <u>KSU:</u> We will perform time-resolved momentum-resolved coincidence ion mass spectroscopy experiments on quadricyclane, norbornadiene, and methylated cyclopentadiene at variable pump wavelengths using our new deep-UV TOPAS. <u>UNL:</u> We will carry out UED experiments on 1,2,3,4-Tetramethyl-1,3-cyclopentadiene, excited at 267 nm. While previous Rydberg spectroscopy experiments by the Weber group at Brown have not detected significant structural transformations in the excited state, the method is not sensitive to changes that occur one the molecule returns to the ground state. Our UED experiments will probe structural changes that take place in the ground state. In order to reach a temporal resolution approaching 200 fs, we will set up a tilted laser pulse for the excitation to minimized group velocity dispersion. We previously successfully used tilted laser pulses at 800 nm in UED experiments. The vapor pressure of the sample is 6 Torr at room temperature, which is comparable to toluene, which we have previously investigated. <u>Brown:</u> Time-resolved photoionization-photoelectron spectroscopy experiments via Rydberg states will elucidate the pathway of ring conversion reactions through excited electronic states. Experiments will be performed on quadricyclane, norbornadiene and cyclopentadiene.Following intriguing indications from the prior experiments, we will explore the excitation wavelength dependence of these reactions. Work on a new photoelectron spectrometer will begin.

Theory: To facilitate interpretation of the X-ray and electron scattering simulations, we will continue work on developing methods for high-throughput first-principles simulations. This will include a range of techniques including DFT, TDDFT, CASSCF, with the goal of rapidly screen candidate structures for idenification in a scattering experiment. In a related but distinct direction, we are continuing efforts to quantify how X-ray scattering can be used as probe of attosecond electron density currents in molecules.

In a complimentary direction, our previous results suggest that given sufficient time-resolution, electron density flows can be measured via X-ray scattering. This opens the door to measuring the dynamics immediately preceding ring-opening, where ring-currents may play a role such as by selectively softening particular bonds. Many questions remain, however, including the role of initial state (specific core-hole, pump, ionization, etc) and the effect of nuclear motion. To answer these questions, we will continue work on implementing a time-dependent scattering

module directly in the real-time TDDFT code, followed by the addition of Ehrenfest electron/nuclear coupling.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

Yanwei Xiong, Kurtis Borne, Andrés Moreno Carrascosa, Sajib Kumar Saha, Kyle J. Wilkin, Mengqi Yang, Surjendu Bhattacharyya, Keyu Chen, Wenpeng Du, Lingyu Ma, Nathan Marshall, J. Pedro F. Nunes, Shashank Pathak, Zane Phelps, Xuan Xu, Haiwang Yong, Kenneth Lopata, Peter M. Weber, Artem Rudenko, Daniel Rolles and Martin Centurion, *Strong-field induced fragmentation and isomerization of toluene probed by ultrafast femtosecond electron diffraction and mass spectrometry,* Faraday Discussions 228, 39 (2021). https://doi.org/10.1039/D0FD00125B

Andrés Moreno Carrascosa, Mengqi Yang, Haiwang Yong, Lingyu Ma, Adam Kirrander, Peter M. Weber and Kenneth Lopata, *Mapping Static Core-Holes and Ring-Currents with X-ray Scattering* Faraday Discussions, 228, 60 (2021). DOI: 10.1039/D0FD00124D.

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Early Career: Probing Attosecond Bound Electron Dynamics Driven by Strong-Field Light Transients (DE-SC0019291)

Michael Chini

Department of Physics and CREOL, the College of Optics & Photonics

University of Central Florida, Orlando, FL 32816

E-mail: Michael.Chini@ucf.edu

Program Scope

The ability to measure and control ultrafast dynamics in electronically excited states of atomic and molecular systems has 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, with durations close to (or potentially below) a single optical cycle. The dynamics will be followed using extreme XUV spectroscopies based on the interference of the coherence emission with an isolated attosecond pulse produced via high-order harmonic generation.

The proposed measurements are based on attosecond interferometry, a technique which uses interference between of XUV light generated in two spatially-separated targets to characterize energy-dependent phases in photorecombination, and thereby characterize the structure of the electronic states of the target as well as the laser field-driven photoionization dynamics. To date, the technique has been used to characterize scattering phase shifts associated with electron scattering in atomic gases[1], including the Cooper minimum in argon, as well as strong-field effects such as Coulomb-laser coupling[2]. In these previous demonstrations, the XUV sources consisted of attosecond pulse trains generated by high-order harmonic generation (HHG), and therefore the interferences could be resolved, and the phases quantified, in discrete harmonic orders. Applying the same technique to characterize XUV coherences generated via strong-field excitation, for which the XUV emission spectrum is generated by XUV free-induction decay (XFID) of excited electronic states, is more challenging for several reasons. First, to generate an electronic wave packet with a high degree of coherence requires the use of intense, single-cycle field transients as the excitation pulses[3,4]. Furthermore, the coherent XFID signal therefore consists of discrete peaks in the vicinity of bound state resonances, thus requiring that the interfering pulse have a supercontinuum spectrum in the XUV. Finally, due to the low flux of XFID in comparison to HHG, it is preferred to perform experiments at high repetition rates. These three requirements necessitate the use of a high-repetition rate source of single-cycle field transients, both for exciting

coherent electronic wave packets and for generating the isolated attosecond pulses necessary for interferometry. While progress has been somewhat hampered by personnel restrictions in the laboratory associated with COVID-19, we have made substantial advances to the project goals.

To date, our efforts have largely focused on the generation and characterization of a high-repetition rate attosecond source based on pulse compression of a commercial ytterbium (Yb)-doped laser amplifier with pulse energy of up to 400 μJ, 280 fs pulse duration, and average power of up to 20 W (50 kHz maximum repetition rate at 400 μJ pulse energy, with higher repetition rates available at lower pulse energy). While Yb-based laser technology offers significant advantages over Ti:Sapphire and other femtosecond laser platforms in terms of high average power, excellent power and pointing stability, and low thermal load, the long pulse durations have prevented their widespread application to attosecond science. However, in 2020 we demonstrated 50-fold nonlinear compression of a Yb:KGW amplifier (400 μJ pulse energy, 280 fs pulse duration, maximum repetition rate of 50 kHz) to a duration of 1.6 optical cycles, through the use of a hollow-core fiber filled with N_2O gas and a chirped mirrors-based compressor[5] (Fig. 1). This was achieved with a fundamentally new approach to spectral broadening, in which "delayed" nonlinearities, such as those associated with rotational alignment in molecular gases[6], cause a dramatic enhancement of the spectral broadening when driven by lasers with relatively long pulse durations. The coherent supercontinuum generated in N_2O gas exceeded two optical octaves (~500-2100 nm), supporting sub-cycle pulse durations. However, the broad bandwidth far exceeds that of our chirped mirror compressor. The spectral phase of the supercontinuum was found to be well-behaved, and pulses of 5.8 fs (1.6 optical cycles at the central wavelength of 1074 nm) were compressed from a reduced bandwidth spanning ~700-1400 nm (Fig. 2). The complex electric field structure of the compressed pulses were measured using a new technique we developed based on multiphoton excitation in solids[7], and the 1.6-cycle source was found to be suitable for attosecond pulse generation and XUV supercontinuum generation in carrier-envelope phase (CEP)-integrated measurements.

The above measurements were performed at reduced repetition rates of <1 kHz and without CEP stabilization. However, the application of the XUV pulses we have generated to attosecond interferometry to the proposed attosecond interferometry measurements requires high repetition rate and CEP stability.
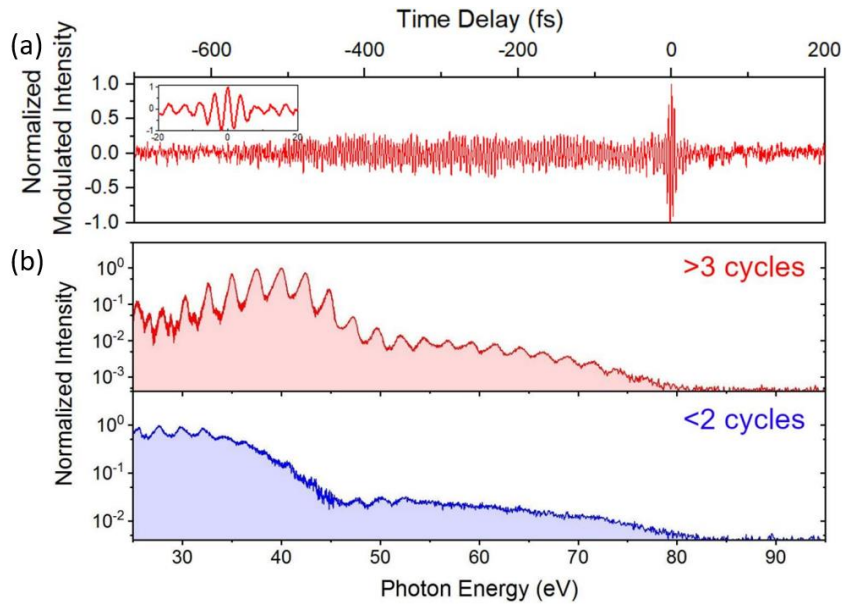
Figure 1: (a) Experimental waveform measured for pulses compressed in N_2O. (b) XUV spectra generated from pulses compressed in Xe (top) and N_2O (bottom).

Unfortunately, we have found that the use of molecular gases is likely unsuitable for use at high-repetition rates. This is because the repetitive laser interaction with the molecular gas leads to rotational heating of the gas medium and a loss of rotational coherence necessary for molecular alignment[8]. For repetition rates above 1 kHz, we observe a substantial reduction in both the spectral broadening and the energy throughput of the molecular gas-filled fiber, which is not the case when using atomic gases. As the "heating" is associated with the excitation of internal degrees of freedom, the spectrum is reduced after only a few pulses (e.g. on ~100 microsecond time scales, as shown in Fig. 3) and therefore conventional approaches to cooling the fiber are not suitable. For this reason, we have had to reconsider our approach to generating single-cycle transients. Instead of using a single fiber filled with a molecular gas, we will construct a two-stage compression system based on two consecutive fibers. In order to avoid losses in the two-fiber geometry, we have purchased a new fiber system with high transmission exceeding 90%. We plan to use this new fiber to compress the pulses to a duration below 30 fs, as we previously demonstrated using the standard fiber technology[9], and use our current fiber to further compress the pulses to single-cycle duration. This work is ongoing.

To convincingly demonstrate the generation of isolated attosecond pulses, it remains necessary to stabilize the CEP of the driving laser. After the COVID-19-related laboratory closures, we had significant difficulty to lock the CEP of our laser oscillator. After consulting with the manufacturer, we discovered that this was due to a fault that had somehow developed in the CEP detection electronics. We returned the unit to the company earlier this year, and only recently received it back. We anticipate that we will be able to stabilize the CEP of the driving laser, and characterize the CEP of the compressed pulses, in the coming months.

Finally, we have completed construction of our experimental setup for attosecond interferometry. In addition to the proposed experiments, the versatile instrument will also allow us to perform attosecond experiments in transient absorption and photoelectron velocity map imaging modes. We have so far used the setup to measure the high-order harmonic generation spectrum with long laser pulses, while the upgrade of the fiber and CEP stabilization are completed.

The research outcomes described above have also led to some work which, while somewhat beyond the scope of the original proposal, will have significant benefits to the program. These include the development of a novel technique for characterizing few-cycle laser waveforms and a collaborative project with Argonne National Laboratory to produce few-cycle pulses in the visible (~515 nm central wavelength) and ultraviolet (~343 nm central wavelength) regions of the spectrum. Results from these studies are expected to lead to a better understanding of how intense laser waveforms can be tailored for control of atomic and molecular excitation processes and to improvements in both the peak intensity and average power of isolated attosecond sources, due to favorable scaling of the high-order harmonic flux with shorter wavelength driving lasers. They will also allow us to drive XUV coherences in different regimes (e.g. multiphoton vs tunneling excitation) by varying the driving laser wavelength.

Future Plans

In the next year, we aim to characterize isolated attosecond pulses and XUV coherences using *in situ* perturbations of the driving laser field. This requires that we characterize the carrier-envelope phase (CEP) stability of the compressed pulses and measure the CEP dependence of both

the high-order harmonic spectrum and the XUV free-induction decay driven by the single-cycle pulses. These measurements will be completed using the recently constructed attosecond interferometry setup. Finally, we will perform the first measurements of attosecond interferometry using two isolated attosecond pulses before moving on to the proposed measurements of bound coherences.

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Peer-Reviewed Publications Resulting from this Project (2018-2021)
1. J. E. Beetar, M. Nrisimhamurty, T.-C. Truong, Y. Liu & M. Chini, "Thermal effects in molecular gas-filled hollow-core fibers," Optics Letters 46, 2437-2440 (2021).
2. Y. Liu, S. Gholam-Mirzaei, J. E. Beetar, J. Nesper, A. Yousif, M. Nrisimhamurty & M. Chini, "All-optical sampling of few-cycle infrared pulses using tunneling in a solid," Photonics Research 9, 929-936 (2021).
3. J. E. Beetar, M. Nrisimhamurty, T.-C. Truong, G. C. Nagar, Y. Liu, J. Nesper, O. Suarez, F. Rivas, Y. Wu, B. Shim & M. Chini, "Multioctave supercontinuum generation and frequency conversion based on rotational nonlinearity," Science Advances **6**, eabb5375 (2020).

Early Career: Atomic View of Molecular Photocatalysis using X-Ray Lasers

Amy Cordones-Hahn

SLAC National Accelerator Laboratory

2575 Sand Hill Rd., Menlo Park, CA, 94025

acordon@slac.stanford.edu

Project Scope:

Molecular photocatalysts have the potential to deliver an alternative sustainable method to produce fuels or other value-added chemicals using solar energy. Identifying the molecular properties that influence their excited state reactivity is a critical first step to creating new and efficient photocatalysts. This research program aims to pinpoint and control the electronic excited state reaction pathways of transition metal complex photocatalysts.

Nickel-based hydrogen-evolving catalysts with 'non-innocent' ligands, known to actively participate in the electron and proton transfer reactions of the catalyst, will serve as platforms to identify how catalyst charge distribution influences the excited state character and reaction mechanism. Achieving the ultimate goal of controlling photocatalytic reactivity first requires the ability to identify and manipulate the excited state charge distribution, relaxation mechanism, and geometry of the reaction site, which may involve metal or ligand atoms. These requirements inform the technical approach of this research, which exploits the atomic specificity and ultrafast time-resolution of X-ray spectroscopy at the Linac Coherent Light Source (LCLS) X-ray free electron laser.

Ultrafast X-ray spectroscopy probing metal and ligand atomic sites will be used to map the excited state charge distributions, determine the transient catalyst structures, and differentiate the mechanistic roles of metal vs. ligand reactive sites. Through these experiments, this research will establish: 1) how catalyst excited states initiate electron and proton transfer reactions, 2) the specific role of metal vs. ligand atom reactive sites, and 3) how to use ligand composition to influence critical excited state properties and reactivity. This novel approach using ultrafast X-ray methods to identify excited state reaction pathways and inform catalyst design will lead to new classes of molecular photocatalysts that efficiently convert solar energy to high value chemicals.

Recent Progress:

In the first year of this research program we have initiated studies of excited state relaxation processes and photochemical reaction mechanisms for two classes of Ni-based molecular photocatalysts for hydrogen evolution that contain 'non-innocent' ligands. First, Ni catalysts containing pyridine-2-thiolate (pyS) ligands were investigated to identify the role of metal versus ligand active sites in the light-driven proton reduction reaction of the catalyst, the first step of the hydrogen evolution catalytic cycle. Protonation has long been assumed to occur on the pyridyl N atom of the pyS ligand, accompanied by partial decoordination of the ligand at this site.[1–4] This proposed mechanism transforms the catalyst from a six-coordinate to a five-coordinate species that

is proposed to act as acceptor in the subsequent photo-induced electron transfer reactions. However, this proposed active species has never been isolated or characterized experimentally. Using a combination of in situ Ni K-edge and S K-edge x-ray absorption spectroscopy we directly probed the protonation mechanism of the catalyst. The Ni K-edge spectrum reports on the coordination geometry of Ni and the first coordination sphere bond lengths, while the S K-edge spectrum reports on the protonation state and metal coordination state of the pyS S atom. Our results indicate a new mechanism for protonation, not realized in previous optical spectroscopy measurements. We find that protonation of the pyS ligand N atoms results in total decoordination of the ligand, followed by solvent coordination at the open sites of the metal. This newly realized protonation mechanism results in two possible active species, a solvated Ni(II) species or a protonated pySH ligand, which can act as electron acceptor. We find that the solvated Ni complex accepts electrons in the subsequent photo-induced reduction reaction. These results highlight an important role for x-ray spectroscopy methods in identifying precise chemical reaction mechanisms, even differentiating metal versus ligand reactive sites, which is critical to understanding the role of 'non-innocent' ligands in photocatalysis.

The second goal we have addressed in the first year of this program extends this same combination of the metal and ligand atom x-ray absorption spectroscopy to the time domain to investigate the excited state relaxation processes of Ni-based hydrogen evolution photocatalysts with 'non-innocent' ligands. This work has focused on Ni bis(dithiolene) and related complexes that are characterized by their large metal-ligand covalency in their valence orbitals.[5,6] While this covalency is known to play a large role in dictating the redox reactions of the catalysts, little is known about how the ligands dictate their excited state charge distributions or excited state relaxation mechanisms, both critical to understanding how light absorption initiates the proton reduction reactions of the catalysts. We have focused on combining ultrafast Ni K-edge and S K-edge transient x-ray absorption spectroscopy to probe the excited state charge distribution on metal and ligand atomic sites and relaxation mechanism. We have recently measured the S K-edge transient absorption, which is sensitive to the changes in charge density on the ligand S atoms and the excited state electron configuration of the valence orbitals containing S character. Our preliminary analysis reveals that at early time delays the ligand S atoms undergo a partial oxidation, consistent with a ligand-to-metal charge transfer excitation. At longer time delays the difference spectra may be consistent with a high-spin excited state that is expected to also result in large changes in the Ni coordination geometry. Upcoming Ni K-edge transient absorption experiments will provide complementary information on the excited state charge distribution on the metal site, and will be particularly sensitive to any predicted changes in the photocatalyst structure in the excited state.

Future Plans:

The future plans for this research program will continue to emphasize a combination of metal and ligand atom x-ray spectroscopies to understand how strong metal-ligand covalency influences the photochemical reactions and excited state relaxation processes of Ni-based hydrogen evolving

photocatalysts. Our immediate plans focus on the completion of time-resolved Ni K-edge x-ray absorption experiments at the LCLS to identify the changes in structure and metal-based charge distribution following excitation of the Ni bis(dithiolene) and related photocatalysts, to complement the time-resolved S K-edge absorption experiments recently completed. As high repetition rate soft x-ray methods become available with the LCLS-II upgrade, these studies will be extended to the soft x-ray regime to focus on the Ni L-edge as a direct probe of metal-ligand covalency in the excited state. This work will focus on a series of photocatalyst ligand composition and charge states with varied metal-ligand covalency to identify the influence of this design property on excited state reactivity.

In parallel, this program will also focus on using metal and ligand atom x-ray spectroscopy to probe the longer photochemical reaction timescales to identify the light driven electron and proton transfer reaction mechanisms of this same class of molecular catalysts. We will identify the metal or ligand-based reactive sites of the photocatalysts by mapping how charge is localized following photoreduction and by identifying the proton binding sites. Again, soft x-ray spectroscopy probes sensitive to the metal or ligand atomic charge and protonation state will enable sensitivity to these properties on the slower timescales of chemical reactivity. We will identify how the changes in ligand composition described above influence not only excited state character, but also photochemical reaction pathway.

The later stages of this program will build on the understanding of how covalent ligands influence excited state character, dynamics, and reactivity (established as described above). We will systematically tune ligand design in order to promote more reactive excited states (e.g., ones that localize charge on the reactive atomic site of the catalyst) and extend their lifetimes. Besides the ligand design strategies described above, we will also explore heteroleptic complexes that undergo excited state charge transfer from one ligand to another.

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Peer-Reviewed Publications Resulting from this Project (Project start date: 09/2020):

No publications to report.

Probing electron and vibrational excitations, and their interactions, using coherent multidimensional techniques
DE-SC0021171

Steven T. Cundiff

Department of Physics, University of Michigan, Ann Arbor, MI 48109

cundiff@umich.edu

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Project Scope: This project will develop and demonstrate multidimensional coherent spectroscopy (MDCS) [1] techniques to fully map wave-packet dynamics in simple molecules. The MDCS techniques will allow the wave-packet evolution to be recorded continuously. The initial experiments will be performed using the existing MDCS apparatus in the lab to record the evolution of the wave-packet's energy. A version that is compatible with using an XFEL as a probe will be developed. Using the XFEL will allow the evolution of the position of the wave-packet, not just its energy, to be determined [2].

Recent Progress: This project started in August of 2020. Progress has been made over the last year, however it has been significantly impacted by the COVID pandemic, due to both restrictions on laboratory access and procurement/supply chain delays.

An important first step was to replace the existing, out-dated laser system with a new one, which was procured using a combination of grant and university funds. We identified a ytterbium based bulk optic oscillator/amplifier combined with a non-colinear optical parametric oscillator as the best solution and initiated the procurement process. The delivery of the system was delayed by several months as it is manufactured in Europe and the vendor had supply chain issues. Once it was delivered, installation was also delayed due to travel restrictions for vendor field-service personnel. Final installation and commissioning was completed in May, 2021, approximately 6 months later than the original timeline. The system is working and meeting specification.

In parallel with the acquisition of the laser system, we designed and procured the iodine cell. While iodine cells for stabilizing laser are available off-the-shelf, they are typically several centimeters long, which is not compatible with the crossed-beam geometry of the MDCS experiment. The optimum cell thickness is determined by balancing several considerations. The aforementioned length of the beam crossing regions is one. The vapor density as a function of temperature, which is limited by the maximum temperature for the cell based on the cell material, also needs to be considered. The optimum vapor density should result in approximately 50% absorption and the peak of the absorption lines to minimize distortion of the MDCS spectra [3]. Based on balancing these we conclude that a 0.5 mm thickness was optimum and found a vendor that could fabricate a cell of this thickness at a reasonable cost.

After finalizing the cell design, we designed and fabricated in-house a sample holder with integral heater. A temperature controller was also assembled using off-the-shelf components. Upon receipt of the sample cell, it was installed in the holder and basic checks performed including taking absorption and fluorescence spectra.

Changing the light source for the ultrafast pulses used for the spectroscopy, also meant that a separate CW laser was needed for the reference beam used to implement active locking of the path lengths in the Multidimensional Optical Nonlinear SpecTrometer (MONSTr). The previous ultrafast system used a 532

nm CW pump laser, from which we split off a small portion to use as a reference laser. The new system is fully integrated and directly pumps the ytterbium gain medium with diode bars. Thus we acquired a 50 mW CW double Nd:YAG laser to provide the reference beam.

The new light ultrafast light source and the new reference laser have been aligned into the MONSTr. Time-zero for the ultrafast pulses has been determined. We are in the process of tuning the feedback loops that lock the pathlengths of the arms. Once this is complete, we will begin producing 2D coherent spectra and begin a science campaign of tracking wave-packet motion.

Future plans: The science goals for the next two years of the project will focus on answering the following questions:

- Can the evolution of the energy of a wave packet in a diatomic molecule be fully mapped using multidimensional coherent spectroscopy?
- Can wave packets on different potential energy surfaces be separated using coherent techniques?
- Can these methods be adapted to using an XFEL as a probe to map the internuclear distance of the wave packet rather than just the energy?
- Do these methods open the door to studying wave packet dynamics in more complex molecules?

The goal of the first phase of the project is to use MDCS to provide a complete and detailed map the energetic evolution of wave-packets, starting with simple molecules with known potential energy surfaces. Building on this initial step, we will attempt to invert the problem and seek to use the wave-packet dynamics to characterize the potential energy surfaces to develop a tool for measuring the surfaces in molecules where they are not known. We will also look at molecules that have more complex electronic structure, for example, many potential energy surfaces that can be simultaneously excited, avoided crossings and conical intersections that result in non-adiabatic dynamics.

The key concept is that MDCS correlates the frequency at which the nonlinear signal is emitted with the corresponding absorption energy, even though the optical pulses that produce the initial excitation and stimulate the final signal are broadband. By scanning the waiting time, T, between the initial pulse pair that creates the excitation and the third pulse the stimulates the signal, it will then be possible to map the energy shift between excitation and emission, even if there are multiple wavepackets evolving simultaneously. This method is directly analogous to tracking the energetic shifts during spectral diffusion of excitons [4]. These data will provide continuous tracking of the energy of a wave-packet. However, the data will not directly measure the position of the wavepacket, the position will have to be inferred from the potential energy surfaces. To directly measure the position of the wave-packet will require using the diffraction pattern provided by a time-resolved hard X-ray probes, as can be done at the LCLS and discussed below.

Although the 2DCS data will not directly give the position of the wave-packet, it may be possible to infer the position of the wave-packet through kinematics. Since the 2DCS tracks the change in potential energy of the wave-packet, the velocity of the wave-packet can be estimated since the change in kinetic energy is equal to the change in potential energy, the velocity can be determined and integrated to get the position. The confounding factor will be that the measured potential energy is the difference between the electronic states, not the absolute potential energy, thus the ground state potential energy curve must be taken into account. However, the excitation process will also launch a wavepacket in the electronic ground state through a Raman process. If this packet can be simultaneously tracked, it may be possible to fully determine both surfaces.

The initial experiments will be performed in iodine to connect with the previous pump-probe measurements [5] and the LCLS experiments [2] and because its transition energies are a good match for the wavelengths produced by the laser system. However, the large changes in the potential energy surfaces mean that even the enhanced bandwidth of the NOPA will be insufficient to probe the wavepacket dynamics over a large enough range of nuclear motion, thus we will look at using continuum generation to produce even

more bandwidth, either for all pulses, or just the final pulse plus local oscillator.

Once we have established the basic concepts using iodine, we will investigate other simple molecules, specifically those with more complicated potential energy surfaces than iodine. The exact molecule will be determined once the initial results on iodine are obtained. One set of possibilities are alkali metal dimers as the PI's lab has experience with making vapor cells for these atomic species, which always contain some fraction of the atoms bound in dimers.

A 3D coherent spectrum allows individual pathways to be isolated and characterized [6]. The concept of a well-defined pathway applies when a discrete level picture applies. In a molecular system this is the case when there are well define vibrational levels for the ground and electronically excited state. The oscillations evident in prior work show that is the case in iodine. However there are also clearly non-oscillatory components corresponding to motion of the wavepacket that is not vibrational. In this situation, the wavepacket will disperse. The dispersion of the wavepacket with time corresponds to a loss of internal coherence, which will also be revealed by a 3D coherent spectrum.

A sequence of 2D coherent spectra, which are generated by Fourier transforming with respect to delays τ and t as a function of the waiting time T between the second and third pulses, will be a function of three dimensions, they do not necessarily allow the generation of a full 3D *coherent* spectrum. To do so requires that the overall phase be stable between successive 2D spectra such that the real and imaginary parts are properly defined and the Fourier transform with respect to T produces the appropriate sign for the frequencies.

We will take full 3D coherent spectra on iodine to start with, again to connect to the prior work, both by others and by the PI's group. By analyzing the lineshapes in a 3D space we will be able to separate the effects of dephasing versus anharmonicity in the potential surfaces on the dispersal of the wave-packets. For unbound wave-packets, there will not be distinct peaks in the 3D spectra, nevertheless an analysis of the spectrum will allow the dispersion of the wave-packet due purely to deterministic evolution on the potential energy surface to be separated from lost internal coherence due to dephasing processes.

In some situations a 3D spectrum can also distinguish between wave-packets on the ground state potential versus the electronically excited state potential. If the thermal excitation of the higher vibrational modes of the ground-state potential is minimal, then the Raman coherence in the ground state must evolve at a negative frequency, whereas those in the excited state can evolve with either positive or negative frequency. Thus the positive frequency components must be due to excited state Raman coherences and the difference between positive and negative frequency components are due to the ground state Raman coherences.

The work described thus far will be purely optical, in the sense that the excitation and observable signal are all optical. While these experiments can provide unprecedented detail in mapping the evolution of the energy of a wave-packet, by monitoring the frequency and phase of the emitted signal, they do not directly measure the inter-nuclear separation of the molecule. Directly measuring the inter-nuclear separation can be achieved by using diffraction of hard x-ray pulses from an XFEL, however that data does not indicate the origin of the wave-packet, which can be done with multidimensional coherent methods, as described in the previous sections.

To marry multidimensional coherent methods with x-ray probes, requires a different approach than used by our current apparatus. The current apparatus uses excitation beams with distinct directions, such that their interference results in a spatial modulation of the excited state populations, which forms the grating that is mapped into the absorption and acts as a diffraction grating to scatter the final pulse into the signal directions. The resulting spatially inhomogeneous excited state populations would give spatially varying x-ray diffraction patterns, which would average out. To overcome this problem, fully collinear beams are needed to realize a spatially uniform excitation. The simplest implementation is to use pulse pair for the excitation in an experiment similar to that performed by Glownia et al. [2]. The challenge will be to separate the diffraction due to the pulse pair rather than the individual pulses. This can be realized by exploiting the sensitivity to the relative phase of the two pulses and cycling the phase such that the signals due to the

individual pulses cancel, whereas that due to the pair adds constructively.

There have been several approaches to using fully collinear excitation pulses to implement multidimensional coherent spectroscopy. A very early implementation used a pulse shaper to generate 4 phase locked pulses and a fluorescence signal as the observable [7]. Another approach uses a pulse shaper to generate a phase locked pulse pair and a separate beam as a probe, which also acts as the local oscillator [8]. The use of acousto-optic based pulse shapers, such as the commercially available 'Dazzler' are limited to low repetition rates of 30 kHz and below, which makes them incompatible with the planned upgrade to LCLS. Static pulse shapers based on liquid crystal spatial light modulators are a possibility, but are relatively inefficient and have limitations on handling high power pulses. Thus neither of these seem like a good option and we propose two alternate approaches.

As part of this project we will develop methods that are compatible with using LCLS to probe nuclear motion. The goal would not be a full MDCS experiment, but rather using a phase locked pulse pair to replace the excitation pulse and show the phase cycling can be used with LCLS diffraction experiments to tag the initial excitation energy of the observed wave-packet. The basic concepts will be demonstrated in the PI's laboratory using an optical probe, rather than an x-ray probe. Where appropriate, the relevant apparatus would be built in a modular fashion such that it could be shipped to SLAC and used with laser sources available there. Of course, doing so would require a successful proposal for beam time on a future LCLS run.

Peer-Reviewed Publications resulting from this project (2019-2021): None as this project started in 2020.

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

DOE Grant No. DE-SC0002325

Marcos Dantus, dantus@msu.edu

Department of Chemistry and Department of Physics and Astronomy, Michigan State University, East Lansing MI 48824

Project Scope

Advances over the past two decades in our understanding of laser-matter interactions allow us to consider strategies for not only observing but also *controlling* the different processes and reactions that these interactions cause. The proposed research on the chemical processes occurring in polyatomic molecules under intense laser excitation, and on quantum control of electronic, vibrational, and rotational dynamics of molecules prior to and during strong-field interactions, is in line with Grand Challenge questions that have been proposed in recent DOE- and NSF-sponsored workshops. This project augments the chemical perspective, as strong-field science addresses interactions with larger molecular systems. We consider important chemical reaction dynamic and mechanistic questions occurring in large molecules that can be uniquely answered by strong-field methods. In the coming period we plan to explore the influence of electronegativity and molecular strain on the primary reaction mechanisms that lead to the production of H_3^+. In addition, we propose to explore the dynamics and control of two types of systems, one producing H_3^+, where the key aspect involves controlling the ionization at a sulfur or oxygen atom, and the second involving controlling the coupled electronic and nuclear dynamics to determine the fragment that carries the charge following strong-field induced (SFI) induced pericyclic reactions.

Recent Progress

(a) Control of electron recollision and molecular nonsequential double ionization

S. Li, D. Sierra-Costa, M. J. Michie, I. Ben-Itzhak and M. Dantus, *Commun. Phys.* **3**, 35 (2020).

Intense laser pulses, lasting a few optical cycles, ionize molecules via different mechanisms. One such mechanism involves a process whereby within one optical period an electron tunnels away from the molecule and is then accelerated and driven back as the laser field reverses its direction, colliding with the parent molecule and causing correlated nonsequential double ionization (NSDI). Here we report control over NSDI via spectral-phase pulse shaping of femtosecond laser pulses. The measurements are carried out on ethane molecules using shaped pulses. The results are shown in the partial mass spectrum obtained with shaped pulses, as shown in Figure 1. We find that the shaped pulses can enhance or suppress the yield of dications resulting from electron recollision by factors of 3 to 6. This type of shaped pulses is likely to impact all phenomena stemming from electron recollision processes induced by strong laser fields, such as above threshold ionization, high harmonic generation, attosecond pulse generation, and laser-induced electron diffraction.
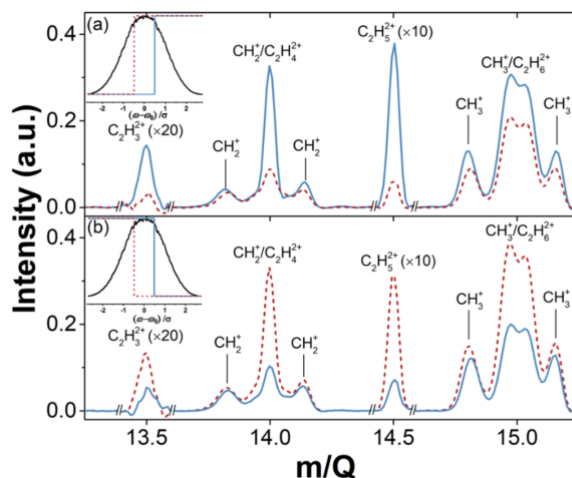
Figure. 1. *Portion of the mass spectrum of ethane obtained using shaped pulses with a positive (top) or negative (bottom) ¾π phase step in either the high energy (blue) or low energy (red) portion of the laser spectrum. The position of the phase step is indicated in the laser pulse spectrum shown as an inset in the upper left corner. The phase step serves to enhance or suppress the yield of doubly charged fragment ions.*

(b) Milliradian precision ultrafast pulse control for spectral phase metrology
J. Stamm, J. Benel, E. Escoto, G. Steinmeyer, M. Dantus, *Opt. Express* **29**, 14314–14325 (2021).

An early revelation in our search to determine the cause for the observed control of NSDI discussed in the previous project was finding that a phase-step with amplitude $\pi/2$ causes drastic changes in the second harmonic generation (SHG) of femtosecond pulses. This observation has resulted in a significant advancement in ultrafast laser technology, namely, the introduction of milliradian precision ultrafast pulse control for spectral phase metrology. Figure 2 shows how pulses compressed by this new method achieve outstanding pulse compression, as evidenced by interferometric frequency-resolved optical gating (FROG). Independent analysis of the measurement by our collaborators revealed the pulse duration was 17 fs with < 1 fs^2 uncompensated chirp and ~ 20 fs^3 third-order dispersion.
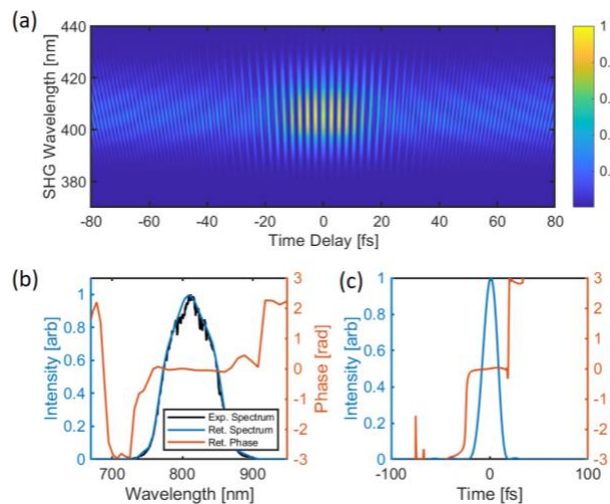
Figure. 2. *(a) Experimental 2D Interferometric FROG after compression using MIIPS and the $\pi/2$-step method. (b) Experimental and retrieved power spectrum of the laser with the retrieved spectral phase. (c) Retrieved temporal intensity and phase.*

(c) Femtosecond dynamics and coherence of ionic retro-Diels-Alder reactions
S. Li, B. Jochim, J. E. Jackson, M. Dantus, *J. Chem. Phys.* **155**, 044303 (2021).

The question of concertedness in retro-Diels-Alder (rDA) reactions in molecular cations has interested chemists because there is indirect evidence that such reactions occur in EI-MS. Our femtosecond time-resolved studies following SFI-pump and near infrared disruptive probing revealed that the rDA reaction in cyclohexene occurs in ~80 ps. The reaction in norbornene and DCPD takes place in ~2.5 ps, and we observed evidence for coherent vibrational motion that correlates with product formation (see Figure 3). In-depth analysis of the norbornene data together with quantum calculations allowed us to identify the 270 cm^{-1} long lived coherent vibrational motion, which correlates with product formation in what is likely a concerted process.
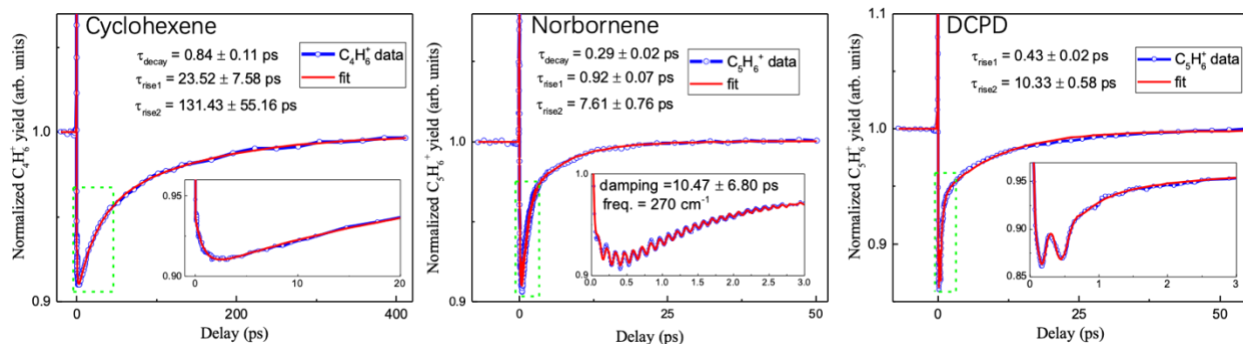
Figure 3. *The main product from the rDA reaction in cyclohexene (left), norbornene (middle), and DCPD (right), is plotted as a function of time delay between the pump pulse causing SFI, and the weak probe pulse that disrupts product formation.*

(d) Pulse shaping in strong-field ionization: theory and experiments

S. Li, B. Jochim, J. Stamm, D. Peng, H-C. Shao, J. M. Ngoko Djiokap, M. Dantus, *Phys. Rev. A* submitted (2021).

Intense ultrafast pulses cause dissociative ionization and shaping the pulses may allow control of both electronic and nuclear processes that determine ion yields. We report on a combined experimental and theoretical effort to determine how shaped laser pulses affect tunnel ionization, the step that precedes many strong-field phenomena. We carried out experiments on Ar, H_2O, N_2 and O_2 using a phase step function of amplitude $\frac{3}{4}\pi$ that is scanned across the spectrum of the pulse. Semiclassical as well as fully quantum mechanical time-dependent Schrödinger equation calculations are found to be in excellent agreement with experimental results, as shown in Figure 4. We find that precise knowledge of the field parameters in the time and frequency domains is essential to afford reproducible results and quantitative theory and experiment comparisons.
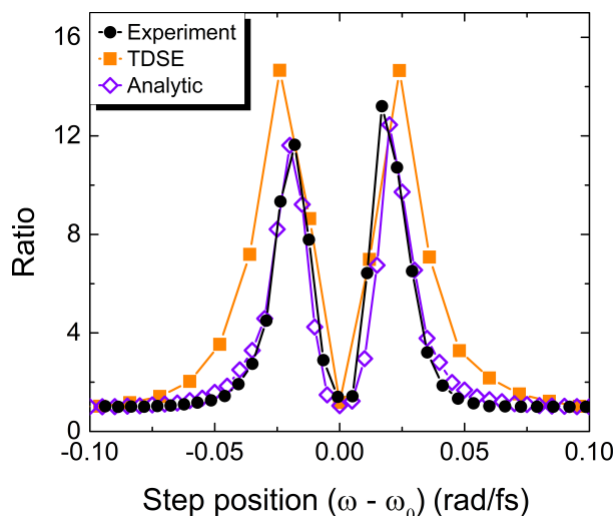
Figure. 4. *Results from simulations based on an analytic ADK formula and from quantum mechanical TDSE calculations for Ar atoms. The analytic results are scaled down by a factor of 5 to match the experimental figure, and the TDSE results have not been scaled, showing excellent agreement with experiment.*

(e) Ultrafast Disruptive Probing: Simultaneously keeping track of tens of reaction pathways

B. Jochim, L. DeJesus, M. Dantus, *Phys. Chem. Chem. Phys*. In review (2021).

Ultrafast science depends on different implementations of the well-known pump-probe method. Here we provide a formal description of ultrafast disruptive probing, a method in which the probe pulse merely perturbs a transient species that may be a metastable ion or a transient state of matter. Disruptive probing has the advantage of allowing simultaneous tracking of the yield of tens of different processes. We describe the model and the expected signals based on a kinetic model. Experimental data on multiple products resulting from the strong-field ionization of two different molecules, methanol and norbornene, are then analyzed using the model. Disruptive probing in combination with ion imaging and/or coincidence momentum imaging, or as complementary to atom-specific probing or ultrafast diffraction methods, is a particularly powerful tool for the study of strong-field laser-matter interactions.
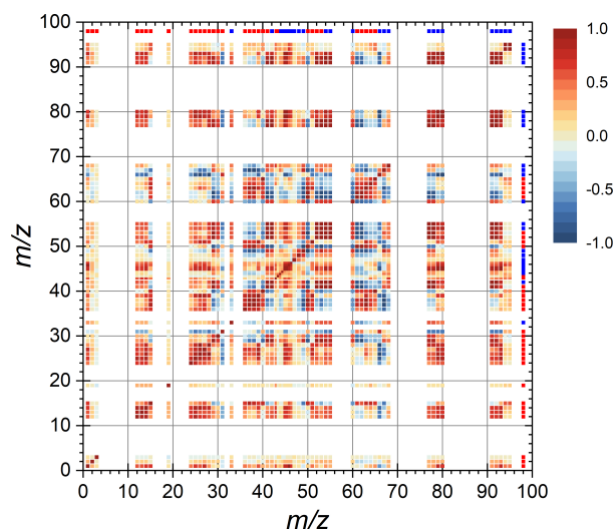
Figure. 5. *Pearson correlation map of the 60 distinguishable ions detected following strong-field ionization of norbornene. Most transient signals show either a short-lived enhancement (red) or depletion (blue) as shown in row/column98.*

Future Plans

i. We have obtained time resolved for assessing the formation of H_3^+ following the dissociative ionization of ethane. We find H_3^+ on average forms in 490 ± 80 fs, while D_3^+ forms in 530 ± 80 fs. These timescales are almost a factor of 5 longer than those measured for H_3^+ formation in CH_3OD, indicating a very different mechanism is at play. In collaboration with Prof. Benjamin Levine, we find that doubly ionized ethane favors hydrogen migration. This is quite different from the isoelectronic system, methanol, which we have previously demonstrated undergoes an unusual H_2 roaming mechanism in 100 fs. A π-backbonding interaction in ethane prevents roaming but facilitates H migration. For methanol, this backbonding interaction is weaker, thus facilitating roaming H_2.

ii. We plan to carry out a series of measurements on substituted methanes (CH_3X). Photoelectron experiments on CH_3I have failed to form H_3^+, and those on CH_3Br form only a trace. However, it is known that CH_3Cl and CH_3F will more readily form H_3^+. We surmise that this is due to their higher electronegativity, and the resulting reduced electron density at the carbon will prevent π-backbonding to the H_2 moiety. Following experiments on CH_3Cl and CH_3F, we will explore compounds containing the pseudohalogens NCS, N_3, and NCO, which are functional groups listed in order of increasing electronegativity. Preliminary experiments on CH_3NCS show that H_3^+ is formed readily. In addition, we find the product ion CH_3S^+, a result of intramolecular rearrangement.

iii. We plan to explore the dynamics and control of two types of systems. For 2-mercaptoethanol (2ME, HS CH_2CH_2OD), H_3^+ or H_2D^+ formation will depend on controlling the ionization at the sulfur or oxygen atom. The second project will involve controlling the coupled electronic and nuclear dynamics in substituted dicyclopentadiene molecules to determine which fragment carries the charge following SFI induced pericyclic reactions.

iv. We look forward to taking advantage of the traveling velocity map imaging instrument from Kansas State University, and the Timepix3 camera we recently obtained through a collaborative (Augustana, MSU, UVA, KSU, U of Mary Washington) NSF-MRI grant. In addition, we are planning to collaborate with Oliver Gessner and Stephen Leone on time resolved X-ray absorption spectroscopy experiments on 2ME, where the L edges of sulfur will indicate if the -SH proton has been lost and the K-edge of oxygen will indicate if the -OH proton has been lost. Finally, we are planning to collaborate on time-resolved electron diffraction experiments with Martin Centurion to be carried out on dicyclopentadiene, a molecule which upon strong-field ionization produces two cyclopentadiene fragments within one picosecond and shows evidence of vibrational coherence.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

M. J. Michie, N. Ekanayake, N. P. Weingartz, J. Stamm, M. Dantus, "Quantum coherent control of H_3^+ formation in strong fields" *J. Chem. Phys.* **150**, 044303 1−7 (2019).

S. Li, D. Sierra-Costa, M. J. Michie, I. Ben-Itzhak M. Dantus, "Control of electron recollision and molecular nonsequential double ionization," *Commun. Phys.* **3**, 35 1−8 (2020).

J. Stamm, J. Benel, E. Escoto, G. Steinmeyer, M. Dantus, "Milliradian precision ultrafast pulse control for spectral phase metrology," *Opt. Express* **29**, 14314–14325 (2021).

S. Li, B. Jochim, J. E. Jackson, M. Dantus, "Femtosecond dynamics and coherence of ionic retro-Diels-Alder reactions," *J. Chem. Phys.* **155**, 044303 (2021).

J. Stamm, M. Dantus, "A comparison of strategies for state-selective coherent Raman excitation," *J. Raman Spectroscopy* **29**, 14314–14325 (2021).

PROGRAM TITLE: ATTOSECOND, IMAGING AND ULTRA-FAST X-RAY SCIENCE

AWARD NUMBER: DE-FG-04ER15614

PI: Louis F. DiMauro
Department of Physics
The Ohio State University
Columbus, OH 43210
dimauro.6@osu.edu

1.1 PROJECT SCOPE

The grant aims at exploring the realm of ultrafast electron and molecular 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 utilizing 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) commissioning and application of the strong field simulator concept using combined mid-infrared and attosecond pulse trains, (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 FY2020

The description below reflects our progress while facing the challenges of COVID. The end of abstract includes a statement of COVID impact.

The Strong Field Simulator concept. A main thrust in our laboratory was to develop a new instrument capable of fully exploiting quantum trajectory control, we dubbed this method the strong field simulator. In typical strong field ionization experiments, a single high-intensity MIR 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). In this program, we are interested in simulating these processes in Helium and other systems. Helium is an ideal platform for studying electron-electron interactions in strong-field processes since it is most accessible multi-electron system for theoretical investigation.

In the semi-classical 3-step view, tunnel ionization and wave packet propagation are directly coupled by the same low-frequency (MIR) strong field. This significantly constrains the ability to control the abovementioned processes. To circumvent this, we employ the strong field simulator (SFS) scheme, which replaces the tunnel ionization (step 1 in the 3-step model) with photoionization by an attosecond XUV pulse. The decoupling of ionization and propagation, driven by a low-frequency MIR dressing field, 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 MIR field. Tuning other properties of the XUV and MIR pulse opens additional avenues for investigation.

In 2019, we proposed to build a new attosecond beamline dedicated and optimized for performing SFS measurements. The SFS beamline focused on improving sensitivity based on three criteria which limited our pre-2019 exploratory experiments: (1) increased XUV flux in the interaction region (better S/N), (2) background contamination in our detection chamber (reducing noise), (3) passive interferometric stability (improved temporal resolution) and (4) better spectral selection near the helium threshold (24.6 eV). 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

Figure 1: The SFS concept is illustrated by the four PES taken by exciting helium with a APT centered at 25 eV and a 90 TW/cm², 1.7 μm MIR pulse. The spectrogram inset shows the ω_{MIR}-frequency, phase-dependence of the SFS PES.

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 Argon gas used previously. In addition, 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. Criterion (4) is accomplished 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 16, 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. Another benefit is tighter focusing of the XUV light enhancing our ability achieve higher dressing field intensity for driving the continuum wave packet. The end-station is an electron-ion coincidence spectrometer that was developed for our helium double ionization studies back in 2000.

Figure 2: (a) Spectrogram of the double ionization of argon using an APT centered at 25 eV and a 30 TW/cm², 1.7 μm MIR pulse. (b) The FFT of the spectrogram shows an expected $2\omega_{MIR}$-oscillation indicative of rescattering.

The SFS apparatus construction started in early part of 2020. Unfortunately, the COVID-19 shut down halted construction until July 2020. Upon restart, the construction was completed, and commissioning experiments conducted in the Fall 2020. Based on these measurements we estimated that the S/N improved by at least 100-fold compared to our 2019 exploratory experiments. Starting in 2021, we started a set of survey measurements in helium, neon and argon using the SFS apparatus. Figure 1 illustrates the SFS concept. An intense MIR pulse is phased-locked with respect to an attosecond pulse train (APT) derived from the same MIR field. A stable Mach-Zehner interferometer controls the relative delay between the two fields. Figure 1 shows photoelectron spectra (PES) taken with (1) APT XUV alone (purple), (2) MIR (1.7 μm) alone (red dot-dash), (3) SFS: (MIR+APT fields) averaged over an optical cycle (purple dash) and (4) difference [(3)-(2)] (black line). Notice that the SFS spectrum is greatly

enhanced in amplitude and energy compared to the single-color measurements. There exist several reasons for the energy enhancement including streaking and rescattering but the source of the increased amplitude is still under investigation. The inset shows the phase dependence of the PES which oscillates at ω_{MIR}. Currently, measurements using different MIR intensities are being conducted.

Finally, a clearer, background-free signature of classical rescattering is double ionization. In the three-step model, double ionization results when the field-driven wave packet returns to the core with sufficient energy to free a bound electron via (e,2e) inelastic scattering. For strong field studies in helium at 0.78 μm this produces a maximum of ~ 1 part in 500 of He^{2+} compared to He^+. To date, we have not been successful at observing double ionization in helium but we are working of increasing the sensitivity of our measurement. However, we have observed the phase-dependent double ionization in argon driven by the (MIR+APT) SFS concept. The experiment is conducted by measuring the total ion yield using an (m/q) time-of-flight mass spectrometer. Figure 2(a) shows that the Ar^{2+} signal oscillates at 2ω (see FFT in [b]) while each color alone does not produce measurable double ionization. One caveat, the 25 eV mirror used result in XUV photoionization with ~10 eV excess kinetic energy, thus not mimicking the near zero energy initial condition of tunneling. However, these results are the clearest signature to date that we are driving in (e,2e) process in our simulator and a starting point for a host of investigations.

Investigations at the LCLS. Clearly, COVID restrictions curtailed our ability to travel to the LCLS at SLAC in 2020 and first half of 2021. Our scheduled "LCLS Run 19" campaigns in the Fall 2020 were postponed and rescheduled for 2021. These campaigns occurred in April and May 2021, but travel was still not permitted. However, we were able to participate in the two campaigns by remote login. The group was able to travel to SLAC for an August 2021 run.

Quantum beats in Auger-Meitner decay: Analysis of data collected in a beam time awarded in November 2018 entitled "Time-resolving correlated continuum electron and core-excited state wave packets by photoemission streaking" was completed. The run was led by SLAC scientist Dr. James Cryan, Dr. Peter Walter and Dr. Ago Marinelli, and focused on the attosecond capabilities of the LCLS, aka XLEAP. The streaking results revealed a rather unexpected feature which upon analysis was identified as a coherent beating, i.e. quantum beat, from an Auger-Meitner decay channel. A manuscript has been submitted to Science and is currently under review.

Time-resolved Auger decay: From the inception of the LCLS XFEL, our team had proposed a self-referencing technique based on the streaking method. The aim was to validate the efficacy of XFELs for measuring core hole dynamics. Over the course of several LCLS campaigns, we develop an approach termed 'self-referenced attosecond streaking' that provides sub-femtosecond resolution in spite of jitter, enabling time-domain measurement of the delay between photoemission and Auger emission in atomic neon excited by intense, femtosecond pulses from the LCLS XFEL. Using a fully quantum-mechanical description that treats the ionization, core-hole formation and Auger emission as a single process, the observed measured delay yields an Auger decay lifetime of 2.2 (+0.2 -0.3) fs for the KLL decay channel, consistent with spectral domain measurements. These results are published in a 2021 Nature Physics article [7A].

1.3 FUTURE PLANS

Over the next year, we will pursue the following studies.

Strong field simulator: We have now completed an initial survey of both energy resolved photoelectron and ion yield for Argon, Neon, and Helium. The oscillation in the rate of Argon double ionization as a function of MIR/XUV delay suggests we could be driving a two-color recollision process, a promising direction for future studies. (i) To study the double ionization of Argon as a function of relative polarization between the XUV and MIR fields, and the corresponding photoelectron distribution. (ii) Substitute our XUV mirror for one with a bandwidth centered on Argon's ionization potential (16 eV), to better approximate the strong field tunnel ionization mechanism, and repeat experiments on double ionization. (iii) Pursue our primary goal of extending these studies to the double ionization of Helium,

where more precise calculations can model the role of electron correlation in non-sequential ionization processes. By completing (i) and (ii) we will gain the necessary knowledge and insights to more effectively carry out campaign (iii). Ken Schafer (LSU) and Abraham Camacho (OSU postdoc) will provide theory support for this program.

Imaging: The goal for FY21 is the application of LIED/FABLES to study ultrafast molecular dynamics using pump-probe geometries. This work is being performed in collaboration with Prof. Cosmin Blaga (KSU). Currently, a junior OSU graduate student is at KSU working with his group. KSU and OSU are developing a new LIED detector scheme which will increase the data rate by a factor of ten, thus enhancing the ability to perform delay scans efficiently. Once this is demonstrated, investigation will explore: (1) 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.

LCLS: The DiMauro group has participated in the LV39 run that occurred during August 9-12, 2021. The campaign led by Dr. Matthias Kling aims at performing time resolved measurements of the cage and plasmon dynamics of endohedral fullerene, specifically $Lu_3N@C_{80}$. Currently, the data from the run is being evaluated. The group will also participate in the submission of proposals and continued analysis of experimental runs associated with the LCLS Directors Attosecond Campaign.

1.4 Peer-Reviewed Publication Resulting from this Project (2019-2021)

1A. *"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.

2A. *"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.

3A. *"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.

4A. *"High relative-phase precision beam duplicator for mid-infrared femtosecond pulses"* A. Camper et al, Opt. Lett. **44**, 5465 (2019). doi: https://doi.org/10.1364/OL.44.005465.

5A. "Attosecond transient absorption spooktroscopy: a ghost imaging approach to ultrafast absorption spectroscopy", Taran Driver *et al.*, Phys. Chem. Chem. Phys. **22**, 2704 (2020). doi: 10.1039/c9cp03951a.

6A. "High-power few-cycle Cr: ZnSe mid-infrared source for attosecond soft x-ray physics", Vyacheslav Leshchenko *et al.*, Optica **7**, 981 (2020). doi: 10.1364/OPTICA.393377.

7A. "Clocking Auger electrons", D. C. Haynes *et al.*, Nat. Phys. **17**, 512 (2021). doi: 10.1038/s41567-020-01111-0.

COVID-19 Impact Statement

There were no changes to the approach over the course of the COVID crisis. However, the COVID-19 crisis has had a disrupted impact on our laboratory operation and student training. The entire DiMauro group was in a stay-at-home state since OSU closed the university on March 14. Fortunately, the Physics building allowed entry in early July 2020 but under reduced occupancy (25%) and following strict CDC protocol. Reinstating equipment took an additional 1-2 months of recommissioning. We continue to run under reduced capacity for the majority of 2021 but in the Fall 2021 the university allowed 100% occupancy with a mandated indoor masking. A major impact during this past year and a half was the challenge of training our most junior students. A final factor was cancellation of our LCLS campaigns in 2020. Our LCLS campaigns were rescheduled for the first half of calendar 2021 but participation was limited to virtual. The first in person run at SLAC did not occur until August 2021.

Strong-Field SENE and Comparison of Exact Solutions vs Few-State Counterparts
Grant No. DE–FG02-05ER15713

J. H. Eberly
Department of Physics and Astronomy
University of Rochester, Rochester, NY 14627

October 1, 2021

Project Scope: Our continuing work [1, 2, 3, 4] builds on an extended exploitation of the SENE approach to quantum ionization events. Additionally, to test the possible utility of well-designed few-state model calculations as an exploitable strong-field approach, we are just beginning to analyze comparatively [5] two new strong-field calculations. Non-perturbative ionization is being investigated by integrating the fully space-time-dependent Schrödinger equation (TDSE) to obtain a numerically exact all-states solution for 3D *ab initio* hydrogen irradiated by an intense quasi-monochromatic pulse, and we use that for comparison with the much more direct solution for an "equivalent" model atom built from just three quantum states but endowed with correct *ad hoc* hydrogenic energies and transition dipole matrix elements.

Recent Progress: Our SENE method refers to a quantum-classical coordination of **S**chrödinger **E**quation dynamics and **N**ewton **E**quation dynamics. The coordination is initiated and controlled by virtual numerical detector (VND) operation. It has been providing [2, 6, 7] a new avenue of theoretical access to far-field quantum coherences that are remnant characteristics of the ionization event (without assuming tunneling). These characteristics have importance because ionization is the process whereby photons liberate electrons from atoms as well as from more complex targets, creating potentially useful correlations to understand and to exploit when possible.

In whatever way such strong-field non-perturbative photo-ionization is initiated [8], its most common alternative formulation is still mainly guided by a weakly justified intuition labeled "adiabatic tunneling" [9]. The value of our continuing work in this direction has been recognized by the designation of our RMP review [10] as an ISI Highly Cited paper, and by an invitation to contribute to Vrakking's special issue of the Journal of Physics B [2], plus the invitation to present the opening plenary talk [11] at the International Conference on Matter and Radiation at Extremes (2017, Beijing). The driving force of all such investigations is the creativity being employed experimentally in applying ultra-

1

short (fs and sub-fs scale) pulses with intensities in the range approaching, and above, $I = 0.1$ PW/cm^2, with wavelengths in ranges both longer and shorter than near-visible. This is producing a stream of new experimental results that continue to challenge theoretical explanations.

We will be advancing development of the theoretical SENE approach by a careful extension of the Feuerstein-Thumm virtual numerical detection (VND) method by introduction of Feynman-type path summation over the trajectory paths of quantum-initiated VND trajectories that arise from numerical detector signals. As demonstrated by momentum interference fringes in far-field distributions we can achieve recovery, before path summation, of the quantum phase information removed by the detectors. Very importantly, along the way we can retain the numerical advantage of tracking via Newtonian, rather than Schrödinger, dynamics all of the ongoing laser action on the post-ionization phase-restored VND trajectories.

Speculative Initiative: While going forward with SENE extension to non-perturbative two-electron ionization, we are beginning to explore a speculative approach to strong-field theoretical calculations. It is based on the recognition that simplified few-level models of quantum coherences in atomic systems are accepted widely as valid. This is based on their successes in explaining or even predicting unusual or counter-intuitive quantum-coherent processes previously undiscovered (recall early analyses: [12]). Phenomena of this kind certainly include strong state dressing, both without ionization [13] and accompanying ionization [14].

Here we are engaging exact numerical solutions of the non-relativistic time-dependent Schrödinger equation (TDSE) in two cases: (a) when used to obtain an exact *ab initio* treatment of radiative excitation of the single electron in 3D hydrogen, and (b) as used to obtain solutions for hydrogen when it is described by only three(!) active quantum states, 2p and 3d and Ep. In both cases, the hydrogen atom and its three-state model analog, are exposed to a quasi-monochromatic optical pulse with frequency near to resonance with the 2p-3d Balmer transition.

In both cases (a) and (b) we are subjecting the two "hydrogens" to strong-field short-pulse excitation with an intensity great enough to reveal strong-field state dressing effects as well as to lead to observable non-perturbative ionization. Several non-perturbative coherences are shown in the figures below.

First Results: Recognizable strong-field effects are multi-cyclic non-perturbative Rabi oscillations of Balmer inversion, as evident in the right figure below, as well as intensity-dependent splitting of the hydrogenic ATI spectrum that arises from the strong-field dressing of the same 2p and 3d Balmer levels, seen in the left figure. The latter results in a two peaked distribution of the probability for excitation of the high-lying Ep state in the model, thus yielding a usefully extended version of the Autler-Townes effect [15], one that includes end-pulse completion by ionization under the single strong field.

The few-state model incorporates a finite decay rate for the high-lying non-Balmer state,

giving a width to the Autler-Townes dressing and this gives a lifetime that is directly linked with the time dependence of the *ab initio* calculation. The left figure displays the splitting of positive electron energy ionization probabilities, and the evident decay rate on the right exactly matches the width of the split peaks in the left figure.

The Autler-Townes splitting in the continuum is wider if the Balmer transition is more off-resonant, as measured by the intensity-dependent Rabi frequency Ω, which is shown in the end-of-pulse red curve on the left. The right figure shows the decay of Balmer probability accompanying the transition Rabi oscillations. The model has desirable flexibility in several directions, such as permitting its third-state probability decay rate to be adjusted to match the rate determined by the *ab initio* exact solution.

Taken together, these results show familiar coherences. What we emphasize, and what is not widely known or examined, is the degree to which a coherence can be expected to be reliably present in the real atom, even if the coherence first became evident only in a highly artificial few-state quantum system, one designed to permit an uncharacteristically very rapid non-perturbative solution of the truncated strong-field Schrödinger equation dealing with only very few states.
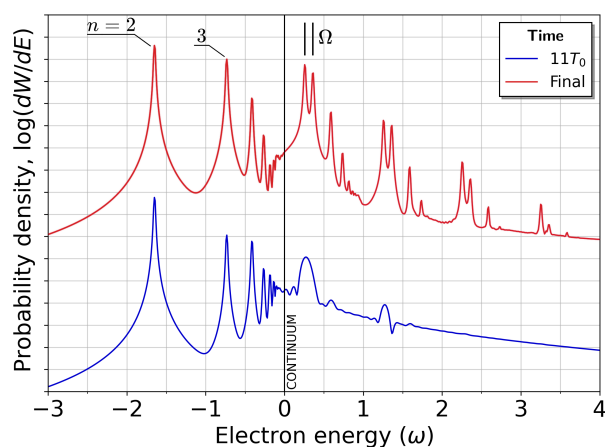
Figure 1
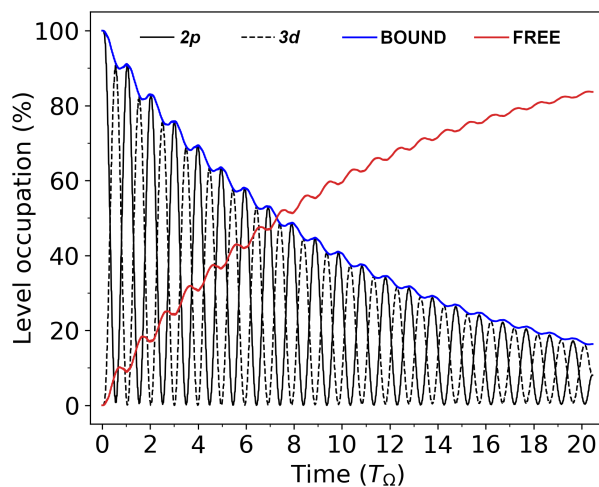
Figure 2

Recent publications with DOE-AMOS support shown by *** in the listing.

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Probing ultrafast XUV/x-ray induced electron correlation in the molecular frame
Award number: DE-SC0021336
Principle Investigator: Li Fang
Department of Physics, University of Central Florida, Orlando FL 32816
Email: Li.Fang@ucf.edu

Project Scope:
Electron-electron correlation is a fundamental process where momenta and energies are exchanged in multielectron atomic and molecular systems. This project investigates photo-induced electron correlations in molecules in the time domain and in the molecular frames. Specifically, the investigation focuses on the temporal profile of the energy and momentum redistribution during electron correlations, the impact of the electron-electron correlation dynamics on the consequent chemical bond activities, and the dependence of the electron correlation dynamics on molecular orbital properties and molecular axis alignment or orientation. Three phenomena driven by electron correlation will be studied with direct comparison between experimental data and theoretical calculations: 1) autoionization, 2) single- and two- photon double ionization, 3) shake and core-hole decay processes. To achieve the needed temporal resolution and the multiple-observable measurement, ultrafast (atto- and femto- second) lasers and a reaction microscope (REMI) will be used to retrieve the transient 3-dimensioanl momentum of charge particles as a function of time. The ultrafast lasers to be used include table-top XUV/x-ray attosecond lasers and facility-based free-electron-lasers. The target molecules are prototype or small molecules, such as N_2, CO_2, and C_2H_2.

Future Plans:
We will continue the construction of the XUV beamline and the spectrometer which are the in-house tools for this project. We expect to have the commercial pump laser installed in February 2022 and adapt the home-built secondary XUV light source to the pump laser. A graduate student in the group will be building the phase tagging apparatus for this project. Meanwhile, we will carry out experiments, in collaboration at existing attosecond XUV/x-ray beamlines, on autoionization of N_2 and/or C_2H_2, when the main laser is back inline in our collaborator's research lab on campus. We aim to use laser aligned molecular target in these experiments. The experiment on N_2 will be carried out at an XUV beamline equipped with a magnetic bottle spectrometer and an XUV (~20-50eV)/NIR (800nm) dual-pulse scheme will be applied. Attosecond streaking measurement will be performed. Correspondingly experiments of the same molecular targets will be carried out at an existing XUV beamline that is equipped with a time-of-flight spectrometer for ion measurement. The ion fragmentation information will be combined with the electron data to obtain implicative information of the correlation between the electron and ion dynamics. (We will take electron and ion spectra separately at the existing beamlines before the REMI spectrometer construction is complete.) We expect that LCLS II at high-repetition-rate will become operational next year and will submit proposals when the corresponding submission cycle is open. (The previous submission cycles have been for standard LCLS configurations, according to the LCLS website.)

Peer-Reviewed Publications Resulting from this Project (Project start date: 9/2020):
No publication to report.

Physics of Correlated Systems
Award DE-SC0010545
Chris H. Greene
Department of Physics & Astronomy, Purdue University, West Lafayette, IN
47907-2036 chgreene@purdue.edu

Project Scope

Whenever multiple degrees of freedom affect each other in a quantum mechanical treatment of an atomic, molecular, and optical system, those degrees of freedom are said to be *correlated*, or in some contexts, *entangled*. This project concentrates on developing a theoretical description of systems where those correlations are strong and often require the development of specialized methods to adequately represent the experimental phenomena. The present project broadens the traditional case of electron correlations to consider expanded types; for instance, in addition to electron-electron correlations, we also consider the correlations between internal and external fields that one or more atomic electrons experiences, and correlations between an electronic coordinate and an internuclear or dissociative coordinate in small molecules. For those systems, we have developed specialized techniques based on different concepts and different approximations than are traditionally utilized in atomic, molecular, and optical physics, namely multichannel quantum defect theory, R-matrix theory, and frame transformation methods.

In many cases, it is 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 had only a limited theoretical interpretation or understanding, while others attempt to predict new opportunities for future experiments relating to energy transfer, chemical reactivity, and photofragmentation.

Recent Progress

(i) Multiphoton ionization of strongly correlated atoms

The current funding period has seen significant progress in ramping up our capability to describe ultrafast or strong laser pulses interacting with an atom, in regimes where either two electrons are nonperturbatively correlated with each other, or where a single electron is highly excited and can readily exchange energy with the ionic core of a many-electron atom. The prototype atom for studies of electron correlation is helium. A much-studied consequence of the accidental degeneracy of He+(n), neglecting the tiny fine structure, is the modified classification of helium doubly-excited states according to correlated SO(4) group theory quantum numbers $\{K,T\}^A$ formulated long ago in studies by D. Herrick and later by C. D. Lin. Our treatment of helium two-photon ionization considered final state energies in the vicinity of the doubly-excited states near the N=2 and N=3 ionization thresholds.[1] The two-photon excitation process with linearly-polarized photons reaches $^1S^e$ and $^1D^e$ autoionizing levels, and it allowed us to explore propensity rules for excitation and decay that have been well-characterized previously only for the $^1P^o$ states reached in single-photon ionization. For excitation, the propensity rules suggest that the A=`+' states should be the most strongly excited; our numerical results obtained using R-

matrix theory and multichannel quantum defect theory confirmed that this is still the case for the excitation step by two-photons in the above-threshold ionization regime that reach the final states via one-photon intermediate states in the singly-excited ionization continuum. On the other hand, a surprise that emerged from our Wigner-Smith time-delay analysis of the two-electron resonance was that while the autoionization decays of *some* states do agree with the $\Delta A=\Delta v=0$ propensity rule that has been shown to be valid for $^1P^o$ states, other doubly-excited state decays violate that rule and populate other decay channels with substantial probability. Our study [1] thus predicts that some of the rules of thumb previously verified for states reached in 1-photon excitation need to be modified for the states reached by two-photon above-threshold absorption. The calculations in [1] have also extracted finer details about the ionization, namely the photoelectron angular distributions, characterized by β_k coefficients of the k-th Legendre polynomial with even k only, for either linearly polarized incident light, or for absorption of two opposite circularly polarized incident photons which produces the trefoil polarization field. Not surprisingly, there are rapid variations of the angular distributions in the vicinity of autoionizing resonances.

Another motivation for our study of two-photon ionization of helium in [1] came from our desire to eventually carry out a detailed study of angular distributions in the presence of simultaneous photoionization by coherent one-photon and two-photon absorption processes that reach the same energy, i.e., from photon sources of respective frequencies 2ω and ω, respectively. The phase-dependent interference of those two processes, using parallel linearly polarized photon sources along a z-axis can produce electron current that is directed preferentially along positive or negative z, depending on the phase difference between the photon sources. One reason such an experiment is of fundamental interest is because the final photoelectron state has broken the parity as a good quantum number. Our most recent publication [2] treats that case, again for the prototype system of atomic helium in the vicinity of doubly-excited final state energies. That effort predicts the angular distribution, and directional asymmetry (strength of positive z current versus negative z current) as a function of final state energy, and its dependence on the atomic and laser phase contributions. Moreover, we point out an alternative way of redirecting the photoelectrons by changing the laser frequency, but with a fixed relative phase and field strength ratio, showing how to use this scheme to redirect photoelectrons by manipulating final state energies across the S-wave $2p^2$ resonance.

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

Most of the molecular physics problems of current interest in our theoretical treatments are those that involve energy interconversion between electronic and vibrational/dissociative degrees of freedom; such processes are controlled by a breakdown of the Born-Oppenheimer approximation. Indeed, gaps exist in current theory that ultimately desires a fully quantitative description of electron-nuclear correlation that can predict in full detail how energy gets interconverted between electronic and nuclear degrees of freedom, and the the relative likelihood of populating the different energetically open final state channels. Dissociative recombination via indirect Rydberg pathways 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. A notable system

involves an electron collision with HeH^+ at low energies where there is no identifiable direct dissociative Born-Oppenheimer potential curve.

In just the past couple of years, it has become possible to carry out DR experiments with a very cold (<10K) ion storage ring experiment at the Cryogenic Storage Ring (CSR) in Heidelberg. Their dissociative recombination measurement of cryogenic molecular HeH^+ ions that collide with low energy electrons has permitted the sharpest test of theory yet. Specifically, they measured this process at low energy with sufficient energy resolution and sufficiently low rotational temperatures to resolve individual resonances. That experiment pointed out inaccuracies in previous theory published by many groups including our own. Our new variant of the energy-dependent frame transformation theory[5] was implemented to quantitatively test the improved theory, in collaboration with the Prague research group of Roman Curik. Following the development and careful benchmarking of our new formulation that we denote as the backpropagated frame transformation method [5], its application to describe the new HeH^+ experiment has proven to give a significant improvement [4] over all previous theoretical implementations of the rovibrational frame transformation method in combination with multichannel quantum defect theory. We are continuing to work on the theory with the Curik group to treat dissociative recombination and vibrational autoionization in systems that have more than one relevant ionic potential curve, as is the case for the gerade symmetry of H_2. This will represent a major expansion of these theoretical capabilities.

In contrast to the rovibrational frame transformation, which 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 unusually high excited states of a diatomic molecule. With former postdoc Teri Price, we treated [7] class of correlations using the *local* frame transformation which involves a transformation between spherical and prolate spheroidal coordinates. Some experimental groups have also sought out our collaboration for understanding complex bound and autoionizing spectra of heavy atoms, and we have collaborated with one group to interpret a complicated region of multichannel perturbers in the erbium atom.[3]

Our efforts 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, our theory does reasonably well in describing the complex resonances that an exact calculation produces in a dissociative recombination calculation. The largest discrepancies are infrequent occurrences of a low principal quantum number perturbing state that is sometimes located at a slightly shifted incorrect energy, and theory 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 approximations, it apparently gave the first estimate of the ungerade contribution to the H_2^+ dissociative recombination cross section. Study of this prototype system will help to understand other systems like polyatomic dissociative recombination where there is too much complexity to treat every relevant degree of freedom by brute force.

Future Plans

A major new direction started within the past year, which we expect to come to full fruition in the next 12 months, involves short pulse absorption and ionization processes in atomic argon. A sequence of two or three ultrafast pulses can produce time-dependent quantum beats between the alternative pathways, and remarkable regularities are emerging in this system from Arvinder Sandhu's experimental group. Promising avenues have emerged and our multichannel quantum defect toolkit is well-suited to describing the phenomena they are observing.

Further multiphoton ionization and coherent control studies are underway and should be completed within the coming year. A graduate student, Yimeng Wang, has made good progress in developing our first theoretical treatment of interfering 1-photon and 2-photon ionization of complex 2-electron atoms (i.e. atoms with 2-electrons plus closed subshells), concentrating on photoelectron angular distributions in the vicinity of doubly excited autoionizing states for barium, a richly complicated multichannel atom. That effort broadens our treatment beyond atomic helium to handle the alkaline earth atoms, where we can treat the combination of autoionizing intermediate and final states, whose decay is mediated by the interplay of electron-electron interaction and spin-orbit coupling. Another exploration underway with Ms. Wang is related to photoionization processes triggered by two frequency- and time-entangled photons.

Significant progress has also been achieved and work will continue in the coming year in developing a new full implementation of rovibrational frame transformation theory, for dissociative recombination or photofragmentation processes, in the more complex regime that arises when there are multiple Born-Oppenheimer potential curves of the positively charged molecular target ion. We will also treat highly excited long-range states of the Sr_2^+ molecule that are beyond capabilities of modern quantum chemistry, by using a recently developed implementation of the spherical-to-spheroidal coordinate frame transformation that interfaces smoothly with generalized quantum defect theory.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

[1] *Two-photon above-threshold ionization of helium*, Yimeng Wang and C. H. Greene, Phys. Rev. A 103, 033103 (2021). DOI: 10.1103/PhysRevA.103.033103

[2] *Resonant control of photoelectron directionality by interfering one- and two-photon pathways*, Yimeng Wang and C. H. Greene, Phys. Rev. A 103, 053118 (2021). DOI: 10.1103/PhysRevA.103.053118

[3] *Spectroscopy of Rydberg states in erbium using electromagnetically induced transparency*, A. Trautmann, M. J. Mark, P. Ilzhöfer, H. Edri, A. El Arrach, J. G. Maloberti, C. H. Greene, F. Robicheaux, and F. Ferlaino, Phys. Rev. Research **3**, 033165 (2021). DOI: 10.1103/PhysRevResearch.3.033165

[4] *Dissociative recombination of Cold HeH$^+$ Ions,* Roman Curik, David Hvizdos, and C. H. Greene, Phys. Rev. Lett. **124**, 043401 (2020); DOI: 10.1103/PhysRevLett.124.043401

[5] *Backpropagated frame transformation theory: A reformulation,* David Hvizdos, C. H. Greene, and Roman Curik, Phys. Rev.A **101**,012709(2020);DOI:10.1103/PhysRevA.101.012709

[6] *Low-energy scattering properties of ground-state and excited-state positronium collisions,* M. D. Higgins, K. M. Daily, and C. H. Greene, Phys. Rev. A **100**, 012711-1 to -10 (2019); DOI: 10.1103/PhysRevA.100.012711

[7] *Local frame transformation theory for two classes of diatomic molecules,* T. J. Price and C. H. Greene, Molecular Physics **117**, 3171-3183 (2019); DOI: 10.1080/00268976.2019.1617446

Early Career: Theory of the femtosecond and attosecond dynamics of molecules in complex regions of their potential landscapes

Loren Greenman

Dept. of Physics, Kansas State University, Manhattan KS, 66506

lgreenman@phys.ksu.edu

Project scope

This project seeks to determine to what extent small molecules can be controllably excited to highly excited states and whether the subsequent dynamics can be controlled as well. To determine this, methods for describing the dynamics of molecules in highly excited states will be developed and tested. Excitation to highly excited states like Rydberg states, doubly excited states, and other excited configurations will be considered. State-to-state transfers will be among the processes considered to be controlled, along with directed energy flow into specific degrees of freedom. Observables corresponding to those that can be measured in coincidence experiments will also be optimized to provide experimental signatures of the dynamics.

Recent progress

In addition to providing new resources for calculating and controlling highly excited molecules, this project will build on existing methods and control schemes. Grid-based methods previously used for photoionization and electron-molecule scattering calculations [1–4] will be employed to explore the limitations of Gaussian basis sets in describing highly excited molecules. Perturbative dynamics will be described with codes developed previously for controlling photoionization in chiral molecules [5–7]. These codes, as well as previously determined potential energy surfaces for molecules such as CH_2I_2 will provide a foundation to build on for this project.

Future plans

To evaluate the limits of control in highly excited states, this project will focus on molecules like CH_2I_2, for which significant data is available regarding potential energy surfaces and some features of excited-state dynamics [8, 9]. Additionally, experiments that include the absorption of multiple ultraviolet photons in CH_2I_2 (private discussions) access states that lie high in the manifold of the neutral as well as some low-lying ionic states that may exist in a dense manifold (preliminary calculations). The calculation of highly excited neutral states is complicated by a lack of well-established quantum chemistry methods, and also these methods are implemented on Gaussian basis sets which cannot easily describe excited states with large spatial extents. For these reasons, this project will develop model potentials for small molecules like CH_2I_2 and extend grid-based methods [1, 2] to calculate the highly excited molecular states. Recently developed methods for calculating highly excited states in

quantum chemistry [10, 11] will also be used for comparison, as well as benchmark methods for correlation, which can be performed only for small or moderate-size basis sets.

The ultimate objectives of the control schemes will be to maximize the transfer of energetic inputs into specific degrees of freedom. These may include specific charge motion or internal nuclear coordinates. To begin, a ground-state to excited-state transfer will be attempted. For excited states in dense manifolds, multiphoton schemes may be required to obtain these transfers with optimal populations and desired phases. Transfer of population between excited states will also be considered. The highly excited states, in addition to existing in dense manifolds, couple to each other with different strengths than those found between the ground state and low-lying states. This may be a feature that can be exploited to optimize state-to-state transfer. Control schemes will also be developed to optimize observables, especially those that can be detected via coincidence measurements. Excited-state populations and dynamics can also be initiated by ionization; this project seeks to understand the dynamics of doubly excited states that arise from double ionization of neutrals.

The extension of the methods described above is also a goal. The grid methods, which thus far have been used for scattering processes and will be extended here to describe excited states in model systems, will also be modified to include additional effects of electron correlation. The perturbative dynamics methods will be supplemented with correlation terms and extended to higher orders of perturbation theory. Additional perturbative pathways will allow more complex control schemes which may prove crucial to achieving the goal of controlling these states.

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Peer-reviewed publications resulting from this project (Project start date: 08/2021)

No publications to report.

Manipulating and Probing Ultrafast Atomic and Molecular Dynamics
DE-FG02-00ER15053

Robert R. Jones, Physics Department, University of Virginia
382 McCormick Road, P.O. Box 400714, Charlottesville, VA 22904-4714
bjones@virginia.edu

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 electron bursts which can serve as fast probes of optical fields as well as molecular structure and dynamics.

II. Recent Progress

As part of our study of THz enhancement near nano- and micro structures, and potential uses of that enhancement for influencing strong-optical-field processes and preparing better experimental targets by improving the degree of THz induced field free molecular orientation, we have worked to increase the maximum field strength attainable from our 1.5 mJ, 1 kHz Ti:Sapphire. We can now produce single-cycle THz waveforms with peak fields of ~150kV/cm at 1 kHz, roughly a third of what we have produced at 15 Hz using Ti:Sapphire pulses with 10x the pulse energy. During the process of characterizing those pulses, via electro-optic sampling in non-linear materials, we recognized the significant potential of an angle and time-resolved optical cross-phase modulation technique for measuring the non-linear index of refraction of materials at THz frequencies. Briefly, the change in the frequency spectrum of a 100 fs 800 nm laser pulse is monitored as a function of its delay relative to a co-linearly polarized THz pulse co-propagating through a non-linear crystal (e.g. ZnTe). The THz induced spectral shift is typically dominated by the Pockels effect, which is linear in the THz field, However, our preliminary experiments suggest that measurement of the spectral response vs crystal angle (relative to the laser polarization) can be used to separate out the contribution of the weaker non-linear Kerr effect, due to its different angular dependence. The non-linear index, n_2, over the broad THz spectrum, can then be determined. Our analysis of this technique is continuing.

We have also continued our development of a new method that employs electron field emission from nanotips as an *in situ*, sub-wavelength probe of the time-dependent electric field in a focused THz beam in vacuum. The ultrafast waveform imaging method utilizes two THz pulses, with a variable time-delay, and takes advantage of two principal features of high-energy electron field emission driven by intense (near) single-cycle THz pulses [1]. First, the emission of high energy electrons is temporally confined to a brief window near the peak of one half-cycle of the THz field. Second, over a wide range of THz field strengths, both the maximum energy of the emitted electrons and the total high energy electron yield are proportional to the peak electric field at the tip. Accordingly, if a relatively intense single-cycle THz "source" pulse generates high energy electrons from a nanotip, then when a second relatively weak "signal" waveform is temporally scanned through the source field, the changes in the (net) maximum field at the tip will be directly reflected in the net high-energy electron yield. By repeatedly scanning the relative delay of the signal and source pulses as the spatial position of the nanotip is varied, we can map out the spatio-temporal waveform of the signal field. While all optical techniques, like the electro-optic sampling method mentioned previously, also allow for full spatio-temporal sampling of THz waveforms, the need to locate a non-linear crystal where the field is to be sampled precludes their use for many potential applications. In addition, as alluded to above, the non-linear THz response of materials significantly complicates (or rules out) the use of electro-optic sampling to characterize strong THz fields. As an alternative, nano-tips can be easily and finely positioned near other objects, throughout a tight sample volume, and in high-vacuum. A manuscript describing the technique is nearly ready for submission.

III. Future Plans

With the restart of our laboratory research following the full COVID-19 shutdown and subsequent limitations to single person occupancy in the labs through May 2021, we are working to make progress on several fronts. First, we 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, we hope to return to our investigation [2,3] of the roles of electron correlation [4] and coupled electronic- nuclear dynamics in directional multi-electron dissociative ionization of small molecules, through pump-probe experiments with bichromatic fields. Third, now that research related travel is again allowed, and once the back-log of COVID delayed experimental projects in both labs is resolved, we plan to continue our work in collaboration with the DiMauro group at OSU [5] on new time-resolved measurements to demonstrate the ability of attosecond photo-electrons to capture ultra-fast changes in the molecular binding potentials of their parent ions.

IV. References

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V. Peer-Reviewed Publications Resulting from this Project (2019-2021)
No publications to report.

Attosecond Physics with XFEL sources

Award number: DE-SC0022093

Principal Investigator: Alexandra Landsman

191 West Woodruff Avenue
Ohio State University
Columbus, Ohio 43210
Email: Landsman.7@osu.edu

PROJECT SCOPE

In the past two years, the very first attosecond X-ray pulses have been produced at LCLS (4), with additional LCLS experiments planned in the near future by our experimental collaborators and other groups. These new experiments are in many aspects different from the conventional attosecond pump probe experiments and provide access to new physics, calling for a development of novel theoretical approaches. In particular, the high energy of XFEL attosecond sources make both inner-core electron dynamics accessible and allow for a single electron to absorb many photons, leading to the break-down of first-order perturbation theory. From a fundamental viewpoint, high field intensities push the study of strong field interactions into the X-ray regime. This allows one to explore a full range of wavelength scaling in strong field ionization, from the mid-infrared to the X-ray. From a practical viewpoint, new theoretical tools need to be developed to interpret, guide, and suggest new experiments. The broad aim of this project is therefore twofold:

> *1. Develop theoretical framework to interpret attosecond ionization delays in atoms and molecules interacting with newly available high intensity attosecond X-ray sources.*
> *2. Explore the scaling of strong field interactions in the high intensity and high frequency regime recently made accessible by XFELs.*

To address these aims, we will develop a new theoretical description of strong field ionization based on the Wigner phase-space representation. Our Wigner phase-space approach has been recently used to describe ionization delay experiments which rely on perturbative single photon ionization using XUV pulses created by table-top laser technology (5; 6). The extension of this approach to attosecond high-intensity X-ray sources made recently available by XFELs promises to address some crucial outstanding questions, as expressed in the aims above.

Wherever possible, we plan to compare the newly developed theory to existing complementary approaches, based on the Strong Field Approximation, or a solution of a time-dependent Schrodinger equation (TDSE). Broadly speaking, our key goal is to expand the number of theoretical tools that one can tap into to interpret ionization experiments using newly available attosecond XFEL sources.

As part of the broader LCLS measurements campaign, my theoretical physics group's progress on this project will be meaningfully amplified: through our own research, by helping network members make further developments in their own programs and through increased opportunities for dissemination of techniques and results. Finally, NSF recently awarded

OSU a mid-scale infrastructure grant to build a National Extreme Ultrafast Science (NEXUS) facility, led by Robert Baker (Chemistry) and Louis DiMauro (Physics), providing additional opportunities for experimental collaboration.

FUTURE PLANS

The focus of this proposal is on investigating ionization delays in atoms and molecules. However, the theory developed in the context of ionization delays will be applicable to the study of other phenomena involving interaction of matter with attosecond XFEL sources. Of particular interest are experiments which use elliptically polarized light, obtaining electron momenta distributions in the plane of polarization. I would like to use these 2D momenta distributions to explore fundamental aspects of the inner-core single photon ionization process, in a manner analogous to how 2D electron momenta distributions were previously used to explore the fundamental aspects of the strong field ionization process using high intensity infrared fields (7,8).

In the future, I would also like to better understand charge migration and the correlated electron dynamics that lead to molecular dissociation following ionization. One question of interest is whether the time evolution of a molecule following single photon absorption and ionization can have a measurable impact on the final momentum of the ionized electron. This opens the possibility of being able to extract the time-evolution of the molecular potential landscape following ionization from the measured electron momenta distributions.

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

Guillaume Marc Laurent (PI)
Department of Physics, Auburn University, Auburn, AL, 36849
Email: glaurent@auburn.edu

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:

Over the last year, we have completed the development of the experimental system that combines a source of shape-controlled attosecond pulses and a multi-particle imaging system (Coltrims). In addition, the experimental system has been moved to a new laboratory over the spring semester, which offers high-stability and temperature-controlled conditions suitable for the long-term experiments. Before moving to the new laboratory, we have completed (and published) a study on control of the electron emission at the attosecond timescale [B. Unzicker *et al.*, NJP, **23**, 013019 (2021)]

1- Electron choreography at the attosecond time scale

Coherent control of quantum phenomena in matter through its interaction with light is a fast-growing field in ultrafast science driven by the ultimate goal of controlling the complex dynamical properties of quantum systems at the heart of many scientific fields. Over the last four decades, femtosecond laser technology has led to remarkable advances in our ability to control the ultrafast femtosecond dynamics in a vast number of systems (from simple to complex molecular systems, clusters, nanostructures, ...). With the recent development of extreme ultraviolet (XUV) light sources with attosecond duration, new capabilities emerge for controlling quantum dynamics in matter with an unprecedented level of precision down to the natural timescale of electron motion. Even though the first attosecond pulses were generated nearly two decades ago, their use for

controlling electron dynamics in matter has been elusive so far. Attosecond control has been mostly achieved with pump/probe schemes where an attosecond-pump pulse triggers a given electronic process and a phase-locked femtosecond-probe field is used to steer its dynamics. The system under scrutiny is thus controlled by varying the time delay between the two pulses. Such an approach has been successfully employed to manipulate benchmark systems such as the electronic charge distribution within a molecular target or the photoelectron emission from atoms.

Despite these impressive proofs-of-principle, attosecond control of quantum phenomena in matter is still in its infancy, though, mainly because attosecond pulse shaping techniques are still developing. Even though several schemes have already been reported to tailor both the spectrum and the polarization of these pulses, shaping their spectral phases for attosecond control, on the other hand, still remains a challenging endeavor for the attosecond community. Indeed, the low intensity of the attosecond pulses currently produced via high-harmonic generation (HHG) together with the high absorption rate of XUV radiation by most optical materials circumscribe the use of traditional pulse shaping techniques (like chirped mirrors, ...) to manipulate the spectral phase of the pulses after generation. An alternative approach consists of shaping the spectral phases of attosecond pulses directly during the generation process. Within the widely accepted three-step model describing attosecond pulse generation via high-harmonic generation, the spectral phases of the frequency components making up the pulse are directly related to the recombination times, which in turn are defined by the electron wave-packet trajectories (also referred to quantum orbits) in the driving laser field. By tailoring the temporal waveform of the femtosecond driving field, the quantum orbits and the recombination times can then be tuned giving some control over the spectral phases of the APT.
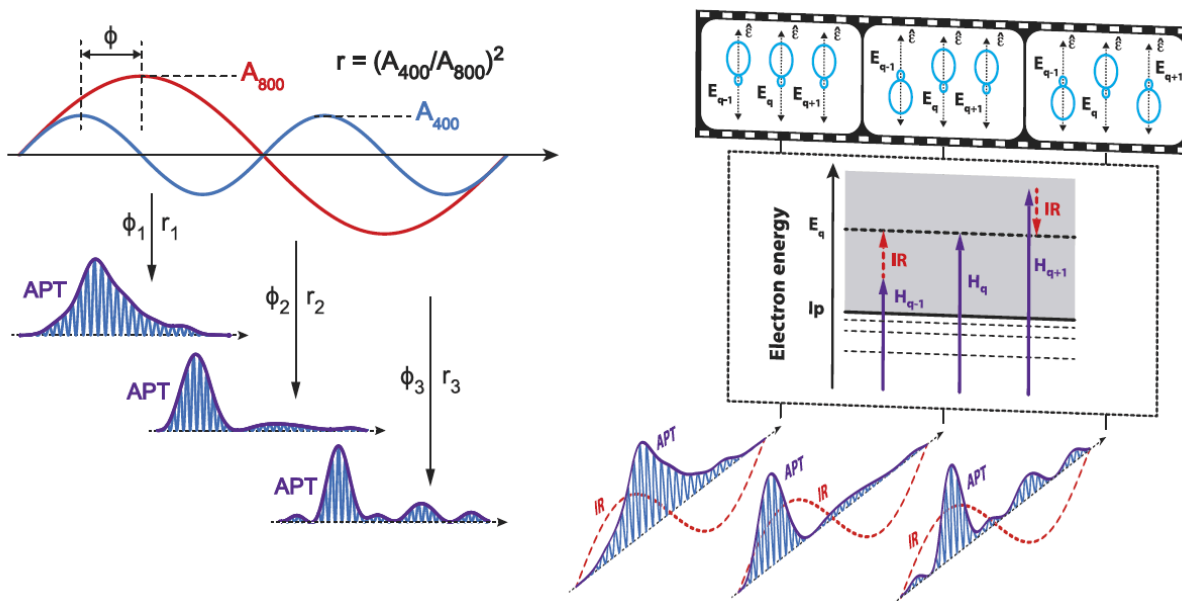
Figure 1: Principle of the experiment: APTs with tailored temporal profile are generated with a two-color femtosecond field (800 + 400 nm) by varying both the intensity ratio r and the relative phase φ between its two components. The pulses are then used to ionize argon gas in the presence of a relatively weak IR field ($\sim 10^{11}$ W cm^{-2}). Three quantum paths contribute to the generation of an electron wave-packet at a given energy Eq. These interfere, leading to an energy-dependent asymmetric electron emission along the direction of polarization of the light that is controlled by tuning the temporal profile of the APT.

Two-color femtosecond waveforms made of a fundamental field and its second harmonic have been proved to be very efficient to manipulate quantum orbits in the HHG process. The literature is rich with experimental and theoretical studies reporting the dependence of the resulting APT's spectrum on the temporal profile of such synthetized waveforms. On the other hand, the dependence of the APT's spectral phases on the temporal profile of the two-color field still remains elusive, though. We have investigated how these phases can be manipulated by varying the intensity ratio and the relative phase between the two components of the driving field. We show that the spectral phases exhibit high tunabilty for an intensity ratio between the two colors in the range of 0.1 to 5%. As an application for such a spectral pulse shaping technique, we have performed a coherent control experiment where the photoelectron emission from atoms generated by tailored attosecond pulses is manipulated along the direction of polarization of the light by tuning the spectral phases of the APT. Attosecond pulse trains with tailored spectral components (amplitude and phase) were used to ionize an atomic target in the presence of a weak IR field. An asymmetric electron emission along the polarization vector was produced through the interference between electron wave-packets generated by one- and two-photon transitions [8]. The photoelectron emission pattern was then controlled by tuning the spectral components of the APT (see figures 1 and 2).
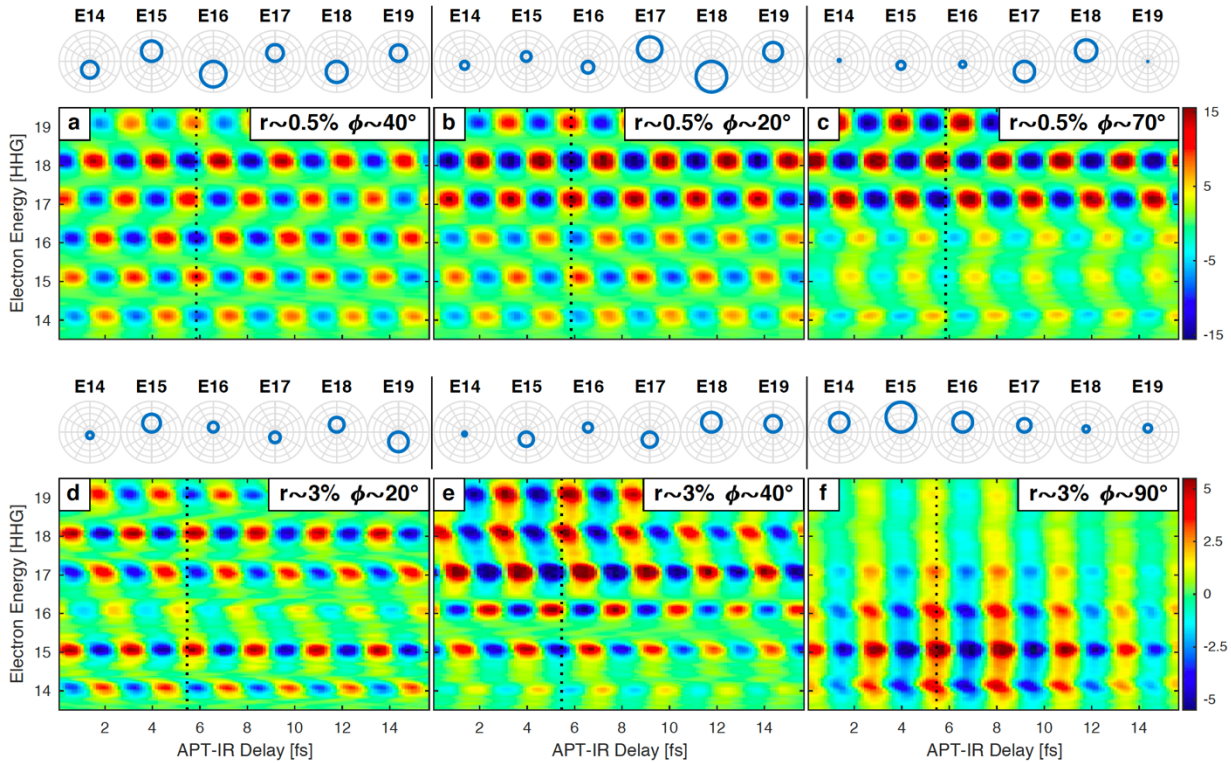
Figure 2: Density plot of the asymmetric component of the photoelectron emission (in %) as a function of the time delay between the APT and IR fields and the photoelectron energy, for different intensity ratio r and relative phase φ between the two colors of the HHG driving field.

2- Completion of the multi-particle imaging system.

Another major step forward has been the completion of the multi-particle imaging system (COLTRIMS). This includes the design and assembly of both the spectrometer and the end-station chamber, as well as the development of the data-acquisition system and the data analysis program. The spectrometer is now operational. Concurrently, we have also assembled and tested the data acquisition system and we have developed expertise with the multi-parametric data analysis. It is important to note that the data analysis for COLTRIMS-type experiment is equally time-consuming as setting up the experiment itself.

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

1- "*Electron choreography at the attosecond time scale*", B Unzicker, J Vaughan, S Burrows, B. Tatum, D Arthur, T Olsson , S Jain, T Hart, P Stringer and G. M. Laurent, New Journal of Physics, **23**, 013019 (2021)

2- *"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, **27***, 30989 (2019)

3- *"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)

Beating electronic decoherence

Wen Li, Wayne State University (wli@chem.wayne.edu)
H. Bernhard Schlegel, Wayne State University (hbs@chem.wayne.edu)

Program Scope

This proposal aims to study and suppress electronic decoherence in molecular systems with two subtasks: (1) developing experimental approaches that will capture the extremely fast decoherence process in the time-domain for the first time. (2) devising atomistic schemes that can suppress decoherence and produce long-lived electronic coherence in molecular system.

Recent Progress

1. Probing attosecond electronic wave packet dynamics in the first two femtoseconds

We have made major progress toward the first goal: we have developed an ultrafast method for measuring the temporal and spatial evolution of an electronic wave packet. Due to the delocalized nature of electronic orbitals, electronic wavepackets initiated by strong field ionization typically have significant spatial evolution other than electron density oscillation at one site. However, the spatial evolution was not previously accessible to experimental investigations at the attosecond time scale. Our method has achieved this capability. Using the 3D-two-electron-angular-streaking (*3D-2eAS*) method developed in the Li group, we carried out measurements on xenon and krypton, in which the yields of double ionization were measured

with a time range between 0 and 2.4 fs. This was performed in a newly developed high-performing apparatus that is capable of covariance measurements (Fig. 1). We observed a clear difference in the time-resolved double ionization yield between xenon and krypton: at around 1.3 fs, xenon shows a higher double ionization yield than krypton. Note at this time, the ionization site is roughly about 180 degrees from that of the first ionization. This suggests that the second ionization is modulated by a dynamical process evolving at one femtosecond time scale. We attribute this to a spin-orbit electronic wave packet produced by the first ionization. A simulation using the time dependent configurational

Fig. 1. The time- and angle-dependent double ionization (DI) yields of krypton and xenon obtained using the *3D-2eAS* technique. The suppression of the minimum at ~1.2 fs in xenon in comparison with krypton was attributed to the temporal-spatial evolution of the wave packet.

interaction with single excitation (TDCIS-IP-CAP) method was carried out by the Schlegel group to model the ionization yield of a coherent superposition between two spin-orbit (SO) states. The calculation shows clearly that due to the difference in SO splitting, the wavepackets

evolves different temporally and spatially and the measured ionization yields have captured these detailed dynamics. The spatial evolution of the wavepackets was modeled by applying different carrier envelope phase (CEP) to the probe laser. We are currently drafting a manuscript on these results for publication.
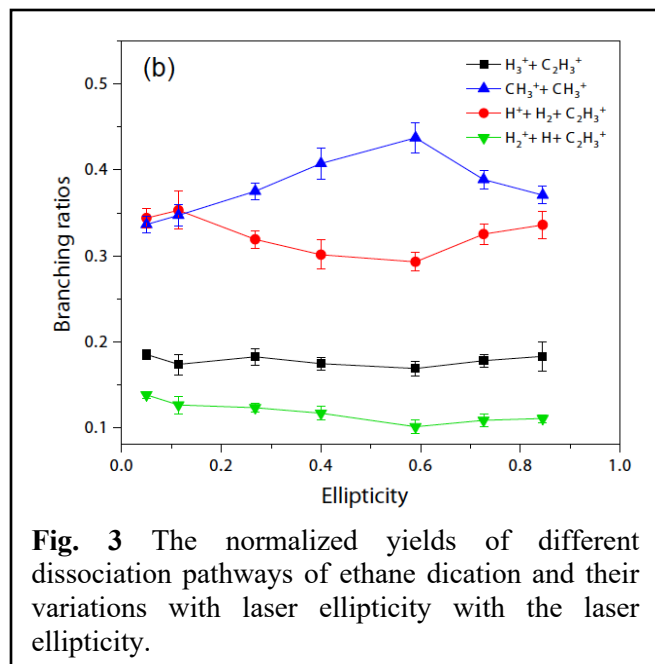
Fig. 3 The normalized yields of different dissociation pathways of ethane dication and their variations with laser ellipticity with the laser ellipticity.

2. Ellipticity controlled dissociative double ionization of ethane by strong laser fields

In this joint work by the Li group, the Schlegel group and the Remacle group, we demonstrated for the first time that the ellipticity of strong laser fields can be used to control branching ratios of strong field double ionization/fragmentation. The Li group carried out fully momentum-resolved coincidence experiments and showed that the major dissociation channels are $H_2+C_2H_3^++H^+$ and $CH_3^++CH_3^+$. Interestingly, the branching ratios changed as the ellipticity of the ionizing laser (Fig. 2). Dynamical calculations by the Remacle group suggest ground state alone could not account for the production of high CH_3^+ yield. The dissociation dynamics of different highly excited dication states were computed with surface hopping method and it was found that significant CH_3^+ production can be achieved, and the branching ratios match the experimental observation. This suggests that excited states play a far more important role that previously assumed. The Schlegel group calculated the overall double ionization yields of two different
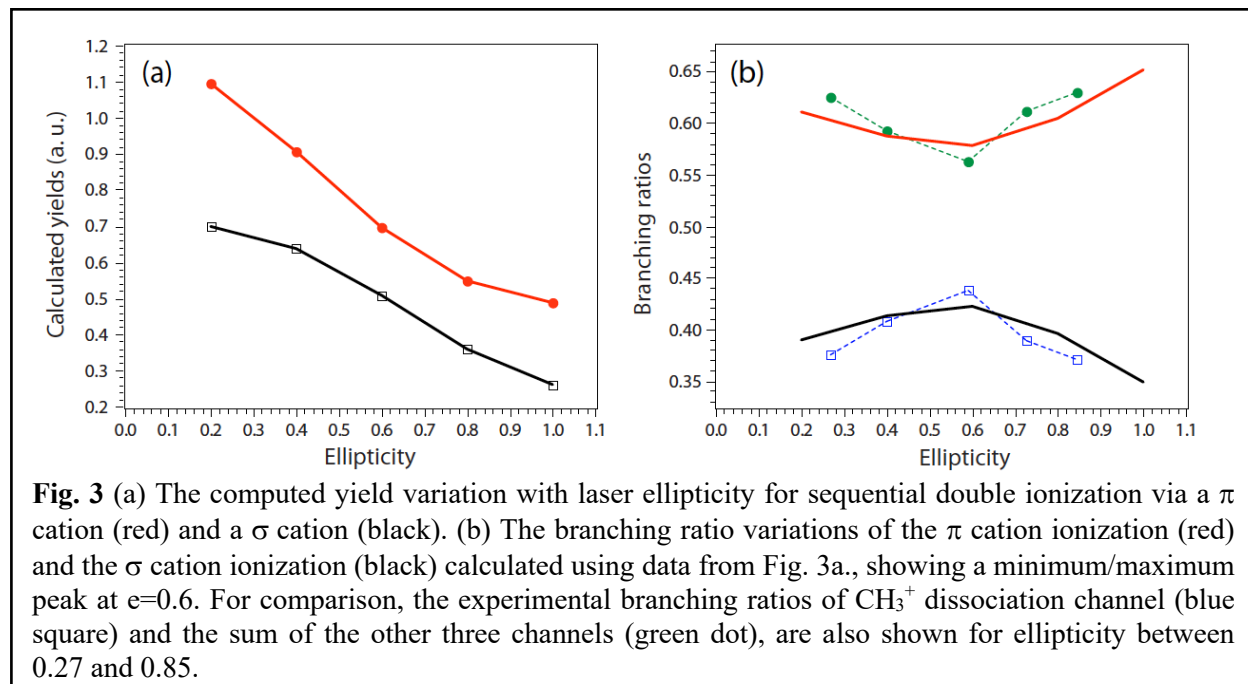
Fig. 3 (a) The computed yield variation with laser ellipticity for sequential double ionization via a π cation (red) and a σ cation (black). (b) The branching ratio variations of the π cation ionization (red) and the σ cation ionization (black) calculated using data from Fig. 3a., showing a minimum/maximum peak at e=0.6. For comparison, the experimental branching ratios of CH_3^+ dissociation channel (blue square) and the sum of the other three channels (green dot), are also shown for ellipticity between 0.27 and 0.85.

ionization pathways: one via a σ cation and one through a π cation. The ellipticity dependent branching ratios are in good agreement with those of experiments. The different angle dependent ionization yields of the two cations lead to distinct ionization yield variations with ellipticity and thus branching ratios (Fig. 3). This work is currently under review in *PCCP*.

3. Characterizing momentum correlation among three electrons in triple ionization

In this work, we demonstrated for the first time that three momentum-resolved electrons can be capture in coincidence. Such a capability is crucial for studying multi-electron correlation driven by strong fields. This was achieved by combining a camera-based momentum imaging system and varying polarizations. We carried out the first measurements on two molecular systems: benzene and methyl iodide, both with significant triple ionization yields. We didn't observe momentum correlation among the three electrons. This was attributed to the sequential triple ionization process initiated by a high laser intensity, which was required for accumulating decent statistics within a finite acquisition time. Future work employing high repetition rate lasers might enable us to study momentum correlation directly in nonsequential ionization regime. This work was published on in Molecular Physics.

4. All-optical 3D momentum imaging of electrons

We developed a new 3D momentum imaging method by employing a fast scintillator and a fast silicon photomultiplier tube. With this method, we have achieved unprecedented deadtime reduction of detecting two electrons in coincidence. This will be utilized in our future experiment of pump-probe 3D-2eAS. This was published in JPCA.

Future Plans

The Li group will continue to develop pump-probe attosecond spectroscopy by probing two electrons arising from double ionization initiated by two phase-controlled laser pulses. The method will be applied to methyl iodide and paraxylene, in consultation with the Schlegel group. The Schlegel group recently developed methodology for simulating sequential double ionization and this method will be employed to screen molecular systems for experimental studies.

With *3D-2eAS,* we obtained experimental evidence of multi-dimensional electronic wave packet dynamics in methyl iodide. However, modeling the dynamics is quite challenging. The Schlegel group will develop a new method to speed up the TDCIS-IP-CAP method.

Peer-Reviewed Publications Resulting from this Project (2019-2021)
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2. Orunesajo, E.; Basnayake, G.; Ranathunga, Y.; Stewart, G.; Heathcote, D.; Vallance, C.; Lee, S. K.; Li, W., All-Optical Three-Dimensional Electron Momentum Imaging. J. Phys. Chem. A 2021, 125, 5220
3. Cooper, G. A.; Alavi, S. T.; Li, W.; Lee, S. K.; Suits, A. G., Coulomb Explosion Dynamics of Chlorocarbonylsulfenyl Chloride. J. Phys. Chem. A 2021, 125, 5481

4. Schlegel, H. B., Ab Initio Direct Dynamics, Acc. Chem. Res. 2021, 1c00390
5. Basnayake, G.; Hoener, P.; Mignolet, B.; Lee, M. K.; Lin, Y. F.; Winney, A. H.; Debrah, D.; Popaj, L.; Shi, X. T.; Lee, S. K.; Schlegel, H. B.; Remacle F.; and Li, W., Ellipticity Controlled Dissociative Double Ionization of Ethane by Strong Fields, Phys. Chem. Chem. Phys. (in revision)

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

Award number: DE-SC0017868

Kenneth Lopata

Department of Chemistry, Center for Computation and Technology,
Louisiana State University, Baton Rouge, LA 70803

klopata@lsu.edu

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. Attosecond transient X-ray absorption, is a power tool for measuring these processes, as the elemental specificity, and corresponding spatial localization, of X-ray absorption can be exploited to probe the time-evolving electronic density in a particular region of a molecule or material. Interpretation of these spectra can be complex, however, as it requires one to relate the intensity and frequency modulations of a spectrum to the underlying dynamics.

First-principles simulations are an ideal tool for "reversing" from time delay to real-time, allowing one to reconstruct electron dynamics from the observed transient spectra. In contrast to simulations of the electron dynamics themselves, there has been less work on computing corresponding attosecond transient X-ray spectra from first-principles. To address this, the overarching goal of this project is to develop quantum chemistry techniques for simulating attosecond electron dynamics and X-ray observables on equal footing, for both solid-state and molecular systems.

Recent Progress

During the past year of this project, we focused on two interrelated thrusts: developing methods for computing attosecond transient X-ray absorption from first-principles, and using these simulations to determine the relationship between observed spectral modulations and the underlying electron dynamics. These are briefly summarized below:

I. Atom-Centered Basis Set Methods for Transient X-Ray Absorption Spectra

Time-dependent density functional theory (TDDFT) using Gaussian basis sets is a natural approach for simulating attosecond transient XAS, as it does not require pseudopotentials and allows for rapid evaluation of hybrid (Hartree-Fock + DFT) functionals. These basis sets, however, give a poor description of high energy virtual states due to their limited spatial extent, and when doing real-time (time-domain) simulations can exhibit non-physical "intruder" peaks in their absorption spectrum arising from transitions from a higher inner-shell edge to a high energy virtual states [Kadek2015]. For a simple absorption spectrum, these spurious peaks can often be identified and removed by inspection. In the case of transient X-ray absorption spectroscopy (XAS), however, intruder peaks not only pollute a computed spectrum, but also exhibit highly nonphysical time-dependent modulations in their energies and oscillator strengths. The net result is, that in molecular systems, atom-centered basis set calculations of transient XAS can be unexpectedly and catastrophically wrong.
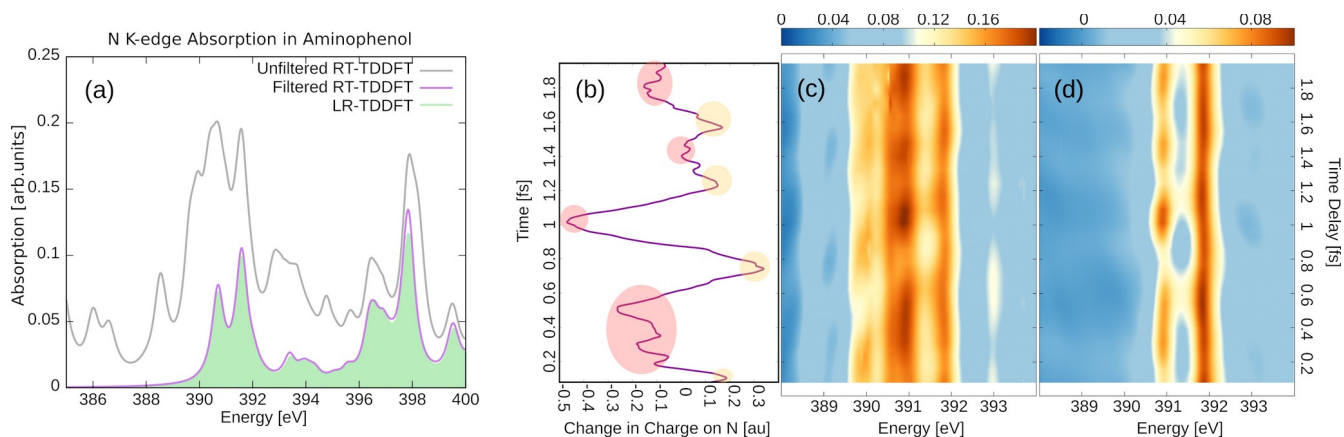
Figure 1: (a) The standard real-time TDDFT computed N K-edge XANES spectrum of aminophenol (gray) exhibits multiple nonphysical "intruder" peaks, while our filtered version (gray) matches the expected linear-response (green). (b) Time-dependent charge on the N atom following UV pumping of the molecule, along with the corresponding computed transient N K-edge XAS (c,d). The unfiltered spectrum (c) is congested with multiple intruder peaks that have nonphysical time-delay dependence, whereas the corrected spectrum (d) shows a clear correlation with the dynamics in the molecule.

To address this, we have recently developed a method of removing peaks using a filtered dipole operator that weeds out the transition amplitude between all unwanted molecular orbitals. Since this is only applied when computing the expectation value of the dipole moment, it keeps interaction with the laser field untouched. Thus, unlike complex absorbing potentials or phenomenological lifetimes, this method can be safely be utilized for simulating transient absorption spectroscopy. In the past year, we validated this method for attosecond transient absorption in atomic, molecular, and solid-state systems.

Fig. 1 shows the results for the case of UV pump/X-ray transient absorption in aminophenol. The unpumped spectrum computed using real-time TDDFT (gray curve in (a)) shows multiple nonphysical excitations spanning the N K-edge XANES region. Using our filter method (purple curve), the spectrum agrees well with the expected linear-response spectrum (green shaded curve). Fig. 1(b) shows the change in atomic charge on the nitrogen atom as a function of time following UV pumping of the molecule, with this charge oscillating from negative (less electrons; red circles) to positive (more electrons; yellow circles). The corresponding transient absorption spectra computed using standard TDDFT is shown in panel (c). Due to the presence of intruder peaks is congested and cannot be easily correlated with the electron dynamics in the system. The filtered (corrected) TDDFT spectrum (d), on the other hand, can be immediately related to the charge oscillations, with the increased absorption at the 391 eV peak occurring at time delays when the nitrogen atom has less electrons around it. This technique has proven instrumental in our ongoing basis set calculations of transient X-ray absorption in molecules and materials, and is likely to find utility in a wide range of related inner-shell spectroscopy simulations.

II. Reconstructing Electron Dynamics from X-Ray Pump/X-Ray Absorption

We previously reported a TDDFT-based method for computing the XTAS of molecules following a UV pump, and showed that for the case of carbon monoxide, aminophenol, and a charge transfer dimer (tetracyanoethylene—tetracyanoethylene), there is a general correlation between the density in a molecule and the observed XTAS spectrum: the optical density decreases and the frequency blue-shifts at the times when there is an increased electron density around an absorbing atom [Chen2020]. In a density picture, increased electron density around the particular heteroatom being probed with XAS reduces the transition probability for an inner-shell probe excitation from that atom. Building on these results, we recently determined how core-hole triggered electron dynamics can also be probed with

XTAS. Dynamics initialized by core-holes are the focus of recent interest due to the availability of short intense pulses for X-ray pump/X-ray probe transient absorption experiments at free electron lasers facilities. Rapid core-hole ionization has been shown theoretically to create a superposition of valence states that manifests as attosecond valence electron dynamics, but relatively little work has been done towards simulating the corresponding X-ray absorption step from first-principles.

Inspired by ongoing inner valence shell experiments at LCLS, we used real-time TDDFT with the PBE0 hybrid functional to determine how N 1s and O 1s core holes trigger valence electron motion, and how this motion can be probed with N and O K-edge attosecond transient XAS. These core-holes result in valence electron oscillations along the long axis of the molecule, with periods of 0.7 fs and 0.6 fs, respectively, and primarily involve a HOMO (π)$\rightarrow$LUMO (π*) superposition, with a small a mixture of other valence orbitals.

Fig. 2 shows the corresponding computed TXAS spectra for the case of N 1s ionization. The transient O K-edge XAS (panel (b)) is strongly correlated with the instantaneous local density around the oxygen atom. For example, when the O has extra electron density around it (time delay d), the optical density of the O K-edge peak at ~521 eV (O 1s $\rightarrow$ π*) is reduced ~50%. Conversely, when the O has less electron density (time delays c, e) the absorption is greater. Additionally, there are pre-edge features in the spectrum at ~515 eV that correspond to O 1s $\rightarrow$ depopulated π orbitals. As with the pumped case [Chen2020], these pre-edge features occur at frequencies outside of the ground-state absorption, and may be useful as "background-free" features in experiments. In contrast to the O K-edge spectrum, the N K-edge TXAS is mostly insensitive the to N core-hole triggered dynamics, with only subtle modulations in the absorption. Core-hole ionization of an alpha N 1s electron results in alpha spin-dominated valence dynamics, thus the transition from the remaining N 1s beta electron is not as sensitive to these dynamics. A similar effect was noticed for the O pump/O probe case (not shown).
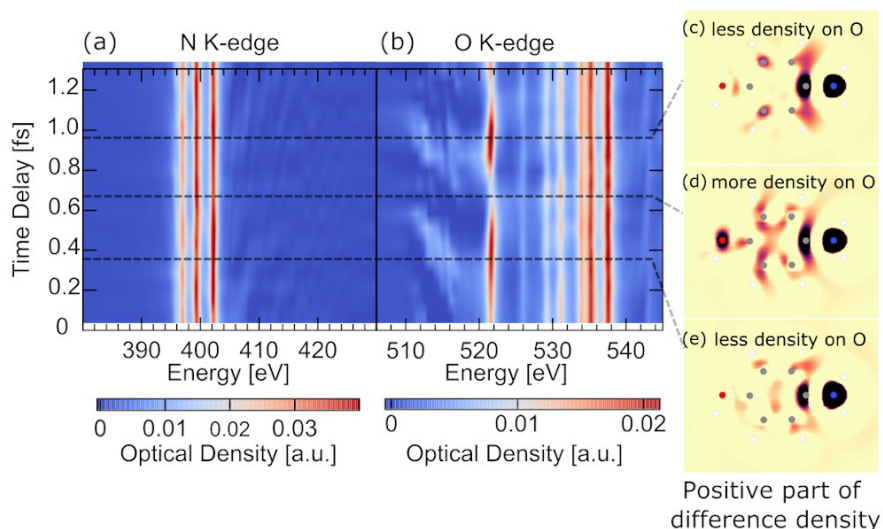
Figure 2: Simulated transient attosecond X-ray absorption following N K-edge ionization in the aminophenol molecule. (a) The N K-edge spectrum is relatively insensitive to the dynamics, whereas the O K-edge spectrum (b) exhibits reduced absorption at time delays when there is more electron density around the O atom.

These results suggest a set of general trends for X-ray pump/X-ray probe transient absorption: the optical density decreases around a probe atom when there is an increased electron density around an absorbing atom, and (ii) pump/probe schemes are most sensitive when using different heteroatoms (e.g., pump@N, probe@O). We have a draft manuscript detailing these results that will be submitted shortly [Chen2021].

III. Attosecond Transient Metallization in Wide-Gap Materials

Finally, building on our work on field-modulated XANES in semiconductors [Darapaneni2020], transient absorption in molecules [Chen2020, Chen2021], and our recently validated filtered real-time TDDFT for XAS [Yang2021], we continued work on simulating transient metalliation in wide gap materials subjected to fields with intensities near their breakdown threshold, and how this can be probed with inner-valence and core-level transient absorption. We completed work [Sissay2021] on transient metallization of α-quartz (SiO_2) probed with Si L-edge XANES using using filtered real-time TDDFT, bulk-mimicking clusters, and range-separated functionals, and found good agreement with experiment [Schultze 2013] and Schrodinger equation calculations [Krausz 2014]. Extensions to other wide gap materials is ongoing.

Future Plans

In the coming year, we will continue simulating transient X-ray absorption in a wider range of cases, including molecules with different heteroatoms (N,O,S) and different excitation types (UV, X-ray, ionization) to further determine how the how spectra can be used to reconstruct the electron dynamics. Additionally, we will focus on attosecond processes in solid-state systems subjected to fields near their breakdown threshold. The emphasis will be on wide-gap materials probed with inner-shell spectroscopy. From a methods standpoint, we will continue to implement and validate our prototype Ehrenfest dynamics code in the NWChem software package. Once complete, this will enable coupled electron/nuclear dynamics to be incorporated into both the molecular and solid-state calculations.

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Peer-Reviewed Publications Resulting from this Project (2019-2021)

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Complexity and Correlated Motion of Electrons in Free and Confined Atomic Systems

Steven T. Manson, Principal Investigator
Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303
(smanson@gsu.edu)

Project Scope

The goals of the research program are: to further 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 free and 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}; and studies of Wigner time delay on the attosecond time 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 the attosecond dynamics of electrons in the photoemission process, as revealed by Wigner time delay [1-3], were explored. Time delay of photoemission was scrutinized within a relativistic framework [4] with a focus on the variation of time delay in the vicinity of the Cooper minima. It was found that the Cooper minimum in one channel has a strong effect on time delay in other channels *via* interchannel coupling, and that relativistic effects strongly affect the time delay in regions of Cooper minima. In addition, we made a systematic study of the dipole phase and Wigner time delay in inner-shell photoionization [5] and found that the time delay, as a function of photoelectron energy, follows essentially a universal shape. And the angular distribution of Wigner time delay was investigated, revealing a strong angular anisotropy of the time delay occurs near Cooper minima while the spin-orbit splitting affects the time delay near threshold [6]. Near autoionizing resonances, the time delay spectrum can become quite complicated, exhibiting both positive and negative delays across the resonance profile [7,8]. And our work indicates that the angular distribution is also quite complex [9]; at certain energies, the time delay can be positive in one direction of photoemission, and negative in another direction, a very odd result from a physical point of view.

To obviate the effects of the Coulomb field near threshold, which dominate the time delay for neutral atom photoionization [5-7], we have studied attosecond time delay in negative ion photodetachment where the emerging photoelectron sees no long-range Coulomb field and low-energy shape resonances are emphasized in the time-delay spectrum. For Cl^- $3p$, the results show significant differences, both qualitative and quantitative, between the time delays for Cl^- and (isoelectronic) Ar photoemission at low photoelectron energy [10]; 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 (isoelectronic) Ar.

Multielectron correlations in the form of interchannel coupling have been found to be crucial determinants of photoemission time delay for outer subshells near inner thresholds [11], i.e., time delay is a sensitive probe of many-body interactions. Thus, we have conducted investigations of valence photodetachment near inner-shell thresholds [12]. 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. The results show time delay spectra dominated by many-body correlations along with very complicated energy dependence over a broad spectral range, also revealing that relativistic effects are of importance 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 [13], 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 [14] 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, an investigation 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 [15]; confined Xe $4d$ was chosen because its cross section has already been studied experimentally [16], thereby suggesting the possibility of experimental study of the Wigner time delay of Xe@C_{60}.

Our program on confined atoms is aimed at mapping out their properties (especially photoemission) to guide experiment and uncover new phenomena. We have found a huge transfer of oscillator strength from the C_{60} shell, near 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 in the photoelectron emission from the cavity, were predicted and confirmed experimentally [16]. Further, in the photoionization of endohedral atoms within nested fullerenes, the multi-walled structure makes the confinement resonances 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 [22], an effect which occurs solely owing to relativistic interactions. We have also explored the interatomic Coulomb decay (ICD) 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 [13-16], making these ICD resonances excellent candidates for experimental study. And to augment the confined atom work, we have performed a density function theory calculation of the photoionization of all 32 valence levels of free C_{60} with full account of the molecular symmetry [22]; the calculation revealed a wealth of detail on the cross sections and is the most accurate calculation to date.

Since high-Z atoms are excellent laboratories to study the combination of relativistic and many-electron correlation effects in electronic structure and dynamics, a new initiative, properties of superheavy elements, has been started [23,24]. We have studied Z=102, 112 and 118 (the heaviest known element) and significant anomalies in the subshell binding energies are found. Also, the photoionization properties show very large differences as compared to lower-Z

atoms in the same column of the periodic table. Specifically, the subshell cross sections are completely dominated by relativistic and many-body interactions. These calculations are of particular interest since experimental studies are now possible [25,26].

Future Plans

We will continue investigating attosecond time delay in photoemission, including a focus on many-body effects, negative-ion photodetachment, and nondipole effects and we will work to further our understanding of how confinement affects time delay. To provide a "road map" for experimental investigations, we will explore photoionization at high energies (tens of keV) to predict where many-body interactions alter simple behavior; preliminary indications are that this can be very significant. In the area of confined atoms, we will 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 and to include relativistic interactions to be able to deal with heavy endohedrals accurately. In addition, we shall focus on the full molecular symmetry of atomic systems confined in C_{60} to understand the limits of simple models and to deal with off-center endohedral confinement. And we shall respond to new experimental capabilities and results as they occur.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

● "Strong Dependence of Photoionization Time Delay on Energy and Angle in the Neighborhood of Fano Resonances," S. Banerjee, P. C. Deshmukh, V. K., Dolmatov, S. T. Manson and A. S. Kheifets, Phys. Rev. A **99**, 013416 (2019).
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● "Wigner time delay in photodetachment," Soumyajit Saha, Jobin Jose, Pranawa C. Deshmukh, G. Aravind, Valeriy K. Dolmatov, Anatoli S. Kheifets and Steven T. Manson, Phys. Rev. A**99**, 043407-1-8 (2019).
● "X-rays put molecules into a spin," John T. Costello and Steven T. Manson, Proc. Nat. Acad. Sci. **116**, 4772-4773 (2019).
● "Photoionization of C_{60}: Effects of Correlation on cross sections and angular distributions of Valence Subshells," A. Ponzi, S. T. Manson and P. Decleva, J. Phys. Chem. A **124**, 108-125 (2020).
● "Photoemission from hybrid states of Cl@C_{60} before and after a stabilizing electron transfer," Dakota Shields, Ruma De, Mohamed El-Amine Madjet, Steven T. Manson, and Himadri S. Chakraborty, J. Phys. B **53**, 125101 (2020).
● "Effects of Spin-Orbit Interaction Activated Interchannel Coupling on Photoemission Time Delay," Sourav Banerjee, Pranawa C. Deshmukh, Anatoli S. Kheifets, and Steven T. Manson, Phys. Rev. A **101**, 043411-1-8 (2020).
● "Outer-Shell Photodetachment of Li⁻ Near Inner-Shell Thresholds," T. W. Gorczyca and S. T. Manson, J. Phys. B **53**, 195203 (2020).
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● "Photoionization of Superheavy Atoms: Correlation and Relativistic Effects," A. K. Razavi, R. K. Hosseini, D. A. Keating, P. C. Deshmukh and S. T. Manson, J. Phys. B **53**, 205203 (2020).
● "A density functional theory based comparative study of hybrid photoemissions from Cl@C_{60}, Br@C_{60} and I@C_{60}," D. Shields, R. De, Esam Ali, M. E. Madjet, S. T. Manson, and H. S. Chakraborty, Eur. Phys. J. D **74**, 191 (2020).
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"Photoionization of Open-Shell Nitrogen Confined in C_{60}," T. W. Gorczyca and S. T. Manson, J. Phys. B **54**, 035202 (2021).
● "Electronic structure and dynamics of confined atoms," P. C. Deshmukh, J. Jose, H. R. Varma and S. T. Manson, Eur. Phys. J. D **75**,166-1-32 (2021).

● "Double Photoionization of Atomic Oxygen: Feshbach Resonances in the Two-Electron Continuum," T. W. Gorczyca, M. Wickramarathna, C. P. Ballance, S. T. Manson, D. Kilcoyne and W. C. Stolte, Physica Scr. **96**, 064005-1-10 (2021).

● "Nonstatistical Behavior of the Photoionization of Spin-Orbit Doublets," Ralph Püttner, Jessica B. Martins, Tatiana Marchenko, Oksana Travnikova, Renaud Guillemin, Loïc Journel, Iyas Ismail, Gildas Goldsztejn, Dimitris Koulentianos, Denis Céolin, Maria Luiza Rocco, Maria Novella Piancastelli, Marc Simon, David A. Keating, C. Rasadi Munasinghe, Pranawa C. Deshmukh and Steven T. Manson, J. Phys. B **54**, 085001 (2021).

● "Wigner-Eisenbud-Smith Time Delay in Atom-Laser Interactions," P. C. Deshmukh, S. Banerjee, A. Mandal, and S. T. Manson, Eur. Phys. J. Spec. Top. (Published online, June 2021).

● "Density functional study of the variants of inter-Coulombic decay resonances in the photoionization of Cl@C_{60}," Ruma De, Esam Ali, Steven T. Manson, and Himadri S. Chakraborty, Physica Scr. **96**, 104007-1-9 (2021).

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● "Photoionization of endohedral molecules: N_2@C_{60}," P. Decleva and S. T. Manson, Physica Scr. **96**, 124005-1-7 (2021).

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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 (DE-SC0020141)

Principal Investigator: Jeffrey Moses

School of Applied & Engineering Physics, Cornell University
142 Sciences Dr./223 Clark Hall, Ithaca, NY 14853

email: moses@cornell.edu

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.

Recent Progress

Our program was largely put on hold due to the pandemic during this reporting period. However, we have made some progress towards our initial phase goals of instrumentation development. Our major activities have been focused on verifying that we can perform a hyperspectral (pulses spanning more than three octaves of bandwidth) optical pump-probe spectroscopy experiment with 10-15 fs IRF.

In order to precisely assess and optimize the IRF, we have been developing methods of *in situ* full pulse amplitude and phase characterization of octave-spanning pulses at the location of the transient absorption experiment. We have constructed a new ultrafast pulse characterization scheme for our octave-spanning near-IR (1.1-2.2 micron) and mid-IR (2-4 micron) probe pulses based on the recent FROSt (frequency resolved optical switching) approach [10], which uses phase-matching-free ultrafast transient absorption in a semiconductor and a ptychographic retrieval algorithm to reconstruct the electric field of the probe pulse. Transient absorption is used as a temporal pulse gating mechanism, in which an ultrashort pump pulse changes the temporal absorption profile of a thin semiconductor relative to the moving frame of the pulse to be tested. This allows the technique to be particularly suitable for our ultrabroadband transient absorption experiments, as it can be performed *in situ* in the experiment. Since the technique does not rely on a nonlinear conversion process, there is no phase-matching bandwidth limiting its applicability for ultrashort pulses, and the test pulse bandwidth can in fact span the full transmission window of the semiconductor medium. We have collaborated with the group of François Légeré at INRS, Quebec, Canada, to implement this in our laboratory.

We completed development of the FROSt optical apparatus, which included the construction of an independent 15-fs (700-900 nm) beam line using chirped mirror pairs to serve as the instrument gate pulse and implementation and testing of our pulse retrieval algorithm. We performed first data collection with mid-IR (2-4 micron) probe pulses, and we have optimized the device for the probe bandwidth and gate pulse power level.

In order to simplify the design of our ultrafast IRF transient absorption spectrometer, we are testing a new approach for generating compressed 10-15 fs mid-IR probe pulses that will eliminate the need for a dedicated pulse shaper. This approach is based on a new technique of adiabatic frequency down-conversion using intrinsic pulse shaping to achieve zero group-delay dispersion during conversion (i.e., a 15-fs near-IR pulse input generates a 15-fs mid-IR pulse output), a technology that we have predicted in prior work but have not yet demonstrated [11]. To this aim, we implemented a quasi-phase matching device with intrinsic pulse shaping and observed efficient conversion. We constructed a new home-built frequency-resolved optical gating (FROG) pulse characterization device and used it to verify a 11-fs duration of the input near-IR pulse. We obtained initial data indicating success of the technique – the delivery of a 10-15 fs compressed mid-IR output pulse – and we are currently assessing it using the FROSt pulse characterization apparatus described above.

Future Plans

Our next step is to finalize the testing of the pump-probe IRF, and to test the transient absorption experimental apparatus in first experiments. Using FROSt, we will first characterize the IRF of a pump-probe beamline consisting of ~10-fs near-IR (~670-1010 nm) and mid-IR pulses (~2000-4000 nm). We intend to perform a spectroscopy benchmarking experiment on graphene, by observing ultrafast Pauli-blocking using our hyperspectral transient absorption spectroscopy approach. As the sample is much easier to handle than rhodopsin and the spectroscopy signal will have a very high SNR, this is a relatively simple yet scientifically interesting (as it would provide insight into the phenomena of Pauli blocking [12]) stepping stone towards our major program goals of ultrafast transient absorption experiments of the rhodopsins and DNA. We will collaborate with Dr. Giulio Cerullo of Milano Polytechnic to complete these experiments.

We are also continuing the development of our instrumentation. We are currently integrating the new spectrometers into our computer controlled pulse shaping and detection system. On the laser side, we are adding to our 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. We have designed and received the adiabatic frequency conversion crystal for the near-IR source and we will implement it after performing a first round of transient absorption experiments. Eventually, our system will possess nearly three octaves of near-continuous spectral coverage for probing the dynamical transition energy of the rhodopsin chromophore and DNA UV-absorption photosystem.

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

P. Margules, J. Moses, H. Suchowski, and G. Porat, "Ultrafast Adiabatic Frequency Conversion," J. Phys. Photonics **3**, 022011 (2021).

Theory and Simulation of Nonlinear X-ray Spectroscopy of Molecules

Shaul Mukamel
University of California, Irvine, CA 92697
smukamel@uci.edu

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, and ultrafast electron diffraction. Optimal control techniques are used to enhance desired weak features.

Recent Progress

Quantum optimal control of conical intersection dynamics in stimulated X ray Raman spectroscopy: Interesting dynamical effects in molecules, especially the ones stemming from coherences, often show up as weak spectroscopic features. It is desirable to amplify these signatures to extract detailed information about decisive events in molecular dynamics.

Optimal control theory (OCT) is a powerful tool to shape laser pulses that steer molecular motion in favor of a specific quantum pathway, with numerous successful applications in chemistry and biology. In OCT, the target is usually expressed in terms of the molecular wavefunction, a quantity that is not directly observable in experiment. In Ref. [11], we put forward a formulation of OCT that maximizes the signal itself, thereby connecting much closer to experiment. The study is exemplified on uracil photorelaxation through conical intersections. The TRUECARS signal that is sensitive only to molecular coherences emerging at conical intersections is simulated. While being background-free from populations, the signal is intrinsically weak and must compete with Auger-Meitner decay or photoionization. We employed our new method to maximize the TRUECARS signal at desired times. In contrast to an unshaped excitation (Fig. 1a), the TRUECARS signal initiated by an optimized pump (Fig. 1b) is located precisely at the desired time and amplified by 2 orders of magnitude. Our procedure is directly applicable to many other spectroscopic signals that rely on the expectation value of a positive definite operator in the optical and infrared regimes.
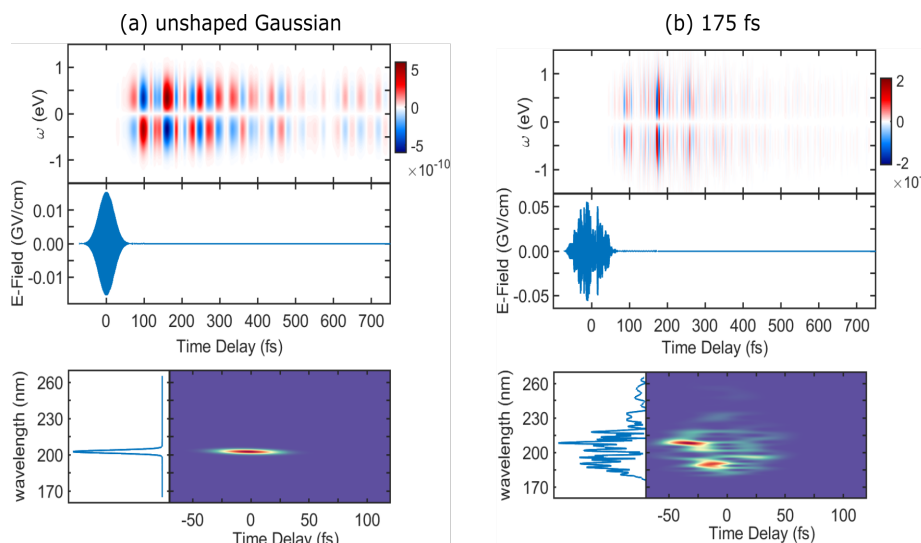
Figure 1 *Optimal control theory of the TRUECARS signal in uracil photorelaxation.* (a) *TRUECARS signal (top), UV pump initiating the excited state dynamics (middle) and its spectrogram (bottom).* (b) *same as (a), but after OCT optimization to maximize the signal at 175 fs.*

A unified approach to time resolved X-ray and electron diffraction:

In Ref. [10], we put forward a unified framework to simulate both X-ray and electron diffraction on an equal and rigorous footing. The X-ray diffraction signals include elastic scattering from (excited) state populations and inelastic scattering terms from coherences that are often missed. The latter gives detailed information about conical intersections by recording a momentum-space image of the electron transition density. In Ultrafast Electron Diffraction (UED), all terms from X-ray diffraction contribute in the same manner. Additionally, there are scattering terms from the nuclear charge density, and mixed nuclear/electronic terms. The latter contain information about the coupled nuclear and electronic motion that move on comparable timescales at conical intersections and cause the breakdown of the Born-Oppenheimer approximation. In the presented framework, all time-resolved diffraction techniques can be treated in the same language and without neglecting specific terms.

Ultrafast X-ray Imaging of Conical Intersections in thiophenol

The conical intersection dynamics of thiophenol is simulated using stimulated X-ray diffraction. The technique employs a hard X-ray narrowband/broadband hybrid probe field and provides a
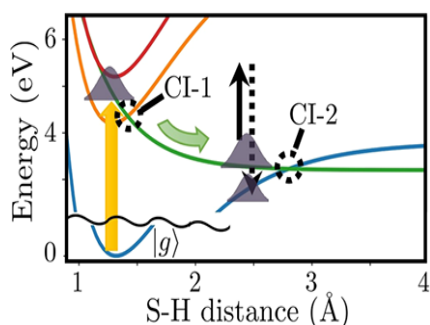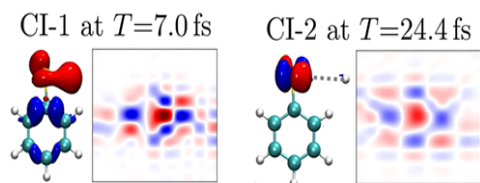
real-time and real-space image of the passage through conical intersections [7]. The signal, calculated using the minimal-coupling radiation/matter Hamiltonian, carries phase information, and the real-space image of the transition charge density can be reconstructed by its Fourier transform. The two conical intersections (S2/S1 ($11\pi\pi^*/1\pi\sigma^*$) and S1/S0 ($1\pi\sigma^*/S0$)) can be distinguished and identified by the diffraction patterns.

Figure 2: Real-time imaging of conical intersections in thiophenol

Stimulated X-ray Raman signal (SXRS) of an Iron complex in optical cavities:

We demonstrate how the electronic excitations of a transition-metal complex, ferricyanide [Fe(III)(CN)$_6$]$^{3-}$, in aqueous environment can be manipulated using UV/Vis and X-ray cavities [12]. The spectroscopic signatures of the valence- and core-polariton states in UV/Vis and X-ray absorption, and stimulated X-ray Raman signals were predicted. In an UV/Vis cavity, the absorption spectrum exhibits the single-polariton states arising from the cavity photon mode coupling to both resonant and off-resonant valence-excited states. Nonlinear stimulated X-ray Raman signals can selectively probe the two-polariton states via cavity-modified Fe core-excited states (Fig. 3). This unveils the correlation between valence polaritons and dressed core-excitations.
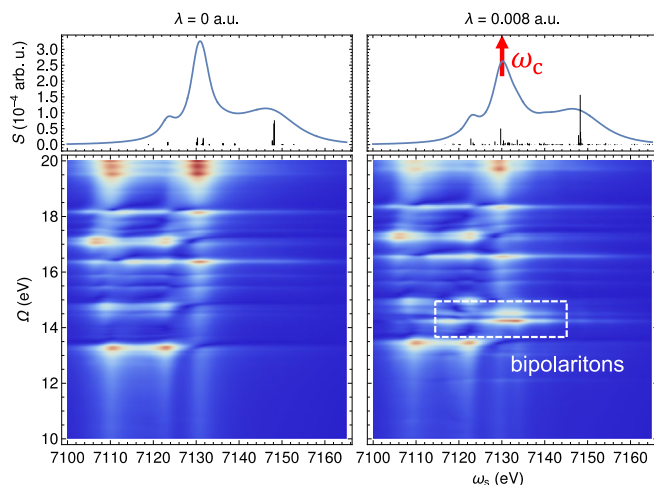
Figure 3: *(top) X-ray near edge structure and (bottom) stimulated X-ray Raman signals for bare molecules and cavity polaritons in an optical cavity. The cavity frequency is indicated in red arrow.*

Future Plans

Quantum control for diffraction signals: Our developed OCT procedure applied to Raman spectroscopy [11] will be extended to other signals. This is particularly promising for ultrafast diffraction. Adding spatial information to the signal opens new observation windows. Specific molecular features will be optimized in time and in space. This gives the possibility to distinguish and determine the spatial profile of conical intersections in the molecule, showing up at different momentum transfer amplitudes in the diffraction pattern. Application will be made to thiophenol

Resonant Stimulated X-ray Raman signals: Resonant stimulated X-ray Raman techniques offer atomic site-specificity in molecules. This was demonstrated for the detected signal and will be exploited in the excitation process. In contrast to optical excitations that usually prepare delocalized valence states, local molecular wavepackets will be excited via a stimulated X-ray Raman process involving different chromophores. This opens a novel control knob to sensitively excite different molecular pathways, which can be subsequently temporally and spatially probed, e.g., by off-resonant X-ray diffraction.

Two-dimensional X-ray spectroscopy of conical intersections: We will extend our previous proof-of-concept work to two-dimensional (2D) X-ray signals. Different chromophores in a small molecule were shown to cause cross-peaks in 2D X-ray signals when they are coupled to the same valence state. Extending this work to the dynamical regime offers higher sensitivity to. monitoring conical intersection. We will simulate transient two color 2D X-ray signals for a molecule undergoing conical intersection dynamics. A change in electronic state character will modulate the cross-peaks between different atomic sites depending on whether they are coupled via the valence state before or after the conical intersection. This will add local information to conical intersection spectroscopy.

Time-resolved photoelectron spectroscopy of conical-intersection dynamics: Time-resolved X-ray photoelectron spectroscopy (XPS) has been successfully used to probe ultrafast molecular dynamics. In XPS, an X-ray pulse ionizes the molecule and the energy of the emitted photoelectron is measured. By varying the arrival time of the ionizing X-ray pulse, the resulting time- and energy-dependent X-ray photoelectron spectrum provides information about the ultrafast dynamics undergone by the molecule. Predictions and simulations of the photoelectron spectrum are typically based on the semiclassical approximation, and only include contributions from the populations of the electronic states in the molecule, neglecting additional contributions from the molecular coherences. The latter, however, carry most valuable information about the evolution of the molecule, especially in the presence of nonadiabatic dynamics such as at the passage through conical intersections. We shall simulate time-resolved XPS taking explicitly into account the coherence contributions, in order to show how signatures of the coherence dynamics can be revealed in the signal. Calculations will be performed in molecules that can be directly tested with existing free-electron laser sources.

Peer-Reviewed Publications Resulting from the Project (2020-2021)

1. *"Stimulated X-ray Resonant Raman Imaging of Conical Intersections", Daeheum Cho and Shaul Mukamel. J.Phys.Chem. Lett , 2020, 11, 33-39*
2. *"Interferometric two-photon absorption spectroscopy with three entangled photons", Lyuzhou Ye and Shaul Mukamel. Appl. Phys. Lett. 116, 174003 (2020)*
3. *"Visualizing Conical Intersection Passages via Vibronic Coherence Maps Generated by Stimulated X-Ray Raman Signals", Daniel Keefer, Thomas Schnappinger, Regina de Vivie-Riedle and Shaul Mukamel. PNAS (2020) http://arxiv.org/abs/2008.06191*
4. *"Chiral Four-Wave-Mixing signals with circularly-polarized X ray pulses," Rouxel, Jeremy; Rajabi, Ahmadreza; Mukamel, Shaul. J. Chem. Theory Comput. 2020, 16, 9, 5784–5791*
5. *"Direct observation of coherent femtosecond solvent reorganization coupled to intramolecular electron transfer." Zachary Fox , Dr. Amity Andersen , Kathryn Ledbetter , Dr. Kasper Skov Kjær , Dr. Roberto Alonso-Mori , Julia Carlstad , Dr. Matthieu Chollet , James Gaynor , Dr. James Glownia , Dr. Kiryong Hong , Dr. Thomas Kroll , Jae Hyuk Lee , Chelsea Liekhus-Schmaltz , Marco Reinhard , Dr. Dimosthenis Sokaras , Yu Zhang , Gilles Doumy , Anne Marie March , Dr. S. Southworth , Prof. Shaul Mukamel , Prof. Kelly Gaffney , Robert Schoenlein , Dr. Niranjan Govind , Dr. Amy Cordones , Prof. Munira Khalil. Nature Chemistry 2021. DOI: 10.1038/s41557-020-00629-3*
6. *"High temporal and spectral resolution of stimulated x-ray Raman signals with stochastic free-electron-laser pulses", Stefano M. Cavaletto, Daniel Keefer, and Shaul Mukamel. Phys. Rev. X 11, 011029 (2021) DOI: 10.1103/PhysRevX.11.011029*
7. *"Stimulated X-ray Resonant Raman Spectroscopy of Conical Intersections in Thiophenol", Daeheum Cho, Jeremy Rouxel and Shaul Mukamel. J. Phys. Chem. Lett., 2020, 11, 4292–4297*
8. *"Probing delocalized current densities in selenophene by resonant x-ray sum-frequency generation" Stefano Michele Cavaletto, Shaul Mukamel. Journal of Chemical Theory and Computation. 2020 DOI: 10.1021/acs.jctc.0c00886*
9. *"Monitoring Aromatic Ring-Currents in Mg-porphyrin by Time-Resolved Circular Dichroism", Yeonsig Nam, Jérémy R. Rouxel, Jin Yong Lee, and Shaul Mukamel. Physical Chemistry Chemical Physics, 2020, 22, 26605*
10. *"Signatures of electronic and nuclear coherences in ultrafast molecular X-ray and electron diffraction", Jérémy Rouxel, Daniel Keefer, and Shaul Mukamel. Structural Dynamics 8, 014101 (2021) DOI: 10.1063/4.0000043*
11. *"Selective Enhancement of Spectroscopic Features by Quantum Optimal Control", Daniel Keefer and Shaul Mukamel. PRL 126,163202 (2021)*
12. *"Manipulating valence and core electronic excitations of a transition-metal complex using UV/Vis and X-ray cavities", Bing Gu, Stefano M. Cavaletto, Daniel R. Nascimento, Munira Khalil, Niranjan Govind, and Shaul Mukamel. Chemical Science, 2021, 12, 8088 – 8095*

Theory and Simulation of Ultrafast Multidimensional Nonlinear X-ray Spectroscopy of Molecules

Shaul Mukamel[1,*], Niranjan Govind[2], Sergei Tretiak[3], Marco Garavelli[4]

1) *Department of Chemistry and Physics &Astronomy, University of California, Irvine, CA*
2) *Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA*
3) *Theoretical Physics and Chemistry of Materials, Los Alamos National Laboratory, Los Alamos, NM*
4) *Dipartimento di Chimica Industriale "Toso Montanari", Università di Bologna, Italy*
*smukamel@uci.edu

Project Scope

Emerging X-ray free electron laser (XFEL) beam sources offer novel probes of matter with unprecedented spatial and temporal resolutions. These experimental advances call for 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.

This 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 and vibrational excitations and 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 non-adiabatic dynamics focuses on computing the nonlinear response to X-ray pulse sequences, using multidimensional Raman signals and X-ray time resolved diffraction to study non-adiabatic dynamics at conical intersections. Four-wave mixing 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.

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. Efficient simulation protocols will be designed for the description of multiple-core excited state energetics and dynamics and for the interpretation of their spectroscopic signatures. Nonlinear spectroscopy techniques well established in the visible and the infrared regimes (e.g., time-resolved photoelectron spectroscopy, time-resolved broadband stimulated Raman, and wave mixing) will be extended to the X-ray regime and applied to a large variety of molecular systems,

thus laying out 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*
  The focus of this Thrust is the integration of the capabilities of software developed by the various groups, and the development of new software, to produce state-of-the-art numerical techniques for the simulation of photo-induced molecular dynamics and different spectroscopic signals.

1. (UNIBO-UCI-PNNL) We have completed and released the implementation of iSPECTRON, a Python-based interface code parses data from popular quantum chemistry software packages (e.g., NWChem, OpenMolcas, Gaussian, Cobramm, etc.), produces the input files for the simulation of linear and nonlinear spectroscopy of molecules with the SPECTRON code (developed at UCI), and analyze the spectra with a broad range of tools. Linear and nonlinear vibronic spectra are expressed in terms of the electronic eigenstates obtained through quantum chemistry computations, and vibrational/bath effects are incorporated in the framework of the displaced harmonic oscillator model, where all required quantities are computed at the Franck-Condon point. A paper highlighting the interface capabilities has been published in the Journal of Computational Chemistry, where the pyrene linear and nonlinear spectra have been computed and analyzed. Regarding nonlinear spectra, iSPECTRON was used to simulate both one-dimensional pump-probe and 2DES spectra, to characterize the spectral diffusion of the main GSB/SE peak and to link the beating along the t_2 time to the actual molecular modes via Fourier transform analysis of the spectra. The effect of the finite time resolution of realistic experiments was also demonstrated. [Segatta2021a] [Segatta2021b]

2. (LANL-PNNL-UCI) An advanced full ab initio Multiconfigurational Ehrenfest with multiple-cloning (MCE-AIMC) formalism has been developed and implemented in the NWChem suite

Fig 1. Schematic of AIMC algorithm. (Song2021a)

[Song2021a], which allows simulating multiple-core excited-state dynamics at the TDDFT level. This MCE-AIMC approach combines two developments: First, the multiconfigurational Ehrenfest (MCE) approach uses many Ehrenfest (EHR) trajectories to guide the center of Gaussian basis functions. Second, the ab initio multiple cloning (AIMC) sampling technique improves the Gaussian basis. Each Ehrenferst mean-field trajectory is allowed to clone into two copies (Fig 1.) when crossing states have sufficiently different PESs. Each time the trajectory is cloned, the original EHR trajectory is replaced by two new trajectories and does not change the wave function. Both configurations then evolve independently. Combined with the pervious implemented Surface Hopping (SH) [Song2020], and Ehrenfest [Song2021a] functions, all three nonadiabatic dynamics methods (AIMC, SH, and EHR) and their implementation allow for different levels of sophistication (NEXMD [Freixas2021] and NWChem [Song2021a]). Altogether this constitutes a powerful simulation capability to obtain the atomistic and electronic structure information from a broad variety of chemical systems and photoexcited reactions ranging from semi-classical approaches to multiconfiguration ab initio dynamics. Details of the implementation and applications recently

were published for EHR and for MCE-AIMC [Song2021a, Freixas2021]. All three capabilies will be available to the broader community in an upcoming NWChem and NEXMD releases. [Song2020] [Song2021a] [Freixas2021] [Song2021b]

3. (PNNL-UCI) An excited-state couplings protocol within the TDDFT pseudo-wavefunction framework was developed. In this approach, we neglect the second-order response and constructed the excited state couplings directly from the amplitudes obtained from a linear-response TDDFT calculation. This simplification bypasses the need to solve the computationally expensive TDDFT quadratic response equations, which are typically limited to narrow excitation windows. This approach may also be used to access sequential double excitations within TDDFT, which in turn can be used to calculate the excited-state absorption. The code has been implemented as a post-processing standalone (Python/C++) program based on an NWChem TDDFT calculation. [Cavaletto 2021a] [Gu 2021b][Segatta2021b]

4. (UNIBO) The multi-configurational RASSCF/RASPT2 approach developed at UNIBO to describe single- and multiple-core excited/ionized states was combined with the displaced harmonic oscillator model to describe the coupling between electronic transitions and intra-molecular modes. The protocol was tested against a set of small organic molecules at the K-edges of the second-row elements carbon, nitrogen, oxygen and fluorine. This set of molecules comprises i) a series of differently fluorinated ethylene systems (to study the method sensitivity to atom substitution), ii) two stable conformers of glycine (to inspect the ability of detecting formation of intra-molecular hydrongen bonds) and iii) formaldehyde (to access the method performance in reproducing vibronically resolved spectra). XANES and XPS spectra were reproduced with a sub-eV accuracy and a correct description of the spectral line-shapes was achieved. Insights for the effects caused by removing a core-electron from a given atom in terms of bond rearrangement and its influence on the resulting spectral shapes were provided. Duschinsky and Herzberg-Teller effects were discussed in detail, highlighting their important role in core-excitation/ionization. Eventually, a path to systematically improve the accuracy of the simulated spectra and facilitate the interpretation of existing experimental techniques while guiding the development and validation of new ones was outlined. [Montorsi2021]

- **Thrust 2:** *New multi-pulse experiments designed to make use of LCLS-II capabilities*

In this thrust we focus on designing and predicting novel signatures that are enabled by recent and future progress at LCLS-II and similar sources. They provide unprecedented temporal and spectral resolutions over a large spectral detection window, thereby opening new windows into ultrafast molecular dynamics. The unique signatures we focus on are coherences that emerge at conical intersections (see Fig. 2). A combination of high-level methodologies in the static and dynamic regime, provided by the symbiotic expertise of our team members, is necessary to accurately simulate these events.
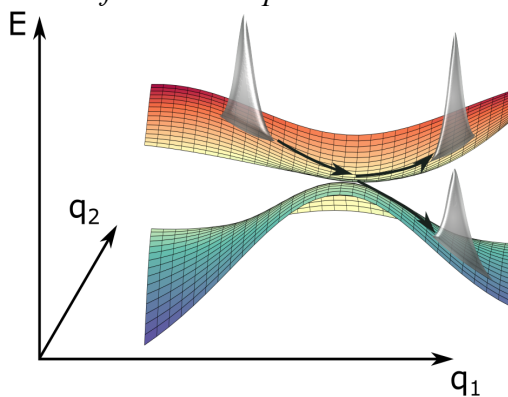
Fig 2. Two electronic states forming a conical intersection. An approaching nuclear wavepacket bifurcates and a vibronic coherence emerges.

1. TRUECARS (UCI-LANL)

Following initial design on a model system, we have significantly deepened our understanding of the TRUECARS signal. This technique uses a hybrid broadband (attosecond) + narrowband (femtosecond) X-ray pulse pair to induce a stimulated Raman process between the two electronic states forming the conical intersection. It reads

$$S(\omega, T) = 2 I \int_{-\infty}^{\infty} dt \, e^{\{i \, \omega(t-T)\}} \varepsilon_0^*(\omega) \varepsilon_1(t - T) \langle \psi_a(t) | \hat{\alpha}_{ab} | \psi_b(t) \rangle$$

and only emerges once there is nuclear wavepacket in both electronic states, i.e., once the conical intersection is reached.

We have demonstrated that the vibronic coherence structure can be extracted directly from the signal and that it gives detailed information even for large molecules including all possible nuclear degrees of freedom and thereby a large decoherence reservoir [Keefer2021b]. Overcoming earlier experimental limitations, we have redesigned the signal to specifically take into account the stochastic nature of current FEL sources and thereby make it readily available at LCLS-II [Cavaletto 2021b].

2. Time-resolved X-ray and electron diffraction (UCI-UNIBO)
   Continuous technical progress at XFELs pushes scattering-based measurements to the single-molecule and femtosecond limits. We have put forward a rigorous quantum-electrodynamical formalism to treat photon and electron diffraction signals on equal footing and account for all contributions, including the usually neglected inelastic scattering events and especially coherences. The latter contribute as weak signatures in the time-resolved diffraction signal [Keefer2021], requiring sophisticated strategies to extract them. We have demonstrated that this can be achieved by realizing high momentum transfer amplitudes requiring very hard X-rays [Keefer2021], by separating the inelastic contributions containing the coherences with frequency-resolved stochastic diffraction [Cavaletto2021a], or by direct coherence enhancement via resonant IR fields [Keefer2021c]. [Keefer2021a] [Cavaletto2021a][Keefer2021c]

3. Complementary information (UCI-UNIBO)
   TRUECARS and time-resolved X-ray diffraction provide complementary information about conical intersections. While energetic distributions of the electronic states and vibronic coherences are available via TRUECARS, diffraction patterns yield spatial information about electron densities. More specifically, the transition density associated with the electronic excitation is encoded in the coherence term, holding the promise to record spatial images of conical intersections. In a comparative study [Nam2021], we are highlighting these differences to give LCLS-II users a detailed overview of what information is accessible with which signal. The preliminary results are depicted in Fig. 3. [Nam2021]

TRUECARS

(a)

(b) real-space

(c) *q*-space

TXRD

(d)
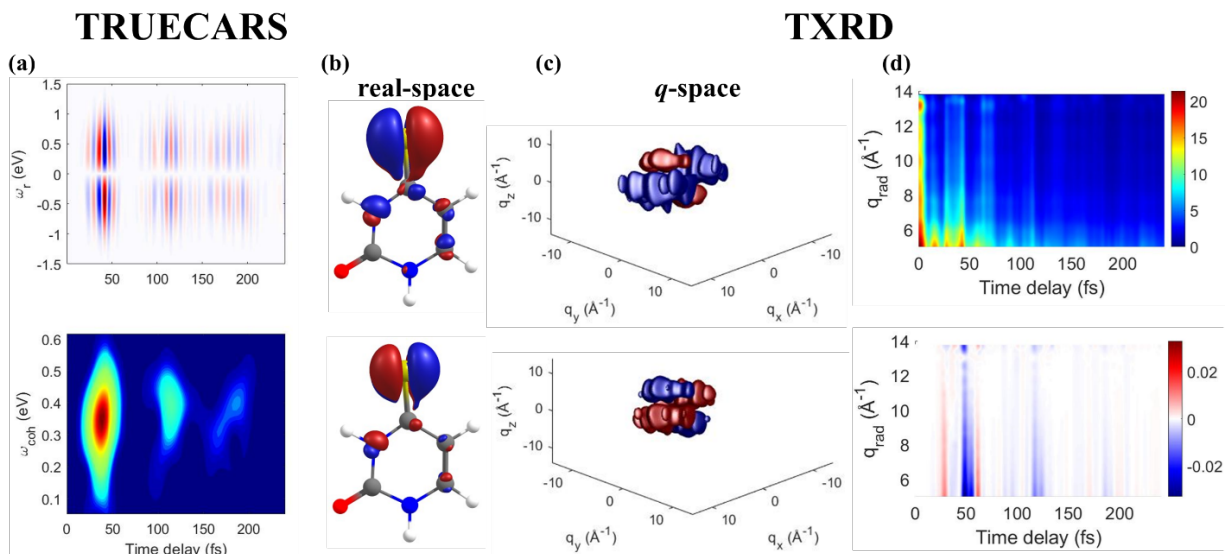
Fig. 3: Stimulated X-ray Raman spectroscopy and Time-resolved X-ray diffraction on 4-thiouracil. (a) TRUECARS measurement and its FROG spectrogram, (b) Electron transition densities, (c) Three-dimensional coherence contribution to the diffraction signal in momentum-space. (d) Radially averaged TXRD signal (top) and coherence

- **Thrust 3:** *Applications to specific molecular systems*

1. (LANL-UCI-UNIBO) We have applied the Surface Hopping formalism and semiempirical Austin Model 1 potential in the NEXMD package to preform non-adiabatic (NAMD) and adiabatic molecular dynamics simulations for the transition-state dynamics of photoexcited cyclooctatetraene (COT). COT is a prototype molecule acting as photo-switch owing to its ability to change geometry upon optical excitation. An active excited to ground state relaxation pathway accompanied with a $S_3/S_2(D_{2d}) \rightarrow S_1(D_{8h}) \rightarrow S_0(D_{4h}) \rightarrow S_0(D_{2d})$ double-bond shifting mechanism are determined through the excited state non-adiabatic dynamics simualtion (Fig 2). The simulated excitation lifetime is in good agreement with experiment. The first excited singlet state S_1 is found to play a crucial role in the photochemistry and a photoswitching fucntion. The

Fig 4. Transition-state dynamics of photoexcited COT. (Song2021b)

obtained critical molecular conformations, energy barrier, and transition state lifetime results will provide a basis for further investigations of the bond order inversion and photo-switching process of COT using more accurate AIMC approach. [Song2021b]

2. (UCI-UNIBO) Azobenzene is a textbook photochemical switch with applications in photopharmacology, optoelectronics and many more. Based on the quantum dynamics simulations on the extremely accurate potential energy surfaces of azobenzene isomerization computed by UNIBO, a series of quantum dynamics studies focusing on different X-ray signals were carried out. In [Keefer2021a], time-resolved X-ray diffraction patterns of the cis→trans photoisomerization were simulated, with a special focus on the mixed elastic/inelastic scattering

from coherences that emerge in the decisive moments of photochemistry and photophysics (such as passage through conical intersections sketched in Fig. 2). These vibronic coherences give rise to relatively weak contribution to the signal. A novel and effective strategy that employes a resonant IR field to enhance the coherence was discussed in reference [Keefer2021c]. A different route was taken in Ref. [Cavaletto2021a], where we demonstrated a time- and frequency-resolved X-ray diffraction technique, which can employ existing stochastic X-ray pulses to separately image the coherence contributions. By suggesting these techniques on real molecules that are easily accessible experimentally, like azobenzene, we aim for maximal impact on current and future LCLS-II experiments. [Keefer2021a] [Cavaletto2021a] [Keefer2021c]

Future Plans

- **Thrust 1: Methodology**

1. (PNNL-UCI-UNIBO-LANL) ***SXRS Protocols Combined with Excited-State Molecular Dynamics***: We will extend our TDDFT-based excited-state couplings protocol by combining it with our excited-state dynamics capabilities to calculate the necessary ingredients to perform SXRS simulations on ultrafast excited-state trajectories of molecular complexes (including transition metal centers) in realistic solvation environments. These studies will be benchmarked against protocols based on accurate wavefunction approaches (RASPT2). To mitigate the high computational cost of wavefunction-based approaches, we will use smaller complex surrogates of the full complexes. These calculations are relevant for experiments planned for LCLS-II in the tender and hard x-ray regimes. Valuable insights into the electronic configuration of transition element complexes like the nature of the metal-ligand interactions, nature of the charge separated states, solvent effects, and d-d interactions, respectively, can be gained from these calculations.

(PNNL-UCI) ***Probing Local Molecular Chiralitity on the Excited-State***: We are developing TDDFT-based X-ray spectroscopy approaches to probe chirality on the excited state combined with excited-state dynamics. Circular dichroism (CD) is a widely used method for measuring enantiomer excess. Time-resolved CD spectroscopy can monitor variation in the molecular chirality on a femtosecond timescale. Both UV and X-ray radiation can be used as a probe for the chirality. While UV radiation is more delocalized, X-ray probes (for example, XCD) are element specific transitions which can be particularly useful for targeted measurements. As an initial test case, we have chosen the fomamide molecule which is achiral in the ground state but become chiral in the S_1 excited state potential energy surface. First, we ran an ab-initio molecular dynamics (AIMD) calculation on S_1 excited state using time-dependent density functional theory (TDDFT). Excited CD and XCD spectra of S_1 excited state have been calculated using geometries extracted from the AIMD trajectory at 30fs intervals. Figures 5 and 6 shows the time-resolved CD and XCD spectra.
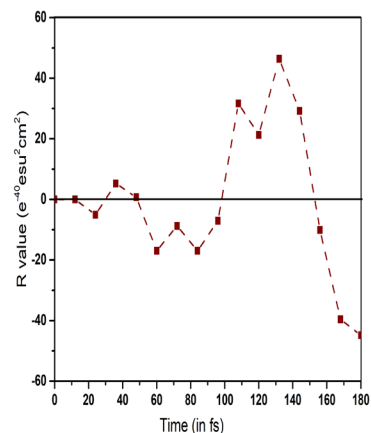

Fig 5. Time-resolved CD spectra of formamide for S1−>S2 transition

We will extend this study to larger molecules and explore the dependence on the distance between the chiral center and the X ray chromophore.

Fig 6. Time-resolved XCD spectra of formamide for S1 at the O and N K-edges

2. (UNIBO) *Extending the RASSCF/RASPT2 approach to larger molecules*: a semi-automated selection of the active space orbitals for large molecular systems will be explored: the method is designed to include the "fundamental" orbitals based on the brightness of the transitions they will be involved in. This step aims at large systems (where a "standard" selection of the active space orbitals would quickly result in unfeasibly long computations) and when multiple-core excited states have to be considered. This will extend the applicability of the accurate RASSCF/RASPT2 protocol.

3. (UNIBO-LANL-UCI) *Connecting ab-initio multiple cloning dynamics with RASSCF/RASPT2 core-excitation calculations*: based on the success of combining quantum dynamics on a grid with accurate simulation of relevant quantum chemistry quantities for X-ray signals with the RASSCF/RASPT2 approach, we plan to apply a similar protocol on the trajectory-based MCE-AIMC dynamics (see Recent Progress – Thrust 1). This will allow to: a) consider all the nuclear degrees of freedom (instead of very few); b) focus only on the important pathways explored during the dynamics (instead of performing computations from large grids of points); and c) consider system of larger size. To that end, we will explore how to properly interface very different levels of theory (dynamics performed at semi-emirical level, single point calculations performed at RASSCF/RASPT2 level) and to select, out of the large number of molecular geometries explored along the MCE-AIMC dynamics, a limited number of key points on which higher level core-excitation computations should be performed.

4. (UNIBO- UCI) *Towards exact multidimensional quantum dynamics***:** the Multi Configuration Time Dependent Hartree (MCTDH), which constitutes one of the most efficient and accurate standards for efficient quantum dynamics modeling, will be extended toward routine on-the-fly simulation of X-ray spectroscopies. The UNIBO unit had recently developed a diabatic multi-dimensional MCTDH protocol [Aleotti2021] that allows to parametrize the quantum dynamics Hamiltonian by employing RASPT2 energy inputs. Its capabilities were demonstrated for a challenging benchmark, the pyrene molecule, where the dynamics of 7 excited states linearly coupled to 49 normal modes, undergoing multiple crossings, was successfully simulated and validated against time-resolved experimental spectra in the UV-VIS window. [Aleotti2021] The same approach will be applied and coulpled to the RASSCF/RASPT2 approach to model X-ray signals and will be applied to other systems (including nucleobases, DNA and retinal proteins). [Aleotti2021]

5. (UCI-UNIBO) *Quantum optimal control for signal enhancement:* Expanding on recent ideas to amplify specific signatures in convoluted signals, different implementations of quantum optimal control will be employed. In [Keefer2021c], we have shaped an additional infrared field to enhance coherence signatures of conical intersections. In the future, we will explore how shaping the probe pulse itself can enhance and modulate the signal to highlight different contributions. Phase
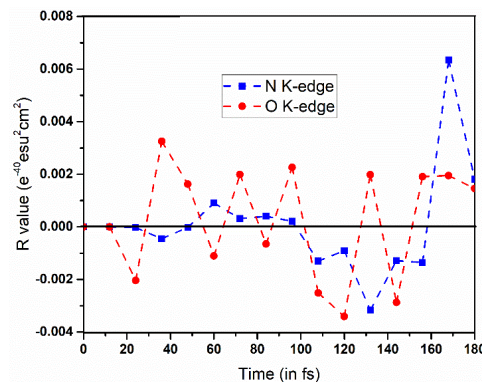
modulation of the probe pulse can potentially eliminate specific quantum pathways, and bandwidth modulation can suppress or enhance different spectral windows where specific contributions are dominating. This will motivate and accelerate the design of X-ray pulse shaping devices currently performed at LCLS-II.

- **Thrust 2: Application Areas**

1. (PNNL-UNIBO-LANL-UCI) ***Early Time Dynamics and Interplay of Spin and Geometry in the Ligand Exchange Reaction of Aqueous Fe(II) Hexacyanide****: Ligand exchange reactions are ubiquitous in transition metal complexes, and controlling reactions using light is attracting interest for a wide range of applications. The mechanisms and timescales for ligand exchange reactions depend upon ligand-ligand repulsion, ligand-metal electron donation, crystal field effects, and metal spin state. $[Fe^{II}(CN)_6]^{4-}$ is known to have two UV induced reaction channels: photo-oxidation, where a hydrated electron is produced, and photo-aquation, where a solvent H_2O molecule replaces a CN- ligand. Despite being a well-known model system, the mechanism underlying the photoaquation reaction has only recently begun to be addressed. The initial step of the photoaquation reaction involves a symmetry forbidden d-d excitation, which results in the formation of a penta-coordinated intermediate species, $[Fe^{II}(CN)_5]^{3-}$, that is in a triplet state. We would like to ask the following questions to shed light on the early time dynamics. What is the timescale of the early time dynamics of the transition from the initially excited singlet state to the triplet state? What is the role of the solvent (water)? We will calculate linear and nonlinear X-ray signals at the Fe K-edge to establish the fingerprints of the early time spin state transition. Since this is a model single-center transition metal complex, we will also be able to complement these calculations with higher-order wavefunction-based approaches (RASPT2) for comparison. We will also compute the SXRS signals to reveal the correlations between valence excitations and Fe core-excitations. This is an active area that is being explored with state-of-the-art ultrafast spectroscopies at LCLS at SLAC. This study will be able to provide new insights and intepretation of experimental data.

2. (PNNL-UNIBO-LANL-UCI) ***Ultrafast Photoinduced Spin and Charge Dynamics in Multiple Center Mixed Valence Transition Metal Complexes***: Mixed valence transition metal complexes are the ideal platform to quantify how electronic correlations, spin transitions, vibronic couplings, and local solute-solvent interactions control intramolecular electron motion on the femtosecond time scale. To explore electron transfer coupled to solute and solvent nuclear motions, we will study solvated mixed-valence complexes, where the ultrafast photoinduced electron transfer between metal centers occurs on a timescale of ~100 fs. An interesting system is the $Co^{III}Fe^{II}$ Prussian blue analogue, a mixed-valence transition metal complex, where it has been recently shown that the initial photoinduced process is a spin transition at the Co center, which occurs within ~50 fs, which in turn drives the metal-to-metal (Fe-to-Co) CT within ~200 fs. Can nonlinear X-ray spectroscopies elucidate further details on the coupled dynamics in these complexes? We will design two-color pump–probe pulse sequences, by tuning the pump and probe pulses to the transition energies of different element-specific core excited states to study the couplings between valence and core excited states.

3. (PNNL-UCI) ***Stimulated X-ray Raman spectroscopy of electronic excitations in core-ionized metalloporphyrins:*** We will develop and apply TDDFT-based protocols to explore the valence electronic excitations in metalloporphyrins prepared by a sudden metal core ionization induced by an attosecond X-ray pump pulse. The created superposition of cationic excited states will be probed with two-dimensional transient X-ray absorption and by three dimensional attosecond stimulated X-ray Raman signals. The latter generated by applying a second broadband X-ray pulse combined with a narrowband pulse tuned to an X-ray chromophore in the ligands (for example, S, P, F, O) should reveal the complex coupling and dynamics between valence and core-excited manifolds of the cation.
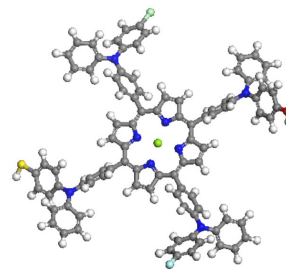
4. (LANL-PNNL-UCI) ***Light harvesting, Energy Transfer (ET), and Charge Transfer (CT) Processes.*** The chlorophyll A dimer (Fig.5) is a minimal essential unit of the light-harvesting complex I (LHC-1). Our preliminary study using NEXMD and SH algorithm shows that the overall B→Q_y internal conversion occurs in the sub-picosecond timescale, in agreement with the time-resolved spectroscopy. In photosynthesis, intermolecular excitation energy relaxation details are critical to ET since many pigments are excited simultaneously and participate in global energy flux. To study the presence of coherence effects during the intermolecular energy exchange, the TDDFT level MCE-AIMC dynamic combining with the TRUECARS Raman signal analysis will contribute to elucidate the underlying mechanisms. This will also be explored using our quantum dynamics modeling with a direct simulation of coherent X-ray spectroscopic probes.
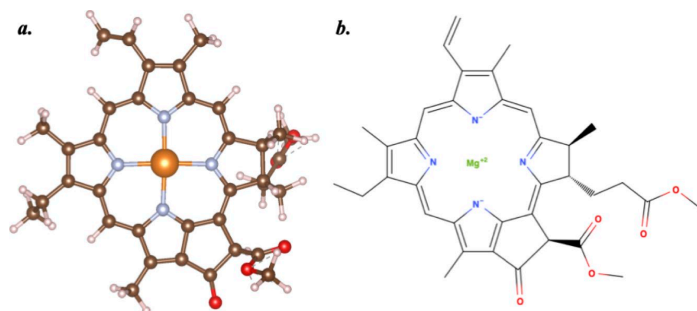

Fig.7 Target Chlorophyll molecular unit for light harvesting, Energy Transfer, and Charge Transfer process study.

5. UCI-LANL-UNIBO-PNNL) *Conical Intersection (CI) passages, Aromaticity, and Molecular Currents*. Cyclooctatetraene (COT) is a conjugated cyclic 4n p-electrons system that is non-aromatic in the ground state (where it assumes a non-planar boat-like (D_{2d}) symmetric structure with localized single and double C-C bonds), but gains aromaticity (with a planar (D_{8h}) symmetric structure yielding equalized C-C bond lengths) in the first singlet excited state S_1, reachable upon UV irradiation (Fig.1*a, c*). Its non-radiative decay via a polyradical S_1/S_0 conical intersection does also promote a bond order inversion in the ground state. COT thus appears as an ideal candidate for studying the non-aromatic (S_0)/aromatic (S_1) photo-switching process. This can also be employed to control the photoinduced charge transfer (CT) involving suitably designed push/pull substituted COTs. While the CT between the two push/pull substituents is allowed by the aromatic character of the excited S_1 state (ON STATE), which creates conjugation between them, CT is interrupted on the ground state (OFF STATE), where a stable non-aromatic de-conjugated cyclic system exists, preventing conjugation between ring substituents. Additionally, the abrupt inversion of aromaticity into anti-aromaticity occurring at the conical intersection (Fig. 6*b*), when the system decays back to the ground state, provides an ideal target for stimulated Raman signals to probe this process. On top of our pervious non-aromatic/aromatic/anti-aromatic transition-state dynamics study [Song2021b], these upcoming studies will use the new developed MCE-AIMC method to provide the electron structure during the photo-switching process, then apply the TRUECARS, TXRD and MCD analysis to identify signatures of photoinduced structural transformation, conical intersection dynamics and predict a photo-controlled current (Fig.1*d*).
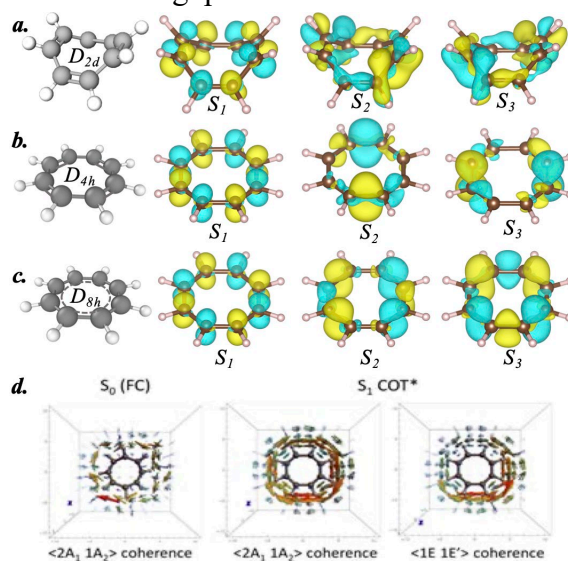
Fig 8. Optimized geometries and transition density plot of *a.* Ground state (S_0) boat-shaped non-aromatic D_{2d} symmetric, *b.* Ground state (S_0) metastable planar anti-aromatic D_{4h} symmetric, and *c.* 1st excited-state (S_1) natural minimum planar aromatic D_{8h} symmetric of COT. *d.* Transition current density maps for coherence, which can generate a directional ring current.

6. (UNIBO-UCI) *Exploring canonical and non-canonical nucleobase dynamics with X-rays*: based on the experience acquired in modeling the azobenzene photo-induced dynamics on a reduced-dimensionalty grid with accurate quantum dynamical approaches, and describing a large variety of resonant and non-resonant X-ray signals capable of capturing relevant events such as passage through conical intersecitons (see Application 2 in Thrust 3), we will extend this protocol to other relevant molecular systems. The family of thio-substituted uracils is particularly relevant here: not only we will consider the effect of the substitution in different positions by means of X-ray techniques, but this will be achieved at multiple possible K-edges of the different atoms that composes the molecules. These studies will first characterize the signals from resonant and non-resonant core-excitations (at the different edges) for different molecular geometries. The potential energy surface of the relevant states along the photo-induced dynamics will be eventually described as a grid over key molecular coordinates, at the RASSCF/RASPT2 level of theory. Quantum dynamics over these surfaces will then be coupled with a large variety of resonant/non-resonant X-ray signals, aimed at differentiating the different deactivation pathways that may

follow the initial photo-excitation.

7. (UCI-LANL) ***TRUECARS for charge migration in large dendrimers***: Recently, we had extended our methodology to simulate signals based on the MCE-AIMC approach [Keefer2021b]. In Fig. 9, we present our next molecular target, a dendrimer with three equivalent arms.
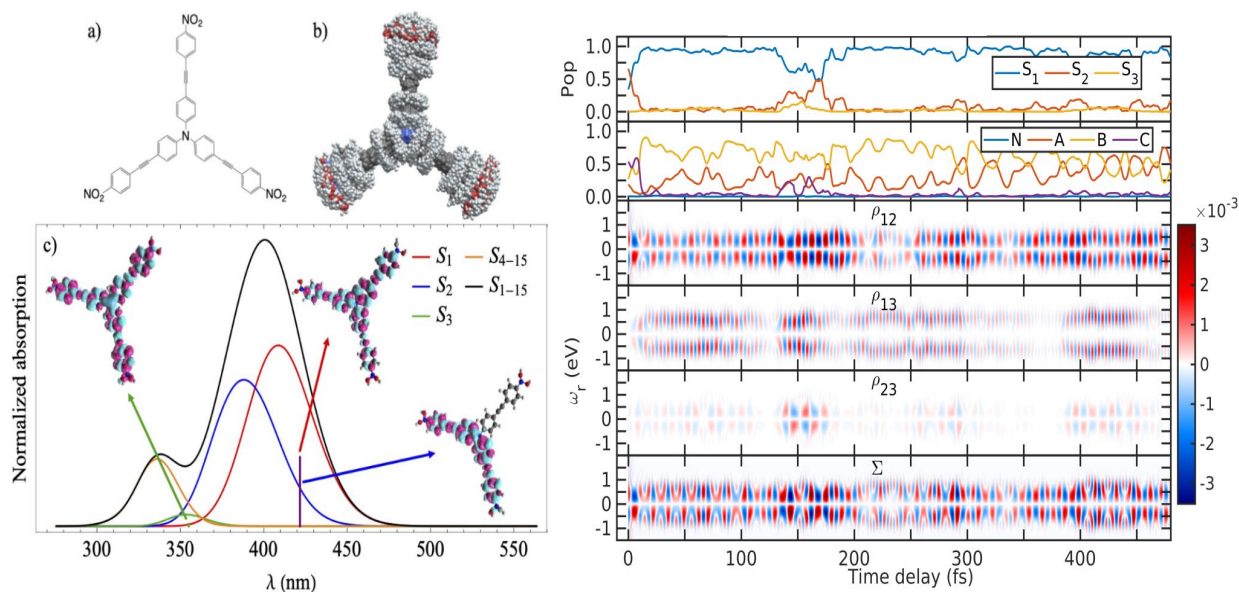
Fig.9 (a) Dendrimer with three equivalent arms (b) overlayed structures after ground-state sampling (c) transition densities localized over different arms depending on the structure (right) Population dynamics, transition density localization in arms A, B and C, and TRUECARS signal of the three different coherences between S_1, S_2 and S_3 along a sample trajectory.

In a preliminary study, we have simulated the non-adiabatic dynamics in several hundred trajectories. Obtained trajectories exhibit charge fluctuations where the electron transition density is either delocalized across all three arms or localized in one or two arms. For a representative trajectory, we have calculated the TRUECARS signal monitoring the coherences between three involved electonic states. In a future continuation, we will simulate the TRUECARS signal and its spectrogram for all trajectories and closely examine of the charge fluctuations and other physical behavior can be monitored via the signal. Additionally, the arms will be chemically modified such that different X-ray chromophores are present in each arm, offering the possibility to monitor local charge densities via resonant signals, or their coupling via off-diagonal signatures in multi-dimensional signals.

Peer-Reviewed Publications Resulting from this Project (2020-2021)

[Aleotti2021] Aleotti, F., Aranda, D., Jouybari, M., Garavelli, M., Nenov, A., Santoro, F., J. Chem. Phys., (accepted 2021), DOI: 10.1063/5.0044693

[Cavaletto 2021a] Stefano M. Cavaletto, Daniel Keefer, Jérémy R. Rouxel, Flavia Aleotti, Francesco Segatta, Marco Garavelli, and Shaul Mukamel. "**Unveiling the spatial distribution of molecular coherences at conical intersections by covariance X-ray diffraction signals**", *PNAS 2021 Vol. 118 No. 22 e2105046118*

[Cavaletto 2021b] Stefano M. Cavaletto, Daniel R. Nascimento, Yu Zhang, Niranjan Govind, and Shaul Mukamel. "**Resonant Stimulated X-ray Raman Spectroscopy of Mixed-Valence Manganese Complexes** ", J. Phys. Chem. Lett. 2021; 12:5925-5931. Doi: 10.1021/acs.jpclett.1c01190 J Phys Chem Lett

[Dorfman 2020] **Nonlinear spectroscopy with quantum light**", Konstantin E. Dorfman, Frank Schlawin, Shaul Mukamel. "Roadmap", 2020 *J. Phys. B: At. Mol. Opt. Phys.* **53**, 072002.

[Freixas2021] Victor M Freixas, Alexander J White, Tammie Nelson, Huajing Song, Dmitry V Makhov, Dmitrii Shalashilin, Sebastian Fernandez-Alberti, Sergei Tretiak, **Nonadiabatic Excited-State Molecular Dynamics Methodologies: Comparison and Convergence.** *The Journal of Physical Chemistry Letters*, 2021, *12*(11), pp.2970-2982.

[Gu 2020a] Bing Gu, Artur Nenov, Francesco Segatta, Marco Garavelli, and Shaul Mukamel. "**Manipulating core-excitations in molecules by X-ray cavities**", *Phys. Rev. Lett. 126, 053201 4 February 2021 DOI: 10.1103/PhysRevLett.126.053201*

[Gu 2021b] B. Gu, S.M. Cavaletto, D. R. Nascimento, M. Khalil, N. Govind, S. Mukamel, "**Manipulating valence and core electronic excitations of a transition-metal complex using UV/Vis and X-ray cavities**"
DOI: 10.1039/D1SC01774H (Edge Article) *Chem. Sci.*, 2021, **12**, 8088-8095

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[Keefer 2021b] Daniel Keefer, Victor M. Freixas, Huajing Song, Sergei Tretiak, Sebastian Fernandez-Alberti, and Shaul Mukamel. "**Monitoring Molecular Vibronic Coherences by Ultrafast X-ray Spectroscopy**", *Chemical Science, 2021, 12, 5286-5294 DOI: 10.1039/D0SC06328B*

[Keefer 2021c] "Keefer, Daniel; Rouxel, Jérémy; Aleotti, Flavia; Segatta, Francesco; Garavelli, Marco; Mukamel, Shaul. **Diffractive Imaging of Conical Intersections Amplified by Resonant Infrared Fields**", *Journal of the American Chemical Society (2021 accepted)*

[Montorsi 2021] Montorsi, Francesco; Segatta, Francesco; Nenov, Artur; Mukamel, Shaul; Garavelli, Marco. "**A high-level multireference approach to simulating soft X-ray spectroscopy of molecules; methods, spectra and insights**", *(2021, JCTC, in review)*

[Nam2021] Yeonsig Nam, Daniel Keefer, Artur Nenov, Irene Conti, Flavia Aleotti, Francesco Segatta, Jin Yong Lee, Marco Garavelli, and Shaul Mukamel, "**Conical Intersection Passages of 4-Thiouracil Probed by X-ray Diffraction and Stimulated Raman Spectroscopy**", *Chemical Science (submitted 2021)*

[Segatta2021a] Francesco Segatta, Daniel R. Nascimento, Artur Nenov, Shaul Mukamel, Niranjan Govind, Marco Garavelli, "**iSPECTRON: a simulation interface for linear and non-linear spectra with ab-initio quantum chemistry software**", *Journal of Computational Chemistry. 2021; 1-16* **DOI:** *https://doi.org/10.1002/jcc.26485* **https://github.com/ispectrongit/iSPECTRON/**

[Segatta2021b] F. Segatta, M. Russo, D. N. Nascimento, D. Presti, F. Rigodanza, A. Nenov, A. Bonvicini, A. Arcioni, S. Mukamel, M. Maiuri, L. Muccioli, N. Govind, G. Cerullo and M. Garavelli, "**In silico ultrafast nonlinear spectroscopy meets experiments: the case of perylene bisimide dye**", *(2021, JCTC, under revision)*

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[Song2021b] Huajing Song, Yeonsig Nam, Daniel Keefer, Marco Garavelli, Shaul Mukamel, Sergei Tretiak, "**Non-adiabatic molecular dynamic study of the relaxation pathways for the photon-excited cyclooctatetraenes**". *Journal of Physical Chemistry Letters, 2021, 12, 5716-5722, DOI: https://doi.org/10.1021/acs.jpclett.1c01397.*

Quantum Dynamics Probed by Coherent Soft X-Rays

Margaret M. Murnane and Henry C. Kapteyn
JILA and Department of Physics, University of Colorado at Boulder
Phone: (303) 210-0396; E-mail: Margaret.Murnane@colorado.edu

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 2019, with 13 peer-reviewed papers published or in review 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), Los Alamos (2), Argonne (1), SLAC (1)). Finally, in other distinct research efforts, we have several collaborations with DOE laboratories, including LBNL and LANL, to probe dynamics in quantum systems using coherent extreme UV (EUV) and soft X-ray (SXR) sources.

Fig. 1. Tunable, low-divergence high harmonic combs via necklace-driven HHG. a Two linearly polarized vortex beams create a necklace-structured intensity and phase profile, to drive HHG. The intensity lobes at the necklace focal plane represent a phased array of HHG emitters which interfere on-axis to form a comb of harmonics with a spacing dependent on the OAM of the driving fields. **b** Time-frequency analysis of necklace-driven HHG. **c** HHG spectrum for necklace-driven and Gaussian-driven HHG. The harmonic spacing, $\Delta\omega=10\omega_0$, (15.5 eV), in the necklace-driven on-axis HHG spectrum is a result of OAM conservation, and is tunable by varying the OAM of the laser. The on-axis harmonics are emitted with a divergence which is significantly reduced compared to that of Gaussian-driven HHG, and decreases with increasing harmonic order.

Recent Progress

Tailoring the Spectrum and Structure of Extreme-Ultraviolet Beams [3,7,8,11]: In recent research we made significant progress in creating spectral, polarization and phase structured HHG beams (spin and orbital angular momentum, SAM and OAM) that can be used to enhance contrast, and to implement unique excitations and probes of chiral structures in molecules, magnetic materials and nanostructures. We demonstrated the first bright, phase-matched, extreme UV (EUV) and soft X-ray HHG beams with circular (or elliptical) polarization, as well as the ability to generate HHG

beams with unique polarization and phase structure. These new HHG capabilities are ideal for a suite of ultrafast X-ray absorption spectroscopies, photoelectron spectroscopies and magneto-optic spectroscopies. Moreover, through selection rules, they allow us to sculpt the HHG spectrum, to tailor the spectral, polarization and phase structure for particular applications. In our most recent work that is currently under review, we demonstrated that by structuring the driving laser beam into a necklace shape with a modulated spatial phase, we can control the spectrum and divergence of EUV and soft X-ray HHG beams. This allows us to create a phased array of HHG sources, that give rise to low-divergence, EUV HHG combs with tunable line spacing. This is in contrast to the supercontinuum spectra that are generated when mid-IR lasers are used to drive soft X-ray HHG.

Reaction dynamics probed using ultrafast VUV light [2,4,5]: In research in collaboration with the Labbe group in Engineering at CU Boulder, we used our unique VUV source to address unanswered questions surrounding enol chemistry. Experimental detection is difficult because mass spectrometry cannot distinguish between enols and their thermodynamically favorable ketone isomers, or distinguish between direct products and dissociative ionization products in combustion. Vacuum ultraviolet (VUV) light can ionize just above the ionization potential, imparting low energy to the molecule, making it possible to identify the presence of an enol by its lower ionization energy compared to the isomer. By combining this novel VUV light source with an established microreactor, we observed the thermal tautomerization of acetone to propen-2-ol for the first time. We also observed the thermal tautomerization of cyclohexanone to 1-cyclohexenol and methyl vinyl ketone to 2-hydroxybutadiene. Our measurements can be used to constrain models, inform future experimental studies of enol reactivity, and enhance current understanding of combustion and environmental chemistry.

Mapping electron-phonon coupling and hot electron cooling in copper nanoparticles in the warm-dense matter regime: Understanding matter under extreme conditions of temperature and pressure is critical for many areas of science. Despite recent advances, it remains very challenging to directly probe the nature of the strongly-coupled interactions within WDM e.g. electron-ion couplings and hot electron cooling, particularly on femtosecond-to-attosecond timescales. This makes it difficult to validate advanced theories. In an exciting advance, with theory collaboration from LBNL and LANL, we overcame these long-standing challenges by uniformly
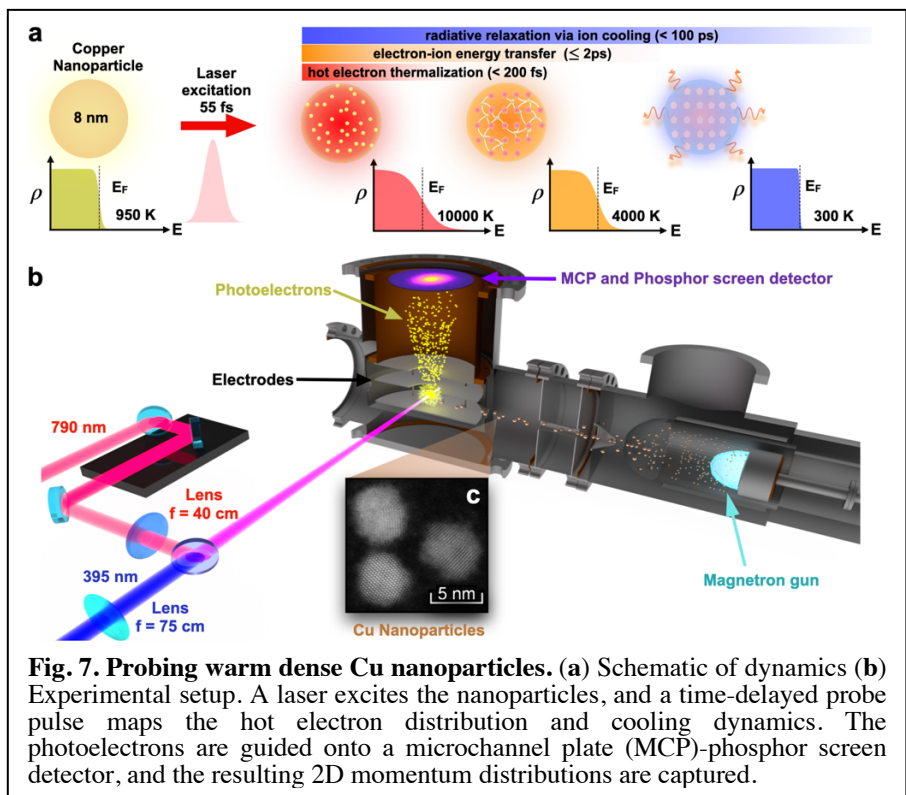
Fig. 7. Probing warm dense Cu nanoparticles. (**a**) Schematic of dynamics (**b**) Experimental setup. A laser excites the nanoparticles, and a time-delayed probe pulse maps the hot electron distribution and cooling dynamics. The photoelectrons are guided onto a microchannel plate (MCP)-phosphor screen detector, and the resulting 2D momentum distributions are captured.

collaboration from LBNL and LANL, we overcame these long-standing challenges by uniformly

heating isolated ~8nm metallic nanoparticles with a strong ultrafast laser field to very high electron temperatures (>10,000K) – while staying below the ablation threshold. We then mapped the resulting WDM dynamics using photoelectron spectroscopy. This enabled unique and accurate measurements of this exotic state of matter. We made three surprising findings. <u>First</u>, we extracted higher values of the electron-ion coupling than had been observed in previous experiments. <u>Second</u>, we were also able to experimentally validate advanced theories of highly-excited strongly-interacting matter. We found that the state of matter we produced lies at the boundary between hot solids and plasmas. <u>Third and finally</u>, we observed a strong modulation of the electron temperature on ~ 1 ps timescales during cooling, by hundreds of K, that had never been observed before in WDM.

Some insights can be derived from past experiments we performed on laser-excited 2D charge-density-wave materials probed using using angle-resolved photoemission. We made the first observation of a modulation of the electron temperature by the breathing mode of the coherent phonon. Some of these observations can be explained by the coherent phonon shifting the band position and the density of states periodically near the Fermi level, leading to an oscillation of the electron temperature at the same frequency—*but with opposite phase*—in order to compensate for the change in electronic entropy. Thus, the breathing mode can modulate the electron temperature directly, and exhibit a π-phase difference from the oscillation of the band shift. Thus, we speculate that a similar modulation of the electron temperaure by the breathing mode in a WDM nanoparticle is occuring. However, to make direct comparisons, we need to correlate the coherent phonon (breathing mode in the nanoparticle) dynamics with the electron temperature modulation, to determine the relative phase. Our student, Dr. Quynh Nguyen, is now a postdoc at SLAC, may be able to address some of these questions using the ultrafast electon diffraction (UED) and XFEL capabilities at SLAC.

Future work

We will extend bright structured high harmonic beams 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 to implement dynamic EUV and soft x-ray spectroscopies in samples excited using mid-IR – UV light. We will also capture dynamics in molecules and nanosystems using photoelectron spectroscopies.

Peer-Reviewed Publications/Patents Resulting from this Project (2019-2021)

1. M. Murnane, X. Shi, H. Kapteyn, "Probing and manipulating magnetic and 2D quantum materials using ultrafast laser and high harmonic sources, Journal of Physics: Condensed Matter **33**, 353001 (2021), doi: 10.1088/1361-648x/abfe21.

2. D. Couch, Q. Nguyen, A. Liu, D. Hickstein, H. Kapteyn, M. Murnane, N. Labbe, "Detection of the keto-enol tautomerization in acetaldehyde, acetone, cyclohexanone, and methyl vinyl ketone with a novel VUV light source, "Proc. Combustion Institute **38**, 1737–1744 (2021). DOI: 10.1016/j.proci.2020.06.139

3. Two papers currently in revision, following peer-review (2021).

4. D.E. Couch, M. M. Murnane, D. D. Hickstein, and H. C. Kapteyn, "High-Flux MHz Vacuum Ultraviolet Light Source," Optics and Photonics News **31**(12), 34-34 (2020). DOI: 10.1364/OPN.31.12.000034

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harmonic generation in negative-curvature hollow-core fibers," Optica **7**, 832 (2020). doi.org/10.1364/OPTICA.395688

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7. L. Rego, K. Dorney, N. Brooks, Q. Nguyen, C.-T. Liao, J. San Roman, D. Couch, A. Liu, E. Pisanty, M. Lewenstein, L. Plaja, H. C. Kapteyn, M. M. Murnane, C. Hernandez-Garcia, "Generation of extreme-ultraviolet beams with time-varying orbital angular momentum," Science **364**, eaaw9486 (2019). DOI:10.1126/science.aaw9486. *Featured on cover*.

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10. F. Bencivenga, R. Mincigrucci, F. Capotondi, L. Foglia, D. Naumenko, A. Maznev, E. Pedersoli, A. Simoncig, F. Caporaletti, V. Chiloyan, R. Cucini, F. Dallari, R. Duncan, T. Frazer, G. Gaio, A. Gessini, L. Giannessi, S. Huberman, H. Kapteyn, J. Knobloch, G. Kurdi, N. Mahne, M. Manfredda, A. Martinelli, M. Murnane, E. Principi, L. Raimondi, S. Spampinati, C. Spezzani1, M. Trovo, M. Zangrando, G. Chen, G. Monaco, K. Nelson, C. Masciovecchio, "Nanoscale transient gratings excited and probed by extreme ultraviolet femtosecond pulses," Science Advances **5**, eaaw5805 (2019). DOI: 10.1126/sciadv.aaw5805

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DYNAMICS OF TWO-ELECTRON ATOMIC AND MOLECULAR PROCESSES

Principal Investigator: **Jean Marcel Ngoko Djiokap**, Award Number: **DE-SC0021054**
The University of Nebraska, Department of Physics and Astronomy
855 North 16th Street, 208 Jorgensen Hall, Lincoln, NE 68588-0299
Email: marcelngoko@unl.edu

PROGRAM SCOPE

The goals of this project are to develop state-of-the-art numerical toolboxes and theoretical tools to describe, understand, control, and image ultrafast correlated two-electron atomic or molecular processes involving energy and spin angular momentum transfers from intense, short-wavelength, ultrashort, arbitrarily-polarized, external electromagnetic fields eventually delayed in time to matter. More generally, we aim to study the time-dependent correlated dynamics of interacting few-body quantum systems. Investigations of current interest are in the areas of strong field physics, linear attosecond 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 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 induce and control electron dynamics in atoms and molecules using attosecond pulses, how to transfer energy and spin angular momentum from electromagnetic radiation to matter, how to image electron correlation processes while they occur, and how to characterize the ionizing pulses.

RECENT PROGRESS

A. *Interference of photoelectron wave packets in ionization of atoms by two time-delayed crossing arbitrarily polarized ultrashort pulses:* Ramsey interference [1] of electron wave packets created by atomic photoionization using two time-delayed, single-color, crossing ultrashort pulses are studied both analytically using first-order perturbation theory (PT) and numerically using ab-initio quantum mechanical calculations. The use of orthogonal pulses is shown to lead to two counterintuitive electron phenomena that are absent for co-propagating pulses (see for instance [2-7]). First, when the initial pulse is linearly-polarized along the propagation direction of the circularly-polarized (CP) later pulse, we predict detection geometries in which the CP single-photon absorption leads to regular single-arm Fermat spirals in the photoelectron momentum distribution (PMD). Second, while copropagating oppositely elliptically-polarized pulses are known to lead to distorted (irregular) spirals, it is shown here that crossing elliptically-polarized pulses with the same or opposite helicity can produce regular spirals or Newton's rings depending on the detection geometry, which even become distorted for CP pulses. Our prediction, illustrated for the case of photoionization of H and He atoms, is quite general as may hold for any S-state. *(See publication [P1] in the list of project publications below.)*

B. *Generation of torqued-electronic vortices: Atomic photoionization by multiple pairs of slits*

We study interactions of multiple temporal pairs of slits in coherent control of photoionization of S-state atoms using a pulse train of N+1 pairs evenly delayed in time by τ, in which the two pulses in a pair with a delay τ_0 are counter-rotating CP. For interacting two double-slit experiments, while Ramsey interference [1] between two identical Archimedean spirals yields pairs of principal

spirals in the PMD in the polarization plane, interference of two spirals with opposite handedness does not lead to spirals, but instead to crocodile-eye-like patterns with nictares. For more than two interacting experiments, the resulting patterns turn out just to be those two novel reference patterns modulated by different kinds of N-dependent time-energy Fraunhofer functions exhibiting diffraction-grating-like patterns. *(See publication [P2] in the list of project publications below.)*

C. Temporal coherent control of resonant two-photon double ionization of H₂ via doubly-excited states: We use time-delayed, oppositely, CP few-cycle attosecond nonoverlapping pulses to study the temporal coherent control of resonant two-photon double ionization (TPDI) of fixed-in-space H_2 molecule via doubly excited states. For light propagating along the molecular axis ($\mathbf{k}\|\mathbf{R}$) and the carrier frequency of 36 eV resonantly populating the $Q_2{}^1\Pi_u^+$ doubly-excited state (DES) and other $^1\Pi_u^+$ DESs, it is shown that the indirect ionization path via these DESs changes the character of the kinematical vortex-shaped PMD produced by the two direct ionization paths from fourfold to twofold rotational symmetry, which is similar to TPDI of helium atom [8]. However, angular distributions exhibiting a quantum beat effect between the ground state and a DES seen for the He atom are observed here for its molecular counterpart with an anomaly in shape and magnitude, not in frequency; which is due to autoionization decays and quantum beats between DESs. For $\mathbf{k}\perp\mathbf{R}$ and a carrier frequency of 30 eV populating several Σ_u^+ and Π_u^+ DESs, the momentum distribution is shown to exhibit dynamical electron vortices with four spiral arms, which stems from mixing the Δ_g^+, Π_g^+, and Σ_g^+ dynamical ionization amplitudes. Our treatment within either the adiabatic-nuclei approximation or fixed-nuclei approximation shows that the latter provides a very good account for this correlated process. *(See publication [P3] in the list of project publications below.)*

D. *On the topological charge of the transition amplitude in atomic ionization by short pulses*

The concept of electron vortex lines (EVL) [9] is useful in various problems of quantum mechanics. In particular, it has been shown in [2-7] for instance that EVL can be seen as spiral patterns in the PMD resulting from the ionization of atoms and molecules by a pair of ultrashort laser pulses. These vortices are characterized by the magnitude of the topological charges describing zeros of the transition amplitude. In our work, we use perturbation theory (PT) to analytically evaluate the topological charge in the multiphoton regime. We show that the topological charge calculated from the transition amplitude for the process of atomic ionization depends not only on the helicity of the laser pulses, but also on the atomic initial state, which has well-defined orbital angular momentum quantum numbers l_i, m_i. *(Authors: J.M. Ngoko Djiokap, A.V. Meremianin, and N.L. Manakov; Manuscript in preparation and will be submitted soon.)*

E. *Electron photoionization for characterization of a train of attosecond pulses or isolated attosecond pulses with time-dependent polarization state:* We study Ramsey interference between a variety of electronic wave packets produced in photoionization of an S-state atom by a train of pulses with arbitrary polarization state and intensity. For a plateau [P2] or Gaussian intensity profile for the pulse train, changing the ellipticity and/or helicity of the composite pulses from pulse to pulse are found to lead to a variety of novel reference interference patterns, including pairs of principal and secondary two-arm spirals, a set of two-arm spirals well separated in energy, a dense two-arm roller coaster spirals, and Newton's rings. We use PT to explain how these reference patterns from TDSE calculations originate from interactions between basic patterns (regular or irregular Archimedean spirals and Newton's rings with variable intensity) in the Ramsey interferometry arms. In all cases, the robustness of these resulting patterns against the

coherence of the pulse train is tested by varying the CEP of the composite pulses in the train. *(Author: J.M. Ngoko Djiokap; Manuscript to be submitted to Phys. Rev. A in October 2021.)*

F. Pulse shaping in strong-field ionization: theory and experiments: Intense ultrafast pulses cause dissociative ionization and shaping the pulses may allow control of both electronic and nuclear processes that determine ion yields. We report on a combined experimental and theoretical effort to determine how shaped laser pulses affect tunnel ionization, the step that precedes many strong-field phenomena. We carried out experiments on Ar, H_2O, N_2 and O_2 using a phase step function of amplitude ¾π that is scanned across the spectrum of the pulse. Semiclassical as well as fully quantum mechanical TDSE calculations are in excellent agreement with experimental results. We find that precise knowledge of the field parameters in the time and frequency domains is essential to afford reproducible results and quantitative theory and experiment comparisons. *(This work is a collaboration with the research group of Prof. Marcos Dantus from Michigan State University; Manuscript to be submitted to Phys. Rev. A in October 2021.)*

FUTURE PLANS

In addition to preparing research described above for publication, we are currently investigating four research problems that should be completed in the remainder of the project period:

(a) ***Effects of attochirp on electron matter-wave vortices***. We shall consider first the case of photoionization of He by a pair of time-delayed, oppositely circularly-polarized attosecond pulses having equal, opposite, or different chirp parameters. Next, we shall consider the investigations B. and E. listed above in the context of chirped pulses. *(This work is being carried out by supervising my graduate student Nathaniel Strandquist at UNL.)*

(b) **Double-slit effects in double photoionization of the ground state of the H_2 molecule by few-cycle, elliptically polarized pulses in the high-photon soft X-ray regime within the dipole approximation**. The first observable we shall consider is the dynamical electron vortex-shaped momentum distribution produced by time-delayed elliptically-polarized pulses [10], which can be viewed as a temporal two-slit experiment. The second observable is the angular and momentum distributions exhibiting dichroic phenomena by a single pulse [11]. For perturbative weak pulse intensities, various high pulse carrier frequencies, and different molecular orientation with respect to the light propagation direction, we shall search for particular detection geometries and energy sharing configurations that enable direct observation and control of two-slit effects by tuning the pulse ellipticity.

(c) **Resonant harmonic generation (RHG) produced by chirped laser pulses**. In previous work (see, e.g., [12]) on RHG of two-electron atoms (He and Be), electron correlation effects via doubly-excited states were evidenced and isolated only when scanning the laser driving frequency. To avoid any frequency scan, we shall use the concept of chirp as a means to be on resonance with transitions from the ground state to doubly-excited states.

(d) **Effects of the time delay between the two laser fields in RHG of He or Be:** Control the multiphoton regime plateau structure (see, e.g., [12]) will be study by considering overlapping and nonoverlapping driving laser pulses at resonant frequencies.

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PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2020-2021)

[P1] J. M. Ngoko Djiokap, A. V. Meremianin, and N. L. Manakov, "*Electron interference in atomic ionization by two crossing polarized ultrashort pulses,*" Phys. Rev. A **103**, 023103 (2021).

[P2] J. M. Ngoko Djiokap, "*Atomic photoionization by multiple temporal pairs of slits,*" Phys. Rev. A **104**, 013115 (2021).

[P3] J.M. Ngoko Djiokap and A.F. Starace, "*Temporal coherent control of resonant two-photon double ionization of the hydrogen molecule via doubly-excited states,*" Phys. Rev. A **103**, 053110 (2021).

Low-Energy Electron Interactions with Complex Molecules and Biological Targets

Award No. DE-FG02-02ER15337

Thomas M. Orlando

School of Chemistry and Biochemistry and School of Physics,
Georgia Institute of Technology, Atlanta, GA 30332-0400
Thomas.Orlando@chemistry.gatech.edu,

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. Electron Spin Polarization Dependent Damage of the Chiral Amino Acid L-Histidine: 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 APS on low energy electron induced damage and stimulated desorption of enantiopure L-histidine vapor deposited on a magnetized Co film. The damage of approximately monolayer films of L-histidine by low energy spin-polarized electrons (SPE) ejected from a magnetized cobalt substrate has been probed using x-ray photoelectron spectroscopy (XPS). Average damage cross sections for N-containing motifs of L-histidine are between 25-30 Mb and 2-5 Mb for zwitterions and neutral molecules, respectively. The magnetization direction of the substrate, which controls the ejected SPE helicity, was reversed in situ, and statistically significant differences in the damage cross sections of 10-30% were measured between positive and negative electron helicities. This is the first
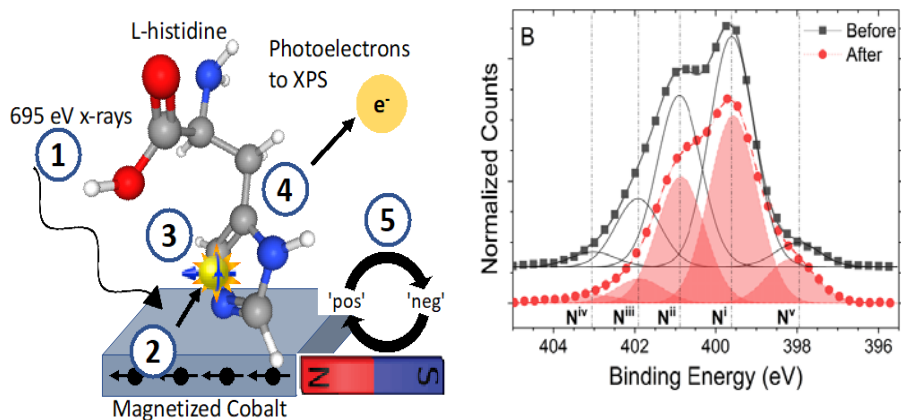

Figure 1: Rough diagram of the experimental setup where (1) 695 eV x-rays are incident on magnetized Co and (2) eject SPE which then (3) interact with adsorbed L-histidine. (4) The chemical state of the molecules is monitored as a function of ejected electron fluence using XPS, and (5) the magnetization direction of the substrate is reversed in situ.

measurement of spin dichroism (SD) in an amino acid. The differential cross sections suggest that inelastic scattering of SPE with chiral molecules could contribute to the persistence of one enantiomer vs. the other under certain irradiation conditions, particularly for the zwitterionic species.

The most recent work at APS used vapor deposited L-isovaline onto a Fe(100) surface magnetized parallel to the surface plane. Film damage due to spin-polarized secondary electrons ejected from the substrate was monitored using x-ray photoelectron spectroscopy (XPS), and reversing the magnetization direction of the substrate in situ allowed the growth/decay rates for the two electron-spin-polarization directions to be compared. However, it was found that only a monolayer coverage of L-isovaline was stable on the surface at room temperature, and that the damage cross sections for the molecule were smaller than others previously investigated. This resulted in very shallow decay curves and significant uncertainty in the cross-section determination, such that a statistically significant cross-section difference could not be determined. The damage cross section in the sub-monolayer region appeared to be linear in concentration indicating the potential dominance of a surface adsorbed negative ion intermediate.

Task 2. Investigating intermolecular Coulomb decay (ICD) at weakly interacting interfaces: We have continued studies of intermolecular Coulomb decay (ICD) in condensed samples composed of weakly interacting rare gases and small polyatomic molecules such as water and ethane. Specifically, we probe ICD at interfaces by monitoring the ejected ion masses and kinetic energies as a function of incident electron energy for pure Xe, Ar and Kr. A direct comparison of the Kr with respect to Ar indicates a bi-exciton process may be occurring in Ar which is capable of producing excimers. This is correlated with the simultaneous production of n=1 surface and bulk 3p excitons on neighboring atoms. This bi-exciton can create a doubly excited Ar_2^{**} which can autoionize in the gas-phase after stimulated desorption into Ar_2^+ or a dissociative $(Ar-Ar)^+$ leading to Ar^+.

Enhanced yields of protonated water clusters are observed from sub-monolayer coverages of water on rare gases, with a particularly large yield for Kr substrates. Only fragment ions and ion-molecule reaction products are observed from sub-monolayer coverages of ethane on all rare gas substrates. This is assumed to be related to ability of holes to localize within the water cluster vs. localization within the bonds of simple hydrocarbons.

Positive ion desorption following electron impact dissociative ionization of ethane adsorbed on the rare gases Ar, Kr and Xe has also been studied as a function of electron energy from
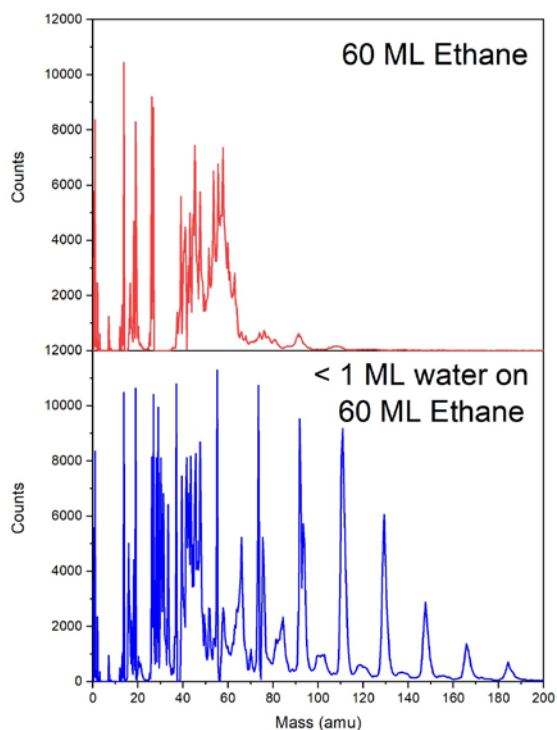

Figure 2. Electron-beam induced ion desorption from 60 ML of ethane and < 1 ML of water adsorbed on 60 ML of ethane. The efficient production and removal of protonated water clusters is likely due to ICD either within the cluster or between the underlying ethane.

threshold to 100 eV. Based on the dependence of ion yields on the identity of the rare gas, it is likely that the majority of ethane molecules undergo indirect ionization following hole transfer from the rare gas (or electron transfer from the ethane). Due to the near-resonant nature of charge transfer, the ethane molecular ion is produced in excited states with occupancy that is defined by the identity of the rare gases. , This leads to differences in ion yields and branching ratios. The quantitative yields increase with the increasing ionization energy gap between the rare gas and ethane, with Ar > Kr > Xe. The ion branching ratios vary with energy from threshold to about 35 eV, showing the fragmentation pattern changes with the availability of excess energy, with C-C bonds more likely to break than C-H bonds over a certain energy range. This effect is most pronounced for Xe, followed by Kr and then Ar. The large increase in yields from 25 eV onwards for all rare gases is likely due to processes like ICD involving Coulomb explosion between neighboring $C_2H_6^+$ localized within ethane clusters.

Future Plans

- We will continue to expand the ICD work on rare gases to condensed clusters and thin-films of molecules such as water, ammonia, ethane, acetylene and tetrahydrofuran, a nucleotide sugar surrogate. The water and ammonia will be dominated by proton transfer, hole delocalization within the cluster and possible ICD. The simple hydrocarbons may undergo dissociative ionization and ion-molecule reactions. ICD in the tetrahydrofuran system was demonstrated in XUV photoionization studies of water:tetrahydrofuran clusters. [6] In this work, the amount of water and the role of proton transfer was not clear. We will correlate the velocity distributions of the departing ions that form as a result of proton catalyzed charge transfer vs. ICD Our proposed efforts will complement the gas-phase cluster experiments and unravel the relative contributions of energy dissipation via ICD, electron transfer mediated decay and proton transfer.

- Low energy electron damage of amino acids and short peptide sequences will be studied in an effort to understand radiation interactions with cell membranes. Damage of films functionalized with amino acids will initially be examined to mimic damage to *Arg–Gly–Asp* intergins and proteins on cancer cell walls. This information will ultimately be valuable to targeted treatment of cancer using radiotherapies.

- 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 in complex solutions containing solvated ions are planned. Initial efforts will focus on examining energy exchange in simple low concentration aqueous (NaOH and NaCl) solutions. Joint proposals with the Argonne AMOP group for LCLS-II beam-time were pursued and beam-time was granted but not until FY2022.

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Recent publications acknowledging support from this program

1. M. Schaible, R. A. Rosenberg, S. Kundu, and T. M. Orlando, "Electron Spin-Polarization Dependent Damage to Chiral Amino Acid l-Histidine", *J. Phys. Chem. Lett.*, 11, 23, 10182–10187 (2020) https://doi: 10.1021/acs.jpclett.0c02855.
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2. S. Kundu, M. J. Schaible, A. D. McKee, and T. M. Orlando, "Direct damage of deoxyadenosine monophosphate by low-energy electrons probed by x-ray photoelectron spectroscopy", *J. Phys. Chem. B.* 124, 9, 1585-1591 (2020), doi.org./10.1021/acs.jpcb.9b08971 (Supplementary Cover Selected)

3. A. D. 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, "Low-energy electron interactions with complex biomolecules and carcinogenesis", Georgia Tech. Petit Institute for Bioengineering and Biosciences, January 14, 2020. (Recording at https://smartech.gatech.edu/handle/1853/62374)

2. T. M. Orlando, "Low-energy electron interactions with complex molecules and biological targets", DOE Atomic Molecular and Optical Physics PI- Program Meeting, Oct. 28-30, 2019.

Structure from Fleeting Illumination of Faint Spinning Objects in Flight

Award Number: DE-SC0002164
Principle Investigator: Abbas Ourmazd
Dept. of Physics, University of Wisconsin Milwaukee
3135 N. Maryland Ave, Milwaukee, WI 53211
ourmazd@uwm.edu

Project Scope

The advent of intense, ultrashort pulses of X-rays and electrons has made it possible to obtain two-dimensional snapshots of individual molecules. The resulting datasets contain invaluable information on the structure and function of key nanomachines, including macromolecular systems. We have developed a series of increasingly powerful algorithms to determine the structure, conformations, energy landscapes, and dynamics of molecular systems. These methods combine techniques from scattering physics, Riemannian geometry, graph theory, and machine learning.

We have recently discovered that the data-driven concepts underlying our work also have important implications for the construction of quantum compilers for classical dynamics.

Recent Progress

We made significant progress on two fronts:

1. Advanced data-driven machine learning algorithms for extracting information from noisy, incomplete data recorded with substantial timing uncertainty; and
2. Data-driven quantum compilers for classical dynamics.

1. Machine learning algorithms for extracting information from non-ideal data

Our latest algorithms extract few-femtosecond, atomic-resolution structural dynamics from noisy, 99% incomplete data recorded with 100fs timing uncertainty. At the same time, our algorithms increase the complexity of systems within theoretical and data-analytical reach from those consisting of ~10 atoms to systems containing more than 2,000 atoms.

More generally, our data-driven approach combines the superb spatial resolution of structural methods, such as crystallography, with the exquisite time resolution of spectroscopy. Our results on the ultrafast, atomic-level changes associated with the femtosecond de-excitation of the Photoactive Yellow Protein (PYP) via a conical intersection reveal novel oscillatory charge dynamics involving often ignored regions surrounding the chromophore. These results are corroborated by independent spectroscopic measurements of PYP in the spectroscopically accessed 3 – 30 THz range. Our results reveal the structure-dynamical trajectories leading to the vicinity of, and through the PYP conical intersection, and elucidate the properties of the potential energy surfaces involved in PYP de-excitation. Finally, our machine learning analysis of experimental data enables simple and numerically accurate quantum-dynamical simulations. This approach constitutes a data-driven route to a wide variety of important processes in complex molecular systems hitherto inaccessible to first-principles calculations.

2. Data-driven quantum compilers for classical dynamics
With D. Giannakis, J. Schumacher, and J. Slawinska

We have developed a framework for simulating measure-preserving, ergodic dynamical systems on a quantum computer. Our approach provides a new operator-theoretic representation of classical dynamics by combining ergodic theory with quantum information science. The resulting quantum compiler enables efficient simulation of spaces of classical observables with exponentially large dimension using a quadratic number of quantum gates. The compiler is based on a quantum feature map that we introduce for representing classical states by density operators on a reproducing kernel Hilbert space, H. Furthermore, an embedding of classical observables into self-adjoint operators on H is established, such that quantum mechanical expectation values are consistent with pointwise function evaluation. In this scheme, quantum states and observables evolve unitarily under the lifted action of the Koopman evolution operators of the classical system. Moreover, by virtue of the reproducing property of H, the quantum system is pointwise-consistent with the underlying classical dynamics. To achieve an exponential quantum computational advantage, we project the state of the quantum system onto a finite-rank density operator on a 2n-dimensional tensor product Hilbert space associated with n qubits. By employing discrete Fourier-Walsh transforms of spectral functions, the evolution operator of the finite-dimensional quantum system is factorized into tensor product form, enabling implementation through an n-channel quantum circuit with an $O(n)$ number of gates and no interchannel communication. Furthermore, the circuit features a quantum Fourier transform stage with $O(n^2)$ gates, which makes predictions of observables possible by measurement in the standard computational basis. We prove theoretical convergence results for these predictions in the large-qubit limit. In the light of these properties, the quantum compiler provides a consistent, exponentially scalable, stochastic simulator of the evolution of classical observables, realized through projective quantum measurement. We implement the framework in the Qiskit platform, and demonstrate its consistency for prototypical examples involving periodic and quasiperiodic oscillators on tori.

Our work opens new directions in quantum information techniques for modeling classical dynamics. This is based on a previously unknown connections between the Koopman operator formalism of classical dynamics and quantum mechanical systems on reproducing kernel Hilbert spaces. The resulting framework leads to quantum computational methodologies for simulating classical dynamics with an exponential advantage over classical computers, and mathematically rigorous convergence guarantees in the large-qubit limit. The topic of simulating classical dynamics on quantum computers is timely, and our work represents a decisive step toward quantum supremacy in this area.

Future Plans
In the remaining few months of the current project term, we plan to use our algorithms to determine the structural dynamics of Bacteriorhodopsin, an exceptionally important photoactive system.

This will allow us to achieve two important goals:
1. Demonstrate the applicability of our algorithmic approach to other key photoactive systems.
2. Highlight the similarities and differences between the way the Photoactive Yellow Protein and Bacteriorhodopsin perform their function. This activity will proceed in collaboration with Prof. Gerhard Schertler and colleagues, who have already signaled their enthusiasm for this project, and provided data.

Peer-reviewed Publications Resulting from this Project (2019 – 2021)

1. A glycan gate controls opening of the SARS-CoV-2 spike protein, T. Sztain et al., **Nature Chemistry**, https://doi.org/10.1038/s41557-021-00758-3 (2021).
2. Selecting XFEL single-particle snapshots by geometric machine learning, E. Cruz-Chu et. al. **Structural Dynamics 8,** 014701 (2021).
3. Observation of substrate diffusion and ligand binding in enzyme crystals using high-repetition-rate mix-and-inject serial crystallography, S. Pandey et al., **IUCrJ 8**, Part 6 (2021).
4. Propagation of conformational coordinates across angular space in mapping the continuum of states from cryo-EM data by manifold embedding, S. Maji et. al., **J. Chem. Inf. Model 60**, 5, 2484-2491 (2020).
5. Diffraction data from aerosolized Coliphage PR772 virus particles imaged with the Linac Coherent Light Source, H. Li et al. **Scientific Data 7**, 404 (2020).
6. Retrieving functional pathways of biomolecules from single-particle snapshots, A. Dashti et al, **Nature Communications 11**, 4734 (2020).
7. Megahertz single-particle imaging at the European XFEL, E. Sobolev et al., **Communications Physics 3**, 97 (2020).
8. Time-resolved serial femtosecond crystallography at the European XFEL, S. Pandey et. al., **Nature Methods 17**, 73-78 (2020).
9. Spatiotemporal pattern extraction by spectral analysis of vector-valued observables, D. Giannakis, A. Ourmazd, J. Slawinska, & Z. Zhao. **Journal of Nonlinear Science 29**, 2385-2445 (2019).
10. Evaluation of the performance of classification algorithms for XFEL single-particle imaging data, Y. Shi, et. al., **IUCrJ 6** Part 2**,** 331-340 (2019).
11. Membrane protein megahertz crystallography at the European XFEL, C. Gisriel, et. al., **Nature Communications 10**, 5021 (2019).
12. Cryo-EM, XFELs and the structure conundrum in structural biology, A. Ourmazd, **Nature Methods 16**, 941-944 (2019).
13. Science in the age of machine learning, A. Ourmazd, **Nature Reviews Physics 2**, 342–343 (2020).

Control of Molecular Dynamics: Algorithms for Design and Implementation

Herschel Rabitz and Tak-San Ho
Award no: DE-FG02-02ER15344
Princeton University,   Frick Laboratory, Princeton, NJ 08540
hrabitz@princeton.edu, tsho@princeton.edu

A. Project Scope:

Achieving control of quantum phenomena with lasers is a long-standing dream going back to 1960s. Advances in ultrafast laser technology along with flexible pulse shaping capabilities have enabled a rapidly rising number of successes in the control of broad varieties of quantum phenomena. The subject is now open for advanced development, and our DOE grant supported research aims to address several key topics in this regard. *The major goal of the project is to develop theoretical concepts and practical algorithms for their transfer into the laboratory to enhance the quality of the experiments as well as to extract greater information from these endeavors.* One item of particular note is that current quantum dynamics studies, especially those seeking to find an optimal control outcome, are limited to only a few particles (i.e., especially of a composite nature, such as with the atoms in a molecule). The research in this area explores artificial neural networks in machine learning aiming to break through this limit, which our preliminary studies indicate is feasible. Success of the research in this domain in itself should dramatically accelerate optimal control simulations of complex unimolecular and bimolecular quantum dynamics of current interest in photochemistry and chemical reactions. Beyond the topic of controlled many-body dynamics, the collective studies will make possible exploration of a number of issues at the foundations of laser control over quantum phenomenon.

B. Recent Progress:

During the current DOE grant period, from October 2020 to September 2021, 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] **Quantum Control Landscapes Beyond the Dipole Approximation:** In this study, we investigated the control landscapes of closed quantum systems beyond the linear dipole approximation. We have performed an extensive exploration of these control landscapes by creating many random Hamiltonians with linear and quadratic terms in the control field, showing that all singular controls are free of local optima. This finding extends recent control landscape work based on the dipole approximation. Importantly, we showed that including a polarizability term in an otherwise uncontrollable dipole coupled system can restore controllability and remove traps on control landscapes. [2] **From Pulses to Circuits and Back Again - A Quantum Optimal Control Perspective on Variational Quantum Algorithms:** The last decade has witnessed remarkable progress in quantum technologies. By leveraging the noisy intermediate-scale quantum devices of today, variational quantum algorithms (VQAs) have been developed for applications including chemistry, optimization, and machine learning. In this study, we presented ways that the efficacy of VQAs could be informed by quantum control theory. In particular, as a major theme throughout, we emphasized the need for sufficient control resources

in VQA implementations and discussed different ways this need can manifest. In addition, we outlined a variety of open questions in the future. [3] **Amplification of quadratic Hamiltonians:** In this study, we developed a powerful *Hamiltonian amplification* (HA) procedure and showed that continuous variable systems described by a certain class of quadratic Hamiltonians can be sped up without full knowledge of the quantum system. The HA method relies on the application of local squeezing operations allowing for amplifying even unknown or noisy couplings and frequencies by acting on individual modes. Specifically, we showed how to combine HA with dynamical decoupling to achieve amplified Hamiltonians that are free from environmental noise and found a significant reduction in gate times of cavity resonator qubits as one potential use of HA. [4] **Ultrafast Photofragmentation of lanthanide complexes:** In this work, we studied the photo-induced dissociative-ionization of lanthanide (Ln) complexes using intense ultrafast transform limited and linearly chirped laser pulses in a time-of-flight mass spectrometry setup. Various fluorine and Ln-containing high-mass fragments were observed in this experiment, including the molecular parent ion, which have not been seen in previous studies relying on relatively long-duration laser pulses of ns or longer. These new high-mass observations provide important formerly missing information for deducing a set of photo-fragmentation mechanistic pathways. An ultrafast control mechanism was proposed by combining insights from earlier studies and the fragments observed in this research. [5] **Optimal control of coupled quantum systems - Application to dipole-dipole-coupled molecular rotors:** In this study, we adopted the first-order Magnus expansion for performing optimal control simulations for coupled quantum systems. Specifically, we have developed an efficient numerical implementation procedure that leverages pairwise couplings and the separability of the zeroth-order time evolution operator to reduce computational cost. A gradient-free stochastic hill climbing algorithm was adopted for optimization. Optimal control simulations have been performed for two and three dipole-dipole-coupled molecular rotors under the influence of a control field. [6] **Assessing closed-loop learning algorithms for high-quality quantum control pulses:** In this study, we examined three learning algorithms, GRadient Ascent Pulse Engineering (GRAPE), improved Nelder-Mead (NMplus) and Differential Evolution (DE), for seeking high-quality control pulses to prepare a Bell state. Each algorithm was implemented experimentally and numerically for a nuclear magnetic resonance system to access the impact of experimental uncertainties. These experiments were successful in preparation of the high-fidelity target state and in agreement with the numerical simulations. [7] **Deprotonation of Phenol linked to a silicon dioxide surface using Adaptive Feedback Laser Control with a Heterodyne Detected Sum Frequency Generation Signal:** In this work, we successfully demonstrated laser pulse shaping control of a surface reaction, in an experiment for laser induced deprotonation of the hydroxyl group of phenol bound to a silicon dioxide substrate, by combining the adaptive feedback control (AFC) technique with surface sensitive spectroscopy. The experiment utilized AFC with heterodyne detected vibrational sum frequency generation (HD-VSFG) as the surface sensitive feedback signal. The combination of AFC with HD-VSFG provides a route to potentially control a wide range of surface reactions. [8] **The Optimization Landscape of Quantum Control Systems:** Optimization is ubiquitous in the control of quantum dynamics in atomic, molecular and optical systems. The ease or difficulty of finding control solutions is highly dependent on the underlying control landscape. In this work, we presented the basic concepts in quantum control landscape theory, especially, the topology at trap-free critical points. The influence of various factors on the search effort were discussed, including control constraints, singularities, saddles, noises and non-topological features of the landscapes, as well as recent

experimental advances. This study provides an overall understanding of the optimization complexity of quantum control dynamics that may lead to more efficient algorithms for quantum system controls and for quantum machine learning. [9] **Multi-Level Evolution Strategies for High-Resolution Black-Box Control:** In this study, we described a multi-level mechanism for Evolution Strategies to address a class of global optimization problems that possess a multi-resolution control nature. In this study, we considered quantum control (QC) problems for which targeted controls may be discretized to increasingly higher resolution. Specifically, we have an automated scheme to facilitate guided-search over increasingly finer levels of control resolution for the optimization problem. We also presented a laboratory proof-of-concept for the proposed approach. [10] **Scalable single-shot mixture characterization:** In this study, we developed a quantum tracking control approach that allows for determining the relative concentrations of constituents in a quantum mixture in a single shot, using a pulse which enhances the distinguishability of components of the mixture and has a length that scales linearly with the number of mixture constituents. Numerical analysis indicated strong performance in two very distinct model systems: (1) mixtures of diatomic molecules in the gas phase as well as (2) solid-state materials composed of a mixture of components. [11] **Quantum tracking control for the orientation of symmetric top molecules in 3D:** In this study, we applied the iteration-free quantum tracking control method to orient symmetric top molecules. We have presented tracking control equations that are free of singularities for the control fields to drive the expectation values of the 3D dipole moment orientation vector along desired paths over time. Numerical simulations have been successfully carried out to illustrate the method. [12] **Machine learning of quantum spin-chain control utilizing artificial neural networks:** In this study, we explored the limit of quantum control simulations for long spin-chains utilizing the artificial neural network technique in machine learning. To this end, we have successfully shown how this technique can render a nearly linear-scaling compressed parameter space via a Hilbert space pruning technique, thus, making feasible large-scale optimal control simulations of long spin-chain systems. The study can be readily extended to optimal control problems involving polyatomic systems.

C. Future Plans:

In the coming year, in addition to continued study seeking a deeper understanding of the topology of control landscapes, we plan to expand our research on controlling quantum dynamics phenomena. There will be a particular emphasis on the study of many-body molecular dynamics control, which is of central importance in wide-ranging applications. Current studies are limited to small molecules of only a few atoms and we aim to break through this key limitation. In this regard, we are especially concerned with the efficiency of finding the accurate solution of the high-dimensional time-dependent Schrödinger equation, which is the key time-consuming step in the determination of an optimal control field. The latter limitation 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 and also explore new avenues, including the Magnus expansion and the application of artificial neural networks (ANN), for performing large-scale molecular optimal control simulations. Specifically, the research plans aim to determine the scaling of effort involved in utilizing the TDH, the Magnus expansion and the ANNs with the aim of

demonstrating 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[SEP] (2019-2021)

[1] Quantum control landscape of bipartite systems, R. Kosut, C. Arenz, and H. Rabitz, J. Phys. A: Math. Theo., **52**, 165305, (2019).

[2] Quantum optimal control of multiple weakly interacting molecular rotors in the time-dependent Hartree approximation, A. Magann, L. Chen, T.-S. Ho, and H. Rabitz, J. Chem. Phys., 150, 164303 (2019).

[3] Assessing the structure of classical molecular optimal control landscapes, C. Joe-Wong, T.-S. Ho, and H. Rabitz, Chem. Phys. *527*, 110504 (2019).

[4] Inherently trap-free convex landscapes for fully qnatum optimal control, R.-B. Wu, Q. Sun, T.-S. Ho, H. Rabitz, J. Math. Chem. *57*, 2154 (2019).

[5] Combining the synergistic capabilities of modeling and experiments: Illustration of finding a minimum-time quantum objective, Q.-M. Chen, X. Yang, C. Arenz, R.-B. Wu, X. Peng, I. Pelczer, and H. Rabitz, Phys. Rev. A 101 (2020*).

[6] An upper bound on the time required to implement unitary operations, J. Lee, C. Arenz, D. Burgarth, and H. Rabitz, J. Phys. A: Math. Theor. 53, 125304 (2020).

[7] Ultrafast Photofragmentation of Ln(hfac)3 with a Proposed Mechanism for forming High Mass Fluorinated Products, J. Chen, X. Xing, R. Rey-de-Castro, and H. Rabitz, Scientific Reports 10, 7066 (2020).

[8] Optimal control of coupled quantum systems based on the first-order Magnus expansion: Application to multiple dipole-dipole coupled molecular rotors, A. Ma, A. Magann, T.-S. Ho, and H. Rabitz, Phys. Rev. A 102, 013115 (2020).

[9] Amplification of quadratic Hamiltonians, C. Arenz, D. Bondar, D. Burgarth, C. Cormick, H. Rabitz, Quantum, 4, 271 (2020).

[10] Optimal control of coupled quantum systems based on the first-order Magnus expansion: Application to multiple dipole-dipole-coupled molecular rotors, A. Ma, A. Magann, T.-S. Ho, and H. Rabitz, Phys. Rev. A, 102, 013115 (2020).

[11] Assessing three closed-loop learning algorithms by searching for high-quality quantum control pulses, X.-D. Yang, C. Arenz, I. Pelczer, Q.-M. Chen, R.-B. Wu, X. Peng, and H. Rabitz, Phys. Rev. A, 102, 062605 (2020).

[12] Quantum Control Landscapes Beyond the Dipole Approximation: Controllability, Singular Controls, and Resources, B. Russell, R.-B. Wu, and H. Rabitz, Front. Phys., 9, 674794 (2021).

[13] From Pulses to Circuits and Back Again: A Quantum Optimal Control Perspective on Variational Quantum Algorithms, A. Magann, C. Arenz, M. Grace, T.-S. Ho, R. Kosut, J. McClean, H. Rabitz, and M. Sarovar, PRX Quantum, 2, 010101 (2021).

[14] Multi-level evolution strategies for high-resolution black-box control, O. M. Shir, X. Xing, and H. Rabitz, Journal of Heuristics, doi.org/10.1007/s10732-021-09483-z (2021).

[15] Optimization landscape of quantum control systems, X. Ge, R.-B. Wu, and H. Rabitz, Complex System Modeling and Simulation, 1, 77 (2021).

[16] Digital quantum simulation of molecular dynamics and control, A. B. Magann, M. D. Grace, H. Rabitz, and M. Sarovar, Phys. Rev. Research 3, 023165 (2021).

[17] Progress toward favorable landscapes in quantum combinatorial optimization, J. Lee, A. B. Magann, H. Rabitz, and C. Arenz, Phys. Rev. A. 104, 032401 (2021).

Atoms and Ions Interacting with Particles and Fields
Award No. DE-SC0012193

F. Robicheaux
Purdue University, Department of Physics and Astronomy,
525 Northwestern Ave, West Lafayette IN 47907
robichf@purdue.edu

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 10/2020-9/2021)

X-ray physics: The graduate student Akilesh Venkatesh led a project, Ref. [7], to understand the possibility of interference between the non-linear Compton scattering of X-rays (2 photons of frequency ω scatter into one photon of frequency near 2ω) and linear Compton scattering of photons at frequency 2ω. In Ref. [3], we demonstrated a method for modeling non-linear Compton scattering. In Ref. [7], we extended these programs to simultaneously include photons of frequency ω and 2ω. We used a perturbative approach to understand the result of the fully numerical calculation. In particular, we investigated the phase difference that appears in the interference term between these indistinguishable processes. We also explored the role that polarization plays in the interference. Of the many different possible combinations of polarization, only two cases exhibit interference. When there is interference, the calculations reveal an intrinsic phase difference between the Compton scattered wave function and the nonlinear Compton scattered wave function of either 0 or π depending on the scattering angle of the X-ray. Akilesh is exploring further calculations of strong field X-ray/atom interactions.

Multichannel effects in Rydberg states of erbium: In collaboration with Chris Greene and the experimental group of Francesca Ferlaino, we performed an in-depth study of the ns and nd Rydberg states of erbium in Ref. [8]. This is an interesting atom to explore because there are relatively few detailed studies of Rydberg states of lanthanide atoms. The experiment used electromagnetically induced transparency through an intermediate state to access even Rydberg states. They identified approximately 550 states. In collaboration with Chris Greene, we developed Multichannel Quantum Defect Theory models for the Rydberg states. For the ns series, we were able to do a fit in terms of energy dependent MQDT parameters that agreed with all the observed states and successfully predicted the positions of originally unobserved states. For the nd series, there were too many MQDT parameters to do an unconstrained fit to the energies. We developed two models that greatly reduced the number of MQDT parameters and allowed for a decent fit of the energies. However, we know these models have limitations because other parameters that could be predicted (mainly the g-factor of the Rydberg states) did

not agree well with the measurements. Further investigations may help untangle some of the unresolved issues.

Orientation effects in collisions: The graduate student Akilesh Venkatesh led a project, Ref. [6], to understand the effect of orientation and alignment of Rydberg atoms on their ionization cross section. He used a classical trajectory Monte Carlo method to calculate the cross sections associated with Penning ionization during the collision of a pair of atoms. Unlike previous studies, we determined the cross section versus the direction of the Laplace-Runge-Lenz vector and of the angular momentum. Differences up to factors of ~2.5 was found depending on the alignment and orientation. An adiabatically conserved quantity was identified which gave qualitative understanding for the dependence of the ionization cross section.

The graduate student supported by this grant, Akilesh Venkatesh, started research in January 2019 and very quickly come up to speed. He has finished two projects involving strong field X-rays to understand non-linear Compton scattering seen at the LCLS and to propose how to use interference in nonlinear Compton scattering. Also, he finished a project involving the orientation and alignment dependence of ionization in collisions between two Rydberg atoms. He is currently investigating basic processes in strong field X-ray scattering.

Future Plans

X-ray physics: The graduate student Akilesh Venkatesh is leading a project to investigate the possibility for detecting properties of electron wave packets using X-rays. If the X-rays themselves are pulsed, then the scattering can depend on the phases of the different components of the electron wave packet. We will use the numerical programs developed in Refs. [3] and [7] to calculate the scattering probabilities for different electron wave packets. We will also develop a method based on the perturbative scattering of the X-rays to benchmark these results and understand the origin of different effects. The goal is to understand what properties of the electron wave packet can be probed with a pulsed X-ray beam.

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 $0.1\,U_p$ and $10\,U_p$ 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 (2019-2021)

[1] X. Wang and F. Robicheaux, "Ionization from Rydberg atoms and wave packets by scaled terahertz single-cycle pulses," Phys. Rev. A **99**, 033418 (2019).

[2] A.O. Hernandez-Castillo, C. Abeysekera, F. Robicheaux, and T.S. Zwier, "Propagating molecular rotational coherences through single-frequency pulses in the strong field regime," J. Chem. Phys. **151**, 084312 (2019).

[3] Akilesh Venkatesh and F. Robicheaux, "Simulation of nonlinear Compton scattering from bound electrons," Phys. Rev. A **101**, 013409 (2020).

[4] P. Giannakeas, M. T. Eiles, F. Robicheaux, and J. M. Rost, "Generalized local frame-transformation theory for ultralong-range Rydberg molecules," Phys. Rev. A **102**, 033315 (2020).

[5] P. Giannakeas, M. T. Eiles, F. Robicheaux, and J. M. Rost, "Dressed ion-pair states of an ultralong-range Rydberg molecule," Phys. Rev. Lett. **125**, 123401 (2020).

[6] Akilesh Venkatesh and F. Robicheaux, "Effect of the orientation of Rydberg atoms on their collisional ionization cross section," Phys. Rev. A **102**, 032819 (2020).

[7] Akilesh Venkatesh and F. Robicheaux, "Interference in nonlinear Compton scattering using a Schrodinger-equation approach," Phys. Rev. A **103**, 013111 (2021).

[8] A. Trautmann, M. J. Mark, P. Ilzhöfer, H. Edri, A. El Arrach, J. G. Maloberti, C. H. Greene, F. Robicheaux, and F. Ferlaino, "Spectroscopy of Rydberg states in erbium using electromagnetically induced transparency," Phys. Rev. Res. **3**, 033165 (2021).

Investigating charge transfer and charge migration on the few- to sub-femtosecond time scale   (DE-SC0019451)

Artem Rudenko[1*], Daniel Rolles[1], Loren Greenman[1], Robin Santra[2,3]

[1] *J. R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS 66506*
[2] *Center for Free-Electron Laser Science, Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg, Germany*
[3] *Department of Physics, Universitat Hamburg, 20355 Hamburg, Germany*
* *rudenko@phys.ksu.edu*

Project Scope:
Intramolecular motion of electronic charge is one of the most important primary events in numerous photo-induced processes in physics, chemistry and biology, ranging from photosynthetic light harvesting to X-ray emission from comets and photocatalysis. Understanding charge dynamics at the microscopic level is essential for achieving fundamental insights into these phenomena and, from a longer-term perspective, for improving technological applications related to energy conversion and storage, which rely on charge motion and separation. Exploiting the fact that X-rays can specifically probe core-level electrons, which are localized at specific atomic sites in the molecule, this project aims at studying ultrafast charge dynamics (charge transfer and charge migration) in gas-phase molecules using ultrashort XFEL pulses. It relies on several novel capabilities recently developed at XFEL facilities, in particular, increased repetition rates, improved synchronization between the XFELs and external lasers, and the ability to produce synchronized pairs of intense, sub-femtosecond X-ray pulses, as well as on recent progress in advanced theoretical modeling. The main goals of the project are to identify the observables most sensitive to such ultrafast charge motion; to develop experimental techniques and theoretical approaches capable of revealing these observables, often relying on few-particle coincidence measurements; and to apply these theoretical and experimental tools to investigate several exemplary processes of interest.

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: *Charge transfer and charge migration dynamics following x-ray photoabsorption;*
Thrust 2: *Nuclear-dynamics-driven charge transfer triggered by UV photoabsorption;*
Thrust 3: *Studies of distance-dependent charge transfer processes in dissociating molecules;*
Thrust 4: *Theory development*

Thrust 1: *Charge transfer and charge migration dynamics following x-ray photoabsorption*
(Rudenko, Rolles, Greenman, Santra)

Recent progress:

Attosecond pump – probe experiments

The main experimental effort in *Thrust 1* over the last year was our active participation in the LCLS "attosecond campaign" - a broad community effort aimed at real-time observation of ultrafast electron motion, led by LCLS scientists James Cryan, Agostino Marinelli and Peter Walter. Utilizing a recently developed capability to generate pairs of few-hundred attosecond X-ray pulses [R1], two campaign beamtimes took place at the TMO end-station at LCLS earlier this year. Our involvement at LCLS is facilitated by the presence of one of our KSU graduate students, Kurtis Borne, at LCLS enabled by a DOE-SCGSR graduate student fellowship.

The focus of both experiments was to investigate attosecond charge migration in para-aminophenol triggered by inner-valence ionization. The photon energy of the pump pulse was set well below the carbon K-shell absorption edge such that only valence and inner-valence ionization was possible as long as no more than one photon from the pump pulse was absorbed. The ensuing electronic wave packet dynamics were then probed by a second sub-femtosecond X-ray pulse at twice or three times the photon energy of the pump pulse ("2ω" and "3ω", respectively), which arrived at a tunable delay between 0 and 10 fs after the pump. In the 2ω case, the probe-pulse photon energy spanned a range of predicted resonant transitions from the oxygen 1s level to the inner-valence hole states created by the pump, leading to the emission of resonant Auger electrons. Alternatively, the induced dynamics were also probed by detecting carbon and nitrogen 1s photoelectrons. The 3ω probe pulse (well above oxygen K-edge), which was used in the second beamtime, additionally enabled measurements of oxygen 1s photoelectrons. Preliminary analysis of the results of both beamtimes show that the delay-dependent resonant Auger spectra consistently manifest a robust transient signal evolving on a 100's attosecond timescale. A more detailed data analysis for both Auger and photoelectron spectra, which also involves a direct comparison with the simulations performed within the attosecond campaign collaboration, is ongoing.

Besides the involvement in the current attosecond campaign efforts, we also continue our work on theoretical modelling of next-generation attosecond pump-probe experiments, which will rely on high repetition rate of LCLS-II. Following up on our earlier study [P1], we have performed a more realistic simulation of correlated multi-particle observables characterizing coherent core-hole wave packet motion in N_2 molecules after ionization with an attosecond X-ray pulse. The details of the calculation and some illustrative results are discussed in *Thrust 4* below.

Tracing ultrafast intramolecular charge dynamics in multiphoton ionization of molecules

Following up on our earlier studies on iodomethane (CH_3I) and iodobenzene (C_6H_5I) systems [R2, P2], we have continued experimental and theoretical work aimed at tracing ultrafast charge dynamics during and after multiphoton ionization of molecules by ultraintense x-rays. To study the interplay between the molecular fragmentation dynamics and charge transfer, we have recently

analyzed the dependence of CH_3I ionization and fragmentation patterns in hard X-ray domain on the duration of the X-ray pulse [P16]. As illustrated in Fig. 1, the pulse duration is the key parameter determining the internuclear distance at which a particular charge state is reached. Correspondingly, the electron transfer from the light elements to the highly charged iodine becomes less efficient for longer pulses. Since the X-ray absorption almost exclusively occurs at the iodine site, this results in a significant reduction of the carbon atom charge for longer pulses (see Fig. 2). Furthermore, while the overall degree of ionization is mainly defined by the pulse energy, our measurement reveals that the yield of the fragments with the highest charge states is enhanced for short pulse durations, in contrast to earlier observations for atoms and small molecules in the soft x-ray domain. We attribute this effect to a decreased charge transfer efficiency at larger internuclear separations, which are reached during longer pulses (see [P16] for details).
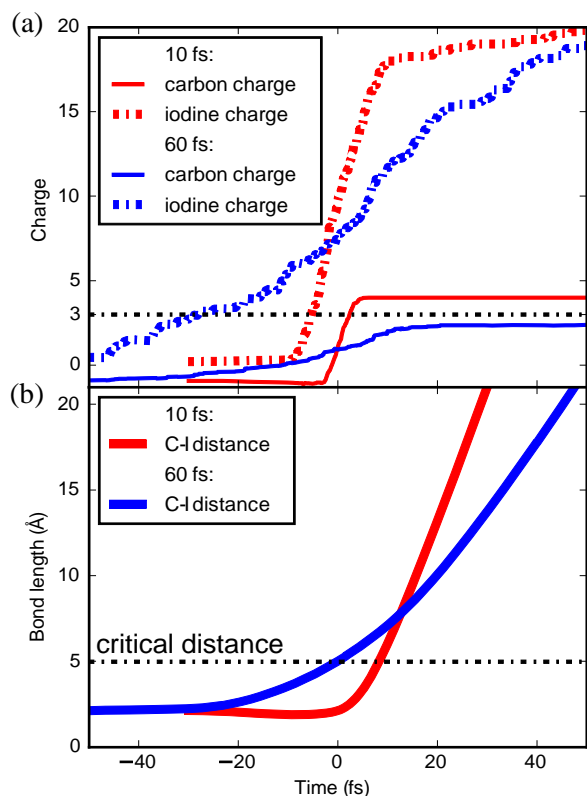
Fig. 1: Simulated average charge evolution (a) and internuclear distance (b) of carbon and iodine for those interaction events ending up with iodine ion charge of 20+, and for pulse durations 10 fs and 60fs. The black dashed line in (a) marks an ion charge of 3+, while the dashed line in (b) is drawn at the critical distance (according to classical over-the–barrier (COB) model) for the charge transfer from C^{3+} to I^{21+}. The time axis is defined such that the peak of the XFEL pulse is at 0 fs *(From [P16])*.
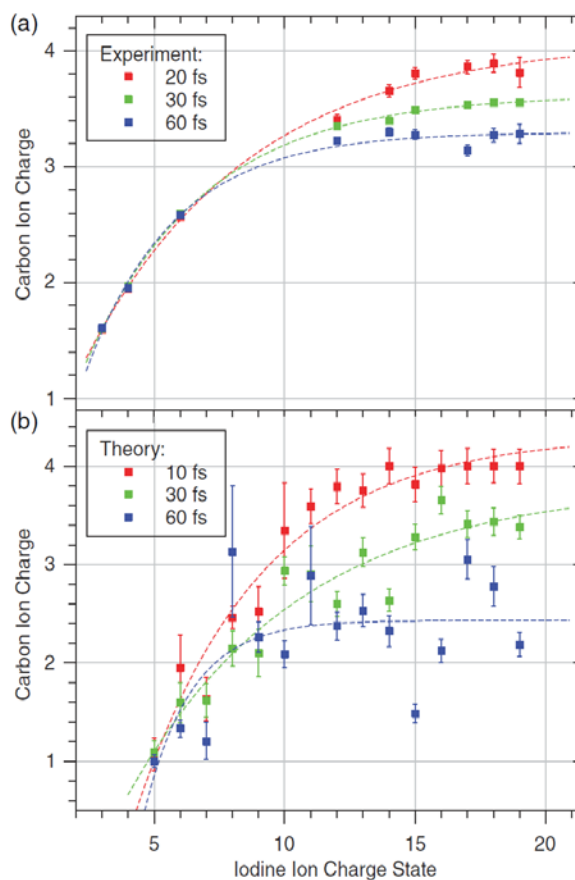
Fig. 2: Measured (a) and calculated (b) charge of carbon ions detected in coincidence with a given iodine ion charge state for different pulse durations with 0.37 mJ pulse energy. The vertical bars show the standard errors (widths) of the carbon ion charge state distributions *(From [P16])*.

In parallel, we have exploited the increase of the repetition rate and the availability of a dedicated "reaction microscope" spectrometer at the Small Quantum Systems (SQS) end station of the European XFEL to obtain a detailed picture of the intramolecular charge transfer following ionization of iodine-containing molecules by soft x-ray pulses. While in the experiments at LCLS we so far focused on the detection of carbon and iodine ions, the parameters available at SQS enable Coulomb explosion imaging of a complete molecular geometry [P20, R3]. This allowed us to trace the charge-up of individual carbon ions in iodopyridine and iodopyrazine molecules as a function of their position in the ring, providing unique insight into the intramolecular charge transfer dynamics [R3].

Future plans:
The next step within the LCLS attosecond campaign will be an experimental investigation of charge migration induced by an X-ray Raman process [R4]. As soon as repetition rates of 10 kHz and beyond are available at LCLS, we are also planning on submitting a proposal to study coherent core-hole motion in N_2, as outlined in [P1]. In parallel, we will continue to work on experimental and theoretical analysis of ion-ion [P19, P20, R3] and ion-electron [P5, P6, P13] coincidence spectra for multiphoton X-ray ionization and fragmentation of molecules, focusing on revealing the correlation between the electronic and nuclear (in particular, hydrogen) dynamics.

Thrust 2: *Nuclear-dynamics-driven charge transfer triggered by UV photoabsorption*
(Rolles, Rudenko)

Recent progress:
Since many photochemical processes relevant for chemistry and other applications are triggered by the absorption of a UV photon, *Thrust 2* of this project is focused on studying charge motion driven by the interaction with UV light. UV-pump X-ray probe experiments with attosecond resolution are currently out of reach at XFEL facilities because of the limited synchronization of the XFEL beam with external lasers. Therefore, we concentrate on charge-transfer dynamics driven by nuclear motion on the timescale of a few tens of femtoseconds. As a prototypical example, we are focusing on the charge-transfer processes in the 2-phenylethyl-N,N-dimethylamine (PENNA) cation, one of the most popular systems for both experimental and theoretical studies of ultrafast charge dynamics.

It has been shown experimentally that in PENNA molecule, which consists of a phenyl and a dimethyl amine group, separated by a $-CH_2-CH_2-$ spacer, a high degree of charge localization can be achieved by site-specific UV ionization [R5]. While resonant two-photon absorption at 266 nm is strongly localized on the phenyl site, three-photon ionization at 400 nm predominantly ionizes the amine site of the molecule. In the former case, the ionization is followed by a "downhill" electron transfer from the amine to phenyl site. Based on prior experimental and theoretical work [R6, R7], the expected time scale for this charge transfer is ~60-80 fs. During the last year, we
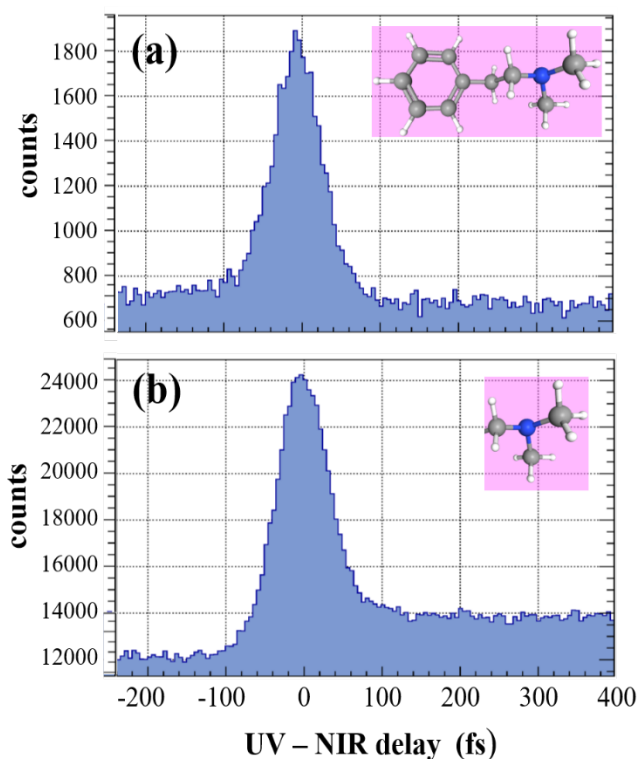
Fig. 3: Yields of the parent PENNA cation (a) and of the $C_3H_8N^+$ fragment (b) measured in the experiment at JRML as a function of the delay between 266 nm pump and 800 nm probe pulses.
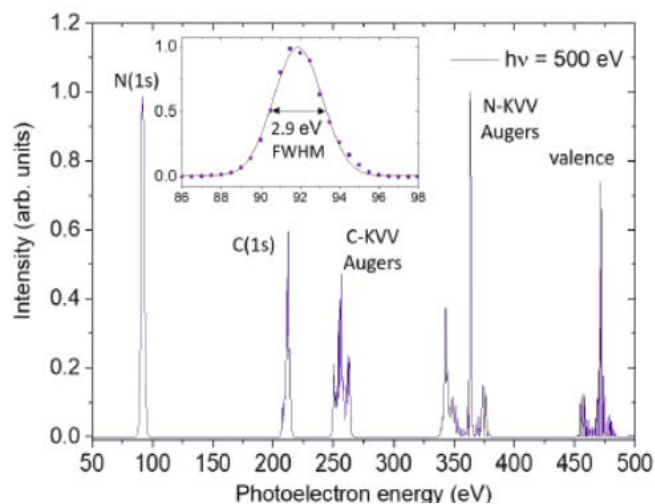
Fig. 4: PENNA photoelectron spectrum recorded at LCLS. Inset: the N(1s) photoline recorded with a higher retardation voltage on the magnetic bottle spectrometer.

have performed experiments on charge transfer in PENNA upon 266-nm ionization at JRML employing dissociation by 800-nm pulses as a probe. As illustrated in Fig. 3, our preliminary analysis indicates that the characteristic charge transfer time of ~80 fs is reflected in the delay-dependent yield of the $C_3H_8N^+$ fragments. However, because of rather large background contribution from dissociative ionization by 800 nm pulses and significant enhancement of the signal at the delays where both pulses overlap, extensive modeling and further experiments are needed to reliably associate these signals with the expected nuclear and electronic dynamics.

A more direct approach for imaging UV-induced charge transfer dynamics in PENNA cation is based on time-resolved X-ray photoelectron spectroscopy upon N (1s) ionization. Since the molecule contains only one nitrogen atom, such an experimental scheme enables site-specific mapping of the (time-dependent) charge density localized at the nitrogen atom position. According to our DFT calculation, based on the molecular orbital picture, the expected binding energy difference for N(1s) electrons for the cations with the charge localization on the amine or phenyl group is between 3.5 and 6 eV.

We first attempted such an experiment in May 2021 at LCLS, employing the magnetic bottle electron spectrometer (MBES) for photoelectron detection. The measured photoelectron spectrum from PENNA obtained with 500-eV, sub-20-fs LCLS pulses is shown in Fig. 4. As can be seen from the inset of this figure, such a configuration would have enough energy resolution to trace the

expected charge-transfer dynamics. Unfortunately, due to technical difficulties at LCLS (network issues and extreme timing instabilities), the pump-probe experiment could not be performed during that run.

Future plans:
We have resubmitted an updated version of our proposal for a time-resolved X-ray photoelectron spectroscopy experiment on PENNA at LCLS. We have also submitted a similar proposal for European XFEL facility, where the higher repetition rate will enable to perform such photoelectron measurement in coincidence with the ionic fragments. In parallel, we will also perform further experiments on PENNA with variable excitation wavelengths at JRML. Besides working on PENNA cation, we have also identified several promising targets for X-ray photoelectron spectroscopy studies of charge transfer in excited states of neutral molecules, in particular, focusing on 4-aminobenzonitrile and its derivatives.

Thrust 3: *Studies of distance-dependent charge transfer processes in dissociating molecules* (Rudenko, Rolles, Santra)

Recent progress:
Our main goal for *Thrust 3* is to study the functional dependence of the charge transfer rate on the molecular geometry and, in particular, on the internuclear distance, for several prototypical fragmenting systems. During the last year, we provided one more example demonstrating that for the case of direct dissociation, the charge transfer dynamics in a dissociating molecule can be reasonably described by the predictions of the classical over-the-barrier (COB) model [P14]. In a recent FLASH experiment [P11], we have also addressed the case where the dissociation proceeds via a relatively long-lived predissociative state, which significantly modifies the characteristic step-function behavior of the delay-dependent signals expected
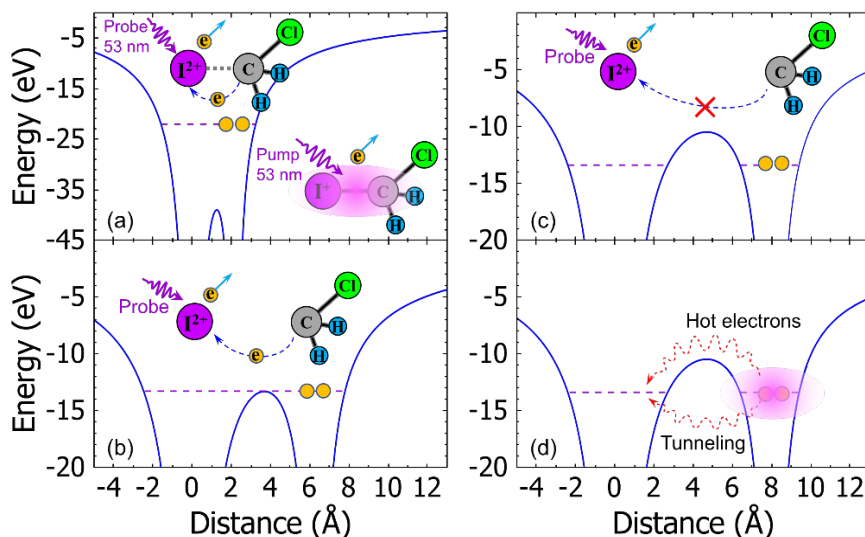
Fig. 5: The pump-probe concept and classical over-the-barrier (COB) model. (a), (b), and (c) show the potential energy barrier for the internuclear distance within, equal to, and outside the critical distance. (d) shows the concept of tunneling effect and thermal-energy-induced electron transfer beyond the COB model.

from COD. Besides that, our effort in *Thrust 3* over the last year mainly focused on data analysis and modelling of the earlier FLASH-II experiment on electron transfer dynamics in dissociating halomethane molecules after valence-shell XUV ionization. A basic idea of this study is illustrated in Fig. 5. Here, one ~30 fs XUV pulse at 23.5 eV triggers dissociative ionization of a molecule, and the second, nearly identical pulse ionizes one of the products. The signatures of charge transfer are then monitored by observing the delay-dependent yields of doubly charged ions.
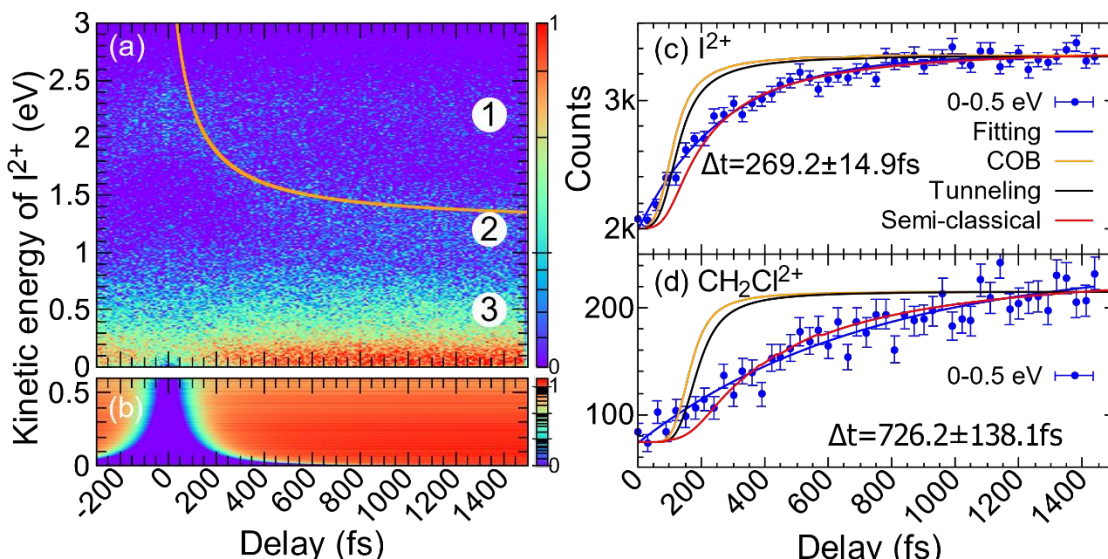
Fig. 6: Measured (a) and simulated (b) map of the delay-dependent kinetic energy distribution of doubly-charged iodine ions from the dissociation of CH_2ClI. The numbers indicate three different channels discussed in text. Left panels show the projections of the low-energy part of the two-dimensional map for I^{2+} (c) and CH_2Cl^{2+} (d). See Ref. [R8, R9] for details of the simulation and experiment.

The outcome of such measurement on CH_2ICl molecule is illustrated in Fig. 6. Three distinct features marked 1, 2, and 3 can be distinguished in the delay-dependent map of I^{2+} kinetic energies shown in Fig. 6(a). The high energy delay-independent band 1 comes from triple ionization of the target, where the molecule remains bound after the pump pulse in some intermediate charge state, and dissociates into $CH_2Cl^+ + I^{2+}$ final state after the probe pulse. The delay-dependent band 2 originates from the target that is first double ionized by the pump pulse and further ionized by the probe. Band 3 with the lowest kinetic energy is the main channel of interest for analyzing the electron transfer process. In this case, the molecule is singly ionized by the XUV pump pulse leading to the neutral-cation precursor dissociation channel $CH_2Cl + I^+$. The iodine ion is further ionized by the probe pulse to the $[CH_2Cl \cdots I^{2+}]$ state. At large delays, this state directly dissociates into $CH_2Cl + I^{2+}$. However, at short internuclear distances, the electron can transfer from CH_2Cl to I^{2+}, resulting in the dissociation limit $CH_2Cl^+ + I^+$ thus, decreasing the I^{2+} production at small delays. In Fig. 6(c) the measured yield of this channel is compared with different theoretical predictions. While both COB and tunneling models strongly deviate from the experiment at small delays, the semi-classical thermal energy model gives the best agreement in that region, although still not completely describing the shape of the experimental curve. Finally, the delay-dependent

yield of the low-energy CH_2Cl^{2+} ions is shown in Fig. 6(d). These events, which show much flatter delay dependence, result from the slower dissociation channel $CH_2Cl^+ + I$. A more detailed discussion of this study is presented in Ref. [R8, R9].

Future plans:
The next steps in *Thrust 3* of this project include (i) experiments with improved time resolution currently available at LCLS and (ii) the extension of this kind of investigations to bound systems, in particular, those with large-scale vibrational motion. The latter part relies on recent progress in characterizing the instantaneous molecular geometry using XFEL-driven Coulomb explosion imaging [P20], and the corresponding experiment at the European XFEL is scheduled for November 2021.

Thrust 4: *Theory development*
(Greenman, Santra)

Recent progress:
Over the last year, the progress on the theory side for this project enabled direct comparison with several recent experiments [P13, P16. P19, R3]. Driven by the availability of multidimensional experimental data, Santra's group paid particular attention to the development of novel schemes to study few-particle correlations [P19, R3, R10], while also working on modelling new experiments [P17] and advancing theoretical tools [P18]. In parallel, Greenman's group has extended the theoretical description of the sequential double ionization process developed in [P1]. In the previous work, an analytical formula for the correlation between the outgoing photoelectrons was achieved by making some simplifying approximations. We have since made a more thorough investigation of the differences between this analytical formula and numerical calculations using more accurate descriptions of the ionization processes. In [P1], the atomic photoionization dipole matrix elements ($\mu_{q,1s}$) are used along with plane-wave continuum states to obtain for the two-site double-core-hole probability:

$$P^{\text{TSDCH}} \propto e^{-\Gamma t_d} |\mu_{\mathbf{q}_1,1s}|^2 |\mu_{\mathbf{q}_2,1s}|^2 \Big(2 - \cos(\mathbf{q}_1 \cdot \mathbf{d}) \cos(\mathbf{q}_2 \cdot \mathbf{d})$$
$$- \cos(\Delta \varepsilon_{gu} t_d) \sin(\mathbf{q}_1 \cdot \mathbf{d}) \sin(\mathbf{q}_2 \cdot \mathbf{d}) \Big).$$

The much more complicated expression required for including the molecular potential in both the dipole matrix elements and the continuum states is [R11]:

$$P^{\text{TSDCH}} \propto \frac{1}{4} e^{-\Gamma t_d} \Big[|\boldsymbol{\mu}^{\text{SODCH}}_{\mathbf{q}_2,1\sigma_g} \boldsymbol{\mu}^{\text{SCH}}_{\mathbf{q}_1,1\sigma_g}|^2 + |\boldsymbol{\mu}^{\text{SODCH}}_{\mathbf{q}_2,1\sigma_u} \boldsymbol{\mu}^{\text{SCH}}_{\mathbf{q}_1,1\sigma_u}|^2 +$$
$$9|\boldsymbol{\mu}^{\text{TODCH}}_{\mathbf{q}_2,1\sigma_u} \boldsymbol{\mu}^{\text{SCH}}_{\mathbf{q}_1,1\sigma_g}|^2 + 9|\boldsymbol{\mu}^{\text{TODCH}}_{\mathbf{q}_2,1\sigma_g} \boldsymbol{\mu}^{\text{SCH}}_{\mathbf{q}_1,1\sigma_u}|^2 +$$
$$\text{Re}\Big\{ e^{i\Delta \epsilon_{gu} t_d} \Big\{ -\boldsymbol{\mu}^{*\text{SODCH}}_{\mathbf{q}_2,1\sigma_g} \boldsymbol{\mu}^{*\text{SCH}}_{\mathbf{q}_1,1\sigma_g} \boldsymbol{\mu}^{\text{SODCH}}_{\mathbf{q}_2,1\sigma_u} \boldsymbol{\mu}^{\text{SCH}}_{\mathbf{q}_1,1\sigma_u} -$$
$$9\boldsymbol{\mu}^{*\text{TODCH}}_{\mathbf{q}_2,1\sigma_u} \boldsymbol{\mu}^{*\text{SCH}}_{\mathbf{q}_1,1\sigma_g} \boldsymbol{\mu}^{\text{TODCH}}_{\mathbf{q}_2,1\sigma_g} \boldsymbol{\mu}^{\text{SCH}}_{\mathbf{q}_1,1\sigma_u} \Big\} \Big\} \Big]$$

The required matrix elements in this expression are calculated from the neutral (single-core-hole or SCH) and the ion (single-orbital or two-orbital double-core-hole SODCH/TODCH) and it uses the molecular orbitals of N_2 ($1\sigma_g, 1\sigma_u$). While the overall nature of the oscillations of the correlated photoelectron spectra at various pump-probe delays does not change, various details are different between the analytical and numerical calculations. There is, for example, a significantly greater amount of structure at intermediate polar angles between 0 and 2π, whereas for the analytical solution the majority of the structure is viewed at these two polar angles.

In addition to analyzing the improved electronic structure and photoionization calculations, we have also begun a search of the parameter space for the best pair of ionization pulses. Knowing this, we can guide the experiments to the optimal configuration in which to see the desired electronic dynamics. We have defined an asymmetry parameter that captures the dynamics where it is strongest. This parameter:

$$\mathcal{A}(t_d, E_1, E_2) = \frac{\mathcal{P}(\theta_1 = 0, \theta_2 = \pi) - \mathcal{P}(\theta_1 = 0, \theta_2 = 0)}{\mathcal{P}(\theta_1 = 0, \theta_2 = \pi) + \mathcal{P}(\theta_1 = 0, \theta_2 = 0)}$$

measures the normalized probability of back-to-back electron ejection, and the maximum and minimum of this parameter with respect to the time delay between pulses illustrates the amplitude of the electron oscillation. The difference between maximum and minimum, therefore, is a good parameter to use to optimize the pulses. Fig. 7 illustrates this parameter as a function of the two photoelectron kinetic energies, and determines a robust maximum near photoelectron kinetic energies of 30 eV and 15 eV.

Fig. 7: Amplitude of the oscillation of the asymmetry parameter $\mathcal{A}$ defined above (maximum vs. minimum) for different values of the photoelectron kinetic energies of the first and second ionized electron.

Future plans:

We will apply the methods developed in [P1] and extended as described above to study different methods of producing and probing attosecond dynamics in molecules. Further exploration of ionization-based methods will be undertaken, including further optimization of the pulses used to ionize N_2. Two key areas of development are planned. First, the extension of the methods developed here to other molecules of interest. The OCS molecule is the target of future studies, and we will describe double ionization in OCS using the same methods as described above. For OCS and N_2, we will study the effects of changing the nuclear geometry on the results as well. While we expect nuclear dynamics to have a small effect on the timescales considered, we plan to account for the effects of vibrational motion in the ground state and confirm our expectations about nuclear dynamics. Another area for future research is the

dynamics induced by different schemes of ionization and excitation. The attosecond dynamics induced by ionizing multiple electrons, both in the core shell as for the case of N_2 and in the valence shell in other molecules, will be compared with attosecond dynamics induced by stimulated Raman x-ray excitation. Quantum optimal control will be applied to each of these schemes to optimize experimental parameters, and in the case of stimulated Raman to minimize unwanted ionization that competes with the electronic dynamics that is the ultimate goal of the project.

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Light-induced couplings to study and control electronic interactions and electron-nuclear dynamics

Award Number: DE-SC0018251
PI: Arvinder Sandhu
Department of Physics and College of Optical Sciences
The University of Arizona
Tucson AZ 85721
asandhu@arizona.edu

Project Scope

We aim to employ light-induced couplings to control correlated and coupled electron and nuclear dynamics in atoms and molecules. This will be achieved by by employing tunable, multi-pulse, pump-probe techniques. The overarching goal of our program is to use light fields to understand and predictably control the charge and energy dynamics. Attosecond transient absorption spectroscopy, non-collinear four-wave-mixing, and coincident velocity map imaging form the main experimental techniques utilized on this project.

The topics to be explored in this project include 1) the study of polaritons formed when autoionizing states are coupled by the laser field, 2) the control of interfering ionization pathways and electron-core interactions, resulting in stabilization of ionization, 3) the investigation of the electronic correlations and electron-nuclear couplings. This project will employ a range of tunable wavelength (600-3400nm) strong 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 use of multi-pulse schemes provides new control possibilities while also providing means to disentangle the role strong fields in XUV-IR experiments. In the second phase of the project, we hope to expand our toolkit to employ attosecond soft-x-ray pulses to obtain elemental and chemical sensitivity in the study of charge dynamics.

Recent Progress

Using tunable spectroscopy, we studied multiple radiatively coupled autoionizing light-induced states in argon and demonstrated their stabilization against autoionization, thus confirming a prediction made nearly forty years ago. We show that this stabilization is due to the destructive interference between the Auger decay and the radiative ionization of the polaritonic components. These results give new insights into the optical control of electronic structure in the continuum and unlock the door to applications of radiative stabilization in metastable polyelectronic systems. We also obtained results on strong-field control, collective effects in dense gases, electron-nuclear couplings, through multi-color ionization and transient absorption experiments. Continuing collaborations with Argenti (UCF), Leone (Berkeley), and McCurdy (LBNL), and Greene (Purdue) groups have been instrumental in these efforts. We are also working towards a new experimental setup for attosecond spectroscopy in the soft-x-ray regime.

Polariton formation and the control of autoionization by light-fields:

Light-induced states and Autler-Townes splitting of laser-coupled states are common features in the photoionization spectra of laser-dressed atoms. The entangled light-matter character of autoionizing Autler-Townes multiplets, which makes them polaritons, however, is still largely unexplored. We employ attosecond transient-absorption spectroscopy in argon to study the

formation of polariton multiplets between the $3s^{-1}4p$ and several light-induced states. We measure a controllable stabilization of the polaritons against ionization, in excellent agreement with ab initio theory.

Laser-dressed autoionizing states (AISs) have been studied theoretically since the 1980s, and theoretical work by Zoller and others indicated the potential of dressing light pulses to stabilize AISs against ionization, because of the destructive interference between the autoionization and radiative-ionization pathways. This quintessential aspect of electron dynamics in the continuum, which has no counterpart in bound states, had not yet received experimental confirmation. We measured the autoionizing polariton multiplets in the delay-dependent absorption spectrum of argon and assigned them with the help of ab initio simulations. Experiment and theory both show clear evidence of the formation of entangled light-matter states with low autoionization rate, due to the destructive interference of the Auger decay amplitude from the different resonant components of the polariton. Our results pave the way to improve coherent control protocols in the continuum thanks to laser-induced Auger decay stabilization.
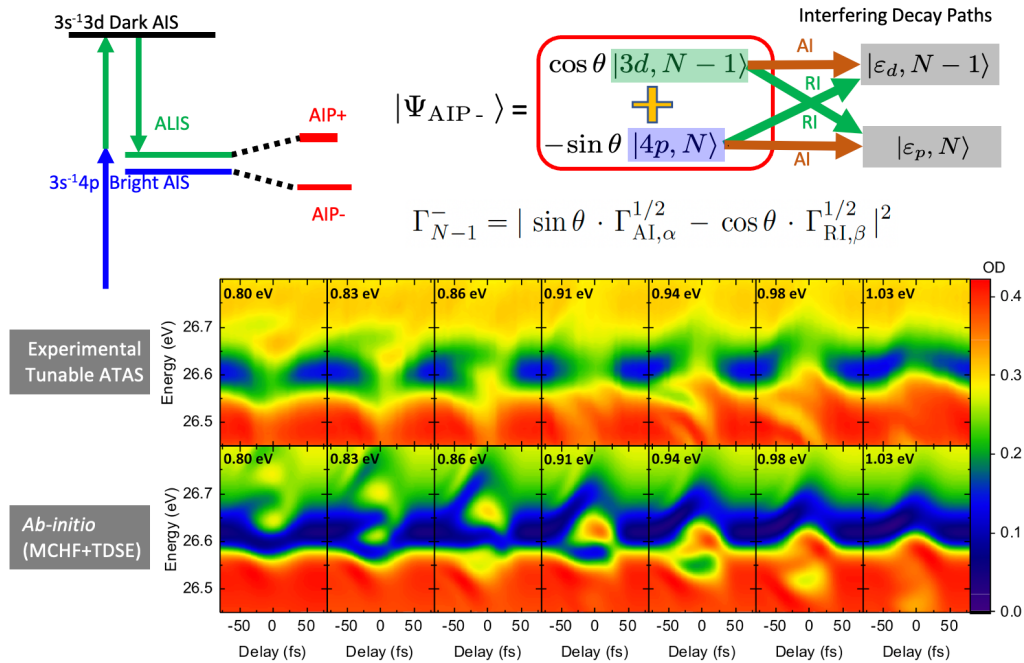

Fig 1. (top) Formation of autoionizing polaritons, AIPs, from mixing between the bright autoionizing state (AIS) and the autoionizing light-induced state (ALIS) of the dark level. Auger (AI) and radiative (RI) decay paths for the AIPs interfere, leading to stabilization seen as narrow spectral width of the lower branch. Experimental (middle) and theoretical (bottom) XUV photoabsorption in the vicinity of argon 4p AIS, as a function of the IR pulse delay, for several values of IR photon energy. Interaction of AIS with ALIS gives rise to the polariton splitting prominently visible between 0.86 to 0.98 eV IR photon energy, with the lower polariton branch width being substantially narrower.

Figure 1 shows the interactions responsible for the formation of polaritonic states and interference mechanisms that lead to the reduction in linewidth of the autoionizing polariton branches, implying a longer lifetime, i.e., stabilization against ionization. We collaborated with Argenti group at the University of Central Florida to theoretically model the light induced modifications of electronic interactions and interferences between active coherent ionization paths. We captured the basic physics with Jaynes-Cummins model that was extended to include autoionizing states, and obtained excellent agreement with ab initio theory, as shown in Fig. 1. These results have been recently published in the Physical Review Letters.

Variation of the linewidth of the upper and lower polaritonic branches with time-delay, which is a proxy for the instantaneous intensity, is shown in the figure 2 for both experiment and ab-initio theory. The results demonstrate that under appropriate condition the lower branch lifetime can be three times longer than the upper branch lifetime.

To systematically explore the control knobs for stabilization, we have conducted additional studies, where we vary the peak intensity of the IR laser pulse over a substantial range and explore the multitude of crossings between the polaritonic components, resulting from the coupling between $3s^{-1}4p$ and neighboring states that are one-photon and two-photon removed. The ability to tune the frequency of IR pulse wavelength, which is unique to our setup, gives us high degree of control, while also allowing quantitative comparison with theory, for identification of the underlying interactions and laser-induced couplings. A manuscript on this study has been prepared for submission.

Fig. 2. Experimental (a) and theoretical (b) polaritonic line shapes for the near resonant case of 0.94 eV IR energy, for several time delays. In the absence of interference between radiative and Auger channels, the two polaritons are expected to have comparable widths. Stabilization is evidenced by the delay-dependent reduction of AIP− width and marked difference between the AIP widths in both experiment (c) and theory (d).

Apart from the study of autoionizing states, we have also conducted XUV-IR multi-wave mixing studies with the bound states in Helium. This work investigates new light-induced couplings and the role of collective effects in transient absorption spectra. We are developing a general theoretical formalism which will serve to quantitatively compute the transient absorption signals under realistic experimental situations.

Coupled electron-nuclear dynamics, conical intersections, and light-induced modification:

We have previously initiated a program focussed on molecular transient absorption studies, where we investigated the autoionizing $nl\sigma_g$ Rydberg series converging to O_2^+ $c^4\Sigma_u^-$ states, and the role of electronic symmetry in determining the transient absorption profile. We also explored the relaxation dynamics of multielectron excited states. The theoretical analysis for this effort was supported by the calculations conducted by McCurdy group at LBNL. However, at that time, we could not experimentally explore the fast (<10fs) autoionization dynamics of $3s\sigma_g$. Fortunately, we were able to collaborate on a recent study of low Rydberg state dynamics, which was an effort led by Newmark and Leone groups. This work led to a better understanding of the impact of the nuclear motion on the autoionization dynamics.

To pursue the study of coupled electron-nuclear dynamics and light induced modification of conical intersections, we are following two-pronged approach that employs both transient absorption and electron/ion imaging. In the case of electronic states of CO_2 molecular ion, we used the 11th harmonic to excite the A and B states of the molecular ion, which have π and σ
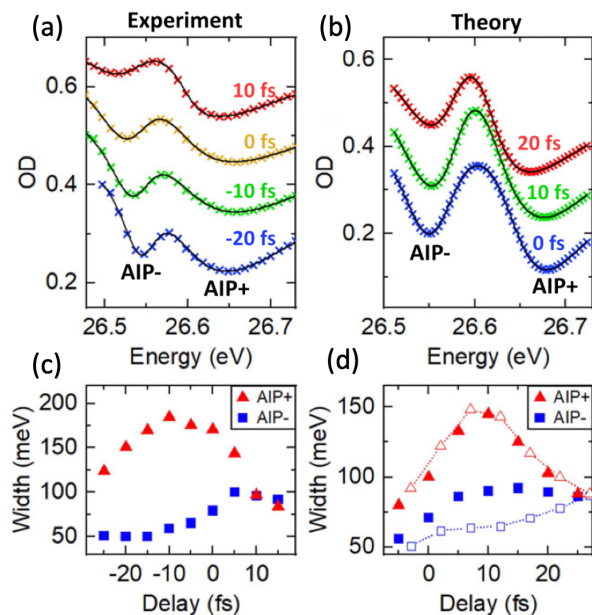
symmetry, respectively. The electron hole is then driven between the σ and π orbitals by the bending and asymmetric stretch vibrations of the molecule. A delayed NIR pulse excites the hole population to a dissociative state and by monitoring the ion-yield we were able to follow the quantum beating of the electron hole density and its decay with time. Now we are using a 'third' tunable IR control pulse to modify the potential energy landscape of conical intersections. We have observed 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^+. We are acquiring additional data at different IR intensities and wavelengths to build a comprehensive picture of this light induced control of conical intersection dynamics. We are also using our transient absorption apparatus to excite the Rydberg states associated with A and B ionic states, which provides another perspective on the electron-hole dynamics in the core.

Future Plans:

Using the unique advantages of tunable laser pulses, we will continue our efforts to obtain quantitative understanding of light-induced electronic couplings in atoms and molecules. These studies will elucidate the potential for the application of light-fields to control the electronic interactions. As another application of this method, we will pursue the characterization of the autoionization dynamics of dark states. We will also further the ongoing experimental efforts which aim to study the modification of electron nuclear couplings with strong light fields by collecting more datas and establishing collaborations with theorist who can simulate the strong-field modification of potential energy landscape in molecules. We will be investing some of our efforts in setting up a new high power, few-cycle MIR laser installed which will be used to 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 resulting attosecond soft-x-ray capability will allow us to conduct elementally specific probing of charge dynamics in complex molecular systems. The tunable, multi-color and multi-pulse spectroscopy techniques developed in these efforts will enhance the attosecond science toolkit by providing new control knobs.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

1) Nathan Harkema, Alexander Plunkett, Arvinder Sandhu, "Tunable high-order frequency mixing for XUV transient absorption and photoelectron spectroscopies", *Optics Express* **27**, 31053 (2019).
2) Alexander Plunkett, Nathan Harkema, Robert Lucchese, C. William McCurdy, Arvinder Sandhu, "Ultrafast Rydberg State Dissociation in Oxygen: Identifying the Role of Multielectron Excitations", *Phys. Rev. A* **99**, 063403 (2019).
3) Yen-Cheng Lin, Ashley P Fidler, Arvinder Sandhu, Robert R Lucchese, C William McCurdy, Stephen R Leone, Daniel M Neumark "Coupled nuclear–electronic decay dynamics of O2 inner valence excited states revealed by attosecond XUV wave-mixing spectroscopy", Faraday Discussions **228**, 537 (2021).
4) Nathan Harkema, Coleman Cariker, Eva Lindroth, Luca Argenti, Arvinder Sandhu, "Autoionizing Polaritons in Attosecond Atomic Ionization", Phys. Rev. Lett. **127**, 023202 (2021).

Transient Absorption and Reshaping of Ultrafast Radiation

DE-SC0010431

Kenneth J. Schafer (kschafe@lsu.edu), Mette B. Gaarde (mgaarde1@lsu.edu)

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803

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Project Scope

Our program is centered on the theoretical study of transient absorption and reshaping of ultrafast extreme ultraviolet (XUV) or X-ray pulses in their interaction with matter. The program emphasizes both fundamental theoretical research and a close connection with experimental groups doing attosecond physics [1], [R1-R6]. 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. We study attosecond transient absorption (ATA) and reshaping using a versatile theoretical treatment that takes account of the laser-matter interaction at both the level of the individual quantum system, via the time-dependent Schrödinger equation (TDSE) [R3,R4,R6], and through propagation of the emitted radiation in the non-linear medium via the Maxwell wave equation (MWE) [2][R1,R2,R5]. Although the majority of the system we have considered are rare-gas atoms, we have also recently considered attosecond transient absorption and reflection in condensed phase systems [R3].

Recent Progress

In this abstract we will focus on recent work aimed at the study of absorption and reshaping of attosecond XFEL pulses in gas media, performed in collaboration with experimental groups engaging with XFEL facilities in the US and Europe [R4-R6].

(i) **Linear and nonlinear reshaping of intense XFEL pulses in rare gases:** We have studied the spectral, temporal, and spatial reshaping of intense sub-to-few femtosecond X-ray pulses as they propagate through an atmospheric-density neon gas, in which the X-ray energy is resonant with a core-to-valence transitions. This work is done in collaboration with the Young experimental group at Argonne National Lab [R5].

We treat the neon atoms as few-level systems that encompass states in both the neutral and singly-ionized species. In the neutral, the 867 eV X-ray pulse resonantly excites an electron from the ground state to the core-excited $1s^{-1}3p$ state, which can subsequently couple to the valence-excited $2p^{-1}3p$ state via stimulated Raman scattering (we can include more np states as desired). The excited $1s^{-1}$ states of the ion is populated (incoherently) by the part of the spectrum above 870 eV, and can couple the ground $2p^{-1}$ state. The TDSE solution includes both stimulated emission, absorption, time-dependent ionization (which
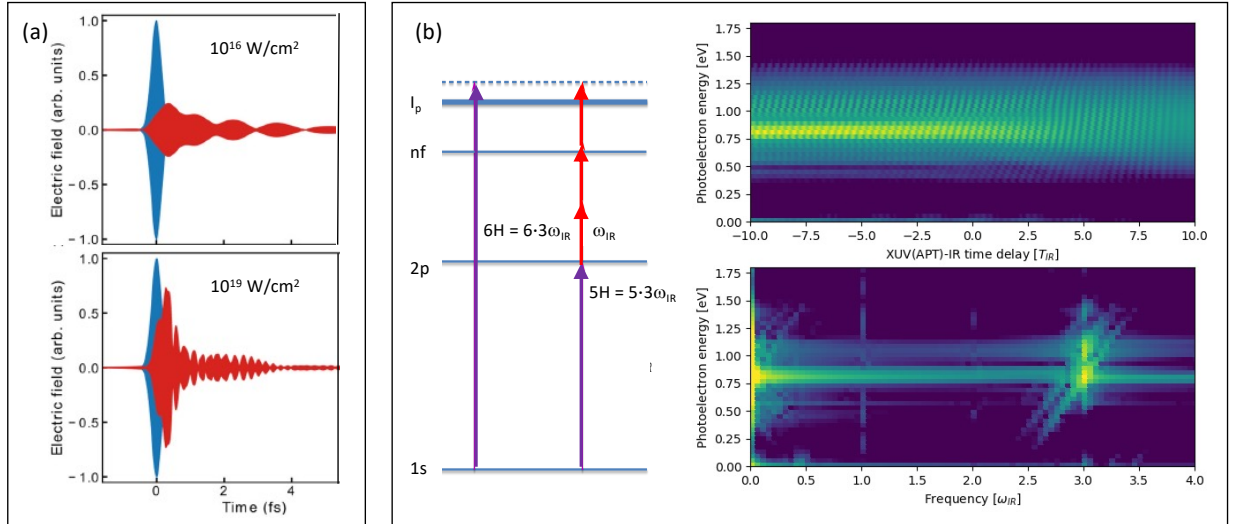
Figure 1: (a) Temporal reshaping of an intense attosecond X-ray pulse in the linear (top) and nonlinear (bottom) regimes (adapted from [R5]). (b) Schematic of FERMI experiment to measure multiphoton ionization phases. Harmonics of the FEL populate both bound and continuum states which are probed by a delayed IR laser pulse. The photoelectron spectrum versus delay (top) can be Fourier transformed to reveal, for example, the effect of intermediate $n = 5, 6$ two photon resonances (diagonal lines near $3\omega_{\text{IR}}$).

populates the ionic states) and Auger-Meitner decay. We simultaneously solve the MWE in 3D to keep track of spatiotemporal reshaping.

In the time domain, we find different reshaping of the pulse in the linear vs. the nonlinear regime; this is for intensities below and above 10^{18} W/cm^2, approximately. As is illustrated in Fig. 1(a), at low intensity the pulse develops a tail on the time scale of the lifetime of the core resonance. The tail represents the emission of light that is out of phase with the driving field and therefore leads to attenuation in the frequency domain. The slow beats build up during propagation, in a self-consistent process where the tail of the pulse again gives rise to additional radiation out of phase with itself. This so-called resonant pulse propagation is well-known in other wavelength regimes [2,3] but has never been documented experimentally in the X-ray regime. In the nonlinear regime, we observe strong emission at 850 eV from stimulated Raman scattering (SRS), initiated by the broad spectral background of the attosecond pulse and strongly enhanced during propagation. This multi-color, intense X-ray pulse in turn drives complex Rabi cycling, which during propagation leads to spectral broadening covering the entire region between 850 and 867 eV and is responsible for the compression of the front part of the pulse visible in Fig. 1(a), bottom panel. In the spatial domain, we additionally observe both absorption-driven reshaping and refractive-index-driven self-focusing at high intensities (not shown in figure).

Experiments measuring initial and final X-ray spectra in a dense rare gas are scheduled to take place at the European XFEL during 2022. In addition, a proposal has been submitted for an LCLS experiment to directly measure the time domain impacts of attosecond X-ray pulses propagating in dense gases.

(ii) Characterization of temporal structure of XUV FEL pulses: The seeded FEL facility FERMI in Milan, Italy generates high intensity, XUV attosecond pulse trains (APT) that have programmable, reproducible wave forms. In collaboration with the Sansone (U. Freiberg) and Mauritsson (Lund U.) experimental groups we have investigated the characterization of XUV APTs produced at FERMI. Because FERMI is seeded by the third harmonic of an IR laser, the harmonics that make up the APT are spaced by three IR photons. This presents a challenge when characterizing the temporal structure of the XUV pulses, since the spectral phases of the XUV harmonics pulses must be measured via an interference of processes involving one and two IR photons absorbed or emitted in the continuum. An additional complication is that the delay between the XUV light and the IR dressing laser can not controlled. The solution, as outlined in [R4], is to plot the correlation between photoelectron sidebands and use the shape of the resulting ellipse to extract the arrival times. At certain set phase differences between harmonics the correlation plot can be used as a "clock" showing the arrival time of the pulses. This scheme has been elaborately tested in our TDSE simulations. A longer paper outlining the theoretical methods has been published [R6] with another on the simulation and verification of complex waveforms at FERMI submitted [4].

Future Plans

Several projects are in progress or planned for the near future:

(i) Propagation and reshaping of intense X-ray pulses We are continuing our studies of temporal and spatial reshaping of intense XFEL pulses in atomic gases. We are currently working on including a description of spontaneous emission in our code to make sure we are not underestimating the seeding of the stimulated Raman scattering. In the longer term, we are also interested in being able to describe different polarizations of the X-ray light.

(ii) Complex XFEL waveforms: Continuing our work with the Sansone group on the characterization of high intensity XUV pulses from FERMI, we will collaborate on a run scheduled for September 2021 to study the continuum phase of two IR photon emission/absorption near the ionization threshold of an atomic system. We know from previous work comparing exact TDSE results to strong field approximation (SFA) simulations that these phases contribute non-trivial effects near threshold [5] and measuring this effect will be the focus of this work. A particular focus is on the effect of the atomic potential, which is elided in the SFA.

In a related but separate experiment, J. Mauritsson will lead an FERMI run devoted to studying two photon below threshold absorption (Rabi cycling) in helium (Figure 1b). As part of this grant we are providing theoretical support on the design and interpretation of the experiment. The aim is to use the XUV harmonics produced by FERMI to measure the phase of the multiphoton absorption process. This involves measuring the phase of the XUV light just above threshold, and so dovetails nicely with the work on the Sansone beamtime.

(iii) Condensed-phase ATA: In the context of another project, we have developed a simple model for how to include excitons in the description of the interaction between light and a 1D condensed-phase system. We are interested in applying this model to the transient absorption of a UV pulse in the presence of a moderately intense IR laser field; in particular how the interaction between the laser-dressed exciton states and the conduction band affects the absorption probabilities.

Peer-Reviewed Publications Resulting from this Project (2019-2021)

R1 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).

R2 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).

R3 R. Geneaux, C. J. Kaplan, L. Yue, A. D. Ross, J. E. Bækhøj, P. M. Kraus, H.-T. Chang, A. Guggenmos, M.-Y. Huang, M. Zürch, K. J. Schafer, D. M. Neumark, M. B. Gaarde, and S. R. Leone, *Attosecond time-domain measurement of core-excitonic decay in MgO*, Phys. Rev. Lett. **124**, 207401 (2020)

R4 P. Maroju *et al.*, *Attosecond Pulse-shaping using a seeded Free Electron Laser*, Nature **578**, 386 (2020)

R5 K. Li, M. Labeye, P. Ho, M. B. Gaarde, and L. Young, *Resonant propagation of x-rays from the linear to the nonlinear regime*, Phys. Rev. A **102**, 053113, (2020).

R6 P. Maroju *et al.*, *Analysis of two-color photoelectron spectroscopy for attosecond metrology at seeded free-electron lasers*, New J. Phys. **23**, 043046 (2021).

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[2] C.-T. Liao, A. Sandhu, S. Camp, K. J. Schafer, and M. B. Gaarde. Beyond the single-atom response in absorption line shapes: Probing a dense, laser-dressed helium gas with attosecond pulse trains. *Phys. Rev. Lett.*, 114:143002, 2015.

[3] MD Crisp. Propagation of small-area pulses of coherent light through a resonant medium. *Phys. Rev. A*, 1(6):1604–1611, 1970.

[4] P. Maroju *et al.* Complex attosecond waveform synthesis at fel fermi. *Appl. Sci.*, 2021 (submitted).

[5] P. Maroju *et al.* Analysis of two-color photoelectron spectroscopy for attosecond metrology at seeded free-electron lasers. *New J. Phys.*, 23:043046, 2021.

Coherent Probes of Molecular Charge Migration

Kenneth Schafer[1,*], Mette Gaarde[1], Kenneth Lopata[2],
Louis DiMauro[3], Pierre Agostini[3], Robert Jones[4]
1) Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA
2) Department of Chemistry, Louisiana State University, Baton Rouge, LA
3) Department of Physics, The Ohio State University, Columbus, OH
4) Department of Physics, University of Virginia, Charlottesville, VA

[*]kschafe@lsu.edu

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 are not yet impacted by the weaker coupling to nuclear 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, 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.

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, at small-, mid- and large-scale facilities, using a concerted effort of theorists and experimentalists. 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. Charge migration studies in the ATTO-CM network are primarily laboratory based but experiments at the LCLS with the participation of members of the ATTO-CM team have started.

Recent Progress

In our effort to understand and observe charge migration (CM) with strong laser fields we have focused our efforts on three main thrusts: "Attochemistry picture of charge migration", "High-harmonic spectroscopy (HHS)", and "Ionization-based initiation and characterization of CM-dynamics". 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* – After establishing simple heuristics for CM in halohydrocarbon chains [Folorunso 2021] we have used nonlinear dynamical tools to uncover the

mechanism that enables sustained CM modes in these systems [Mauger 2021]. We also extended our CM-mode analysis to screen for viable benzene derivatives to use in experimental ionization-based CM investigations (Thrust 3).

2. *Thrust 2: High-harmonic spectroscopy (HHS)* – Building on our wide-ranging expertise in experimental and theoretical HHS [Tuthill 2020], we have pursued several avenues to coherently probe CM with XUV light. Experimentally we have developed (i) attosecond spectroscopy facilitated by a 400-nm driven high-harmonic generation (HHG) source and (ii) HHG from a liquid jet. Theoretically, following our progress with reliably computing HHS signals [Hamer 2021] (iii) we have proposed a novel HHS method for probing CM via the high-harmonic sidebands produced when the CM-mode and driving-laser frequencies are incommensurate [Hamer 2021b].

3. *Thrust 3: Ionization-based initiation and characterization of CM-dynamics* – We have continued our study of strong-field ionization (SFI) with phase-locked two-color fields, as a potential means for controlling initial hole localization and subsequent CM dynamics, and to validate TDDFT predictions on the orientation dependence of SFI. Following our TDDFT predictions of robust CM in halobenzenes (Thrust 1), we have expanded our experiments on CM initiated by SFI to include detection of both doubly charged parent ions and ion fragments that result from double ionization as a function of the laser frequency. The OSU team has also started participating in CM campaigns at LCLS.

Thrust 1: Attochemistry picture of charge migration

Thrust 1 of the ATTO-CM network uses first-principles simulations to address questions underlying the design and interpretation of CM experiments, such as: Which molecules are expected to support CM? Does CM manifest in generic ways so that its periodicity and visibility can be predicted to follow simple rules? Does the way in which CM is initiated influence how it proceeds? Are there generic mechanisms that enable sustained CM motions in molecules? Answers to these questions are crucial for our ongoing efforts to observe CM using HHS and frequency-matched ionization in Thrust 2 and Thrust 3 below. To this end, the LSU team has established general attochemical heuristics for CM in halohydrocarbon chains [Folorunso 2021]. In a complementary approach, we also leveraged tools from nonlinear dynamics to study the mechanisms of CM in these targets [Mauger 2021].

Molecular modes of charge migration in benzene derivatives: The LSU team computes CM modes in complex organic molecules using all-electron TDDFT simulations with atom-centered basis sets and hybrid functionals, as implemented in the open-source code NWChem [Valiev 2010]. Our simulations involve three steps: emulation of a hole via ionization, time propagation, and extraction of CM modes and metrics from the density. To prepare the initial state we use constrained DFT (cDFT) [Eshuis 2009], which self-consistently computes the density of the system with the requirement of having a localized hole on the halogen. This emulates a rapid SFI process that leaves the system in a non-stationary state with a halogen-localized hole. This is a significant improvement over simply creating ad hoc hole(s) in the ground-state Kohn-Sham valence orbital(s), which exhibit significant delocalization errors and give qualitatively incorrect dynamics [Eshuis 2009]. In contrast, the cDFT procedure naturally mixes multiple orbitals, resulting in a more multi-electron, multideterminant-like excitation. We then interpret the resulting dynamics in terms of the hole density, defined as the difference between the neutral ground-state and cation densities. For halohydrocarbon chains, we have shown that conjugation (delocalized double and triple bonds) is required for facile CM, which happens by "hopping" between π bonds; we also established that higher Z halogens result in more stable holes throughout the CM process with Br and I being the most viable candidates for experimental purposes [Folorunso 2021].

Building on our results with halohydrocarbon chains, we have performed CM-mode investigations in benzene derivatives. Like in the chain case, we observe that holes initiated on halogens generally result in periodic CM motions, whereas functionalization with most other functional groups does not. For example,

Figure 1 shows that iodobenzene and iodotoluene support robust CM oscillations with the localized hole moving from the iodine to the far end of the benzene ring. Both have a period of slightly over 2 fs. In contrast, there is no identifiable CM for benzamide. This is a consequence of the electron donating (hole withdrawing) strength of the amide ($-CONH_2$) group, which results in a hole that essentially does not move. These simulations were performed in conjunction with frequency-matched ionization (FMI) measurements from the UVA team (discussed in Thrust 3 below), both for identifying viable target
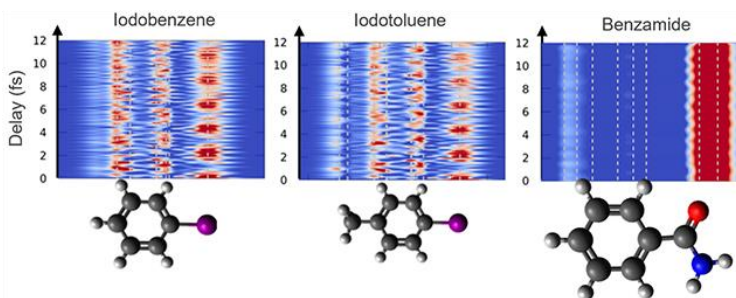

Figure 1: CM-mode analyses in benzene derivatives (see titles). Each panel shows the time-dependent hole density along the molecule backbone. The two halobenzenes show ~2-fs periodic CM modes with the hole migrating between the iodine and ring. By contrast, benzamine does not exhibit any CM following the injection of a hole on the amide group.

molecules and for determining the time scale of the CM dynamics. Calculating the CM time in these molecules is especially critical for interpreting FMI measurements, where modulation in the yield of particular ions is expected to occur when (half) the laser period is equal to the CM period. Going forward, a major focus of our work will be to systematically determine the effect of chemical substitution on CM in a wider range of benzene derivatives, both to understand how chemistry dictates CM, and to guide ongoing and planned FMI experiments.

Nonlinear dynamics of charge migration: The message from our CM simulations is clear: we consistently observe sustained modes in halohydrocarbon chains. But why does this happen in these systems, and how should we think about these modes more generally? To answer these questions, we have employed tools from nonlinear dynamics [Laskar 1999] and investigated the underlying dynamical mechanisms that regulate CM modes. Our motivations for doing so are two-fold: (i) the (TD)DFT framework we use to describe CM motions in molecules is *de-facto* a nonlinear system, because of how electron-electron interactions are accounted for in the Hartree and exchange-correlation functionals; and (ii) general-purpose nonlinear dynamics tools and techniques have been developed to analyze and visualize systems with many degrees of freedom.

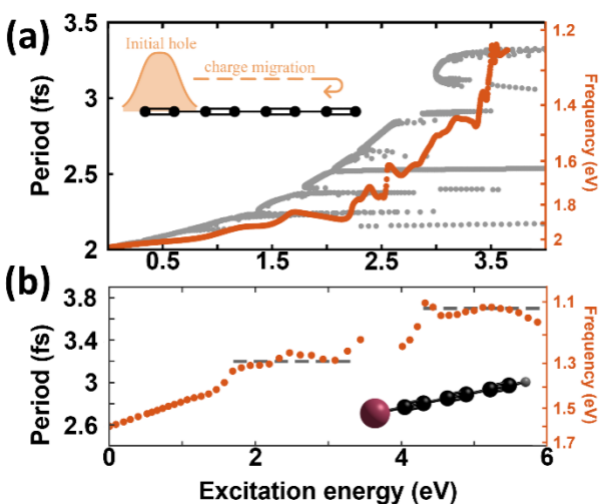To begin with, we have developed reduced-dimension models of the π system that supports CM in

Figure 2: Phase-space analysis of CM. We show the results of CM-mode period analyses in (a) a one-dimensional model π system and (b) full-dimensional BrC_6H molecules. Orange markers show the period of the CM when a variably localized initial hole, here controlled by the electronic excitation energy, is induced on the left/Br side of the molecule (see inset). Both panels show a succession of "plateaus," which are signatures of the attosecond solitons that enable sustained CM modes in those systems. Grey markers in (a) mark periodic modes obtained by investigation of the full phase space of the model π system.

conjugated halohydrocarbon chains – see the inset of Figure 2 (a). These relatively simple models allow us to perform detailed analysis of the CM dynamics; typically involving a few thousand TDDFT simulations. We then tested the most pertinent configurations in full-dimensional simulations in the BrC_6H molecule – see panel (b). Comparison between the model π system and full-dimensional simulations are striking: Both exhibit sustained CM motions, with a localized hole that periodically travels back and forth through the conjugated system, as sketched in the inset of panel (a). In the phase-space analysis of Figure 2, we see that the CM period increases with the electronic excitation in the cation, and that the increase happens in a stepwise fashion. Generally, we have found that conjugated halohydrocarbon chains can support multiple CM modes with periods varying by several hundred attoseconds. Notably, each of these modes span entire regions of phase space where we find essentially the same type of CM, with the same period, irrespective of the details of the initial hole configuration – see the dashed lines in panel (b). This is essential for experimental applications as it ensures some robustness of the CM dynamics against uncertainties in the way the hole might be created. With our nonlinear analysis, we also found that chemical functionalization can be used to control the ability of a molecule to support periodic CM modes. Finally, we established that sustained periodic CM modes in these systems emerge as attosecond solitons, and that they are driven by the nonlinear mean-field multi-electron coupling, instead of resulting from the beating between a few molecular orbitals as is often proposed [Remacle 2006, Calegari 2014, Ayuso 2017]. Interestingly, this attosecond-soliton mechanism provides a novel way to understand CM dynamics directly in the time domain and in real space. A manuscript detailing our results, and their implication for future theoretical and experimental CM studies, is currently under review [Mauger 2021].

Thrust 2: High-harmonic spectroscopy (HHS)

Thrust 2 of the ATTO-CM network focusses on using HHG light as a vehicle to coherently probe CM in a wide range of molecules. While our initial investigations relied on HHS in gas-phase molecules driven by MIR lasers [Tuthill 2020, Hamer 2021], we have expanded the range of our experimental capabilities to cover XUV attosecond spectroscopy and liquid-phase HHG. Theoretically, we have proposed a novel high-harmonic sideband spectroscopy approach for probing the types of periodic CM modes identified in Thrust 1 [Hamer 2021b].

Attosecond spectroscopy: The gas density required for producing detectable HHG in large molecules is typically challenging to achieve, due to their low vapor pressures. As an alternative to HHS in the gas phase for such systems, the OSU team is pursuing attosecond spectroscopy as a coherent probe for time-resolved CM studies. Attosecond spectroscopy uses the XUV radiation produced from a well characterized HHG source to directly probe the molecule of interest. As with the RABBITT metrology, this XUV radiation can be combined with a dressing field to probe ultrafast dynamics.

Figure 3 shows the photoionization spectrum of N_2 using a 400-nm driven HHG radiation. Within each high-harmonic order it clearly reveals multiple cationic states due to the closely spaced energy levels in the target. This demonstrates that ionization with XUV radiation can both probe deep into the valence shell and resolve multiple cationic final states. This is typically not feasible with MIR-driven HHS, which generally probes only the HOMO of the molecule. Previous molecular attosecond spectroscopy has mainly used an 800-nm laser to generate the XUV
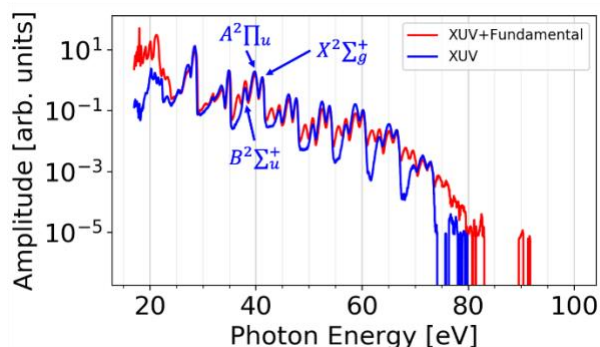

Figure 3: Photoionization spectra of N_2 produced from XUV radiation only (blue) and with the HHG fundamental field added (red). For each harmonic we observe three cationic states (see labels for the 13th harmonic).

radiation. Our novel use of the shorter 400-nm driving wavelength yields a 6-eV harmonic spacing, which reduces spectral congestion from the multiple ionization pathways. Finally, Figure 3 shows that we can produce HHG light beyond 70 eV (in the figure, the drop in the photoionization signal is due to the aluminum filter used to remove the fundamental field). This high cutoff energy will allow us to probe both the inner and outer valence shell of many molecules.

The OSU team has established techniques for using a 400-nm driving field in RABBITT experiments by studying the breakdown of the continuum-continuum phase asymptotic approximation near threshold [Bharti 2021]. Furthermore, by using a two-color RABBITT scheme as illustrated in Figure 4, we can remove the Wigner phase and isolate the continuum-continuum phase difference between the different sidebands. Beyond a test of our 400-nm generating capabilities, this study helps to better measure the continuum-continuum phase and hence improve our ability to remove its contribution to the measurement for better isolation of CM signatures.

Figure 4: Two-color RABBITT: (Left) Ionization pathways from a XUV odd-order harmonic comb produced in neon with 400 nm and an 800-nm dressing field. (Right) Spectrogram obtained by varying the delay between the XUV and dressing fields.

High-harmonic sideband spectroscopy (HHSS): The LSU node simulates HHS in real molecules using grid-based TDDFT calculations, as implemented in the open-source code Octopus [Andrade 2015]. In [Hamer 2021] we have shown that aggressive processing and normalization of TDDFT HHS signals can be used to recover experimentally relevant spectral amplitudes and phases from simulations. These include mimicking the selection of the short quantum-path in individual simulations, which is otherwise obtained in experiments through macroscopic phase-matching, and restricting the TDDFT orbitals that contribute to the HHS signal. We also showed how one can use field-free scattering simulations to mimic the recollision step in HHG and allow the direct calculation of recombination dipole matrix elements without explicitly calculating the scattering states of a molecule.

Next, we have combined our experience from calculating reliable HHS signals, along with initiating particle-like CM (see Thrust 1), into a TDDFT-based study demonstrating that HHSS can be a robust probe of CM in the halogenated carbon chain BrC_4H. Specifically, we have found that we can extract detailed information about the time-domain characteristics of the CM process in our simulations by monitoring the spectrum as we scan either the HHG laser frequency or the relative delay.

Figure 5 (a) illustrates our approach for using HHSS to explore CM, in BrC_4H. We start by creating a one-electron valence hole localized on the Br center, using constrained DFT, as discussed above. This pump step induces periodic CM dynamics as shown in panel (a) with a frequency of ω_{CM}~1.8 eV. Next, a delayed MIR probe pulse drives HHG in the molecular cation undergoing CM. The probe laser is polarized perpendicularly to the molecular backbone, ensuring that it does not drive the CM dynamics [Kraus 2015], and its frequency is incommensurate with ω_{CM}. The
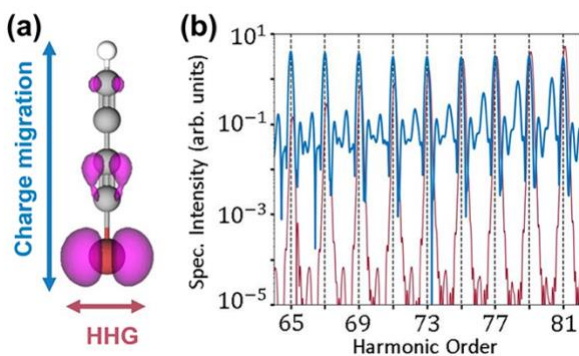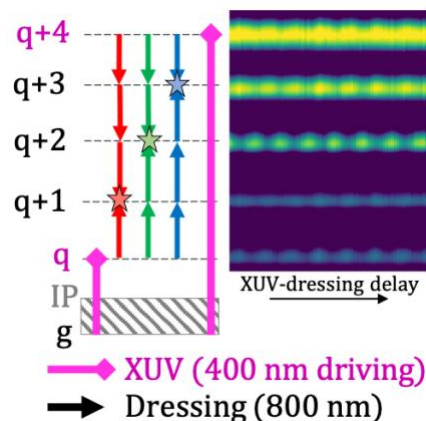

Figure 5: (a) Schematic of HHSS where a delayed HHG probe is driven perpendicular to the pump-initiated CM. (b)The resulting harmonic spectrum for an 1800-nm HHG driver (top curve) clearly shows high-contrast sidebands as compared to the CM-free spectrum (bottom).

periodic CM-induced modulation of the HHG process leads to clear sidebands in the harmonic spectrum, as illustrated panel (b): compare the top and bottom HHG spectra with and without CM, respectively.

In our HHSS analyses we have found that periodic CM motions initiated in the BrC_4H molecule leads to a coherent time-dependent modulation of a time-delayed HHG probe. This modulation is directly visible at the sub-laser-cycle level, as a function of the time delay. In the spectral domain and over several laser cycles, the migration dynamics manifests as sidebands whose energies correspond to the sum and the difference frequencies between the driving laser and the CM. These sidebands constitute a robust background-free, all-optical, probe of the CM motion and one can unambiguously extract the migration frequencies by scanning the laser wavelength. Furthermore, the presence of multiple sidebands per harmonic frequency indicates that HHSS is able to determine whether the system is undergoing particle-like CM as described in Thrust 1 above. A manuscript summarizing these findings is nearly finished and will be submitted soon [Hamer 2021b].

Liquid high-harmonic generation (LHHG): HHS gives access to the attosecond timescales necessary to resolve CM dynamics. One major challenge for its application to many CM-relevant molecules is the difficulty to get sufficiently high gas-phase sample density to obtain detectable HHG light. For this reason, we are exploring if HHS can be extended to liquid-phase targets via LHHG.

The OSU team has developed an apparatus for studying LHHG. It consists of two vacuum chambers: a target chamber housing a ≤ 1-micron thick flowing liquid sheet and an XUV spectrometer chamber. The liquid sheet (inset of Figure 6) is generated with a microfluidic nozzle developed at SLAC by the DePonte group [Koralek 2018]. This sheet is pumped by an IR/MIR laser pulse and harmonics emitted from the interaction are analyzed downstream in the spectrometer. Figure 6 shows data taken with the LHHG apparatus where both the gas and liquid phase HHG of isopropanol are measured. Both phases are isolated simply by placing the laser focus on or off the sheet. This technique could be extended towards targets of interest to CM such as the halobenzenes investigated in Thrust 1 and Thrust 3.
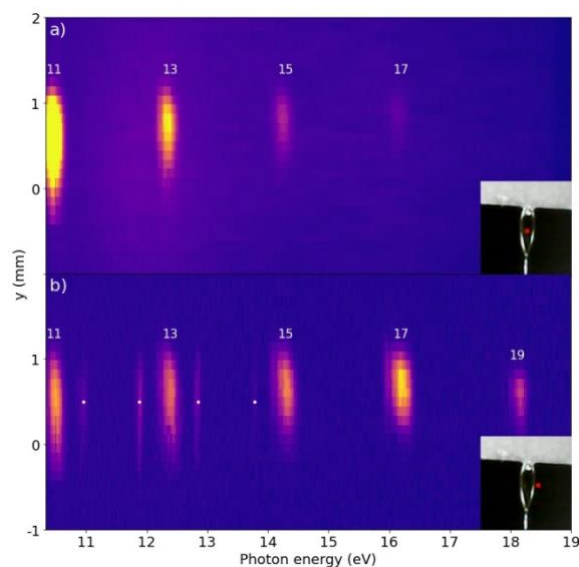

Figure 6: HHG from the interaction of a 1300-nm laser pulse with an isopropanol liquid sheet. The insets show the position of the laser focus relative to the liquid sheet, yielding (a) liquid phase or (b) gas phase HHG. Higher order diffraction in the spectrometer are indicated with white dots.

Thrust 3: Ionization-based initiation and characterization of CM-dynamics

Thrust 3 of the ATTO-CM network focuses on time- and angle-dependent strong-field single, multiple, and dissociative ionization. It plays a central and unifying role across the network because: (i) SFI underlies HHS as the first step in HHG; (ii) the angle between the ionizing laser polarization and the molecular axis can predictably influence the nature of the resulting hole and its subsequent dynamics; and (iii) the single, double and dissociative ionization rates depend on the time-dependent electron distribution within the molecule as well as on the instantaneous value of the oscillating field, potentially providing a time-resolved microscope for probing CM dynamics. As an extension to our attosecond XUV spectroscopy (Thrust 2), the OSU team is participating in LCLS CM campaigns using pump-probe attosecond x-ray spectroscopy.

Frequency-matched ionization (FMI) spectroscopy of halobenzenes: The LSU team has performed TDDFT calculations to identify halobenzene-like molecules that exhibit periodic, particle-like hole dynamics, and similar carbon ring molecules that do not. As discussed in Thrust 1 above, we have predicted robust CM

oscillations in iodobenzene, iodotoluene, and iodoanaline, with the localized hole moving from the iodine to the far end of the benzene ring and back with very similar periods, slightly over 2 fs. In contrast, no identifiable CM is expected for benzamide, which has no halogen functionalization – see Figure 1.

Based on our CM calculations in benzene derivatives, we performed preliminary FMI measurements (at UVA and, more recently, at OSU), exposing unaligned, near room temperature samples of each of the molecules to intense 50-100-fs infrared laser pulses. The molecular ion and ion fragment yields were recorded as a function of laser wavelength $1.2 < \lambda < 2.4$ microns, with the half-period of the laser (*i.e.*, the time between field maxima) equal to the predicted CM period for $\lambda \approx 1.35$ microns. The wavelength dependence of the ratio of the doubly- to singly-charged parent ion yields was used to provide a measure of the changes in the double ionization probability – after accounting for the possible wavelength dependence of the single ionization rate. The ratios for the different molecular species were compared to determine if there was any evidence of wavelength-dependent suppression or enhancement of the double-to-single ionization yield ratio, which would be consistent with FMI of the CM predicted in three of the four molecules.

We observed interesting wavelength dependencies in the yield ratios for iodobenzene and iodotoluene, near the wavelengths where FMI was predicted. Unfortunately, however, fragmentation of iodoanaline and benzamide was essentially complete, and no significant singly or doubly charged parent ion signals were detected, so there was no measurement available for the control molecule. Notably, the greatest changes in the yield ratios in iodobenzene and iodotoluene, near 1.35 microns, were coincident with a significant suppression of the single and double SFI yields, and a concomitant increase in the production of two different singly-charged fragments, the largest being the parent molecule with only the halogen cleaved

Figure 7: Ion time-of-flight spectrum produced during the exposure of iodobenzene to 50-fs, 60-µJ laser pulses. The $C_6H_5^+$ and $C_4H_4^+$ fragment yields are enhanced, at the expense of reduced production of doubly- and singly-charged parent ions, for wavelengths near 1.35 microns where the laser half period is approximately equal to the predicted CM period.

– see Figure 7. Given the substantial decrease in singly charged parent ion production, even at low intensities where the molecular ground-state is not depleted, the enhanced fragment ion production is apparently due to a frequency-dependent, post-ionization coupling between the laser and the parent ion. More analysis is needed to determine if this could be the result of a frequency match between the strong field and SFI-induced electron dynamics. While not successful in terms of unambiguously detecting CM, the results of our initial FMI measurements have played an important role in guiding our next experiments as outlined in more detail in the Future Plans section below.
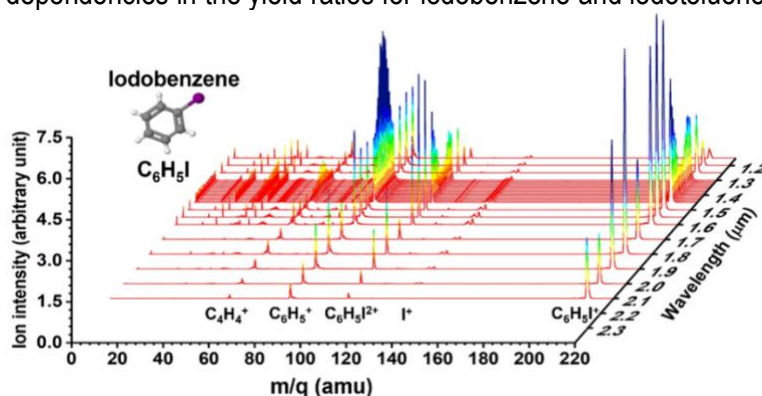
SFI of oriented molecules: Our investigations have advanced from alignment-dependent SFI, in which the relative angle between a molecular axis and a laboratory-fixed axis is well-defined, to orientation-dependent phenomena, where the direction of the applied field and the molecular dipole is known, and controllable. This is significant, as oriented molecular targets open the possibility of using directional fields to drive electrons in specific directions, within or about the molecule, for inducing and probing particular CM modes. Using purely optical techniques based on the application of asymmetric two-color ($\omega+2\omega$) fields, the UVA node has explored angle-dependent SFI of OCS. The two-color fields induce orientation through two distinct (and sometimes competing) mechanisms, hyper-Raman excitation and angle-dependent SFI

[Znakovskaya 2014]. As with transient alignment the orienting interactions coherently redistribute rotational population in molecules, creating rotational wave packets in both the neutral and ion that exhibit preferential orientation at distinct times. Rather than use one asymmetric field pulse to induce orientation and a second to preferentially ionize the molecules using a field with a known lab frame direction, we measure the delay-dependence of the transient orientation of the neutral and ionic molecules induced by the combined hyperpolarizability and SFI mechanisms. We then extract the angle-dependent ionization rate by fitting the delay-dependent orientation measurements to simulations modeling the effects of angle-dependent SFI as well as anisotropic polarizability and hyperpolarizability.

The ionization studies are supported by TDDFT simulations from the LSU team. Specifically, the polarizability and hyperpolarizability values were computed using a finite-difference scheme, where the nonlinear response is extracted from simulations of the dipole moment at five different field amplitudes [Ding 2013]. This method is general and could be applied to other future molecular targets. Additionally, our TDDFT simulations of two-color ionization yields demonstrate a strong similarity between the angle-dependent sub-cycle SFI rates in single- and two-color fields. This validates the assumption that SFI of OCS is essentially adiabatic, depending only on the value of the instantaneous field, rather than its time-dependence. A full analysis of the data and fits is nearly complete, which will allow for a direct comparison of measured and calculated angle-dependent ionization rates. The coherent rotational spectroscopy approach we have developed should be generally applicable to fully characterize angle-dependent SFI in symmetric-top, and perhaps asymmetric-top molecules.

In addition to direct numerical simulations, the LSU team has implemented weak-field asymptotic theory (WFAT) [Tolstikhin 2011,Dnestryan 2016] for DFT orbitals. WFAT is an adiabatic method for the calculation of angle-dependent tunnel ionization yields of a molecule in a static electric field. Since it is a time-independent method, it can give inexpensive estimates of angle-dependent rates. This allows us to perform extensive investigations of the parameter space that would otherwise not be feasible with direct numerical simulations of SFI. While previous studies using WFAT employed Hartree-Fock orbitals, we have used DFT orbitals and built a WFAT module in the NWChem package. Preliminary comparison of ionization yields from WFAT and two-color simulations in NO and OCS have been very encouraging. Figure 8 shows the orientated-SFI yields for NO computed both with TDDFT, using a two-color laser field, and from WFAT, at the corresponding field maximum. The excellent qualitative agreement between the two suggests an adiabatic ionization process (we have observed similar agreement between TDDFT and WFAT computations for OCS).

Figure 8: Angle-resolved SFI of oriented NO. We compare the ionization yields computed using TDDFT with a two-color pulse (blue) and WFAT with a static field of the same peak-field amplitude (red – normalized to the TDDFT curve). The laser pulse has 800/400-nm wavelength, 60-fs duration, and 1.6×10^{14} W/cm^2 peak intensity.

Attosecond pump-probe spectroscopy at LCLS: The visibility of the ATTO-CM network led to an invitation to the OSU group to join the LCLS Director's CM campaign group ("Attosecond Campaign" – PIs: J. Cryan, A. Marinelli, and P. Walter). In 2021, the OSU group participated in one of the first pump-probe experiments using the XLEAP mode at LCLS for investigating CM in para-aminophenol (pAp) (beamtimes LV9418 in April 2021 and LW8819 in May 2021). The XLEAP mode of LCLS enables two-color pump-probe experiments with isolated attosecond soft x-ray pulses [Duris 2020].
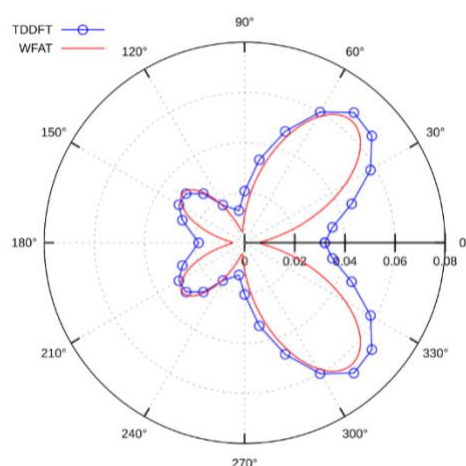
The experiments aim to study CM in pAp using two different techniques: pump-probe x-ray absorption spectroscopy (XAS) and pump-probe x-ray photoelectron spectroscopy (XPS). The XAS and XPS techniques are illustrated in Figure 9 (a). In both measurements the pump-probe delay is scanned between 0.3 and 10 fs. A promising time-dependent signal has been seen in the XAS data. We have observed below-edge absorption at 525 eV (Figure 9 (b)) and the electron kinetic energy distribution at this photon energy matches the oxygen Auger-Meitner decay measured above the K-edge. Furthermore, the strength of this absorption feature varies on attosecond timescales (Figure 9 (c)). This time dependence could be correlated to CM. Comparison with theory from the LCLS collaboration is an ongoing effort as is the analysis of XPS data.
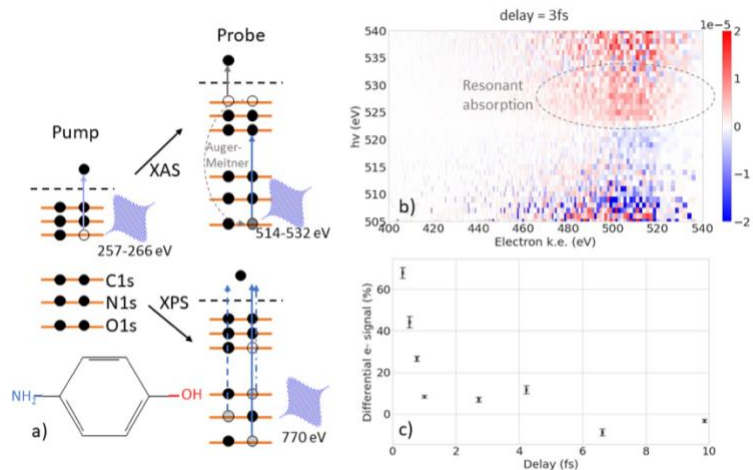

Figure 9: a) Schematic of the XAS and XPS measurements at LCLS. b) XAS differential dispersion plot. The plot is the difference between high-pump pulse energy and low-pump pulse energy data at 0.3-fs delay. An absorption feature is seen between 525 and 530-eV probe photon energy. c) Time dependence of the resonant Auger-Meitner decay signal between 525 and 530-eV probe energy.

Cross-training and interactions between the network partners

We have maintained continuous communication between all the nodes of the network, including:

- Frequent zoom meetings between all partners, together with frequent, internode email, phone, *etc.* 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.
- The COVID-19 pandemic essentially halted our personnel exchange program. We have been able to resume some travel only recently, at limited capacity, with 1 postdoc from UVA spending 1 week at OSU in late June 2021 to perform FMI measurements on the OSU beamline. We plan to resume our in-person operation a soon as it is safe and reasonable to do so.

These active exchanges have allowed us to maintain a strong collaborative community among the PIs, students, and postdocs.

ATTO-CM workshop: Due to the COVID-19 pandemic, we suspended our yearly in-person ATTO-CM workshop for 2021. We expect to resume it in 2022, with an in-person meeting at OSU.

Future Plans

CM modes: In the coming year, we will continue our TDDFT simulations of CM in functionalized benzene derivatives to determine the relationship between chemical functionalization and CM metrics such as its period and contrast. To this end, we will perform systematic studies of para-functionalized halobenzenes with groups of varying electron withdrawing strength. These results will continue to guide our choice of molecular targets for future HHS and FMI investigations.

Nonlinear dynamics of charge migration: So far, our nonlinear analyses have focused on field-free CM motions. Next will extend our investigations to include the influence of an external laser field to generate

HHG. Specifically, our goal is to provide a phase-space analysis to the HHSS results described above. For that we will develop two-dimensional halohydrocarbon models so that we can set the polarization direction perpendicular to the molecular backbone and avoid driving the electronic motion instead of probing it.

Attosecond spectroscopy: We will use attosecond spectroscopy to experimentally investigate the halobenzene series. Related species such as nitrosobenzene [Bruner 2017] and benzene [Despré 2015] have been shown to exhibit CM dynamics. Encouragingly, benzene's CM is initiated by valence ionization and was shown to last at least 10 fs, which is beyond the onset of nuclear dynamics [Despré 2015]. We plan to achieve attosecond resolution by coupling attosecond spectroscopy with a molecular resonance. By initiating CM during ionization through a shape resonance, we expect that the resonance decay will be sensitive to the underlying shift of charge density and observable in the phase retrieved by RABBITT.

High-harmonic sideband spectroscopy: We will investigate the robustness of the HHSS signal by considering other molecules in the halohydrocarbon family as well as including (semi-classical Ehrenfest) nuclear dynamics in our TDDFT simulations [Castro 2013]. So far, we have performed time-resolved HHSS analysis – scanning the delay between the CM initiation and the HHG probe – by sub-cycle resolving our multi-cycle HHG signals [Hamer 2021]. Instead, we will investigate performing the same kind of delay-scan analysis using a more experimentally realistic ultra-short generating pulse.

Liquid high-harmonic generation (LHHG): We have two primary goals for our LHHG experimental efforts over the upcoming year: (i) study the effect of solute molecules on LHHG and (ii) assess whether gas-phase HHS is feasible using the vapor surrounding the liquid sheet. An outstanding question for future LHHG investigations is whether an isolated molecular response can be extracted from the HHG from a solution containing a solvated CM-relevant target. This is likely necessary for liquid-phase HHS of CM dynamics. A second approach in performing HHS with the LHHG apparatus would be to study gas phase harmonics from the solvent vapor surrounding the liquid sheet as demonstrated in Figure 6 (b). We will investigate this question in halobenzene solvents.

Frequency-matched ionization spectroscopy: We will continue our concerted investigations of FMI in halobenzenes. This will involve performing measurements and companion CM-mode simulations in the same carbon-ring targets (see Thrust 3 above). Experimentally, we will focus on trying to detect changes in the yield ratio for doubly to singly charged ions as a function of the ionizing laser frequency. First, we will attempt to increase the yield of singly and doubly ionized parent molecules by employing shorter (~20 fs) two-color pulses with fundamental wavelengths in the range of 0.55-1 μm. With the appropriate two-color phase, the field periodicity of 1.7-3.3 fs will be suitable for detecting charge oscillations with periods in this same range. In addition, we will consider ion fragments with high kinetic energy release, indicative of the Coulomb-like repulsion of two positively charged fragments and utilize the momentum imaging spectrometers available at UVA and/or OSU. For simple two component double ionization channels, such $(C_6H_5)^+ + I^+$ from iodobenzene, the fragment momenta reveal the relative alignment of the molecular axis with respect to the laser polarization (*i.e.*, there is no need for pre-alignment) as well as the approximate separation of the fragments at which double ionization occurs [Gong 2014]. Accordingly, we can select those fragments for which double ionization has occurred very near to the equilibrium configuration of the molecule, with negligible variation in the relevant bond distance (and in the CM period) prior to the probe ionization event. In addition, we can readily compare results obtained with different initial molecular alignments relative to the laser polarization. In particular, we can readily distinguish molecules that were initially aligned perpendicular to the laser polarization, for which CM occurs (primarily) perpendicular to the driving field, so that (as with HHSS) the electronic polarization induced by the laser does not significantly impact the CM dynamics.

FMI computations in systems with charge migration: While a direct simulation of strong-field induced double ionization (or fragmentation) is not feasible in our TDDFT simulations, we expect that our CM metrics, as well as single-ionization computations from molecular cations undergoing CM dynamics, can yield relevant

results when compared to measurements. Specifically, to support FMI experiments, we will use TDDFT with complex absorbing potentials to simulate two-color SFI yields for functionalized benzene molecules when varying multiple parameters such molecular orientation, laser intensity, or the phase between the two color components. Additionally, after starting our simulations with a hole on the molecular halogen center, we will quantify how CM modulates the strong-field sequential double ionization yield. This will shed light on the role of CM in the pre-fragmentation double ionization part of the process.

Attosecond pump-probe spectroscopy at LCLS: We will continue our participation in experimental efforts towards measuring CM using attosecond soft-x-ray pump-probe spectroscopy through the LCLS Director's Attosecond Campaign. The OSU team is actively analyzing data from the XPS measurements taken in the 2021 beamtimes. Our goal is to identify a time dependence in the oxygen 1s binding energy that is related to the XAS signals also recorded during the run. Additionally, we will participate in proposed beamtimes in 2022 that will study CM in aminophenol isomers. These experiments will use the same techniques established in 2021 and will further our understanding of the influence of molecular orbital structure on CM.

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Peer-Reviewed Publications Resulting from this Project (2019-2021)

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Complete spectroscopy in the attosecond regime

Carlos A. Trallero

Department of Physics, University of Connecticut, Storrs, CT 06268

`carlos.trallero@uconn.edu`

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. Such complete measurements involve time-resolved phase and amplitude maps of the quantum state of molecules and atoms.

## Towards zeptosecond-resolved heterodyne experiments

In the last year we have focused on developing techniques for heterodyne measurements of the molecular wavefunction. We employ transient absorption spectroscopy with trains of attosecond XUV pulses in an interferometric configuration (see Fig. 3). Evolution of the interference pattern gives information of the phase, while the overall brightness provides information on the amplitude. Combined, they will provide the complete, energy, angle, and time dependent bound-continuum dipole moment of a molecule.

We have built a new spectrometer with a XUV-Xray camera which provides a much needed linearity in the XUV regime. We spent most of this last cycle building and quantifying the stability of our new setup. Currently we observe interference fringes with both Gaussian and Bessel-like beams (see [3], and the spectra in Fig. 1)
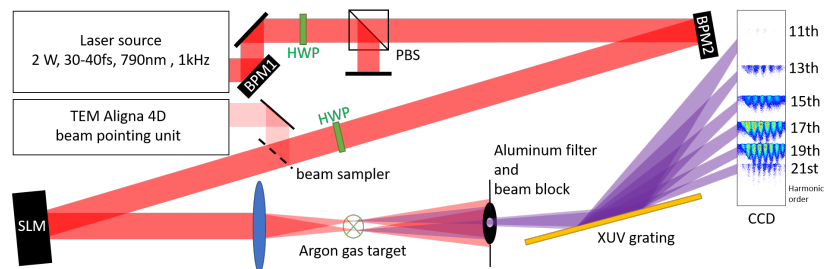
Figure 1: Experimental setup. Phase is controlled via a spatial light modulator (SLM) to generate two phase locked beams. The image on the right depicts spatial interference pattern detected on a CCD.

The most relevant result of this project is that we have achieved temporal zeptosecond resolution and precision in the controlled delay between two trains of attosecond pulses. Delay resolution is achieved by controlling the optical phase of the fundamental with a spatial light modulator (SLM) and the precision is measured by the resolved fringe motion. An example of temporal evolution of the interference fringes is shown in Fig. 2a) and the change in slope with each harmonic in b). So far we have achieved a precision of 120zs in the delay control and a resolution of 413zs, measured as the RMS of the phase jitter over multiple scans performed over 10 hours (see 2c) and d)). We are confident that our setup can be made more stable in the future and that we will be able to achieve a temporal resolution of 300zs.
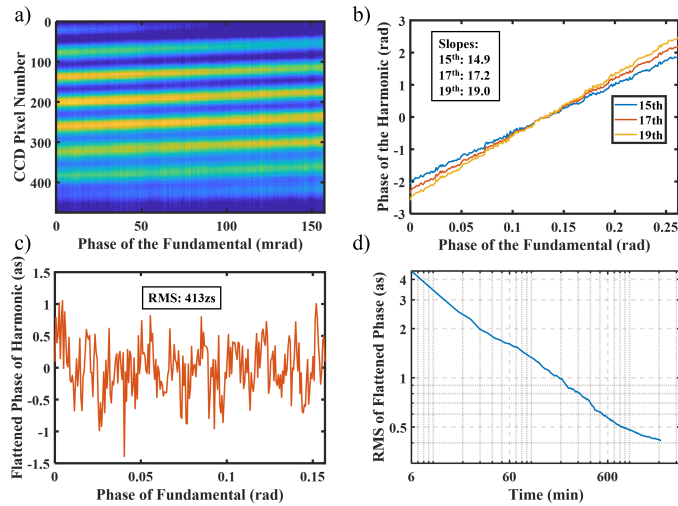
Figure 2: a) Interference fringe evolution of the 17th harmonic and b) comparison of the phase evolution of the 15th, 17th, and 19th harmonics as a function of the relative phase of the two foci of the fundamental. c) Noise of the phase of the 17th harmonics for 350 scans. d) RMS of the noise phase noise over time for harmonic 17th. Step size of fundamental phase corresponds to 120zs.

High harmonic generation enhancement with synthesized fields
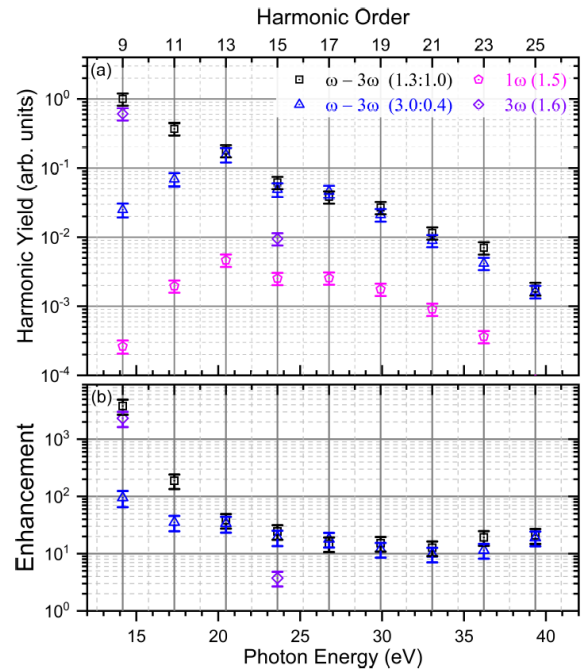*in collaboration with Ben-Itzak*

Project Scope

Experimental demonstration of XUV flux enhancement through HHG with synthesized fields

Recent progress

In the past we have demonstrated the synthesis of two pulses with center wavelengths 800 and 266nm $(\omega - 3\omega)$ with a phase stability of 50as without the need of stabilization or optical feedback. We also performed in-situ ionization measurements, in parallel with the harmonic yield. Because ionization rate in atoms, for a fixed pulse duration, depends only on peak intensity, ionization yields recorded as function of delay between ω and 3ω provides a precise relative phase calibration. We then use this well characterized phase point to determine the influence of electron trajectories on the harmonic yields.

In Fig. 4, we show the measured divergence of the harmonics generated by the bichromatic and single-color diving fields. In particular, Fig. 4(a) shows the measured harmonic spectrum as a function of the photon energy and divergence angle for the 800-66nm driving fields for the (1.3:1.0) intensity ratio. In Fig. 4(b), we compare the yields of the 17th harmonic as a function divergence angle for both two-color intensity ratios as well as the single-color 800nm driver. From this plot, it is clear that the bichromatic fields significantly outperform the 800nm driving field.

Figure 3: (a) Harmonic yields driven by ω (pink), 3ω (purple), and $\omega - 3\omega$ for the (3.0:0.4) (blue) and (1.3:1.0) (black) intensity ratios. (b) Enhancement of harmonics generated by the 800-266nm fields over the optimized single-color 800nm.

In Fig. 4(e) we plot the measured $1/e^2$ divergence angle as a function of harmonic order for the bichromatic and single color driving fields. For the harmonics produced by the two-color fields, we plot the divergence angle at the phase where each harmonic's flux is maximized. One can see that, for most harmonic orders, the bichromatic fields produce less divergent beams than the 800-nm field.

This result is consistent with the assertion of previous theoretical predictions that HHG by fields enhances the short over the long trajectories. Furthermore, the (1.3:1.0) intensity ratio produces smaller divergence harmonics than the (3.0:0.4) ratio, with the exception of the 9th harmonic. This result may arise from the difference in excursion times of the electron trajectories for each intensity ratio, though this calls for further investigation. It is important to note that the reason the 9th harmonic has significantly different divergence angles may be related to its photon energy lying below argon's ionization potential, meaning its generation mechanism is different than the other harmonic orders.

To reiterate the important message of this subsection, the bichromatic fields produce harmonic beams with smaller divergences due to minimizing the contributions of the long trajectories. Since the short and long trajectories have different wavefronts and phases, minimizing the long trajectories allows the resulting beams to have better wavefronts, improving focusing quality and brightness of the photon source. Thus, the synthesized field presents a superior and enhanced XUV pulse.

# High harmonic generation at high repetition rate for photo electron spectroscopy
in collaboration with Tobias Saule and the Max-Planck-Institute of Quantum Optics (MPQ), Munich

Project Scope
Beam time for time-resolved and angle-resolved photoelectron spectroscopy (tr-ARPES) at MHz repetition rate and high energies on tungsten (110).

Results
The supported two-week beam time was used to conducted finishing experiments with the novel high energy attosecond beating by interference of two-photon transitions (RABBITT) setup recently developed at MPQ (up to 72eV photon energy). RABBITT spectrograms from a tungsten (110) target were measured for multiple photon energy ranges and evaluated. The new setup combines, for the first time, a high XUV flux, high photon energies to probe 4-f core states as well as a very good energy resolution (around 100 meV) to resolve resonances. The good energy resolution is due to the high repetition rate, which allows for a high XUV flux while keeping the number of photo electrons emitted per pulse low to prevent space charge effects and the usage of an attosecond pulse train with
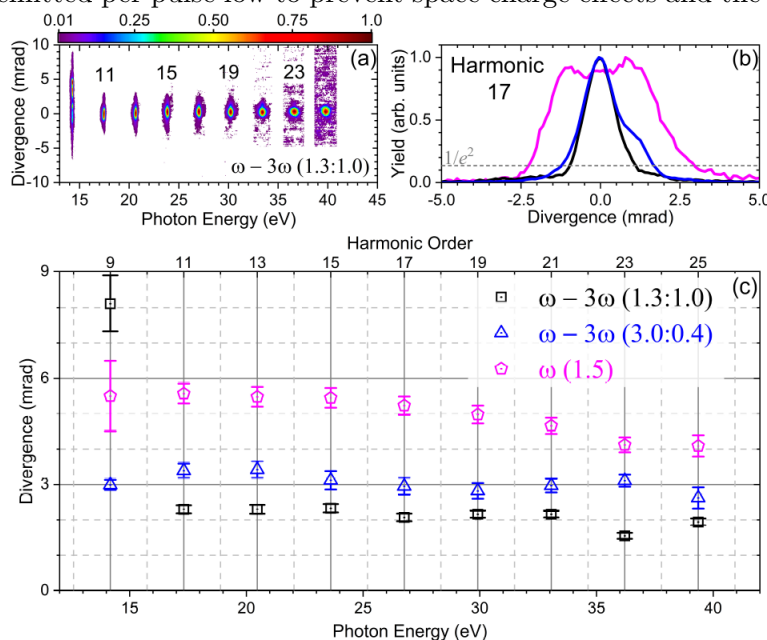
Figure 4: (a) Photon yield as a function of the photon energy and divergence angle for the intensity ratios (1.3:1.0). Several harmonic orders are marked on the figure for clarity. (b) The integrated yield of the 17th harmonic as a function of its divergence angle for the single- and two-color laser fields, normalized so the maximum value is set to unity. The color coding follows the legend in panel (c). (c) Measured full width divergence angle at 1/e2 of the maximum intensity of each harmonic order for the single- and two-color driving fields.

very narrow harmonics. During the beam time, amongst others, a resonant photoemission delay at 62 eV electron kinetic energy was revealed. This resulted in a publication in the journal Nature Communications with the title Attosecond intra-valence band dynamics and resonant-photoemission delays in W(110).

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.

New laser system

A new laser system is greatly delayed due to the covid-19 pandemic. It is expected to be installed in the Spring of 2022. This laser system was made possible through a DURIP, an ONR and AFOSR grants. The laser produces 300W or average power and will have several modes of operation with continuously tunable repetition rates from 25 to 200kHz and possible pulse duration as short as 4fs. We have tested 300 W long term stability at 25 and 200 kHz and currently have demonstrated the generation of 50fs at more than 250W of average power with a repetition rate of 25kHz (10mJ of energy per pulse).

Peer-Reviewed Publications Resulting from this Project (Project start date August 16th 2018)

1. Generation and control of phase-locked Bessel beams with a persistent noninterfering region, Z. Rodnova, Tobias Saule, Richard Sadlon, Edward McManus, Nicholas May, Xiaoming Yu, Sina Shahbazmohamadi, and Carlos A. Trallero-Herrero, Journal of the Optical Society of America B, **37**, 3179-3183, (2020) https://doi.org/10.1364/JOSAB.400801

2. Asymmetric high energy dual optical parametric amplifier for parametric processes and waveform synthesis, Brandin Davis, Tobias Saule, and Carlos A. Trallero-Herrero, Optics Express, **29**, 7379-7388, (2021) https://doi.org/10.1364/OE.417068

3. Higher order harmonic generation and strong field ionization with Bessel-Gauss beams in a thin jet geometry, Michael Davino, Adam Summers, Tobias Saule, Jan Tross, Edward McManus, Brandin Davis, Carlos A Trallero-Herrero, Journal of the Optical Society of America B, **38**, 2194, (2021), https://doi.org/10.1364/JOSAB.420073

4. Enhancing high-order harmonic generation by controlling the diffusion of the electron wavepacket, Travis Severt, Jan Tross, Georgios Kolliopoulos, Itzik Ben-Itzhak, and Carlos A. Trallero-Herrero, Optica, **8**, 1113, (2021), https://doi.org/10.1364/OPTICA.422711

5. Attosecond intra-valence band dynamics and resonant-photoemission delays in W(110), S. Heinrich, T. Saule, M. Högner, Y. Cui, V. S. Yakovlev, I. Pupeza and U. Kleineberg , Nature Communications **12**, 3404 (2021), https://doi.org/10.1038/s41467-021-23650-7

Structural Molecular Dynamics Using Ultrafast Gas X-Ray Scattering

Award # DE-SC0017995

Peter M. Weber
Department of Chemistry
Brown University, Providence, Rhode Island 02912
Peter_Weber@brown.edu

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 phase X-ray scattering, which is pursued at the LCLS light source at SLAC National Accelerator Laboratory. The X-ray scattering experiments are prepared and 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.
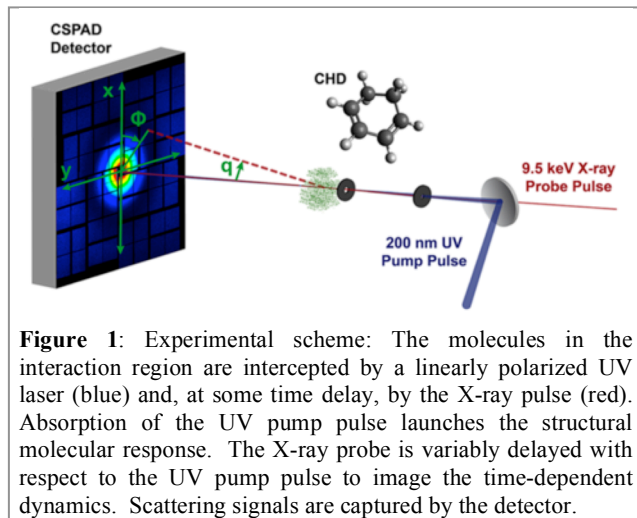
The experiments explore molecular phenomena associated with the nuclear and electron structural dynamics of molecules during reactions. This includes the motions through conical intersections, charge delocalization, the fracture of chemical bonds, vibrational motions and the propagation and spreading of wave packets. Model systems for those investigations include medium-sized organic systems such as cyclohexadiene, trimethyl amine, N-methylmorpholine, N,N-dimethylpiperazine, and 1,2-dithiane. Those systems are 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

Successful beam times at LCLS have resulted in several important advances as reported previously:

- We have measured complete, time-dependent excited state structures of polyatomic molecules. These are largely experimental structures, with only the electronic correction terms derived from theory.

- We learned how to determine the spatial orientation of transition dipole moments within the molecular frame from the anisotropy of the transition dipole moment.

- We developed codes to calculate the total scattering signal from molecules in excited states.

- We observed ultrafast molecular dynamics in trimethyl amine, N-methylmorpholine and 1,3-cyclohexadiene.

- We uncovered how the passage through conical intersections in 1,3-cyclohexadiene is affected by the initial excitation energy.

- We disentangled the contributions of electronic and nuclear geometry changes to the x-ray scattering patterns.

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 detector.

The general principle of these experiments is shown in Figure 1: the molecules are excited by an optical laser pulse to an excited state, a process that initiates the reaction. The time-evolving molecular structures are probed by scattering an X-ray pulse that arrives a short time after the excitation pulse. The scattering pattern is measured on the detector, and its analysis leads to the structure as a function of time. By sequencing the time-dependent molecular structures we obtain a 'molecular movie' showing the motions of atoms while reactions proceed.

X-ray scattering is sensitive to the electron density distributions. Since the core electrons are tightly, and nearly spherically, distributed about the atomic nuclei (except for hydrogen atoms), the X-ray scattering pattern yields the atomic positions. The valence electrons also contribute to the scattering signal, but their spatial distributions depend on the chemical bonding. We have succeeded in observing both the nuclear and the electronic structure parts by separating their respective effects by treating the nuclear and electronic effects as additive terms,

$$\Delta S_{\text{exc}}(q, \mathbf{R}') = \Delta S^{\text{nucl}}(q, \mathbf{R}') + \Delta S_{\text{exc}}^{\text{elec}}(q, \mathbf{R}'),$$

where the nuclear contribution, $\Delta S^{\text{nucl}}(q, \mathbf{R}')$ represents the contribution to the scattering as if the molecular geometry was deformed $\mathbf{R}_0 \to \mathbf{R}'$ on the ground electronic state. The second term is the electronic contribution, $\Delta S_{\text{exc}}^{\text{elec}}(q, \mathbf{R}')$, defined by the difference in scattering from the excited and ground electronic states at a single molecular geometry $\mathbf{R}'$. On a formal level, this decomposition of $\Delta S_{\text{exc}}(q, \mathbf{R}')$ does not involve any approximation regarding the scattering process itself.

The determination of complete, excited state structures from pump-probe scattering data requires the construction of a large pool ($\approx 10^6$) of potential molecular structures. For each such structure the scattering pattern is calculated by including both the nuclear geometry displacement and the changes in the electronic structure. A statistical analysis compares the structures in the pool to the experimentally measured scattering pattern to retrieve the optimal excited state structure. All bonded and non-bonded distances, as well as bond angles and dihedral angles are obtained in this fashion. We have demonstrated that this structure determination method is independent of how the pool of structures is created. Only the correction due to the electronic excitation, which is a comparatively small effect, is contributed by the calculations. This implies that it is the experimental pump-probe x-ray scattering pattern, rather than a computational model, that gives rise to the determined structure.

A Structural View of Charge Transfer

Charge transfer, i.e. the motion of electrons across or between molecules, plays a fundamental role in many areas of chemistry, physics, biology, and materials science. The spatial redistribution of electrons is typically associated with changes in the molecular geometry. A comprehensive understanding of this process requires atomic spatial resolution and femtosecond temporal resolution.
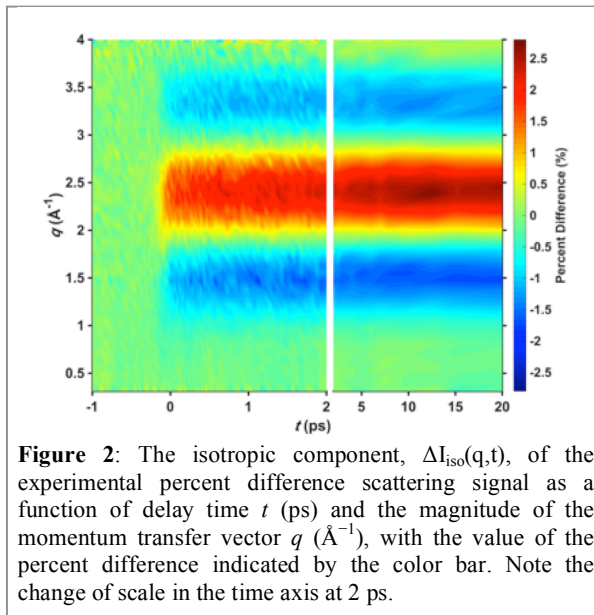
Given the emerging ability of ultrafast gas-phase scattering to record both nuclear and electronic structure as discussed above, we use time-resolved gas-phase x-ray scattering to study the photoinduced intramolecular charge transfer in an organic molecule, N,N′-dimethylpiperazine (DMP, $C_6H_{14}N_2$, see inset in

Figure 2: The isotropic component, $\Delta I_{iso}(q,t)$, of the experimental percent difference scattering signal as a function of delay time t (ps) and the magnitude of the momentum transfer vector q (Å^{-1}), with the value of the percent difference indicated by the color bar. Note the change of scale in the time axis at 2 ps.

Figure 3). In its ground electronic state, DMP has C_{2h} symmetry with two equivalent ionization centers, one on each nitrogen atom. Valence ionization, or in the present case excitation to an electronic Rydberg state, initially creates a state where the charge is located on one of the amine atoms. On a timescale of picoseconds, this charge delocalizes across both nitrogen atoms, implying effectively a transfer of half an electron.

The time-resolved x-ray scattering patterns reflect the chemical reaction in time and in the space of scattering vectors. For kinetic reactions this implies that the time-dependent signal is comprised of separable spatial and temporal parts:

$$\Delta I_{iso}(q,t) = \gamma \left(\sum_\alpha S_\alpha(q)F_\alpha(t) \right) * g(t)$$

Here, $S_\alpha(q)$ is the fitted isotropic scattering pattern of transient structure α, while $F_\alpha(t)$ is the corresponding time-dependent population as determined by the kinetic scheme. The scalar γ represents the excitation probability and $g(t)$ is a Gaussian function that characterizes the instrument response. As a result, the time-dependent scattering pattern, Figure 2, can be separated into orthogonal spatial and temporal contributions. This enables the extraction of experimental scattering patterns of each of the contributing components, Figure 3.

Applying the structure determination method with a large pool of structures enables us to obtain the complete, excited state structures of both the charge-localized and the
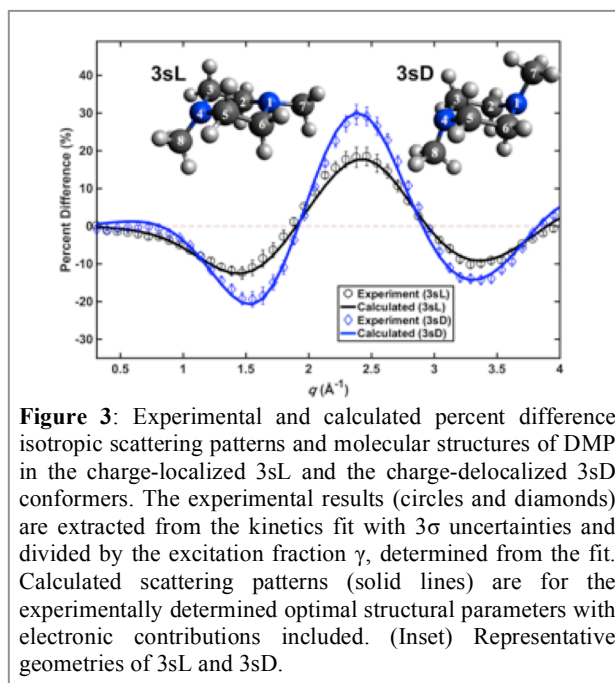
Figure 3: Experimental and calculated percent difference isotropic scattering patterns and molecular structures of DMP in the charge-localized 3sL and the charge-delocalized 3sD conformers. The experimental results (circles and diamonds) are extracted from the kinetics fit with 3σ uncertainties and divided by the excitation fraction γ, determined from the fit. Calculated scattering patterns (solid lines) are for the experimentally determined optimal structural parameters with electronic contributions included. (Inset) Representative geometries of 3sL and 3sD.

charge-delocalized species involved in the charge transfer. The analysis also results in time constants for the kinetics of the charge transfer reaction. In a pleasing confirmation of both the experimental procedure and the analysis methodology, the derived bond parameters reflect chemical intuition of the involved structures. As an excerpt from the complete structure table, the nearby table lists the torsional angles involving the amine groups of DMP. While the angles in the localized structure reflect the positioning of the charge on one atoms, the delocalized charge features both amines with equal angles, as one would expect.

Torsional angles (^{o})	Localized	Error	Delocalized	Error
C_8-N_4-C_3-C_2	92.3	6.9	88.8	3.5
C_8-N_4-C_5-C_6	93.6	0.2	88.1	4.9
C_7-N_1-C_6-C_5	163.9	1.4	89.5	3.2
C_7-N_1-C_2-C_3	165.1	0.5	90.4	4.6

III. Future Plans

We are continuing to analyze data sets obtained at various LCLS beam times. Computational modeling of the dithiane reaction upon optical excitation is ongoing and a manuscript about that work is being prepared.

We have also applied for LCLS beam time to advance our x-ray scattering experiments. Additional experiments with x-ray absorption and MeV electron scattering are planned as well. The goal of these experiments is to uncover important phenomena in chemical dynamics with advanced experiments made possible by the upgraded LCLS.

IV. Peer-Reviewed Publications resulting from this Project (2019-2021)

1. "Ab initio calculation of total scattering from molecules", Andrés Moreno Carrascosa et al., *Journal of Chemical Theory and Computation*, 15, 5, 2836-2846, **2019**, DOI: 10.1021/acs.jctc.9b00056

2. "Simplicity beneath Complexity: Counting Molecular Electrons Reveals Transients and Kinetics of Photodissociation Reactions", J. M. Ruddock et al., *Angewandte Chemie International Edition*, **2019**, 58, 6371 –6375, DOI: 10.1002/anie.201902228

3. "The photochemical ring-opening of 1,3-cyclohexadiene imaged by ultrafast electron diffraction" T. J. A. Wolf et al., *Nature Chemistry*, **11**, 504–509 (**2019**), DOI: 10.1038/s41557-019-0252-7

4. "Femtosecond Molecular Movie Reveals Vibrational Coherence and Dephasing" Brian Stankus et al., *Nature Chemistry,* 11, 716–721 (**2019**). DOI: 10.1038/s41557-019-0291-0.

5. "Roadmap on photonic, electronic and atomic collision physics I. Light-matter interaction," Kiyoshi Ueda et al., *J. Phys. B: At. Mol. Opt. Phys*. 52, 171001 (**2019**). DOI: 10.1088/1361-6455/ab26d7

6. "Scattering off Molecules far from Equilibrium," H. Yong et al., *J. Chem. Phys*., 151, 084301 (**2019**). DOI: 10.1063/1.5111979.

7. "A Deep UV Trigger for Ground-State Ring-Opening Dynamics of 1,3-Cyclohexadiene," Jennifer M. Ruddock et al., *Science Advances*, 5, eaax6625 (**2019**). DOI: 10.1126/sciadv.aax6625

8. "Observation of the molecular response to light upon photoexcitation" Haiwang Yong et al., *Nature Communications*, 11, 2157 (**2020**). DOI 10.1038/s41467-020-15680-4.

9. "Ultrafast X-ray and Electron Scattering of Free Molecules: a Comparative Evaluation" L. Ma et al, *Structural Dynamics*, **7**, 034102 (**2020**); PMCID: PMC7316516; https://doi.org/10.1063/4.0000010.

10. "Advances in Ultrafast Gas-Phase X-ray Scattering," B. Stankus et al., *J. Phys. B., Atomic, Molecular & Optical Physics*, 53, 23 (**2020**). https://dx.doi.org/10.1088/1361-6455/abbfea.

11. "Determination of Excited State Molecular Structures from Time-Resolved Gas-Phase X-Ray Scattering," H. Yong et al., *Faraday Discussions*, **2021**, 228, 104 – 122. 10.1039/D0FD00118J.

12. "Ultrafast X-Ray Scattering Offers a Structural View of Excited State Charge Transfer," H. Yong et al., *PNAS* 118 (19) e2021714118, **2021**. , DOI: 10.1073/pnas.2021714118.

Combining High Level *Ab Initio* Calculations with Laser Control of Molecular Dynamics

Thomas Weinacht

Department of Physics and Astronomy

Stony Brook University

Stony Brook, NY

thomas.weinacht@stonybrook.edu

and

Spiridoula Matsika

Department of Chemistry

Temple University

Philadelphia, PA

smatsika@temple.edu

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:

2.1 Excited State Dynamics in Conjugated Systems

One of the questions that we set out to address in the previous grant cycle was how the structure of conjugated systems affects their excited state dynamics. In order to expand our understanding of photoisomerization with two double bonds, we studied cis,cis-1,3-cyclooctadiene (COD), a molecule similar to cyclohexadiene (CHD) and butadiene (for which there have been a number of studies), but larger and more flexible. We made use of trajectory surface hopping (TSH) calculations and UV-pump VUV-probe time resolved photoelectron spectroscopy (TRPES).The TSH calculations reveal that COD has a very short excited state lifetime, with decay to the ground state occurring through conical intersections (CIs). Several products formed on the ground state have also been observed, including cis,trans COD and 3-methylenecycloheptene. Our calculations and analysis indicate that the internal conversion dynamics for photo-excited COD are highly non-local, with trajectories exploring many different geometries at which non-adiabatic coupling drives hopping between electronic states. In addition to calculating the excited state dynamics, we also carried out calculations of the measurement observables for both time resolved photoelectron spectroscopy (TRPES) measurements and ultrafast electron diffraction (UED) measurements. A comparison of the calculated and measured TRPES signals shows that while our calculations agree qualitatively with the measurements, they do not agree quantitatively on the timescale for decay of the photo-electron signal. We are currently working on understanding this discrepancy, and also carrying out an analysis of UED measurements of the same dynamics. The UED measurements and analysis are carried out in collaboration with the group of Martin Centurion at the University of Nebraska.

2.2 TRPES as a Test of Electronic Structure and Nonadiabatic Dynamics

We have combined TRPES measurements with nonadiabatic dynamics in uracil in order to both resolve discrepancies in the dynamics and benchmark the theory. We performed trajectory surface hopping calculations for uracil excited to the first bright state (S_2, $\pi\pi^*$) using three different levels of theory (CASSCF, MRCIS and XMS-CASPT2) in order to understand the role of dynamical correlation in determining the excited state dynamics, with a focus on the coupling between different electronic states and internal conversion back to the ground state. These dynamics calculations were used to simulate the TRPES (Fig. 1). The comparison of the calculated and measured spectra highlighted the importance of dynamical correlation in being able to reproduce the correct dynamics, and demonstrated that reproducing the experimental observables can lead to accurate assignments and be used to benchmark theory. We also found that the S_2 population decays very fast.
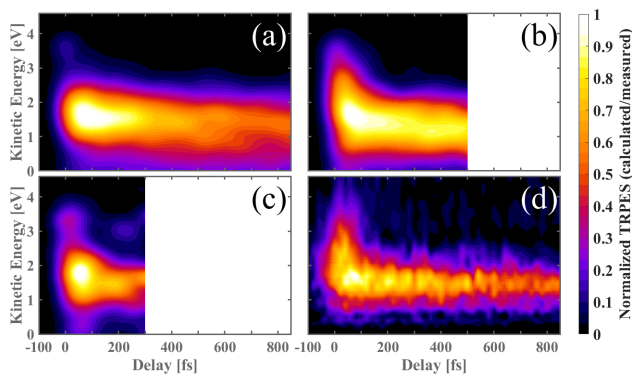
Figure 1: Calculated and measured TRPES of uracil. In this figure, the calculated and measured TRPES signals are plotted as a function of time and kinetic energy (KE). Panels (a), (b), and (c) show the calculated TPRES according to CASSCF, MRCIS, and XMS-CASPT2 levels of theory, respectively, while panel (d) shows the measured TRPES. All the TRPES signals are normalized individually.
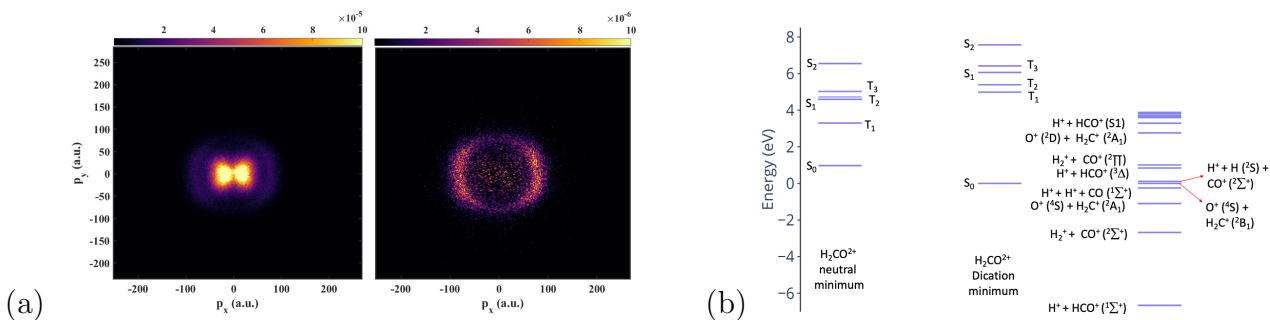

Figure 2: (a) Momentum resolved CD_2^+ yield from strong field ionization of CD_2O. The left panel shows the total momentum resolved CD_2^+ yield, while the right panel shows the momentum resolved CD_2^+ yield in covariance with O^+. The laser was polarized along the x axis for these measurements. (b) Calculated excited states and dissociation limits for CH_2O^{2+} at the EOM-EE-CCSD/cc-pVTZ level.

2.3 Strong Field Molecular Double Ionization

In the past year, we completed the analysis of our measurements of strong field double ionization of D_2O, in collaboration with the groups of Phil Bucksbaum at Stanford University, Robert Lucchese at Berkeley Lab, and Bill McCurdy at UC Davis. Our coincidence measurements of electrons and ions demonstrated momentum resolved above threshold ionization, in which we could separately measure the photoelectron spectrum for electrons produced in coincidence with different fragment ions, and ions with different momenta. We also highlighted non-vertical ionization by comparing our momentum resolved coincidence measurements of the three body dissociation of doubly ionized D_2O with the dynamics calculations. Most recently we extended these measurements to covariance, demonstrating information content equivalent to coincidence measurements, but with data acquisition speeds up to 100 times faster.

We are now applying these covariance measurements to the double ionization of deuterated formaldehyde, which is a natural follow up to our work on D_2O. Fig. 2 illustrates the covariance measurements with a comparison of the total momentum resolved CD_2^+ yield and the momentum resolved CD_2^+ yield in covariance with O^+. The central feature in the total momentum resolved CD_2^+ yield is not present in the covariance yield, indicating that the central spot arises from single ionization, whereas the outer lobes that appear in both graphs come from double ionization that leads to CD_2^+/O^+. Furthermore, the graphs highlight a strong angle dependence for both the single and double ionization yields. Electronic structure calculations help us identify the dissociation energies (Fig. 2), while trajectories are used to identify the states and dynamics associated with each
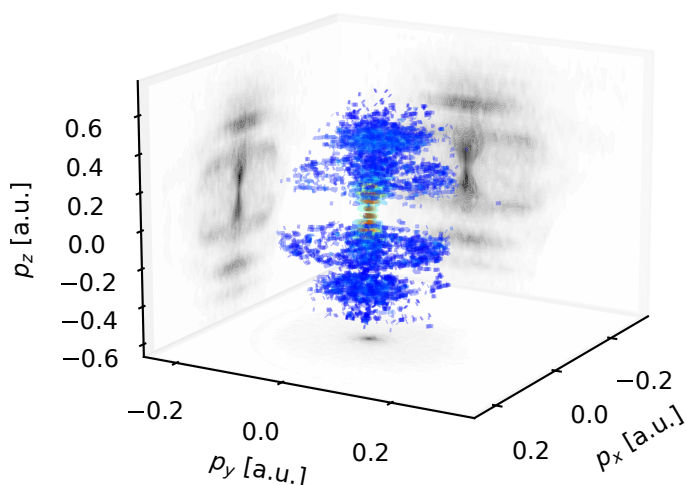
Figure 3: Three dimensional rendering of ATI peaks from strong field ionization of Xenon, with projections onto each plane. Photoelectron yield as a function of p_x, p_y and p_z. The laser polarization is in the z-direction (the time of flight axis pointing towards the detector) as depicted by the red arrow in the figure.

fragmentation channel.

3 Three dimensional Velocity Map Imaging

Making use of our recently acquired TPX3CAM, in collaboration with the group of Carlos Trallero at the University of Connecticut, we have developed 3D VMI for electrons using the fast time to digital converter (TDC) on the TPX3CAM. The $[p_x, p_y, p_Z]$ information for each electron is encoded in the measured [x,y,t] provided by the camera. The camera sensor provides [x,y] information, while the timing information comes from capacitavely coupling to the phosphor screen detector, with a constant fraction discriminator between the phosphor screen and the TDC. Figure 3 illustrates our 3D VMI measurements for strong field ionization of Xenon.

4 Future Plans

We have several goals for the immediate future:

1. Complete our analysis of the trajectory surface hopping calculations, TRPES measurements and UED measurements for COD to form a complete picture of the excited state dynamics.

2. Calculate dissociation dynamics in the formaldehyde dication including non-adiabatic dynamics *en route* to dissociation.

3. Interpret the formaldehyde strong field double ionization measurements for both 5 and 30 fs laser pulses with the dynamics calculations in order to obtain a molecular frame, state resolved picture of the strong field double ionization, including non-adiabatic dynamics in the dication.

4. Further develop our 3DVMI measurements and perform electron-ion covariance measurements.

5 Peer-Reviewed Publications Resulting from this Project (2019-2021)

- "Electron correlation in channel resolved strong field molecular double ionization", Chuan Cheng, Patricia Vindel Zandbergen, Spiridoula Matsika, and Thomas Weinacht, *Phys. Rev. A*, **100**, 053405 (2019)

- "The Generality of the GUGA MRCI Approach in COLUMBUS for Treating Complex Quantum Chemistry", Hans Lischka, Ron Shepard, Thomas Müller, Péter G. Szalay, Russel M. Pitzer, Adelia J. A. Aquino, Mayzza M. Arajo do Nascimento, Mario Barbatti, Lachlan T. Belcher, Itamar Borges Jr., Scott R. Brozell, Anita Das, Silmar A. do Monte, Leticia Gonzalez, William L. Hase, Gary Kedziora, Fabris Kossoski, Francisco B. C. Machado, Spiridoula

Matsika, Dana Nachtigallova, Reed Nieman, Markus Oppel, Felix Plasser, Rene F. K. Spada, Eric A. Stahlberg, Elizete Ventura, David R. Yarkony *J. Chem. Phys.*, **152**, 134110, (2020)

- "Excited State Dynamics of cis,cis-1,3-Cyclooctadiene: UV pump VUV Probe Time Resolved Photoelectron Spectroscopy" Yusong Liu, Pratip Chakraborty, Spiridoula Matsika and Thomas Weinacht. *J. Chem. Phys.*, **153**, 074301 (2020)

- "Excited State Dynamics of cis,cis-1,3-Cyclooctadiene: Non-adiabatic Trajectory Surface Hopping" Pratip Chakraborty, Yusong Liu, Thomas Weinacht, Spiridoula Matsika. *J. Chem. Phys.*, 152, 174302 (2020)

- "Spectroscopic and structural probing of excited state molecular dynamics with time-resolved photoelectron spectroscopy and ultrafast electron diffraction" Yusong Liu, Spencer Horton, Jie Yang, J. Pedro F. Nunes, Xiaozhe Shen, Thomas J. A. Wolf, Ruaridh Forbes, Chuan Cheng, Bryan Moore, Martin Centurion, Kareem Hegazy, Renkai Li, Ming-Fu Lin, Albert Stolow, Paul Hockett, Tamás Rozgonyi, Philipp Marquetand, Xijie Wang, and Thomas Weinacht *Phys. Rev. X*, **10**, 021016, (2020)

- "Simultaneous Observation of Nuclear and Electronic Dynamics by Ultrafast Electron Diffraction", Jie Yang, Xiaolei Zhu, J. Pedro F. Nunes, Jimmy K. Yu, Robert M. Parrish, Thomas J. A. Wolf, Martin Centurion, Markus Guhr, Renkai Li, Yusong Liu, Bryan Moore, Mario Niebuhr, Suji Park, Xiaozhe Shen, Stephen Weathersby, Thomas Weinacht, Todd J. Martinez, Xijie Wang *Science*, 368, 886, (2020)

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Name	Affiliation
Thomas Allison	Stony Brook University
Vadym Apalkov	Georgia State University
Luca Argenti	University of Central Florida
Polly Arnold	Lawrence Berkeley National Lab
Andreas Becker	JILA and Department of Physics, University of Colorado Boulder
Itzik Ben-Itzhak	J.R. Macdonald Laboratory, Physics, Kansas State University
Nora Berrah	University of connecticut
Cosmin Blaga	Kansas State University
Philip Bucksbaum	SLAC/Stanford
Martin Centurion	University of Nebraska - Lincoln
Lan Cheng	Johns Hopkins University
Michael Chini	University of Central Florida
Amy Cordones-Hahn	SLAC National Accelerator Laboratory
James Cryan	SLAC National Accelerator Laboratory
Steven Cundiff	University of Michigan
Marcos Dantus	Michigan State University
Louis Dimauro	The Ohio State University
Gilles Doumy	ARGONNE NATIONAL LABORATORY
Joseph Eberly	univ. rochester
Brett Esry	J.R. Macdonald Laboratory, Kansas State University
Li Fang	University of Central Florida
Chris Fecko	DOE-BES
Tim Fitzsimmons	BES
Bob Forrey	NSF
Matthias Fuchs	University of Nebraska - Lincoln
Mette Gaarde	Louisiana State University
Kelly Gaffney	SLAC National Accelerator Laboratory
Marco Garavelli	Bologna University
Bruce Garrett	DOE-SC-BES
Bonnie Gersten	DOE-BES
Oliver Gessner	Lawrence Berkeley National Laboratory
Shambhu Ghimire	SLAC National Accelerator Laboratory
Tais Gorkhover	SLAC
Niri Govind	Pacific Northwest National Laboratory
Chris Greene	Purdue University
Loren Greenman	Kansas State University
Martin Head-Gordon	LBNL
Tony Heinz	SLAC
Phay Ho	Argonne National Laboratory

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Kevin Jones	National Science Foundation
Robert Jones	University of Virginia
Henry Kapteyn	JILA, University of Colorado
Refik Kortan	doe-bes
Jeffrey Krause	Department of Energy
Vinod Kumarappan	Kansas State University
Guillaume Laurent	Auburn University
Peter Lee	DOE/BES
Stephen Leone	LBNL and Univ of Calif Berkeley
Elliane Lessner	BES/SC/DOE
Wen Li	Wayne State University
Chii Dong Lin	kansas state university
Kenneth Lopata	Louisiana State University
Robert Lucchese	Lawrence Berkeley National Lab
Vyacheslav Lukin	National Science Foundation
Steven T Manson	Georgia State University
George Maracas	DOE BES
Anne Marie March	Argonne National Lab
Todd Martinez	SLAC
Spiridoula Matsika	Temple University
Bill McCurdy	Lawrence Berkeley National Laboratory
Grace Metcalfe	AFOSR
Francesco Montorsi	University of Bologna
Jeffrey Moses	Cornell University
Tia Moua	ORISE
Karl Mueller	Pacific Northwest National Laboratory
Shaul Mukamel	University of California - Irvine
Margaret Murnane	JILA, University of Colorado
Adi Natan	Stanford PULSE Institute
Artur Nenov	Università di Bologna
Daniel Neumark	UC Berkeley, LBNL
Jean Marcel Ngoko Djiokap	The University of Nebraska-Lincoln
Thomas Orlando	Georgia Institute of Technology
Abbas Ourmazd	Univ. of Wisconsin Milwaukee
Mick Pechan	USDOE BES MSE
Herschel Rabitz	Princeton University

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Lucas Reigelsperger	ORISE
David Reis	SLAC
Thomas Rescigno	Lawrence Berkeley National Laboratory
Francis Robicheaux	Purdue University
Daniel Rolles	Kansas State University
Artem Rudenko	Kansas State University
Arvinder Sandhu	University of Arizona
Arvinder Sandhu	University of Arizona
Robin Santra	DESY & University of Hamburg
Kenneth Schafer	Louisiana State University
H. Bernhard Schlegel	Wayne State University
Robert Schoenlein	SLAC National Accelerator Laboratory
Athena Sefat	DOE-BES
Francesco Segatta	University of Bologna (Italy)
Tom Settersten	DOE BES
Linda Severs	ORISE
Wade Sisk	DOE/BES
Daniel Slaughter	Lawrence Berkeley National Laboratory
Steve Southworth	Argonne National Laboratory
Andrew Stickrath	Air Force Office of Scientific Research
Uwe Thumm	Kansas State University
Carlos Trallero	University of Connecticut
Sergei Tretiak	LANL
Xijie Wang	SLAC
Thorsten Weber	Lawrence Berkeley National Lab
Peter Weber	Brown University
Thomas Weinacht	Stony Brook University
Thomas Wolf	SLAC National Accelerator Laboratory
Linda Young	Argonne National Laboratoy
Jane Zhu	DOE-BES