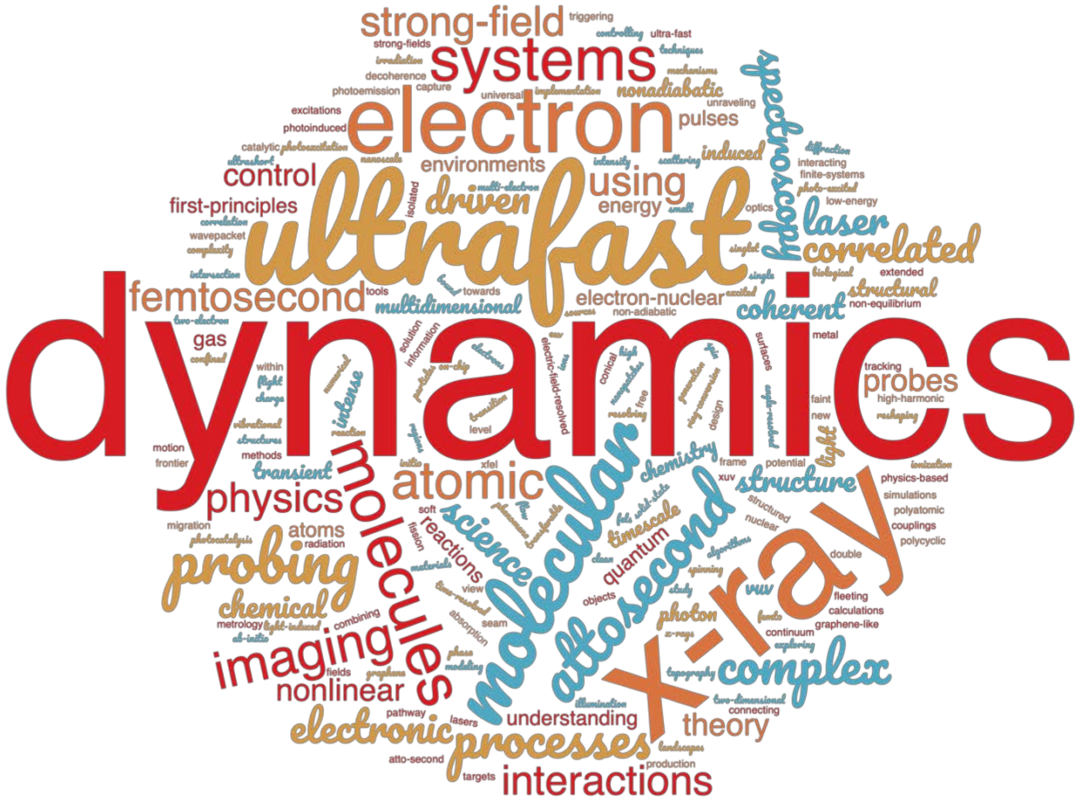
2023
Atomic, Molecular, and Optical Sciences Research PI Meeting



Hilton Washington DC/Rockville
Hotel & Executive Meeting Center
Rockville, Maryland

October 23-25, 2023

U.S. DEPARTMENT OF ENERGY | Office of Science

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

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Program and Abstracts

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Cover Graphics: The input for the Wordclouds.com cover art is based on the titles of the abstracts for this year's meeting.

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

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FOREWORD

This volume summarizes the 43rd 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. In addition to PI presentations on their currently funded research, we are thrilled to include a special session on Day 1 that is inspired by the 2023 Nobel Prize in Physics. The session, “A Long Road to Attosecond Science,” will be chaired by Jeff Krause, the former DOE Program Manager for the AMOS Program and the former Lead for the Fundamental Interaction Team in BES. The session includes four presentations by AMOS PIs, who provide historical perspectives of attosecond physics and a vision for the future in the context of the AMOS Program and BES mission science.

The AMOS program continues to advance fundamental, hypothesis-driven research in ultrafast chemical sciences, with emphasis on ultrafast x-ray science, strong-field and attosecond science, and correlated dynamics. The program supports basic experimental and theoretical research aimed at understanding the structural and dynamical properties of molecular systems. The research targets fundamental interactions of photons and electrons with 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.

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 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.

We are excited to return to the in-person meeting format for the first time since October 2019. Many thanks to Teresa Crockett in BES for her key efforts in coordinating with the staff of the Oak Ridge Institute for Science and Education (ORISE) to help plan and execute this meeting. We are also indebted to Teresa and Angie Thevenot in BES for their indispensable behind-the-scenes efforts in support of the BES/AMOS program over the past year.

Thomas B. Settersten
Chemical Sciences, Geosciences, and Biosciences Division
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Updated October 25, 2023

2023 Atomic, Molecular and Optical Sciences Research PI Meeting

Office of Basic Energy Sciences
U.S. Department of Energy

October 23 – 25, 2023 (Times are EDT)

MONDAY, OCTOBER 23

7:30 AM	*BREAKFAST*	
OPENING REMARKS		
8:30 AM	Welcome and Introductory Remarks **Thomas B. Settersten**	 U.S. Department of Energy, Lead for Fundamental Interactions Team
NEW RESEARCHERS AND PROJECTS		3-minute, 1-slide summary
9:00 AM	**Nikolay Golubev**	University of Arizona
9:03 AM	**Donnie Keathley**	Massachusetts Institute of Technology
9:06 AM	**Guillaume Laurent**	Auburn University
9:09 AM	**Kenneth Lopata**	Louisiana State University
9:12 AM	**Jin Qian**	Lawrence Berkeley National Laboratory
9:15 AM	**Niranjan Shivaram**	Purdue University
9:18 AM	**Carlos Trallero**	University of Connecticut
9:21 AM	**Meng Han**	J.R. Macdonald Laboratory, Kansas State University
9:24 AM	**Jeremy Rouxel**	Argonne National Laboratory
9:27 AM	*BREAK, 18 MINUTES*	
LAB PROGRAMS	**Nora Berrah** (Chair) University of Connecticut	10-minute presentation, 5-minute Q&A
9:45 AM	Ultrafast Chemical Sciences **Philip H. Bucksbaum**	 SLAC National Accelerator Laboratory
10:00 AM	Atomic, Molecular, and Optical Sciences **Oliver Gessner**	 Lawrence Berkeley National Laboratory
10:15 AM	Atomic, Molecular, and Optical Physics **Linda Young**	 Argonne National Laboratory
10:30 AM	Structure and Dynamics of Atoms, Ions, Molecules and Surfaces **Artem Rudenko**	 J.R. Macdonald Laboratory, Kansas State University
10:45 AM	*BREAK, 15 MINUTES*	
SESSION 3	**Nikolay Golubev** (Chair) University of Arizona	20-minute presentation, 10-minute Q&A
11:00 AM	Atomic View of Molecular Photocatalysis using X-ray Lasers **Amy Cordones-Hahn**	 SLAC National Accelerator Laboratory
11:30 AM	*BREAK, 30 MINUTES*	
12:00 PM	*WORKING LUNCH*	

A LONG ROAD TO ATTOSECOND SCIENCE	**Jeffrey L. Krause** (Chair) Former AMOS Program Manager & Lead for Fundamental Interactions Team 25-minute presentation, 5-minute Q&A
1:00 PM	Attaboy, Attosecond **Louis F. DiMauro** Ohio State University
1:30 PM	The Road to Attosecond Science and Technology **Kenneth Schafer** Louisiana State University
2:00 PM	Putting Attosecond High Harmonic Technologies to Work **Margaret Murnane** University of Colorado, Boulder
2:30 PM	Attosecond XFELs: A Tool to Study Ultrafast Electron Motion **James P. Cryan** SLAC National Accelerator Laboratory
3:00 PM	*BREAK, 30 MINUTES*
SESSION 5	**Kenneth Lopata** (Chair) Louisiana State University 20-minute presentation, 10-minute Q&A
3:30 PM	Attosecond and Strong-field Molecular Processes Viewed with X-rays **Philip H. Bucksbaum** SLAC National Accelerator Laboratory
4:00 PM	Photoionization Delays in Atoms and Molecules **Alexandra Landsman** Ohio State University
4:30 PM	Electronic and Nuclear Dynamics in Molecular Photoemission **Robert Lucchese** Lawrence Berkeley National Laboratory
5:00 PM	*ADJOURN, DINNER ON YOUR OWN*

TUESDAY, OCTOBER 24

7:30 AM	*BREAKFAST*
SMALL-GROUP PROJECTS	**Jin Qian** (Chair) Lawrence Berkeley National Laboratory 30-minute presentation, 10-minute Q&A
8:30 AM	Probing Nuclear and Electronic Dynamics in Ultrafast Ring-Conversion Molecular Reactions **Martin Centurion** University of Nebraska
9:10 AM	Coherent Probes of Molecular Charge Migration **Kenneth Schafer** Louisiana State University
9:50 AM	Probing Elementary Molecular Events by Novel X-ray Spectroscopies **Shaul Mukamel** University of California, Irvine
10:30 AM	*BREAK, 30 MINUTES*
SESSION 7	**Donnie Keathley** (Chair) Massachusetts Institute of Technology 20-minute presentation, 10-minute Q&A
11:00 AM	Non-linear Resonant X-ray Interactions: Experiments and Theory **Gilles Doumy** Argonne National Laboratory
11:30 AM	Simulations of X-ray Scattering: Interference and Wave Packets **Francis Robicheaux** Purdue University
12:00 PM	*WORKING LUNCH*
1:00 PM	*COLLABORATION DISCUSSIONS*

SESSION 8	**Niranjan Shivaram** (Chair) Purdue University 20-minute presentation, 10-minute Q&A
3:00 PM	Ultrafast Molecular and Interfacial Dynamics Studied by Time-Resolved Imaging and Inner-Shell Spectroscopy **Oliver Gessner** Lawrence Berkeley National Laboratory
3:30 PM	Imaging Light Driven Molecular Dynamics **Itzik Ben-Itzhak** J.R. Macdonald Laboratory, Kansas State University
4:00 PM	Probing Molecular Wavepacket Evolution Using Multidimensional Coherent Spectroscopy **Steven Cundiff** University of Michigan
4:30 PM	Strong-field-driven Dissociative Ionization Dynamics in Small Molecules **Uwe Thumm** J.R. Macdonald Laboratory, Kansas State University
5:00 PM	*ADJOURN, DINNER ON YOUR OWN*

WEDNESDAY, OCTOBER 25

7:30 AM	*BREAKFAST*
SESSION 9	**Guillaume Laurent** (Chair) Auburn University 20-minute presentation, 10-minute Q&A
8:30 AM	The Physical Significance of the View Observed from the Top of Quantum Control Landscapes **Herschel A. Rabitz** Princeton University
9:00 AM	Correlated Molecular Dynamics in Momentum Space: Theory in Coincidence with Coincidence Momentum Imaging **Loren Greenman** J.R. Macdonald Laboratory, Kansas State University
9:30 AM	*BREAK, 15 MINUTES*
SESSION 10	**Carlos Trallero** (Chair) University of Connecticut 20-minute presentation, 10-minute Q&A
9:45 AM	Probing Excitons in 2D Systems and Interfaces **Tony F. Heinz** SLAC National Accelerator Laboratory
10:15 AM	High Order Harmonic Generation in Extended Systems **Shambhu Ghimire** SLAC National Accelerator Laboratory
CLOSING	
10:45 AM	Closing Remarks **Thomas B. Settersten** U.S. Department of Energy, Lead for Fundamental Interactions Team
11:00 AM	*ADJOURN*

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Argonne National Laboratory

J.R. Macdonald Laboratory

Lawrence Berkeley National Laboratory

SLAC National Accelerator Laboratory

University Research Summaries (by PI)

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AMO Physics at Argonne National Laboratory

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

The Argonne AMO physics program explores the frontiers of x-ray physics as enabled by accelerator-based light sources and, in so doing, lays the foundation for ultrafast x-ray applications in other scientific domains. We utilize the novel properties of accelerator-based coherent x-ray sources, primarily the Advanced Photon Source (APS) synchrotron at Argonne and the Linac Coherent Light Source (LCLS) x-ray free-electron laser (XFEL) at SLAC in concert with ultrafast lasers, to create exotic and/or non-equilibrium states and to probe their rapidly evolving properties with atomic-scale spatial and temporal resolution. The experimental work is supported and complemented by theoretical developments, often taking advantage of massively parallel codes developed for the evolving supercomputer suite 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. 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-resolution 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 attosecond and 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, use the new ChemRIXS beamline at LCLS and optical pump/infrared probe capabilities at the Argonne Center for Nanoscale Materials (CNM).

This past year was particularly notable in terms of upgrades to Argonne-based facilities; the APS began its year-long upgrade to the $\sim$ 500x brighter APS-U in April 2023 and the Aurora Exascale Computer installed its last component in June 2023. The AMO group has made substantial progress in the interpretation of many experimental campaigns of the previous year. In Subtask 1, we have developed a theoretical framework extending beyond the conventional rate-equation approach that shows how x-ray Rabi oscillations can be harnessed to augment the scattering efficiency for single-particle imaging experiments, and, demonstrated high-resolution stochastic stimulated x-ray Raman spectroscopy. In Subtask 2, we have experimentally observed a new nonlinear x-ray process in a small molecule and developed improved theoretical codes to model the interaction, and, used our x-ray science expertise to help develop a new instrument, the Argonne Auger-Meitner Radioisotope Microscope, which characterizes electron multiplicities and energy distributions of radionuclides. In Subtask 3, we have interpreted the first all–x-ray attosecond pump/probe experiment in a condensed-phase target, liquid water. We have also uncovered new insights into a fundamental ligand exchange reaction through the combination of transient x-ray absorption, x-ray emission, and optical spectroscopy coupled with QM/MM MD simulations. Importantly, we have recruited a new staff member, Jérémy Rouxel, whose expertise in both theory and experiment on nonlinear x-ray and chiral spectroscopies will augment our exploration of the scientific frontiers afforded by upcoming capabilities at DOE light sources.

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], L. Cheng[9] 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. A deep 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 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 provided an understanding of x-ray–atom/molecule interactions in the single particle regime [10, 11, 49–58]. However, nonlinear propagation through resonant absorbing media where the back-action of the media alters the propagating field, unavoidable for studies using the powerful transmission-based x-ray transient absorption spectroscopy method, has been much less studied. XFELs now deliver nearly transform-limited pulses with sub-femtosecond duration with the potential for MHz repetition rates [59] over a wide range of x-ray energies thus universally enabling core-level attosecond transient absorption spectroscopy (ATAS) of organic (C,N,O) and inorganic (transition metal and actinide) compounds. The achievable power density also enables stimulated Raman scattering [60, 61], amplified spontaneous emission, pulse compression [62] which are basic to proposed nonlinear x-ray spectroscopies [63, 64].

Building upon our 2020 theoretical/computational study of temporal, spectral, and spatial reshaping of intense, ultrafast x-ray pulses propagating through a resonant medium [7], and our two 2022 experimental campaigns at EuXFEL and the LCLS, our main focus this year has been on the understanding of the experimental results. We have also participated in three beamtimes associated with a community campaign led by J.E. Rubensson where spontaneous x-ray emission is spatially imaged along the XFEL propagation axis. This new observable has promise to provide even more insight into intense x-ray propagation in dense gases.

From the EuXFEL campaign, we demonstrated core-level stimulated x-ray Raman spectroscopy in gaseous neon via covariance methods. The straightforward energy-dispersed transmission measurement after traversal of the target provided x-ray Raman spectra with linewidths of ~ 0.3 eV over the entire incoming SASE pulse bandwidth of ~ 7 eV after accumulating 18000 single-shot images in 30 minutes. Simulation of the propagation of many SASE pulses, using the Argonne Leadership Computing Facility, shows that lower background is obtained by correlating the stimulated Raman spectrum with the *input* SASE spectrum (as opposed to the *transmitted* SASE which suffers from absorption at resonance). Our ghost-imaging method to obtain the input SASE spectrum [13] can be applied for this improvement in future studies. Deeper investigation of x-ray stimulated Raman scattering with SASE pulses quantified the scaling of the covariance signal with the dipole strengths of the "pump" and "dump" transitions, the evolution of the x-ray Raman signal relative to the x-ray laser signal and the differences with respect to spontaneous Raman spectroscopy.

From the LCLS campaign with S. Li, J. Cryan and A. Marinelli, we studied the propagation of resonant attosecond pulses, as opposed to 40-fs SASE pulses, in gaseous neon. The temporal reshaping was monitored with a 2.0 μm streaking laser in a co-axial velocity map imaging detector

[65] and the spectral reshaping with a zone plate spectrometer. While the temporal reshaping data requires continued analysis, the setup allowed us to measure the polarization of the x-ray laser as a function of photon energy of the pump laser.

Future Plans: We have demonstrated core-level stimulated Raman spectroscopy using broadband stochastic SASE pulses and compared its performance with standard spontaneous x-ray Raman spectroscopy. Publications are being prepared [66]. Motivated by upcoming polarization control at XFELs, and our observations of the polarization of the x-ray laser we plan theoretical extensions to the 3D code to include propagation of arbitrarily polarized pulses.

2.2 X-ray Imaging Applications with Femtosecond and Attosecond Pulses

P. J. Ho, A. Venkatesh, L. Young, S. H. Southworth, C. Knight[10], T. Gorkhover[11], S. Kuchel[11], C. Bostedt[12], D. Rupp[13], A. Niozu[14,15], Y. Kumagai[16], K. Ueda[17] 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 nanosized systems.

Recent Progress:

Since the early vision for single-shot imaging experiments with XFELs [67], radiation induced damage has been an important topic [5]. In collaboration with the group of Tais Gorkhover and the group of Christoph Bostedt, we have been reexamining the role of radiation damage in single-particle imaging (SPI) with a coherent x-ray diffractive approach and exploring strategies for improving scattering efficiency of SPI experiments. We are currently revising a paper that reports our combined experimental and theoretical study of x-ray scattering response of Xe nanoparticles in the vicinity of the Xe ionic resonances [68]. The experiment images recorded with few femtosecond and sub-femtosecond pulses are up to 10 times brighter than the static linear model predicts. Our Monte-Carlo simulations [5, 69] attribute the effect of enhanced scattering to transient resonances [5, 51, 54]. Our simulation suggests that ultrafast form factor changes during the exposure can increase the brightness of X-ray images by several orders of magnitude.

This year, we continued to explore the feasibility of modulating and enhancing x-ray scattering efficiency on various fronts. In addition to the soft x-ray regime, we investigated resonant scattering studies in the hard x-ray regime, crucial for achieving atomic spatial resolution. In June 2023, we conducted an x-ray scattering experiment using hard XFEL pulses at SACLA with Fe films. Preliminary data analysis reveals enhanced scattering signals near the photon energy of the $1s \rightarrow 2p$ resonance of Fe^+, as predicted by our theoretical calculations. This enhanced scattering signal is a result of two-photon resonant scattering during the pulse. An incoming photon first non-resonantly ionizes a 2p electron from Fe atom and reveals a hidden ionic resonance [5, 51, 54]. Subsequently, a second photon exploits the ionic resonance to enhance the scattering signals.

In 2022, we performed an experiment to exploit x-ray induced Rabi cycling for damage reduction in the single-particle, coherent diffraction approach. The experiment was performed at TMO endstation at LCLS-II using neon droplets as target. We have recorded coincident time-of-flight ion data and scattering images with XLEAP and 20-fs pulses across the Ne K-edge. To facilitate the data analysis, this year we developed a theoretical formalism to model the impact of coherent Rabi oscillation processes on the total scattering signals by the time-dependent Schrödinger equation. In our formalism, the total scattering signals include both resonant fluorescence ($A \cdot P$) and elastic scattering channels (A^2) and the resonant fluorescence channel is treated as a coherent process. The competing processes of Auger decay and photoionization are also accounted for. Using the Ne^+ ion as a first system, we study the effects of Rabi oscillations (between ground state of $\mathrm{Ne}^+[2\mathrm{p}^{-1}]$ and core-excited states, $\mathrm{Ne}^+[1\mathrm{s}^{-1}]$) on the total scattering signals as a function of pulse duration, pulse intensity and photon energy. The total scattering signal is found to depend strongly on the pulse area. When the fluorescence rate is significantly smaller than the Rabi oscillation rate, we found an upper bound on the total scattered signal, in contrast to the prediction found with the linear scattering model. More importantly, the total scattered signals under resonant conditions are found to be an order of magnitude larger than in the case of non-resonant x-ray scattering from pulses of comparable intensities.

Future Plans: We will write up the results of our theoretical investigation of the effects of Rabi oscillation on the scattering signals in Ne^+ system. We will extend our theory to go beyond single-atom response in order to guide the interpretation of the measured data from the Ne droplet experiment.

2.3 X-ray imaging using higher-order correlations

P. J. Ho, L. Young, A. E. A. Fouda, C. Knight[10], 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 [5, 70]. 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:

By measuring the correlation of photon arrival times on two detectors as a function of the photons' spatial separation, Hanbury Brown and Twiss (HBT) interferometry enables the determination of the size and spatial distribution of a light source [71]. This year, Fabian Trost and colleagues have successfully demonstrated that the temporal correlation of x-ray fluorescence photons on a detector can be used to image the structure of emitters on a copper film (see Fig. 1) [72]. In the experiment, intense, 9-keV and few-femtosecond XFEL pulses were used to excite two spots with micron separation on the film and subsequently induce fluorescence from these spots. This achievement marks a significant milestone toward extending HBT interferometry into high-resolution x-ray imaging [6, 8, 73].

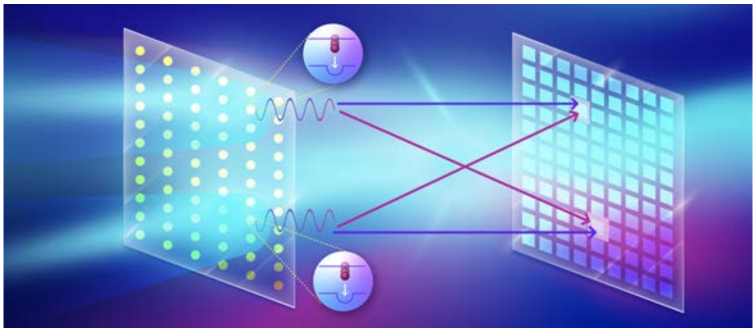

Figure 1: A highly intense x-ray free-electron pulse is diffracted to ionize atoms at two distinct spots on a copper film, resulting in the generation of x-ray fluorescence photon pairs. Each photon pair has two indistinguishable pathways to reach a pair of pixels on a detector, thereby producing a two-photon interference effect that is associated with Hanbury Brown and Twiss interferometry.

This year, we published a paper that discusses the current status and potential of the HBT-based imaging technique [14]. With substantial improvement in spatial resolution, we pointed out that this

technique could eventually enable single-particle imaging of biomolecules and catalysts at the atomic scale, and, with sufficient time resolution, characterization of their reaction dynamics. Continued advances in XFEL technology could also mean that the photon-hungry process of fluorescence excitation can be achieved with sub-fs pulses [9]. To exploit the power of HBT interferometry for chemical imaging with elemental specificity, it is highly desirable to develop multicolor imaging using multiple detectors or detectors with energy-discrimination capabilities. In this same year, we have expanded our theoretical toolkits to predict the necessary conditions for multicolor imaging and to assess the impact of finite detector energy resolution. In collaboration with Chris Knight, we have successfully implemented an initial version of the Monte Carlo/Molecular Dynamics (MC/MD) code, documented in [70] and [69]. This code now efficiently performs energy and force calculations on a GPU. Remarkably, we have observed a substantial 65-fold speedup for the kernel on the A100 GPU compared to a single CPU core, resulting in an overall application speedup by a factor of 32.
Future Plans: We plan to further develop our MC/MD code by exploring schemes to move MC calculations to the GPUs. This strategy will to enable large GPU-accelerated workloads on Polaris and Aurora in the future. Also, to determine the feasibility of an experimental effort with the HBT-based imaging technique, we plan to perform calculations that account for the effect of finite detector spectral energy resolution.

3 Ultrafast X-ray Induced Phenomena

3.1 Resonant inner-shell excitations with intense x-ray pulses

G. Doumy, E. Pelimanni, A. E. A. Fouda, P. J. Ho, R. Puettner[18], G. Grell[19], S. Bokarev[20] and others

Project Scope: The resonant interaction of x-rays with matter is central for exploiting site-selectivity in molecular systems. However, this interaction remains largely unexplored when subjected to intense x-ray pulses, which can trigger subsequent processes like stimulated emission and stimulated x-ray Raman scattering [24]. In addition, there is a need to develop theoretical methods to accurately simulate these processes starting from the initial interaction between the x-ray field and the molecule and extending to the description of the resulting decay products. We use the recently predicted double core-excitation process in small molecules as an experimental and theoretical benchmark.

Recent Progress: The binding energy of core electrons experiences a significant increase upon the first core ionization of a molecule. Our calculations indicate that after core excitation, subsequent core excitations from a different site occur at slightly lower photon energies compared to the ground state. This phenomenon can be qualitatively understood as a consequence of the stabilization of valence shells resulting from a more highly charged core, while the binding energy of core electrons remains largely unchanged in the neutral molecule. We first explored theoretically the unique interaction conditions that a single XFEL pulse can create in nitrous oxide (N_2O). This interaction leads to the formation of neutral, two-site excited double-core-hole states by elevating two core electrons to occupy the same unoccupied molecular orbital [30]. Using time-dependent Schrödinger equation (TDSE) simulations, we established that the creation of double-core-excited neutral molecules is a dominant process. The change in the electron de-excitation spectrum (Auger-Meitner process) between single and double-core-excited states was predicted using a simple Mulliken population analysis. This study motivated a successful proposal application at the EuXFEL facility.

Although N_2O was included in our experiment, the clearest findings emerged from the investigation of the simpler molecule N_2. By comparing the decay spectra obtained at high and low x-ray intensity, we effectively confirmed the formation of the doubly-core excited molecule. This confirmation was established by observing distinct peaks corresponding to the spectator-participator and participator-participator decay channels, where one or both of the excited electrons actively participate in the decay process. Crucially, the photon energy that maximizes these two processes is lower than the single core excitation energy, in line with the prediction of a lower energy for the second excitation step. We are in the process of writing these findings into a manuscript, which will be complemented by additional calculations. These calculations involve refining the computation of the Auger-Meitner decay spectrum by adopting a more realistic approach to account for continuum states [74].

Future Plans: The relative simplicity of the double-resonant excitation process in small molecules, combined with our successful experimental observation, makes it as a good candidate for benchmarking theories related to non-linear x-ray processes. Our first experiment had limited diagnostics, and we expect that knowledge of shot-to-shot spectral content of the SASE pulses could help separate the non-linear signal and increase the energy resolution of the measurement. Furthermore, diatomic molecules like N_2 have raised intriguing fundamental questions regarding symmetry and selection rules. Future improved measurements could contribute to a better understanding and clarification of these issues.

3.2 Time-resolved chemical shifts

G. Doumy, S. H. Southworth, D. Koulentianos, P. J. Ho, A. E. A. Fouda, K. Li, L. Young, L. Cheng[9], A. Al Haddad[12] , C. Bostedt[12], A Picon[19], S. Oberli[12], J. Marangos[21], T. Driver[8], J. Cryan[8], and other collaborators

Project Scope: The interaction between x-ray photons and inner shell electrons within molecules gives rise to localized excitations that undergo rapid evolution. This process involves charge redistribution, cascading decay events, emission of electrons and photons, nuclear motion, and, ultimately, bond breaking. By employing two-pulse, two-color modes at XFELs [75], our goal is to leverage site-sensitivity to track the initial stages of electron dynamics in the core-excited states and monitor the subsequent evolution of the molecule once the initial decay processes have occurred. This knowledge is pivotal for comprehending the photochemical behavior of these molecules following 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 [76]. To identify the transient species created during the interaction and the ensuing evolution of the molecule, we brought to LCLS our hemispherical electron analyzer in the old AMO beamline. 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 [26], which is a focus of the attosecond science campaign at LCLS (3.4).

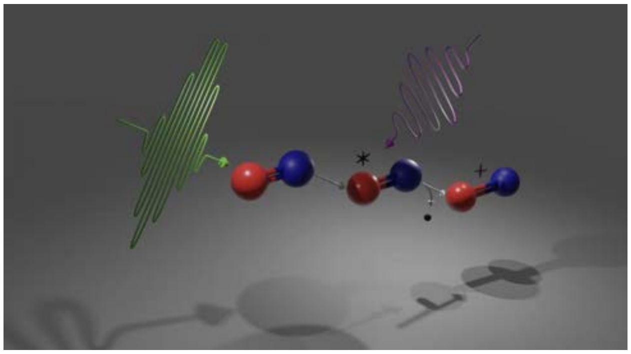

Figure 2: Cartoon representation of site-selective excitation and probing using soft x-ray ultrashort pulses. A first pulse resonantly core-excites a CO molecule at the oxygen site. A second, delayed x-ray pulse only core-ionizes the carbon site, before and after Auger-Meitner decay and subsequent nuclear dynamics. Measurement of the evolution of the chemical shifts (binding energies of the carbon sites) is used to monitor the electronic and nuclear dynamics occuring in the system.

Using x-ray photoemission spectroscopy (XPS), we tracked the behavior of a CO molecule following resonant x-ray excitation of the oxygen $1s \rightarrow \pi^*$ transition initiated by the first x-ray pulse. Concurrently, a second x-ray pulse ionized the $1s$ electrons from the carbon site in the ground state molecule, as well as from all the subsequent products (including the core-excited molecule, cationic molecule following Auger decay, and ionic fragments resulting from dissociation). This allowed us to monitor their distinct and evolving chemical shifts. Conducting these experiments is inherently demanding due to the requisite broad bandwidth of XFEL pulses and the inherent variability in machine conditions. Additionally, these measurements demand advanced modeling that encompasses a multitude of decay pathways to accurately explain the observed data behavior. Signatures of the core-excited molecules, and of both metastable and dissociative ionic states are observed and reproduced by the model [31]. Furthermore, the modeling suggests that within the core-excited molecule, a new equilibrium bond distance could potentially yield an observable XPS signature, provided that there is adequate time and energy resolution.

Future Plans: The CO measurement represents a proof of principle, as well as a demonstration that improved additional diagnostics are crucial to be able to extract the actual pump-probe signal from the large linear background. This includes shot-to-shot spectra as well as shot-to-shot characterization of the two-color pulse conditions. With high-repetition-rate soft x-ray operation now being commissioned at LCLS, advanced experiments with attosecond time resolution and coincidence capabilites are on the horizon, and will be necessary to correctly observe the intended phenomena.

3.3 X-ray and inner-shell interactions and applications

S. H. Southworth, G. Doumy, E. Pelimanni, S. Li, A. E. A. Fouda, P. J. Ho, L. Young, D. A. Walko[22], P. R. Stollenwerk[23], L. Cheng[9], A. Verma[24], M. Simon[24], V. Lindblom[25], S. L. Sorensen[25], R. Püttner[18], S. T. Manson[26], T. W. Gorczyca[27], and other collaborators.

Project Scope: Tunable, high-resolution synchrotron x rays combined with x-ray, ion, electron, and coincidence spectroscopies are used to explore inner-shell phenomena that challenge theory and calculational methods and provide basic information for applications. Instrumentation development, measurements, theory, and calculations are key components of this project.

Recent Progress:

Resonant Auger spectroscopy of the ESCA molecule: Our experimental studies of site-selective C K-shell photoionization and ion fragmentation of ethyl trifluoroacetate, a molecule that has four distinct C 1s chemical shifts, began with photoelectron-photoion-photoion coincidence measurements and Auger electron spectroscopy at the SOLEIL synchrotron facility. In combination with *ab initio* electronic structure calculations, the coincidence measurements demonstrated and explained a lack of site specificity in the ion fragment yields that is attributed to the role of dicationic electron states after Auger decay [78]. The ion fragmentation study was followed by near-edge x-ray absorption (NEXAFS) scans across the four C K-edges using total ion yields that exhibited features from each of the chemically-shifted sites. Identification of the features was aided by core–valence-separated equation-of-motion coupled-cluster (CVS-EOM-CC) calculations [18]. Particularly interesting is comparison of the experimental and computed NEXAFS spectra in which the main site-specific transitions are identified.

Recently, our collaborators at Lund University used the MAX IV synchrotron facility to record the valence photoelectron spectrum of ethyl trifluoroacetate at 120 eV and a two-dimensional spectral map of Auger-electron yields (255-290 eV electrons) across the C K-edges (285-300 eV photons). The AMO group is contributing computational results for valence photoionization and resonant Auger decay across the C K-edges. While the analysis is ongoing, site specific enhancements are observed for the $C_{OO}(1s) - \pi^*$ excitation (288.3 eV) and for the $C_{F_3}(1s) - \sigma^*$ resonance (295.6 eV) [79].

Argonne Auger-Meitner Radioisotope Microscope: Basic information on inner-shell vacancy decays, including charge transfers and dissociation, is important for understanding x-ray damage mechanisms and for applications of radiopharmaceuticals that position radionuclides near cancerous tissues so that emitted Auger electrons destroy the DNA and membranes of tumorous cells [80,81]. For this application, it is important to know the numbers and energies ("Auger multiplicities") of the emitted electrons to model the efficacies and dosages of particular radionuclides. Auger multiplicities are not well known experimentally, particularly for lower electron energies (0-30 eV and 30-500 eV) that are effective in damaging tumorous cells. To fulfill the need for measurements of Auger electron multiplicities, Argonne's Physics Division is building an instrument that will capture electrons, ions, and x-ray photons in coincidence following nuclear decays from radionuclides captured in a cryogenic buffer gas beam [82]. The AMO group is contributing expertise in theory and experimental methods of x-ray and inner-shell processes and support in using APS x rays to commission and characterize the electron, ion, and x-ray detectors. Two beamtimes were conducted at APS using Kr, Xe, and CF_3Br for which the decay processes have been well studied. The electron and ion detectors and the data acquisition and analysis software were commissioned in these experiments.

Double K-shell photoionization of neon: A Scienta EW4000 hemispherical electron analyzer was used at APS beamline 7ID for inner-shell experiments on Ne, Kr, and Xe. High-resolution Auger electron spectra of Ne were recorded using 6 - 8.5 keV x rays to determine KK/K, the double-to-single K-shell photoionization cross section ratio [83]. The APS measurements extend earlier measurements over 2.3 - 6.5 keV made at the SOLEIL synchrotron facility [84]. Measurements of the energy variation of KK/K for Ne are motivated by extending measurements and theory for He [85–87]. The measured KK/K ratios are compared with calculations on He-like Ne^{8+} using the R-matrix with pseudostates (RMPS) method [88, 89]. The experimental measurements on neutral Ne and theoretical Ne^{8+} cross-section ratios show similar variations with energy, but the measured ratios systematically exceed the calculated ratios [33]. The discrepancy is attributed to effects of the eight L-shell electrons not included in the calculations. From the calculations, scaling of KK/K with nuclear charge Z along the He-like isoelectronic sequence was also quantified.

Post-collision interactions in heavy atoms: The Scienta analyzer was also used to measure variations in Kr $L_2 - M_{4,5}N_{2,3}$ Auger electron spectra while scanning the x-ray energy below, through, and above the K-edge at 14327 eV [29]. Below the K-edge, the Auger line is generated by direct L_2 photoionization. In the K-shell pre-edge region and above, the yield increases by ×10 due to L_2 vacancies generated by K-shell photoionization followed by KL_2 x-ray emission. Resonant Auger transitions were observed in the few-eV region below threshold due to 1s → np Rydberg states. Above the ionization threshold, the Auger electron spectrum was observed to increasingly shift in energy and become increasingly asymmetric as the photon energy approaches threshold. These post-collision-interaction (PCI) effects are attributed to energy exchanges between the fast Auger electron and the low-energy 1s photoelectrons. The theoretical analysis accounted for the radiative and Auger decay steps by using an effective lifetime $\tau_{eff} = \tau_{1s} + \tau_{2p}$, i.e., the sum of the 1s and 2p lifetimes, where $\tau_{1s} = 0.24$ fs and $\tau_{2p} = 0.50$ fs. The KL_2 radiative decay step increases the effective lifetime by $\sim 50\%$. As a followup experiment, we measured Xe $KL_2 - L_2M_{4,5}M_{4,5}$ Auger electron spectra while scanning the x-ray energy through and above the K-edge at 34565 eV [90]. In this case, $\tau_{1s} = 0.068$ fs and $\tau_{2p} = 0.22$ fs, so the KL_2 radiative decay step increases the effective lifetime by $\sim 30\%$. The PCI shifts are being compared with shifts of Xe $L_2 - M_{4,5}M_{4,5}$ spectra measured directly through the L_2 edge by our collaborators at the SOLEIL synchrotron facility.

Future Plans: Computational analysis of resonant Auger yields for ethyl trifluoroacetate will be completed and the experimental and theoretical results submitted for publication [79]. An instrumentation and concept paper on the Auger-Meitner Radioisotope Microscope (ARM) will be submitted for publication [82]. Electron/ion/x-ray coincidence data from commissioning the detector section of the ARM using APS x rays will be analyzed to demonstrate the instrument's capabilities. The cryogenic buffer gas beam source will be commissioned and first measurements conducted on radionuclides. Data analysis will be completed on PCI shifts of Xe $KL_2 - L_2M_{4,5}M_{4,5}$ Auger electron spectra that include KL_2 radiative decay in comparison with the shifts measured directly through the L_2-edge. A paper on the Xe measurements [90] will be completed and submitted for publication. From comparison of measured KK/K ratios for Ne with calculations on He-like Ne^{8+}, it would be interesting to extend theory to 10-electron Ne to confirm the effects of L-shell electrons in the process. A 10-electron calculation on Ne could also determine the cross sections for other multielectron hole states that were observed experimentally. It is expected that the RMPS method can be extended to a 10-electron calculation on Ne (T. W. Gorczyca *et al.*).

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 [59] 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. A crucial development of the campaign has consisted in a thorough characterization of the two-pulse mode operating in the w/2w mode, where the pump pulse at the fundamental frequency is generated in the first undulator section, while the probe pulse reuses the initial micro-bunching to generate the second (or higher) harmonic pulse, with the delay being modified by either adding undulators in the second section or through the magnetic chicane delay. An angular streaking measurement in CF_4 was performed and confirmed results from advanced XFEL simulations [91].

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 are the amino-phenol isomers. These rigid molecules exhibit several atomic centers (including unique O and N sites) that can be selectively excited and/or probed using soft x-ray radiation. Three 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. Some of the XPS data was used as a proof of principle attosecond pump-probe experiment in the technical paper. The XAS measurement uses the same experimental method demonstrated with femtosecond pulses in the isopropanol molecule using our Scienta hemispherical electron analyzer [26] but uses a magnetic bottle electron spectrometer instead. It has produced reliable transient signals that are mostly reproduced through a large theoretical effort inside the campaign. A critical observation is that fast damping is followed by a revival around 5 fs, signature of coherent electronic motion in the cation [92].
Future Plans: Extension of the XLEAP project to the high repetition rate capabilities of LCLS-II will happen in late 2023, with anticipation that this will allow further investigation into stimulated x-ray Raman scattering like the one oberved in the smaller NO molecule [16].

3.5 X-ray induced ultrafast electron and fragmentation dynamics in heavy-element containing molecules

P. J. Ho, S. Southworth, R. Dunford, A. E. Fouda, L. Cheng[9], D. Walko[22], and others
Project scope: The goal of this project is to characterize x-ray induced relaxation processes in

heavy-element containing molecules with combined theoretical and experimental approaches. The measured data will guide the development of theoretical frameworks for describing the electron and fragmentation dynamics associated with the multi-step cascades and multiple pathways of the relaxation processes.

Recent Progress: Characterization of the inner-shell decay processes in molecules containing heavy elements is key to understanding x-ray damage of molecules and materials and for medical applications with Auger-electron-emitting radionuclides [93, 94]. The 1s hole states of heavy atoms can be produced by absorption of tunable x-rays and the resulting vacancy decays characterized by recording emitted photons, electrons, and ions [95, 96]. The 1s hole states in heavy elements have large x-ray fluorescence yields that transfer the hole to outer electron shells that then decay by sequential Auger-electron transitions that increase the ion's charge state until the final state is reached. In molecules the charge is spread across the atomic sites, resulting in dissociation to energetic atomic ions [76]. We have used x-ray/ion coincidence spectroscopy to measure charge states and energies of I^{q+} and $\mathrm{Br}^{q'+}$ atomic ions following 1s ionization at the I and Br K-edges of IBr. In addition to IBr, we also have coincidence data for Br_2, $\mathrm{CF}_3\mathrm{Br}$ and $\mathrm{CH}_2\mathrm{IBr}$. As a first step, we present the charge states and kinetic energies of two or more correlated fragment ions associated with core-excited states produced during the various steps of the cascades in IBr. To understand the dynamics leading to the ion data, we develop a computational model that combines Monte-Carlo/Molecular Dynamics simulations [69] with a classical over-the-barrier model [97] to track inner-shell cascades and redistribution of electrons in valence orbitals and nuclear motion of fragments.

Our MC/MD+COB calculation suggests that a model that allows inner-shell decays, electron transfer, and dissociation to occur concurrently is necessary to account for all experimentally observed breakup modes and to show good agreement with the measured ion kinetic energies. Our calculations enable tracking of the multistep cascades, depicting the charging process, and identifying the dominant pathways and participating transient electronic states spanning across multiple time scales from attoseconds to picoseconds. Due to the finite lifetimes of the core-excited transient states, the resulting charging process does not occur instantaneously. Our analysis further shows that the timing of the Br 3d and I 4d hole decays during the fragmentation can affect the probability of the subsequent electron transfer processes and the production of particular breakup modes. Interestingly, we find that during the decay process, molecules can have bond lengths shorter than the initial bond length. Our analysis suggests that at least two factors can initiate nuclear motion that leads to bond contraction, including ion recoil during the emission of electrons and Coulomb attraction between ions and continuum electrons. These results were published this year [34].

Future Plans: We plan to finish the analysis of the experimental data of Br_2, $\mathrm{CF}_3\mathrm{Br}$, and $\mathrm{CH}_2\mathrm{IBr}$. Additionally, we will explore the effect of molecular orbitals during the multistep cascade processes using an in-house ab initio molecular dynamics method. This method utilizes a set of time-dependent trajectory functions for modeling inner-shell decays across multiple potential energy surfaces. The initial implementation of our method uses inner-shell decay rates from relativistic Hartree-Fock-Slater simulations [34], and we will benchmark our results against experimental x-ray/ion coincidence data of the IBr molecule.

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

4.1 Dynamics in ionized aqueous systems

L. Young, S. Li, K. Li, G. Doumy, S.H. Southworth, C. Otolski, A. M. March, P.J. Ho, Z.-H. Loh[7], J. E. Rubensson[6], Y. Kumagai[16], R. Santra[11,28], L. Inhester[28], A. Sopena Moros[28], S. Bhattacharyya[28], K. Kunnus[8], G. Dakovski[8], D. DePonte[8], M.-F. Lin[8], S. Moeller[8], C. Pearce[29], E. Nienhuis[29], J. LaVerne[30], T. Orlando[31], L. Lu[32], X. Li[32] and other collaborators

Project Scope: Time-resolved x-ray spectroscopies in the water window provide a powerful 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 [98,99]. Newly developed XFEL x-ray pump/probe techniques, including the attosecond timescale, enable one to capture initial events following inner-valence and core-ionization, and, in combination with laser-ionization of outer valence orbitals, a means to dissect the full range of ionization phenomena on the ultrafast timescale.

Recent Progress: Previously we reported studies of hole dynamics in valence-ionized liquid water [36, 37]. Pump-probe x-ray transient absorption (tr-XAS) [36] and resonant inelastic x-ray scattering (tr-RIXS) [37] enable water-window probes of transient species produced during water radiolysis (H_2O^+,OH, H_3O^+), are general and readily ported to other situations. This has led to several collaborations aimed at understanding radiolysis on the physico-chemical timescale and in the extreme environments associated with legacy waste management at PNNL through the Energy Frontier Research Center, IDREAM.

This year, we analyzed and interpreted the FY22 LCLS experiments on radiolysis in water, conducted a followup experiment using mid-IR to probe strong-field ionized water at the Argonne Center for Nanoscale Materials (CNM), and submitted a new proposal to study the dynamics of electron solvation at the EuXFEL using their unique beam-splitting off-axis zone plate experimental configuration.

The December 2021 LCLS experiment extended our studies of valence-ionized water to thinner sheet jets in order to capture the signatures of the products of the proton transfer reaction (OH, H_3O^+, e^-(aq)). This x-ray absorption spectrum (XAS) of liquid water near the oxygen K-edge matched with excellent fidelity a reliable synchrotron radiation study [100]. The XAS of liquid water, OH, e^-(aq) and H_3O^+ obtained at 2 ps delay from ionization was reproduced by theory from the CFEL group using small water clusters embedded in a larger system. Further theoretical work used the structural sensitivity of XAS to gain insight into cavity formation dynamics of the solvated electron and will soon be submitted for publication [101].

The April 2022 LCLS experiments represent the first all x-ray attosecond pump/attosecond probe experiment in a condensed phase target, liquid water. This was enabled by the novel XLEAP $\omega/2\omega$ mode [91] which produced tunable attosecond x-ray pulses at $\omega = 250 - 270$ eV and $2\omega = 500 - 540$ eV. We used the powerful attosecond transient absorption (ATAS) method to observe transient changes in the valence hole and pre-edge region. Theory to understand the nature of transient absorption in condensed phase demonstrated the importance of electron collisions and that the ATAS signal at 0.6-fs delay is confined to the subfemtosecond range, i.e. below the oxygen core-hole lifetime of ~ 4.5 fs. This effectively freezes nuclear motion and shows the ability of ATAS to provide attosecond snapshots. With this justification for static electronic structure calculations, multi-reference configuration interaction calculations of a water pentamer were used to gain insight into origin of the observed pre-edge bleach and the valence hole region. These studies in pure liquid water provide the foundations for studies in complex systems. A manuscript is in preparation [102].

Future Plans: Publication of our results is the immediate priority [101, 102]. Next is an analysis of an earlier and planning for a followup experiment on ionized liquid water using IR probes - which can provide sensitivity to hydrogen bonding and complex formation following electron injection. Our EuXFEL proposal "Dynamics of electron solvation in aqueous systems" is scheduled to run in June 2024. We plan to work with LCLS staff in the context of our Scientific Campaign proposal to enable radiolysis studies both in complex liquid and interfacial environments.

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[22], E. Kinigstein[22], S. Heald[22], S. Kelly[22] 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 that has been constructed at Sector 25. Our pump-probe x-ray spectroscopy setup at Sector 7 has started the move to Sector 25 during the upgrade dark period.

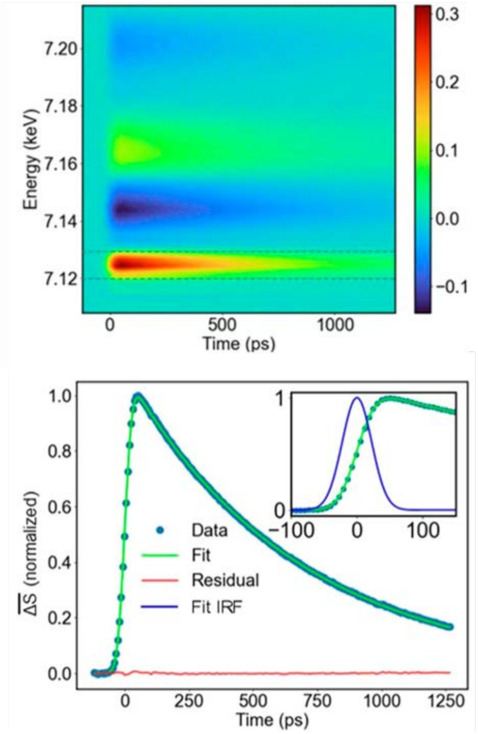

Figure 3: X-ray transient absorption data collected on the Fe K-edge of $[\mathrm{Fe(II)(bpy)_3}]^{2+}$in H_2O excited at 355 nm, collected with the Asynchronous X-ray MultiProbe technique [47]. The 2D plot on top shows the full x-ray transient absorption data surface generated by the first bunch after the laser by simultaneous measurement with $\sim$ 10 ps steps. The bottom plot shows a projection on the time axis of the strongest feature of the 2D plot, overlapped with a fit from the convolution of the instrument response function (IRF), largely due to the x-ray pulse duration, and the exponential decay of the high-spin state produced after photoexcitation.

Recent Progress: We have been collaborating with Xiaoyi Zhang, beamline scientist in charge of the Time-resolved X-ray Research group at APS, to expand the pump-probe x-ray spectroscopy capabilities at APS. We will merge the strengths of our original setup at Sector 7 with the one from Sector 11 to build a highly flexible, powerful endstation at Sector 25 for spectroscopy studies of liquid phase chemistry across a wide range of relevant timescales. As a result of three beamtimes to commission a newly developed data acquisition system [43] at high-repetition-rate pump-probe cycling rates, a new asynchronous pumping strategy was successfully demonstrated. Using this scheme, efficient collection of picosecond, nanosecond, and microsecond data can be achieved in single scans, with the additional advantage of a completely passive scanning of the delay at picosecond to nanosecond timescales providing unprecedented stability. This stability is demonstrated in Fig .3 which captures the rise and decay of the signature of the formation of the high-spin state in photoexcited iron tris-bipyridine. These results and the method are published in Ref. [47].

Future Plans: 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 Tracking the photochemistry of solvated iron-based coordination complexes

A. M. March, G. Doumy, C. Otolski, S. H. Southworth, L. Young, W. Gawelda[19], G. Vanko[33], Z. Nemeth[33], A. Andersen[29], N. Govind[29], D. Hayes[34], M. Chini[37]

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. 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 [103–116], allowed us to track reactions from about 10 ps to the microsecond regime. This setup is presently being moved to the new spectroscopy beamline at Sector 25. Our newly constructed optical transient absorption setup provides critically important complementary information for understanding transient x-ray spectra.

Recent Progress: Our studies have focused on two complexes: aqueous $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ and aqueous ferrate(VI) ion, the latter in collaboration with the group of Dugan Hayes at the University of Rhode Island. The first we use as a model system to understand ligand exchange reactions in water and the second becomes highly reactive in the presence of UV light, suggesting potential uses in water remediation.

For ferrous hexacyanide in water, absorption of UV light initiates an exchange of a $\mathrm{CN^-}$ ligand with a water molecule from the solvent. Using the MHz repetition-rate laser-pump/x-ray-probe capabilities our group has built at the Advanced Photon Source we have investigated the reaction using both absorption spectroscopy at the Fe K-edge and nonresonant Fe 1s emission spectroscopy. Pre-edge XAS resonances sensitive to geometry revealed a 20-ps lived pentacoordinated intermediate species. QM/MM molecular dynamics simulations explain the rather long time for aquation as being due to fluctuations in the geometry of the pentacoordinated complex that leave very short time intervals when there is room for a water molecule to bond [108]. The Kα, Kβ, and valence-to-core emission spectra yield complementary information beyond geometry for the species involved. The measured Kβ line confirmed the triplet spin state of the pentacoordinated intermediate and also revealed an unexpected transient difference signal at long times that was not in agreement with theoretical predictions for the aquated species. A repeat of the measurement confirmed the experimental result. Our newly built optical transient absorption setup allowed us to understand this discrepancy as being due to a small amount of pentacoordinated species surviving in equilibrium with the aquated species at long time. It also allowed us to gather experimental evidence supporting the QM/MM MD simulation's prediction that fluxionality plays a role in the reaction. A manuscript reporting these results is presently being prepared.

X-ray transient absorption results on the ferrate ion at both UV and visible laser excitations have helped disentangle the mechanism of the photophysics and photochemistry of the ion, which had surprisingly never been able to be measured. A combined optical/x-ray spectroscopy study was able to disentangle the dynamics of the complex after photoexcitation over timescales of seven order of magnitude [46]. In addition, comparative optical and x-ray spectroscopy using deuterated water as the solvent has demonstrated a 10-fold increase in the decay of one of the intermediates compared to water, which can be rationalized to the different vibrational coupling of a single solvent molecule. These findings are currently under review [117].

Future Plans: The next steps for our work on $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ include experimental exploration of the fastest timescales. We will incorporate a fiber compressor to reduce the pulse duration of our optical pulses in our OTA setup to the 20-30 fs regime from 230 fs. Preliminary measurements indicate an interesting dependence of the aquation reaction on the counter ion. This will be further explored. For aqueous ferrate(VI) we will examine preliminary transient XES measurements that were taken before the APS dark period.

4.4 Photodegradation mechanisms of Mn-based CO_2 reduction catalysts followed by transient x-ray absorption

A.M. March, C. Otolski, G. Doumy, C. Elles[35], J. Blakemore[35], R. Sension[36], J. Penner-Hahn[36]

Project Scope: This collaborative project with groups at the University of Kansas and Michigan aims to better understand the behavior of a series of Mn-based CO_2 reduction catalysts with the form $\mathrm{Mn(CO)_3(bpy)Br}$, 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: Very rich datasets were obtained during APS beamtimes in June 2018 and December 2019 where we performed transient XANES measurements at both the Mn and Br K-edges on multiple time scales (ps, ns and μs). 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 is suggested as a solvent molecule coordinates with the penta-coordinated intermediate. These results motivated the submission of a proposal at LCLS in collaboration with expert users of the facility (R. Sension and J. Penner-Hahn) to gain direct access to the very first steps of the photoreaction, from the metal-to-ligand charge transfer state to the ligand loss.

This experiment took place in August 2022, and generated a large amount of data on several of the complexes, from the early steps (50fs) up to about 90 ps which matches our earliest APS measurement. Analysis is still ongoing, but a number of preliminary findings demonstrate the great advantage of using x-ray spectroscopy to get local probes in a complex molecule. For example, while both measurements at the Mn and Br K-edges evidence the early formation of a MLCT state and its fast decay, we observed that the signature at the Br site then remains very similar, in contrast to the signal at the Mn edge where at least 4 timescales are extracted. Because the complexes do not have octahedral symmetry, it was expected that polarization sensitive measurement may reveal additional insights. This is indeed the case, and we even observed an unexpected difference between two of the complexes that will require additional measurements, both using time-resolved IR absorption measurements and additional XFEL measurements.

Future Plans: These complexes demonstrate the importance of studies spanning multiple time scales. We now have a full dataset covering these different regions, and the next steps will consist in reconciling the different measurements along with published optical transient spectroscopy data to construct a consistent model for the different mechanisms at play. In addition, additional time at the LCLS was requested, where we would hope to explore further the unexpected asymetric behavior between complexes, as well as study the effect of tuning the optical excitation to specific MLCT absorption bands.

5 Affiliations of collaborators

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Structure and Dynamics of Atoms, Ions, and Molecules

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1. Overview

The J.R. Macdonald Laboratory (JRML) focuses on studying the interaction of short and 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 accessing electronic motion in matter, to femtoseconds and picoseconds for different types of nuclear motion in molecules. To achieve our goals, we are advancing theoretical modeling and computational approaches as well as experimental techniques, studying light-matter interactions in a very broad wavelength range, from the midinfrared to the hard x-ray domain. The synergy afforded by the close interaction of theory and experiment within the Lab serves as a significant multiplier for these efforts. A significant fraction of our research is done in collaboration with others, both at JRML and elsewhere, including many groups within the DOE-AMOS program. Several JRML members conduct experiments at free-electron lasers, such as LCLS, European XFEL, FERMI, and at other FEL and synchrotron radiation facilities. At the JRML site, we run experiments with three femtosecond laser systems, several high-harmonic generation sources, and a large number of complementary charged-particle imaging and spectroscopy instruments. Right now, the Lab is in the process of adding a high-repetition rate 100-kHz, 200-W laser system, which is expected to give a significant boost to many of our coincidence measurements.

On the personnel side, this year Kansas State University approved the hire of Meng Han, who has recently joined the experimental JRML group. He plans to develop a research program focused on attosecond science, in close collaboration with other JRML experimentalists and local theory groups.

Current JRML research projects are organized in three subtasks around the following basic themes: “Strong-field and attosecond science", “Correlated dynamics", and “Ultrafast XFEL science”. These themes serve as broad categories since the boundary between them is not always well defined. The following progress summaries provide brief updates on a select subset of our ongoing projects in each of these subtasks.

2. Strong-field and attosecond science

Strong laser pulses enable us, on one end of a wide range of timescales, to couple multiple electronic states within a small fraction of an optical cycle, launching broad wavepackets and enabling the study of attosecond charge migration. On the other end of the range, they can excite extensive rotational coherences and provide access to the molecular frame. Investigations of the interaction of strong laser fields with atoms and molecules have led not only to attosecond light sources and unprecedented time resolution, but also to a wealth of new tools including impulsive alignment, high-harmonic spectroscopy, laser-induced electron diffraction and time-resolved Coulomb explosion imaging. The main goal of the projects in this sub-task is to exploit the versatility of strong-field physics to both image and control electronic and nuclear motion.

2.1. Strong-Field Excitation and Ionization: Laser-Induced Electron Diffraction - Blaga, Lin

Project Scope: This project explores intense laser-matter interactions with a particular emphasis on ultrafast molecular dynamics studies. Leveraging the λ^2- scaling law and the rescattering mechanism of strong-field physics, we pursued the development of midinfrared ultrafast lasers that allowed us to generate high energy (>100 eV) returning electron wave packets that possess enough resolving power to determine the location of atomic centers inside the parent molecular ion via laser-induced electron diffraction (LIED) [1,2]. In addition, the project also aims to develop ultrafast photoelectron metrologies and novel experimental tools for molecular dynamics studies. High-energy (>100 eV) LIED is a viable ultrafast imaging method because the measured rescattering yields $Y(p,\vartheta)$ in the photoelectron angular distributions (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 wave packet $W(k_r)$, where k_r is the momentum at return [3]. Structural information is contained only in the DCS term, and not $W(k_r)$. Furthermore, at large rescattering angles the DCS is determined by the *field-free, short-range* potential. Therefore, high-energy LIED "sees" the location of the atoms inside a molecule but is insensitive to any chemical information. During the last few years, we concentrated our efforts to extend LIED to lower electron return energies (< 20 eV), a regime where the chemically active valence electrons of the parent play a significant role in the details of the DCS. If these efforts are 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 temporary trapped by the parent.

Recent Progress:

2.1.1 High-energy LIED in alkanes

During the last year, in collaboration with Prof. Louis F. DiMauro (Ohio State University), we began an extensive survey of ultrafast molecular imagining in alkanes. In three joint experimental campaigns during Summer of 2023, we measured photoelectron angular distributions and mass spectra in methane isotopes (CH_4 and CD_4), ethane (C_2H_6), propane isotopes (C_3H_8 and C_3D_8), and butane isomers (n-C_4H_{10} and iso-C_4H_{10}) at two midinfrared laser wavelengths (3.0 and 3.5 µm). The investigations, performed using OSU's midinfrared tunable laser source operating at 1 kHz repetition rate, were devised to address three scientific goals.

The first goal aimed to prove that high-energy LIED can successfully image isomeric targets. As isomers have the same chemical formula, the DCS are similar, as seen in Fig. 1a, where the theoretical DCSs for 50 eV electrons diffracting on neutral n-butane and iso-butane are presented [4]. The main differences between the isomers are a slightly higher DCS for isobutane in the near backscattering geometry (red arrow) and a local diffraction maximum in n-butane at 90 degrees absent in isobutane (green arrow). Our preliminary LIED experimental data shown in Fig. 1b is extremely encouraging, clearly reproducing the expected DCS differences predicted by theory. We are now in the process of modeling the experimental DCS and extracting structural information.

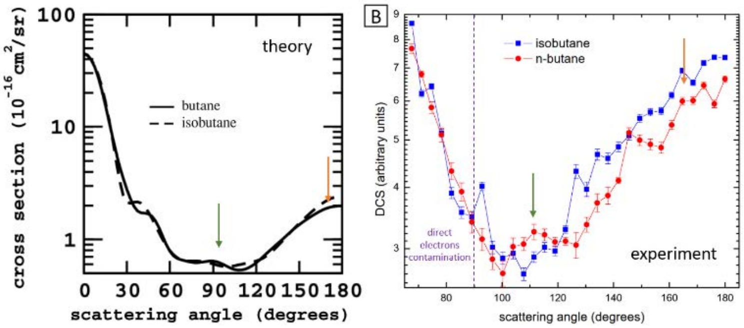


Figure 1. (a) Calculated elastic electron-C_4H_{10} DCS at 50 eV electron kinetic energy [4]. (b) LIED experimental DCS for 50 eV electron return energy, taken with 3µm, 100 fs pulses at 50 TW/cm^2. The red and green arrows indicate similarities between theory and experiment, outlining LIED's ability to distinguish between n-C_4H_{10} and iso-C_4H_{10}.

The second thrust of this project consisted in measuring DCS for n-alkanes as the length of the carbon chain increases. This is an essential and necessary step for UV-pump, LIED -probe experiments aimed at visualizing chain breakup of organic compounds under UV irradiation. For example, UV photoionization of n-butane can result in C-C bond breakup and formation of methyl, ethyl, and propyl radicals. To be able to "visualize" this process, it is first necessary to demonstrate and understand the imaging capabilities of LIED as a probe. For this purpose, the corresponding neutrals (methane, ethane, and propane) are excellent substitutes. Detailed experimental analysis and theoretical modeling are pending.

The final thrust of this project consisted in determining if LIED can be applied successfully when the wavelength of the midinfrared imaging pulse matches a vibrational resonance of the target. When LIED was demonstrated, it was applied only in non-resonant cases. Nonetheless, in previous years, we demonstrated that the mass spectrum of CD_4 at 3.5 µm shows significantly more dedeuteration as CH_4 shows deprotonation, whereas with a 2.9 µm driver, they are identical. This hints that at 3.5 µm, a wavelength at which CD_4 has a C-D stretch resonance, a significant amount of energy from the laser pulse is deposited into the molecules, making it vibrationally hot. Under these circumstances, it is not obvious if LIED could produce a clear molecular image. To investigate this, we had recorded LIED data in C_3H_8 and C_3D_8 at 3 µm (both species non-resonant) and 3.5 µm (first species non-resonant, second resonant). Experimental and theoretical analysis are pending.

2.1.2. Low-energy LIED in alkali atoms

In 2017, we reported the results of an extensive experimental survey aimed at benchmarking various strong field ionization theoretical models [5] in atomic targets. The main finding of this work was the demonstration that the quasistatic, wavelength independent Ammosov-Delone-Krainov (ADK) theory is in excellent agreement with the experiment when the adiabacity (Keldysh) parameter $\gamma=(IP/2U_P)^{0.5}$ is less than 0.7, even for low-IP targets. For LIED, ADK is a required ingredient as in its regime of applicability, the classical electron trajectory approximation is necessary to extract elastic electron-parent ion differential cross sections. Until now, LIED has only been applied to high electron return energies (> 50 eV) so that DCS theoretical modeling with the independent atom model (IAM) was possible. However, if ADK remains valid, LIED should apply even for low electron return energies, although the simplicity of IAM-based DCS modeling is abandoned in favor of more complex theoretical models.

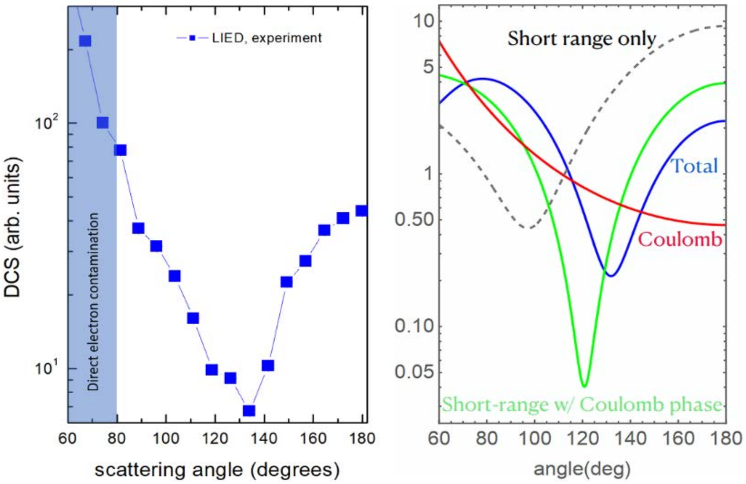


Figure 2. Low-energy laser-induced electron diffraction in sodium at 15 eV electron kinetic energy. Left panel: experimental data. Right panel: theoretical modeling. As seen, including only the short-range potential produces a DCS (dash line) that does not agree with experimental data. Including the long-range Coulomb potential (red line), produces a total DCS (blue line) in excellent agreement with the experiment (the deep diffraction minimum at 130°).

During the last year, in collaboration with DiMauro's group at OSU we successfully extracted and modelled DCSs from the measured photoelectron angular distributions of sodium and potassium under irradiation with intense ~100 fs, 3.6 μm pulses for electron energies in the 7-20 eV range. The theoretical modeling clearly demonstrated that the DCS cannot be accurately modelled with the short-range IAM. However, including the long-tail Coulomb potential the agreement between theory and experiment was excellent. In Fig. 2, the LIED experimental and theoretical DCS are shown in the case of sodium atoms, imaged with 15 eV recolliding electrons. The experiment and the theoretical modeling have been concluded successfully, and the manuscript on these results is in preparation.

Future Plans: For the next year, we will continue our work on both LIED projects highlighted in the previous section. The arrival of a new high average power 100 kHz laser system at JRML in late 2023 will vastly augment our experimental capabilities. Coupled with our new multi-anode double sided TOF apparatus, we will gain nearly three orders of magnitude in data collection rates. This will truly open the possibility to conduct UV/VIS-pump, LIED-probe ultrafast molecular imaging studies. For this purpose, we will continue to work with alkanes, targets we understand well and for which we are developing theoretical models.

2.2. Modelling of Attosecond Charge Migration, Charge Transfer and Sequential Double Ionization - Lin

Project scope*:* Excitation and ionization of a molecule by ultrafast light pulses could create a superposition of electronic states. Subsequent electron dynamics by the coupling of electronic coherence and nuclear motion induces charge migration and possibly charge transfer. In the past decade, based on the three-step rescattering model, high-harmonic spectroscopy (HHS) and LIED have been used to probe change of nuclear geometry immediately (sub- to few-fs) after tunnel ionization. Using the HHG data generated from aligned molecules and applying machine learning algorithms, we have been able to retrieve picometer-scale molecular geometry change and charge migration speeds for individual molecules within the first femtosecond after ionization. In parallel, we developed new schemes for mapping vibronic coherence induced by tunnel ionization using either sequential double ionization or x-ray transient absorption as a probe. Using our new theoretical model based on the density-matrix formulation, we show that both of these probe schemes will reveal different vibronic coherences, and the theory results can be directly compared to experimental data.

Recent Progress:

2.2.1 Characterizing sub-femtosecond charge migration following tunnel ionization of molecules by high-order harmonic spectra

In 2022, we reported charge migration for N_2 and CO_2 using HHS [P29]. Following that work, our collaborators in Wuhan carried out HHG measurements on the linear carbon chain molecule C_4H_2 where tunnel ionization by an 800 nm laser will create two holes, one π_g HOMO orbital and one π_u HOMO-1 orbital. The resulting hole dynamics will migrate along the linear chain. Our reconstruction allows us to obtain how the speed of the center-of-charge (COC) migrates versus the alignment of molecules with respect to laser polarization, ranging from 4.5 Å /fs to about 2.8 Å/fs. The report of this work has been published in [P53] and was featured in SPIE Digital Library in August 2023.

Applying HHS to NH_3 molecules using 800 nm and 1300 nm lasers, the same team was able to extract the NH bond length as well as the bond angle HNH, showing that both increase with harmonic order (due to attochirp), as well as with the wavelength of the 1300 nm laser. Using HHS, we were able to show that the bond length increases by 0.6 pm in about one femtosecond, and 1.5 pm in about two femtoseconds. We have also carried out TDDFT simulation to obtain the change of bond length in NH_3 when an electron is stripped out of the molecule and how quickly the molecular ion changes shape. The calculations are in good accord with the results extracted from the harmonic spectra.

2.2.2. Density matrix theory for dissociative sequential double ionization of molecules

Since last year, our group set out to find a simplified theory that could calculate quantities that can be directly compared to typical pump-probe experiments (the effort led by Dr. Isaac Yuen). Clearly, such a theory should include essential molecular structure, the dependence on the pump and probe pulses, as well as the coherent coupling between electronic and nuclear wave packets. To compare with experiments, average over the orientation of molecules is also essential.

Our first project was to calculate the kinetic energy release (KER) spectra of the dissociative double ionization of N_2 molecules using intense laser fields [P32]. We used the density matrix formulation to calculate the time dependence of the density of the neutral, cation and dication. The laser ionizes the neutral from the ground state to a few low-lying ionic states to create a coherent ionic wave packet. These ionic states are still under the external laser field and can be further ionized to ground and excited dications. For the ionization, we used the MO-ADK theory to calculate the ionization rate. The higher dication states can dissociate to $N^+ + N^+$, where the KERs of the ion can be measured. Our simulation was shown to be consistent with the earlier experiment from JRML. This is the first time that KER spectra for N_2 have been properly simulated by theory. Note that in this work, we account for the average over the molecular alignment and the focal laser intensity distribution. With our model, we do not calculate electronic wave functions. Thus, the computations are about three to four orders of magnitude faster than any full time-dependent *ab initio* quantum calculation. This method was further extended to O_2 molecules [P57] which have open-shell ground state. The results of the calculations yield good agreement with earlier experimental data [6] and with current JRML COLTRIMS experiments on double ionization of O_2.

2.2.3. Unraveling vibronic coherence

To investigate coherence and pump-probe experiments, the theory used in section 2.2.2 needed to be substantially extended. Since the MO-ADK model only calculates the tunneling ionization rate, to account for laser coupling between cation channels, the complex off-diagonal density matrix elements need to be calculated. This was studied in [P54]. With the theory in place, we have found that the population of N_2^+ cations are significantly modified by laser coupling which would have significant implication for air lasing, which currently is a topic of great interest.

So far, the calculations have been limited to pulses that are less than 6 fs such that nuclear degrees of freedom can be fixed when the laser is on. For pump-probe experiments, our goal is to find out how the electron wave packet evolves in time over tens of femtoseconds after the neutral molecule is ionized. This is a topic generally referred to as charge migration. Over the longer time, even when there is no laser field, the coupling between the electrons and the nuclear motion must be accounted for. A theory for addressing vibronic coherence in charge migration as probed by another intense IR laser was investigated. The theory predicts beatings of the KER spectra with respect to the time delay, and that the branching ratios of ionization channels can be directly related to the off-diagonal element of the density matrix of the cation. The model was applied to N_2 molecules but no experiments so far for comparison.

Charge migration can also be probed using the transient absorption spectroscopy. Such experiments have been carried out by a number of experimental groups where the probe pulse is an XUV or soft x-ray. The vibronic coherence in N_2^+ was investigated recently and coherence between two cation states has been extracted from the optical depth measurement. A paper on this work has been submitted.

Future plans: During the last two years, we have developed a theory that can be used to understand the outcome of pump-probe experiments and to produce results that can be directly compared to experimental data. In particular, this approach allows for a quantitative characterization of vibronic coherence which plays an essential role in determining whether charge migration might evolve to charge transfer in a chemical reaction. Future development will depend on specific molecular systems that are suitable for experimentalists and for theorists. Much remains to be done. For mapping charge migration with HHS, the next goal is to examine HHG spectra from molecules that have been excited by a pump pulse. The experimental setup for such measurements is currently being developed.

2.3. Strong-field-driven dynamics in small molecules - Kumarappan, Thumm, Rolles, Rudenko

Project scope: The goal of this project is to understand and image strong-field driven dynamics in excited states of small molecules and molecular ions. In particular, we focus on understanding the role of light-induced potentials and light-induced conical intersections in light-molecule interactions. Experimentally, we use pump-probe measurements of ion (and sometimes also electron) momentum distributions using velocity map imaging (VMI) or COLTRIMS spectrometers to characterize the dynamics. Kinetic energy and angular distributions help us understand both the ionization and/or excitation by the pump as well as the dissociation, further ionization and/or Coulomb explosion by the probe pulse. In addition, we employ channel-selective Fourier spectroscopy to characterize the states populated by the pump pulse. For VMI measurements, long scans enable sufficient resolution in the FFT spectrum that we can identify electronic and vibrational states excited by the pump unambiguously from the rotational coherences that are also simultaneously excited. At the same time, coincident ion-electron spectra can provide further insight into state-specific electronic and nuclear dynamics.

Theoretically, we aim to develop conceptual, analytical, and numerical tools to (i) image and control the effects of intense light pulses of different wavelengths, from NIR to soft x-rays, on the electronic and nuclear dynamics in small molecules; and (ii) extend our investigations from diatomic molecules to larger systems, starting with triatomics. We compare theoretical results with several experimental data sets for one- and two-color pump-probe experiments performed at JRML and in other labs.

Recent progress:

2.3.1. Fourier Spectroscopy of Post-Ionization Dynamics in Molecular Cations: Spin-Rotation Wave Packets in N^+ $A^2\Pi_u$

Strong-field ionization can populate several low-lying electronic states of the cation, depending on the ionization energies, the shape for the molecular orbital from which ionization takes place and post-ionization couplings between states in the cation. We investigate the rotational dynamics of the cation after the ionizing pulse and the role that spin-orbit coupling plays in these dynamics. The experiment consists of ionizing jet-cooled nitrogen by 800 nm, 35 fs pulses and then dissociating the resulting cations with the third harmonic of the pump. Velocity map images of the N^+ ion in a long delay scan are analyzed using pBasex and FFT, and the data is Fourier filtered to isolate the contributions from the two fine-structure-split manifolds. A combination of resonant excitation in the probe, KER and Fourier filtering allows us to isolate spin-rotation wave packets in individual vibrational levels of the cation; note that our pulses are long enough to exclude vibrational wave packet dynamics.

As an example of the information we can extract from these experiments, Fig. 3a shows the time-dependent yield the dissociation of the cation in the $A^2\Pi_u(v = 4)$ state produced by resonance-enhanced three-photon dissociation through the $D^2\Pi_g(v = 3)$ state. Fig. 3b shows the KER distribution from a single line in the quantum beat spectrum where four dissociation channels can be identified. Since the lines from the F_1 and F_2 fine structure levels are well separated in the FFT, we can Fourier-filter the data and reconstruct the time-dependence of the yields from these two levels individually (Fig. 3c). These show strikingly different behaviors. The difference in revival periods is noticeable already at the first half-revival. The revival pattern for F_1 shows sharp single-cycle revivals with no chirp and only a slow variation in carrier-envelope phase. F_2 revivals, on the other hand, show rapid onset of chirp. These differences can be understood in terms of competing influences of centrifugal distortion and spin-orbit splitting in the Hund's-case-(a) Hamiltonian for $A^2\Pi_u$. In F_1, the two largely cancel out the quadratic term in the beat frequency as a function of J, leaving the revival pattern unchirped. In F_2, the quadratic term is enhanced, leading to a larger chirp than centrifugal distortion alone would have caused.

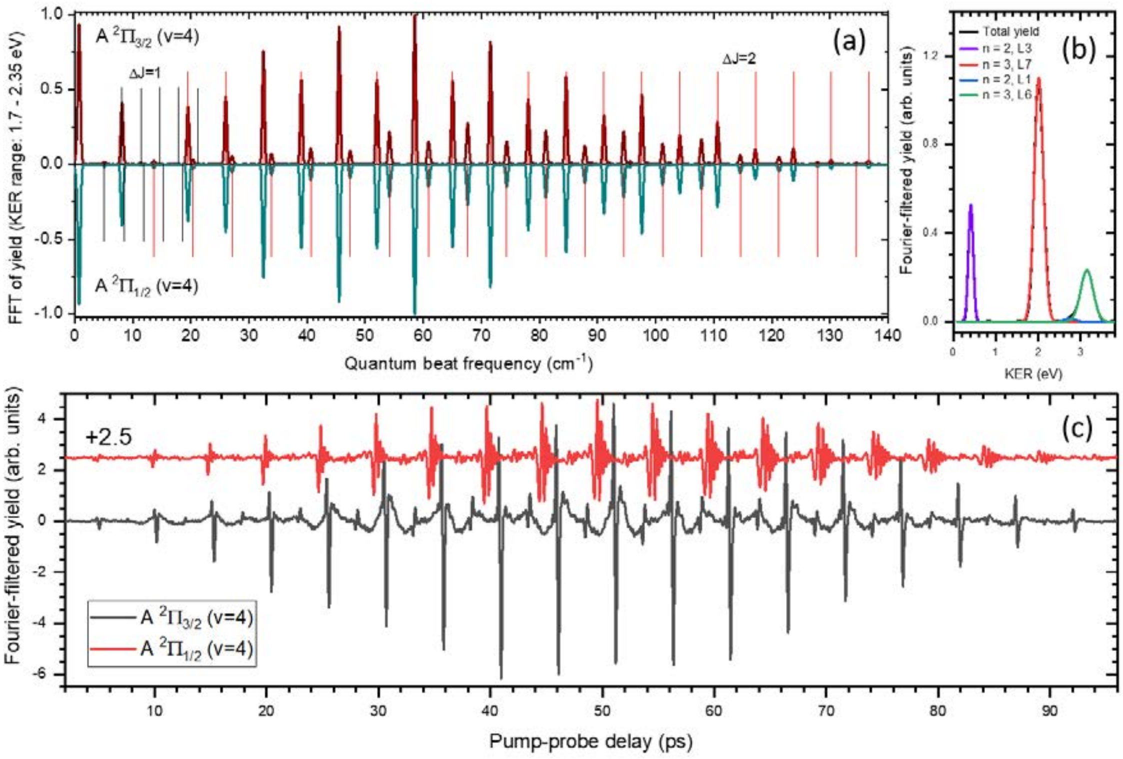


Figure 3. (a) Fourier transform of the yield of N^+ ions produced by a 264 nm probe pulse that dissociates cations left in the $A^2\Pi(v = 4)$ state of N_2^+ produced by an 800 nm pulse. The yield is gated on the KER of ions dissociating to the seventh dissociation limit, L7 ($N^+(^1D) + N(^2p^o)$), reached by three-photon absorption from $A^2\Pi(v = 4)$. The FFT spectrum is mirrored for convenience; vertical lines mark the expected positions of the $\Delta J = 1, 2$ rotational quantum beats within F_1 ($\Omega = 3/2$, top half) and F_2 ($\Omega = 1/2$, bottom half) levels. No electronic lines (transitions between F_1 and F_2) are observed. (b) KER distribution of the yield, gated on the F_1 line at ~78 cm^{-1}. Four channels can be identified; in the legend, n labels the number of 264 nm photons absorbed and L# the dissociation limit in increasing order by energy. (c) Delay dependence of N^+ ion yield retrieved by inverse FFT of the spectrum shown in (a). Frequency filtering separates F_1 and F_2 yields. The broad envelope is an artifact of the Hanning filter used in the FFT.

Similar plots for the Legendre moments ($L = 2$–8) of the angular distribution show that rotational beats extend up to (and likely past) the Nyquist frequency in our experiment with 50 fs steps in delay. These coherences suggest that the cation is tightly aligned near the end of the pump pulse and that, for similar pumping conditions, rotational dynamics could be critical even for sub-ps pump-probe experiments. Already by the first half-revival of alignment at ~5 ps, the behavior of F_1 and F_2 is distinct; simulations of nitrogen lasing that do not include spin may need to do so.

2.3.2. XUV-pump IR/VIS-probe dissociative ionization (DI) of CO_2

Following the sudden single ionization of CO_2 in ultrashort pump pulses with 18 eV central photon energy, we propagated the coupled nuclear motion in CO_2^+ on the $A^2\Pi_u$, $B^2\Sigma_u^+$, $C^2\Sigma_g^+$, $b^4\Pi_u$, and $a^4\Sigma_g$ adiabatic BO potential-energy surfaces of the excited molecular cation, exposed to delayed 780 or 400 nm probe-laser pulses, including all vibronic degrees of freedom (Fig. 4) [7]. We calculated potential-energy surfaces and probe-laser-induced dipole couplings between BO states *ab initio* by applying the multi-configurational self-consistent-field (MCSCF) quantum-chemistry code GAMESS [8]. Due to its dominating Franck-Condon (FC) overlap with the CO_2 ground state, we assumed the ionization step to only populate the $B^2\Sigma_u^+$ (0,0,0) state.

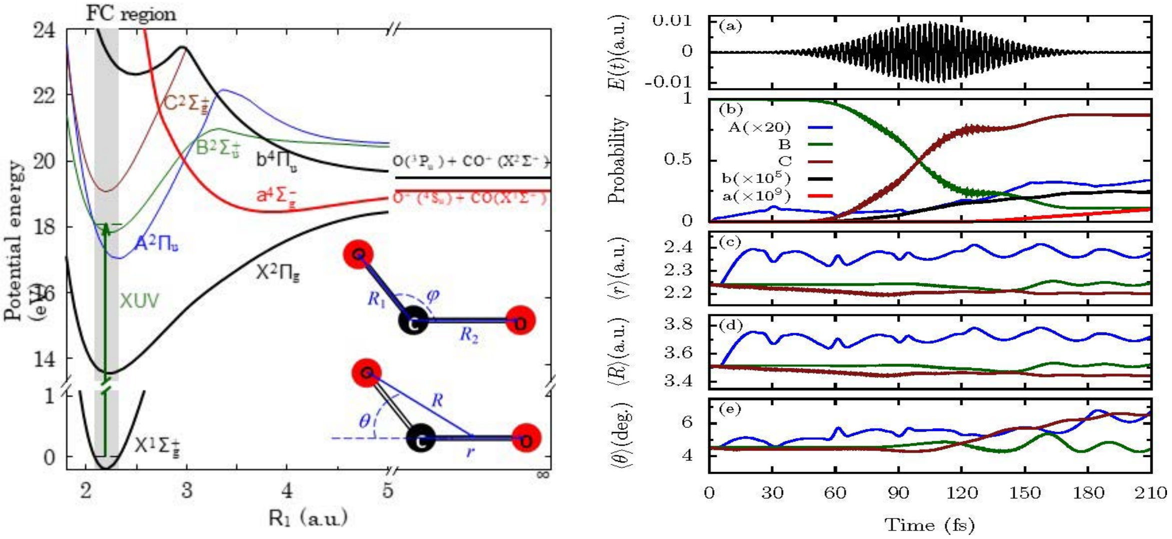
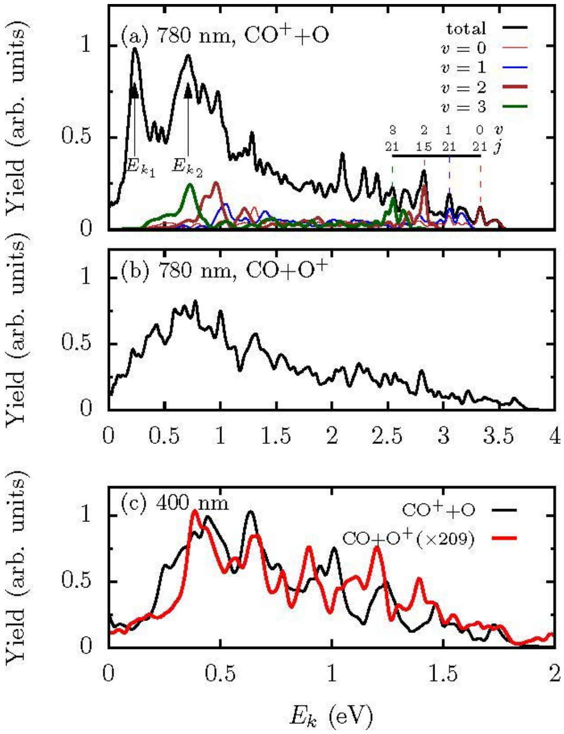


Figure 4. *Left:* CO_2^+ BO potential energies for R_2=2.24 a.u. and $\varphi = \pi$. Green arrow: FC transition to the initial $B^2\Sigma_u^+$ (0,0,0) level. Inset: internuclear and Jacobi coordinates. *Right:* Nuclear dynamics for a pump-probe delay of 105 fs [7]. (a) Laser electric field. (b) Populations in the $A^2\Pi_u$, $B^2\Sigma_u^+$, $C^2\Sigma_g^+$, $b^4\Pi_u$, and $a^4\Sigma_g$ states. (c-e) Expectation values of the Jacobi coordinates.

Nuclear dynamics: Numerically propagating the nuclear motion of the pump-pulse excited CO_2^+ ions across 45 fs, $2x10^{13}$ W/cm^2 peak intensity probe pulses, we find fragmentation into the O(3P_g)



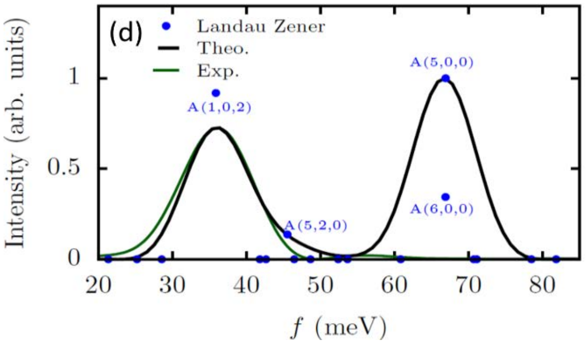


Figure 5. Fragment yields for dissociation into (a,c) O(3P_g) + CO^+($X^2\Sigma^+$) and (b,c) O^+(^4S_u) + CO($X^1\Sigma_+$) at a pump-probe delay of 105 fs as functions of the fragment kinetic energy [7]. (d) Power spectrum of the O(3P_g) + CO^+($X^2\Sigma^+$) yield as a function of the quantum-beat frequency *f*, compared with experimental data [9] and Landau-Zener transition rates between beating $B^2\Sigma_u^+$(0,0,0) and $A^2\Pi_u$ (n_s,n_b,n_a) levels. n_s, n_b, and n_a designate quantum numbers for symmetric stretch, bending, and anti-symmetric stretch modes.

+ $CO^+(X^2\Sigma^+)$ and [$O^+(^4S_u)$ + $CO(X^1\Sigma_g^+)$] dissociation channels to proceed via non-adiabatic transfer at the $A^2\Pi_u \leftrightarrow B^2\Sigma_u^+$ CI, $B^2\Sigma_u^+ \rightarrow C^2\Sigma_g^+$ excitation in the probe pulse by absorption of three [one] photon[s], and spin-orbit coupling to the $b^4\Pi_u$ [$b^4\Pi_u$ and $a^4\Sigma_g$] state[s] (Fig. 4).

Kinetic-energy-release spectra: As a function of the KER, the yield for $O(3P_g)$ + $CO^+(X^2\Sigma^+)$ fragmentation displays internal fragment excitations as a sequence of peaks (Fig. 5a,c). For 780 nm probe pulses, three-photon excitations result in KERs up to 3.38 eV. CO^+ vibrational (ν) and rotational (j) quantum numbers are indicated in the graph. As expected, $O^+(^4S_u)$ + $CO(X^1\Sigma_g^+)$ dissociation yields are much smaller (Fig. 5b,c).

Core-hole dynamics at the $B^2\Sigma_u^+$ - $A^2\Pi_u$ conical intersection of CO_2^+: By quantum-beat analysis [10] of the delay-dependent KER spectra and supported by Landau-Zener transition rates between vibronic levels in the $B^2\Sigma_u^+$ and $A^2\Pi_u$ electronic BO states [7], we unraveled the nuclear wave-packet anatomy with main contributions from a small number of vibronic levels. In particular, we find oscillation periods of 115 as due to quantum beats between the $B^2\Sigma_u^+(0,0,0)$ and $A^2\Pi_u(1,0,2)$ states, reproducing the core-hole oscillation measured in [9]. We also identified strong 62 fs oscillations, due to beating $B^2\Sigma_u^+(0,0,0)$ and $A^2\Pi_u(n_s,0,0)$, n_s=5,6 levels (Fig. 5d).

2.3.3. *Imaging strong-field-induced bending vibrations in SO_2^+*

Light-induced vibrational wave packets play a fundamental role in many types of molecular dynamics and have been studied extensively. In this work, we show that one can directly map coherent bending vibrations in a laser-ionized small molecule using time-resolved Coulomb explosion imaging. As sketched in Fig. 6a, we use a strong 28-fs, 790-nm laser pulse to ionize SO_2 and launch vibrational wave packets in its cationic states. Subsequently, a second NIR pulse of higher intensity is employed to further ionize and dissociate (Coulomb-explode) the molecules. The ionic products are detected in coincidence using a COLTRIMS apparatus.

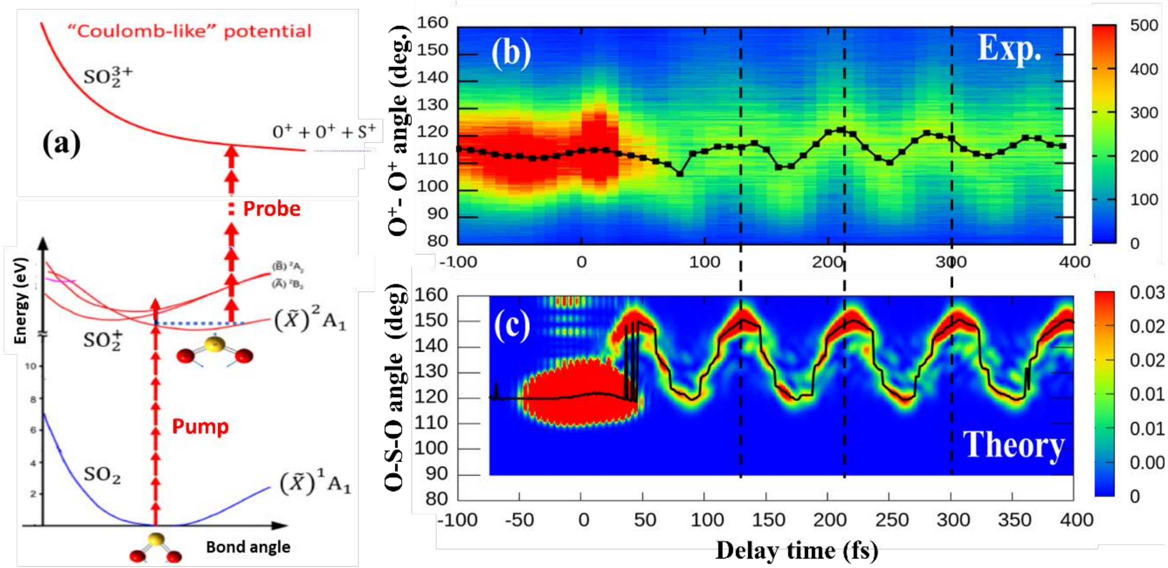


Figure 6. (a) Sketch of a NIR pump – NIR probe experiment and relevant potential curves of SO_2 and SO_2^+. (b) The measured delay-dependent yield of $S^+ + O^+ + O^+$ coincident channel plotted as a function of the angle between the two O^+ momentum vectors. (c) The simulated time-dependent probability density of the vibrational wave packet propagating in the ground state of SO_2^+ shown as a function of the O-S-O bond angle. The solid lines in (b) and (c) indicate the average value of this angle as a function of the delay.

Focusing on the $S^+ + O^+ + O^+$ channel, we observe a pronounced oscillation in the measured angle between the two O^+ ions, which directly reflects the O-S-O bending vibration. The periodicity of observed oscillations (~83 fs, corresponding to the frequency of ~400 cm^{-1}) clearly indicates that we mainly image the vibrational wave packet in the SO_2^+ ground state [11]. In Fig. 6b, the simulated time-dependent probability density of the nuclear wave packet propagating in the ionic ground state is plotted as a function of the O-S-O bond angle. The simulation closely resembles the experimental data, manifesting nearly identical periodicity and phase behavior. Therefore, even though the quantitative relation between the measured momentum-space angle and the real-space bond angle is non-trivial and requires further analysis, these results provide direct and intuitive picture of the strong-field-induced vibrational wave packet in a triatomic molecule.

While the observables for the triply-charged final state presented in Fig. 6 are clearly dominated by the ionic ground-state vibrations, the FFTs of the delay-dependent data for lower charge states as well as the theoretical results also manifest weak but clear signature of the ground-state bending vibrations in the neutral SO_2 molecule. The analysis of the relative phases of ionic and neutral vibrational wave packets based on the frequency filtering and inverse FFT (similar to the procedure described in Section 2.3.1 above) is currently underway.

Future plans: We plan to extend high-resolution Fourier spectroscopy to heteronuclear diatomics like NO and CO, and to triatomic molecules such as CO_2, SO_2 and OCS. We are also planning experiments in which the probe wavelength in the UV is varied to address different vibrational states in the cations. For the dissociative ionization of CO_2^+, we plan to (i) extend the present model by removing its restriction to initially linear (not bent) molecules that are aligned with the pump- and probe-pulse-polarization direction. Allowing for arbitrary molecular orientation and bending entails different, compromised, or no dipole-selection rules, thus altering the population transfer between relevant adiabatic states in the molecular cation. This is expected to affect the coherent nuclear dynamics and, correspondingly, experimentally observable KER spectra and dominant quantum-beat ("core-hole") oscillation periods [9]. Addressing recent experimental findings at JRML [12], we intend to (ii) reveal the cause of comparatively slow 3 ps fragment-yield oscillations in the DI of CO_2, (iii) scrutinize the dependence of KER spectra on the relative linear polarization directions of pump and probe pulses, and (iv) continue our recent investigation of the DI of H_2O and SO_2. Finally, for imaging strong-field-incduced vibrational wave packet, the main challenge for the future work is to connect momentum-space and real-space observables for Coulomb explosion imaging. We plan to address this via improved modelling of the probe step. In addition, we plan to combine different final-state observables and to employ resonant UV probe pulses, which would exclusively map ionic wave packet to a single low-lying repulsive potential energy curve.

2.4. Extracting dynamical pathways - Esry

Project Scope: Identifying the quantum-mechanical pathways followed during a light-induced dynamical process remains a significant challenge, especially in complex systems. In the latter, understanding the dynamical pathways usually relies heavily on theoretical calculations. We are exploring to what extent we can objectively and unambiguously extract pathway information directly from measured observables without elaborate theory.

Recent Progress: Building on our general theory of carrier-envelope phase (CEP) effects [13,14], which showed that the CEP and the net number of photons n is a Fourier-transform pair, we want to “invert” the expansion to find the quantum-mechanical amplitude *i.e.*, the pathway — linking the initial state to the final state through the exchange of n photons. This inversion would be applied directly to measured observables, thereby providing a clear, theory-free procedure applicable even to complex molecules, in principle.

Given that this procedure depends on there being CEP dependence in the observable, it will only be relevant for processes driven by few-cycle pulses (although not necessarily intense). With this caveat, the system’s wave function can generally be written as

$$\Psi(t) = \sum_{n=-\infty}^{\infty} e^{in\varphi}\psi_n(t)$$

for any number of degrees of freedom. This expansion makes the CEP (ϕ) dependence explicit. From this wave function, any observable and its CEP dependence can be written.

For the present testing, we have focused on analyzing the momentum distribution following field-induced breakup into two fragments (which could be either photoionization or photodissociation). The energy-angle distribution — effectively the momentum distribution — can be very generally written as

$$\frac{\partial^2 P}{\partial E\partial\theta_k} = \sum_{n,J,J'}\Big[A^*_{nJ'}(E)A_{nJ}(E) + \sum_{n'\neq n} A^*_{n'J'}(E)A_{nJ}(E)e^{i(n-n')\varphi}\Big]Y_{J'0}(\theta_k)Y_{J0}(\theta_k).$$

All of the information about a particular system in a given laser pulse is contained in the amplitudes $A_{nJ}(E)$ which give the amplitude for the pathway from the initial state to the final state with angular momentum J and energy E via n net photons. These amplitudes necessarily also include the net effect of the time-dependent dynamics that connect these states. Further insight can be had by considering the perturbation theory expressions for the amplitudes. For instance, a net-n photon pathway would include contributions from n photon absorption, n+1 photon absorption with 1 photon emission, n+2–2, and so on.

In our previous work, we used the expression above to construct and interpret CEP-dependent observables from the amplitudes. For example, the expression shows that CEP effects only appear as the interference of different net-n pathways. And, the first contribution will be for $|n-n^1|=1$, which accounts for nearly all of the CEP dependence observed in the literature. More complicated CEP dependence requires higher frequencies $|n-n^1|>1$ which are much less likely (as an example, net-2-photon and net-4-photon pathways are unlikely to contribute at the same energy).

Recently, we have used this expression as the basis for extracting the amplitudes. The procedure would require that the energy-angle distribution be measured as a function of CEP in pulses short enough to show CEP effects. This experimental data is then fit using the above expression to obtain the $A_{nJ}(E)$. There are several ways to carry out this fit, and the one that we are pursuing starts with the Fourier transform with respect to CEP:

$$\begin{aligned} c_m(E,\theta_k) &= \frac{1}{2\pi}\int_0^{2\pi} e^{-im\varphi}\frac{\partial^2 P}{\partial E\partial\theta_k}d\varphi \\ &= \sum_{nJJ'} A^*_{n-mJ'}(E)A_{nJ}(E)Y_{J'0}(\theta_k)Y_{J0}(\theta_k). \end{aligned}$$

This method for extraction of the amplitudes thus has a lot of overlap, for instance, with retrieving the field of a laser pulse via an interferometric technique like FROG. And, like such techniques, uniqueness of the retrieved amplitudes can be an issue and was a concern. Using relatively simple physical arguments to restrict the coefficients — such as energy conservation and dipole selection rules - alleviates much of the problem, however. In addition, careful utilization of minimization routines with sampling a distribution of initial guesses seems to eliminate most of the local minima from the fit. Nevertheless, as the number of amplitudes grows (with, say, intensity or energy), the minimization becomes challenging.

Besides some simple testing, we have also successfully extracted the amplitudes from calculations of strong-field dissociation of HeH^+ from an initial $v = 0$, $J = 0$ initial state in a two-cycle, 4000-nm pulse with intensity 10^{14} W/cm^2. Because at least six photons are required for dissociation and the energy range in our calculation covered six peaks in energy, $n_{\min} = 4$ and $n_{\max} = 15$ were chosen. Similarly, the minimum and maximum J values used were $J = 0$ and $J = 15$. We solved the time-dependent Schrödinger equation to calculate the $A_{nJ}(E)$ directly and construct the energy-angle distribution to fit to. The extracted amplitudes could thus be compared to the calculated amplitudes, showing that we were able to extract the amplitudes to 1% over this whole energy range.

Future Plans: Further testing of this pathway extraction procedure is needed, along with improvements in efficiency to make it applicable to higher intensities. We also want to find ways to get more fine-grained information than $A_{nJ}(E)$. One obvious approach would be to introduce a two-color (or more) field with variable relative phase. Other controllable parameters might provide a route to additional insight. The more immediate next steps, however, will involve application to experimental data.

3. Correlated dynamics

Molecular processes are influenced and, in some cases, dominated by correlations among electrons and between electrons and nuclei. These correlations become increasingly important as larger and more complex molecules are considered. In order to approach a complete understanding of energy flow in complex systems or biological molecular dynamics, we must first build the ability to observe and describe correlations in molecules. We use complementary tools to explore the dynamics of chemical processes, including coincidence detection of neutral and ionic molecular fragments, photoelectron spectroscopy, ultrafast electron diffraction, impulsive alignment of molecules, and *ab initio* theoretical methods. Combining theoretical modeling and computational molecular physics with coincidence and alignment measurements, and employing several complimentary experimental techniques, we seek to gain a more complete picture of the critical role of correlated dynamics in molecular processes.

3.1. Molecular Fragmentation Dynamics with Neutral and Ionic Targets- Ben-Itzhak, Rolles, Rudenko, Esry

Project Scope: The light-induced fragmentation of molecules and subsequent dynamics of the fragments is one example of a process where correlations between electrons and nuclei can result in a high level of complexity. Within this project, we are developing and improving experimental analysis techniques that deconvolve the complex data, resulting in a picture of different dynamic processes. To identify and separate various reaction pathways and to elucidate the role of different initial and intermediate states, we perform coincidence experiments employing both neutral targets and molecular ion beams, and have a close collaboration between theory and experiment. We are also advancing our theoretical ability to describe these complicated processes from first principles.

Recent Progress:

3.1.1. Native frames: Disentangling sequential and concerted multi-body fragmentation

Previously, we reported our studies of the formation of hydrogen-rich fragments from ethanol following double ionization by a strong laser field. In this work, performed in collaboration with E. Wells (Augustana) and M. Dantos (MSU), we determined the probability associated with the site of origin of each hydrogen atom [15]. This was accomplished also for "incomplete-breakup channels", i.e., the cases where there is a missing neutral fragment(s) in addition to the detected ion pair. This year, we explored these 3-body breakup channels employing the native frames analysis method [16,17].

This analysis of the $H_2O^+ + C_2H_3^+ + H$ breakup channel is shown in Fig 7 as a function of the kinetic energy release (KER) of the intermediate $C_2H_5O^{2+}$ dissociation into $H_2O^+ + C_2H_3^+$ and the angle between the conjugate momenta associated with the two fragmentation steps, the first being H elimination from ethanol dication. The measured distribution has a narrow KER peak centered at about 4.9 eV and a broad angular distribution caused by the rotation of the intermediate $C_2H_5O^{2+}$ in the fragmentation plane. The deviation from the expected flat angular distribution [16,17], resulting in dips near the edges of the distribution at 0° and 180°, is due to the relatively poor momentum resolution of the reconstructed slow H fragment, which is determined from momentum conservation. Simulations including the momentum resolution under the present experimental conditions reproduce nicely the measured distribution shown in Fig. 7.

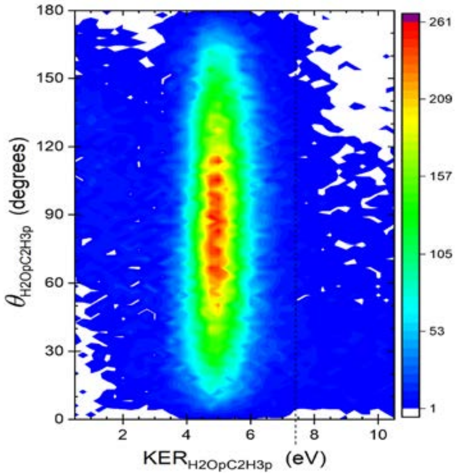


Figure 7. The number of $H_2O^+ + C_2H_3^+$ coincidence events as a function of the KER in $C_2H_5O^{2+} \rightarrow H_2O^+ + C_2H_3^+$ and the angle between the conjugate momenta associated with the 1st and 2nd breakup steps [2,3].

The fragmentation of the ethanol dication into $H_3^+ + C_2H_2O^+ + H$ exhibits a similar sequential breakup involving hydrogen elimination first, i.e., breakup into $C_2H_5O^{2+} + H$ followed by the dissociation of the $C_2H_5O^{2+}$ intermediate into $H_3^+ + C_2H_2O^+$. In addition, this $H_3^+ + C_2H_2O^+ + H$ channel has minor contributions of concerted breakup and sequential breakup following the ejection of an H_3^+ first, followed by hydrogen elimination from the intermediate $C_2H_3O^+$.

In a similar project exploring the HCOOD isotopologue of formic acid, we have observed similar sequential breakup processes involving hydrogen elimination as the first step. The most interesting of these channels involves double hydrogen elimination, namely $H + D + CO_2^{2+}$ followed by the dissociation of the CO_2^{2+} intermediate into $O^+ + CO^+$ after the carbon dioxide rotates for some time in the fragmentation plane. Curiously, in addition to the CO_2^{2+} that survives for a few rotational periods (i.e., a fraction of a nanosecond), we also observe the dissociation of metastable CO_2^{2+} in flight to the detector, with sufficient statistics to evaluate the lifetime to be about 600 ±100 ns. This measured lifetime is different than what we observe following double ionization of CO_2 under similar laser conditions.

Finally, we also employed native frames analysis [16,17] in our studies of two- and three-body fragmentation of $CHBr_3$ driven by intense 28-fs laser pulses (see [P49]). Specifically, we identified sequential fragmentation of the trication proceeding via $Br^+ + CHBr_2^{2+}$ and followed by $CHBr_2^{2+} \rightarrow Br^+ + CHBr^+$. This information was also used in the interpretation presented in [P39].

3.1.2. Predissociation- and photodissociation pathways of OD^+

Previously, we implemented the native frames method [16,17] to analyze single photon double ionization data of D_2O acquired through our ALS collaboration (which includes the LBNL group, R. Dörner, T. Jahnke, A.L. Landers and others). Specifically, we separated sequential fragmentation of the heavy water dication leading to $D^+ + D^+ + O$ via $OD^+ + D^+$, identified two dissociation pathways involving the $b^1\Sigma^+$ and $a^1\Delta$ states of the intermediate OD^+, and followed their breakup step by step (see [P40]). In a follow-up project, we identified the same intermediate OD^+ states in the sequential fragmentation of D_2O^{2+} leading to $D^+ + O^+ + D$ final products. The second fragmentation step in both cases, i.e., the predissociation of the OD^+ intermediate, starts by a $b^1\Sigma^+ \rightarrow A^3\Pi$ (or $a^1\Delta \rightarrow A^3\Pi$) transition driven by spin-orbit coupling. Note that the $A^3\Pi$ state correlates with the $D^+ + O$ dissociation limit, therefore, to reach the $O^+ + D$ products additional transitions are needed. We identified the most likely path in this case to be $A^3\Pi \rightarrow X^3\Sigma^- \rightarrow B^3\Sigma^-$, where the final $B^3\Sigma^-$ state correlates with the $O^+ + D$ dissociation limit. Consequently, the ratio of the number of sequential fragmentation events (for either the $a^1\Delta$ or $b^1\Sigma^+$ intermediate state, $N_{a,b}$) associated with D^+–D^+ or D^+–O^+ coincidence events provides a measure of the $A^3\Pi \rightarrow X^3\Sigma^- \rightarrow B^3\Sigma^-$ transition probability (see [P59]):

$$P_{a,b}(A^3\Pi \rightarrow X^3\Sigma^- \rightarrow B^3\Sigma^-) = N_{a,b}(D^+ + O^+ + D) \,/\, [\, N_{a,b}(D^+ + O^+ + D) + N_{a,b}(D^+ + D^+ + O)]$$

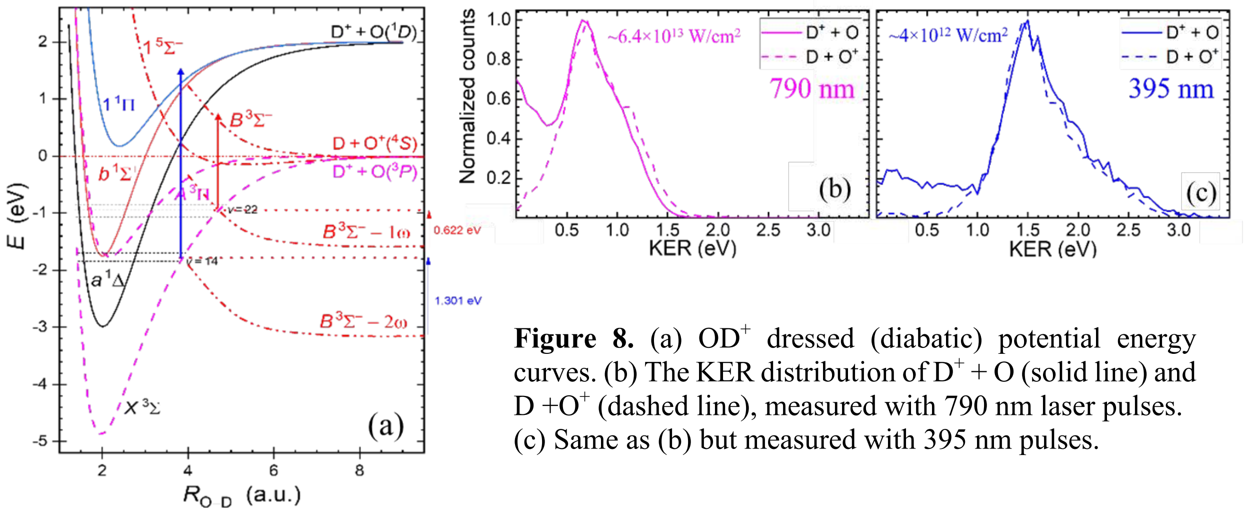


Figure 8. (a) OD^+ dressed (diabatic) potential energy curves. (b) The KER distribution of $D^+ + O$ (solid line) and $D + O^+$ (dashed line), measured with 790 nm laser pulses. (c) Same as (b) but measured with 395 nm pulses.

As a follow up on the project above, we have measured the photodissociation of an OD^+ ion-beam target using NIR and UV photons provided by the PULSAR laser. As shown in Fig. 8a, the single photon absorption excited the OD^+ from its $X\,^3\Sigma^-$ ground state to the $B\,^3\Sigma^-$ state, which dissociates into $D + O^+(^4S)$ with a KER peak around 0.7 eV (790 nm) and 1.5 eV (395 nm), as shown by the dashed line in Fig. 8b,c. The KER distribution of the $D^+ + O(^3P)$ dissociation channel, shown by solid line in Fig. 8b,c, exhibits the same prominent KER peaks (with some low KER contributions associated with other dissociation paths). Here too, the branching ratio of the $D^+ + O(^3P)$ channel, i.e., $N(D^+ + O) \,/\, [\, N(D^+ + O) + N(D + O^+)]$, is a direct measure of the transition probability from the $B\,^3\Sigma^-$ state to the final state leading to the dissociation into $D^+ + O(^3P)$ – either the $X\,^3\Sigma^-$ or $A\,^3\Pi$ state. Calculations are underway to determine the relative importance of these two final states.

Future plans: We plan to continue examining the limitations of native frames analysis, for example, deviations from a uniform $N(\Sigma_{AB,C})$ angular distribution, and exploring other possible signatures of sequential or concerted breakup. In addition, we will extend native frames analysis to four-body breakup following initial studies of formic acid and formaldehyde. We will also continue to probe molecular-ion beams, like CD_n^+ (n=2-4) and D_3O^+, in a strong laser field.

3.2. Ultrafast UV-induced ring opening of thiophenone - Rolles, Rudenko

Project Scope: A significant fraction of the current JRML research program is focused on time-resolved studies of UV-driven ultrafast photochemistry in the gas phase. We have exploited recent advances in Coulomb explosion imaging (CEI) and the availability of several complementary ultrafast probing techniques to study the dynamics of UV-excited halomethanes [18-20,P27,P60,P68]. Over the last year, we extended these studies to more complex systems, in particular focusing on ring-opening reactions. UV-induced ring opening has attracted considerable interest in the ultrafast physics and chemistry community because it generally combines sub-100-fs electronic relaxation via non-adiabatic transitions with large-amplitude, coherent nuclear motion that can ultimately lead to a variety of photoproducts. These characteristics make them an exciting testbed for both experiment and theory. While we have recently carried out time-resolved measurements on several UV-induced ring-opening reactions, here we focus on the example of thiophenone, a five-member heterocyclic molecule, for which we have recently complemented the results of our earlier time-resolved photoelectron spectroscopy (TRPES) study at FERMI [21] with an ultrafast electron diffraction (UED) experiment and with two CEI measurements, which employed intense femtosecond x-ray and NIR pulses as a probe.

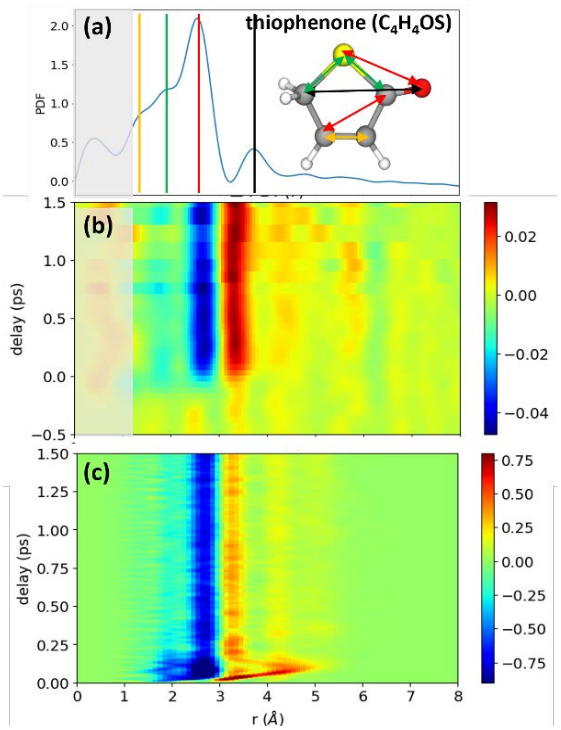


Figure 9: Comparison of MeV-UED results for UV-excited thiophenone with ab-initio molecular dynamics calculations. (a) Experimentally determined static (i.e., no UV-pump) pair distribution function (PDF) with characteristic interatomic distances marked as vertical lines (see sketch). (b) Difference between the PDF for pump-on and pump-off in the experiment. (c) Same difference computed from the theoretical trajectories using the independent atom model to calculate the scattering signal.

Recent Progress:

3.2.1. MeV ultrafast electron diffraction experiment at SLAC

In our previous XUV TRPES experiment on the ring opening reaction in thiophenone triggered by the absorption of a 267 nm UV photon, we achieved an overall excellent agreement with the results of *ab initio* molecular dynamics calculations [21]. However, several key elements of the theoretical predictions, namely the actual ring-opening motion, which is expected to occur within approximately 70 fs, and the actual identification and branching ratio of the photoproducts, were not accessible to the

TRPES experiment. We therefore complemented our experimental investigations of this reaction with an UED study using the MeV-UED user facility at LCLS/SLAC. The results of the MeV-UED experiment, compared to the same molecular dynamics calculations as used to interpret the TRPES experiment, are shown in Fig. 9. Although the temporal resolution of the MeV-UED setup is not sufficient to resolve the ultrafast, large- mplitude motion during initial ring opening (see red "wiggle" in Fig. 9c), the experimental data in Fig. 9b shows unambiguous proof for the production of open-ring photoproducts, as seen by the depletion of the peak corresponding to the O-S distance (blue vertical band) and the enhancement of a new feature at a larger internuclear distance (red vertical band) consisting of several distances in the open-ring photoproducts. Further analysis of the data also yields the time-resolved branching ratios of the photoproducts, which are in good quantitative agreement with the theoretical predictions [22].

3.2.2. Coulomb explosion imaging with XFEL and table-top NIR laser

To resolve the nuclear motion in thiophenone *during* the ring opening, which was too fast for both the TRPES and the MeV-UED experiments, we also performed time-resolved CEI experiments at the European XFEL and with the table-top lasers at the JRML. Both setups have a temporal resolution better than 40 fs for experiments at 266 nm. Preliminary results (Newton plots) for static (i.e., unpumped) thiophenone recorded at EuXFEL are shown in Fig. 10. It is particularly noteworthy that these momentum images can clearly resolve the three-dimensional structure of the molecule, including the positions of the two hydrogen atoms located outside of the molecular plane defined by the 5-member ring.

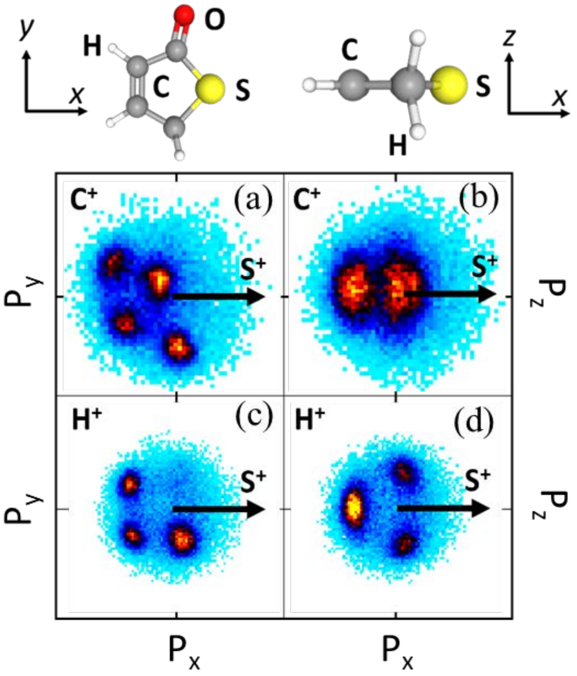


Figure 10: Coulomb explosion images (Newton plots) of thiophenone derived from the H$^+$ + C$^+$ + O$^+$ + S$^+$ coincidence channel, recorded at a photon energy of 2.7 keV at the European XFEL. Panels (a,b) show the C$^+$ momentum images and panels (c,d) the H$^+$ momentum images in the molecular frame (a,c) and in the plane perpendicular to it (b,d), as sketched above. The molecular frame (*x-y* plane) for the Newton plots is defined by the S$^+$ (+*x* axis) and O$^+$ (not shown) fragment ion momenta.

While the analysis of the time-resolved EuXFEL data (not shown here) is still ongoing, signatures of ring opening can be clearly resolved in the results of a similar CEI experiment at the JRML that employed an intense 28-fs NIR pulse as a probe. As illustrated in Fig. 11a, the "static" (probe only) CEI pattern in this case is not as clear as for the data obtained with the x-ray probe (compare with Fig. 10a), mainly because of the higher background contribution, which is considerably suppressed in the EuXFEL experiment performed above the sulphur K-edge. As shown in Fig. 11b, for the static case, clear signatures of the molecular structure can be restored by gating on the "correct" position of the O$^+$ momentum (marked red in Fig. 11a). Fig. 11d-g displays the evolution of the molecular-frame

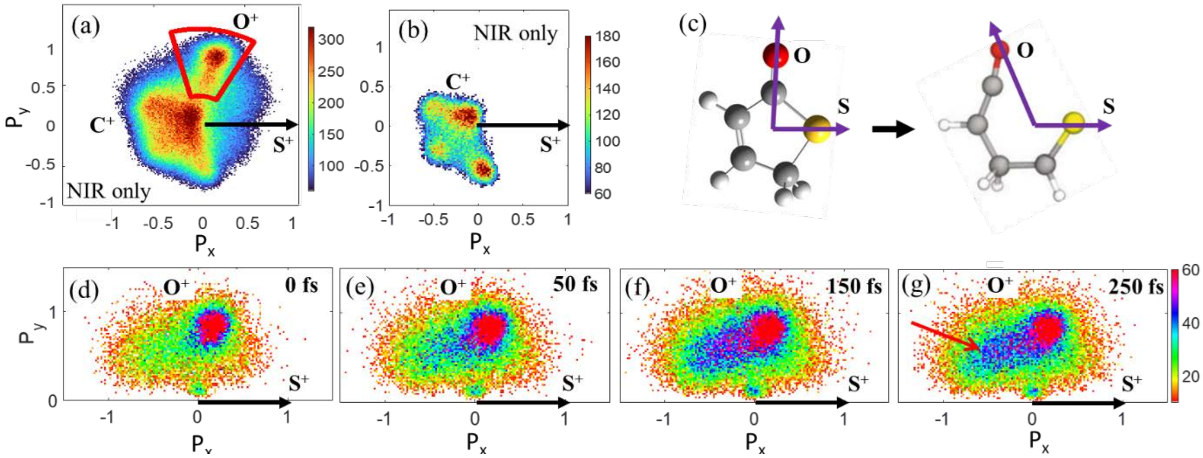


Figure 11. Newton plots of thiophenone derived from the C$^+$ + C$^+$ + O$^+$ + S$^+$ coincidence channel, recorded with the NIR probe pulse at the JRML. (a) "Static" molecular-frame momentum distributions of C$^+$ and O$^+$ fragments obtained with NIR probe pulse only. The molecular frame is defined by the S$^+$ (positive *x* axis) and O$^+$ (*x-y* plane, positive *y*) ion momentum vectors. (b) Same as (a) but including only C+ ions under the condition that the O+ momentum is in the area marked red in (a). (c) Schematic of the (O, S) angle change expected for ring opening. (d-g) Molecular-frame momentum distributions of O$^+$ ions obtained in the UV pump – NIR probe experiment at four different delays. Since the oxygen momentum is chosen to be in the upper hemisphere (positive *y*), only the upper half of the Newton plots is shown.

O$^+$ momentum distributions obtained after exciting thiophenone molecules with 266 nm pump pulse. As the pump-probe delay increases, some of the oxygen fragments appear at significantly higher angles with respect to the S$^+$ momentum (as indicated by the red arrow in Fig. 11g), directly reflecting the ring-opening process.

Although the analysis of both EuXFEL and JRML data sets is still in progress, we preliminarily conclude that the ring-opening motion of the carbon-sulfur-oxygen backbone is easier to resolve in the data from the NIR-laser experiment at JRML, whereas the positions of the hydrogen atoms are better resolved in the EuXFEL data.

Future Plans: Given the success of both the MeV-UED and the laser- and XFEL-based CEI campaigns, we plan to apply both techniques to other UV-induced isomerization and ring-opening reactions. We have already expanded our work (and will continue to do so) to reactions induced at 200 nm, produced as the fourth harmonic of our Ti:Sa laser, and also to variable excitation wavelengths between 200 and 400 nm produced by our new OPA. This significantly increases the range of molecular targets and reactions that we can study.

3.3. Correlating observables with nuclear geometry – Greenman, Rolles, Han

Project Scope: Following on recent work characterizing the effects of nuclear geometry in the chiral observable photoelectron circular dichroism (PECD), we want to determine what observables can be correlated with nuclear geometries, especially those involved in bond breaking. We are particularly interested in photoelectron observables, such as ionization yields and β parameters. By understanding the correspondences between observables, preferably those determined by experiments that can provide significant statistical certainty, and geometry features like bond lengths we can more definitively follow certain dynamical processes using these observables as a guide.

Recent Progress: We have explored photoelectron observables related to the bond breaking of the halomethanes CH_3I and CH_3F (CH_3X). As the C-X bond breaks, the electronic structure becomes more complicated and the scattering calculations even more so. We have determined that the current theories of photoionization are limited in their capability to describe such systems, especially for the CH_3I molecule. Even with this limitation, we have calculated the approximate photoionization yield and β parameters for CH_3F as a function of the C-F bond length (see Fig. 12). We currently limit ourselves to a frozen CH_3 fragment, which, according to our previous work, did not lead to qualitatively different conclusions for the photoelectron observable PECD. We have performed the calculations for CH_3X photoionization with the UK-RMol+ package [23]. Importantly, this package may be used with Gaussians and/or B-splines as a basis for continuum states. Also, a common strategy employed with this and related methods uses monocentric Gaussians to represent the inner part of continuum functions. This method requires converging with respect to partial wave parameters (ℓ) and integration expansion parameters (L). We have performed extensive studies of the convergence behavior for CH_3X, and found the cost of convergence to be quite high (using 4-8 nodes on NERSC). This limits us to moderate convergence parameters for CH_3F and makes converged calculations for CH_3I too expensive even at the equilibrium geometry. Fig. 12 was produced at $\ell = 4$, which gave satisfactory convergence for the cost. Additional correlation made converging this calculations harder. Using a CAS-CI model available in UK-RMol+, we were unable to obtain converged results for CH_3F at its equilibrium geometry even up to $\ell = 7$.

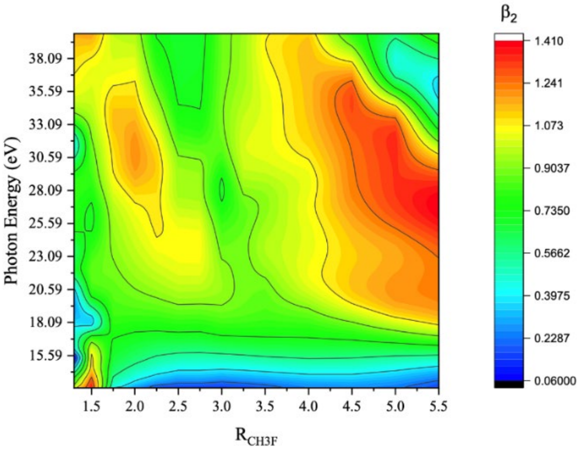


Figure 12: Photoelectron β parameters for CH_3F as a function of C-F bond length. Multiple features may be used to fingerprint bond-breaking geometries.

The photoionization yields associated with Fig. 12, but not shown here, predict a shape resonance near 17 eV at the equilibrium geometry that is quickly suppressed as the bond length increases. A shift in the ionization potential also shows the transition between bonded and unbonded. There is a dip in the ionization potential near intermediate geometries of r = 2.5 Å, which is another feature that can be used to identify the path along the bond-breaking process. This provides one observable that can be used as a reference to determine whether the molecule is near its equilibrium geometry. As we expected, asymmetry parameters provide an even more differential view of the molecular geometry, especially in combination with the shape resonance reference. At higher photoelectron kinetic energies, there are features in β which go from very low values near equilibrium geometries to much higher values as the bond length is stretched by a few Å. Near $r = 4.5$ Å, the β parameter sharply rises to 1.4 from a baseline value of 0.7. This happens at a range of energies from 20 up to 35 eV. We believe that these features are interesting both as an experimental signature of molecular geometry and as a tool for testing photoionization theories.

Future plans: With the previously mentioned work on PECD, we now have multiple systems where we believe that we can observe bond breaking without a direct molecular-frame measurement. For both of these systems, we have concentrated on the ground electronic state.

While there are schemes that can induce bond breaking from the ground state, we also plan to study these observables on low-lying excited states. These observables may be used to identify the state and the geometry in a best case scenario. We also plan to look at observables related to non-linear spectroscopies. In collaboration with the experimental group of Niranjan Shivaram at Purdue, we are attempting to predict experiments that measure components of the third-order hyperpolarizability tensor for molecules. With the arrival of Meng Han, a new JRML experimental PI, part of the local experimental activity will focus on molecular chirality. Correspondingly, we are starting with chiral prototype molecules methyl oxirane and CHClBrF, and we are attempting to determine which components of the tensor best show chiral asymmetries. We are also looking at applying these techniques to ethylene, and determining whether they can be used as a sensitive observable for passage through a conical intersection.

4. Ultrafast XFEL science

Novel capabilities developed at FEL facilities, in particular the ability to produce intense femtosecond or even sub-femtosecond XUV and x-ray pulses, open up new avenues for imaging structure of matter and for studying ultrafast light-induced dynamics. Successful implementation of these new capabilities requires detailed understanding of light – matter interactions at XUV and x-ray wavelengths, both in single-photon regime and at high intensities. The projects in this section use coincident charged-particle imaging and transient absorption techniques in combination with advanced theoretical modeling to improve our basic understanding of FEL-driven dynamics, and to apply element-specific short-pulse XUV or x-ray probes to study ultrafast charge dynamics (charge transfer and charge migration) in gas-phase molecules

4.1. Resonance-enhanced x-ray multiphoton ionization – Rolles, Rudenko

Project Scope: X-ray ionization observed in gas-phase high-intensity XFEL experiments is typically dominated by sequential multiphoton absorption and subsequent relaxation processes. With sufficiently high photon flux, the highest ion charge state created is usually the last ionic charge state that can be reached before its ionization potential rises above the photon energy. However, at certain x-ray photon energies, the ionization level can be drastically enhanced by transient resonances created during the sequential ionization process. If inner-shell electrons can be resonantly excited to high-lying orbitals, higher charge states can be reached via subsequent autoionization of multiply excited states, or by the absorption of an additional x-ray photon. This project aims to study such resonance-enhanced x-ray multiphoton ionization (REXMI), in particular, focusing on the photon energy dependence of this process.

Recent Progress: Our earlier work on the x-ray multiphoton ionization of isolated heavy atoms [24-26] and molecules containing heavy-atom constituents [27,P5,P23] revealed the importance of REXMI processes for both atomic and molecular cases. Following up on these studies and making use of the easy photon energy tunability provided by the variable gap undulators at the European XFEL, we recently investigated the dependence of REXMI on the x-ray photon energy. Fig. 13 shows the measured xenon charge-state distribution as a function of photon energy. Several resonance features that move towards higher photon energy for increasing ionic charge state are observed and their assignment to specific resonance transitions are indicated. These transitions shift up in energy for increasing ion charge, leading to the curved features seen in Fig. 13. Supported by *ab initio* ionization dynamics calculations, which are in good agreement with the

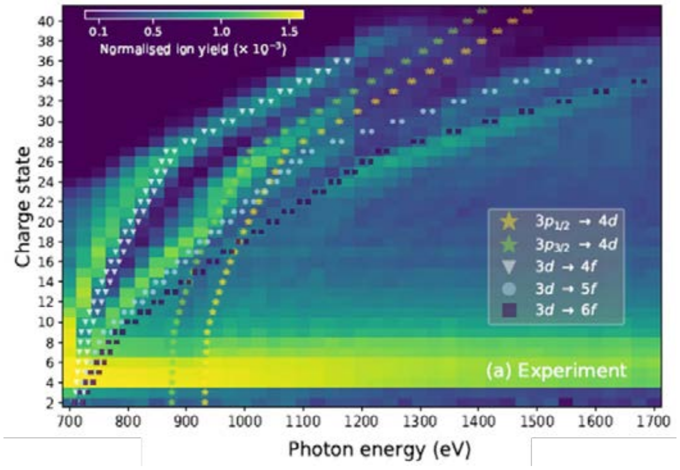


Figure 13: Experimental xenon charge-state distributions as a function of photon energy, recorded with a constant number of photons ($9.3 \pm 0.2 \times 10^{12}$) per X-ray pulse. Colored markers show selected resonant transition energies in the ground-state configuration of each charge state q – 1.

experimental observations [P61], we can identify the formation of massively hollow atoms, featuring up to six simultaneous core holes, during the ionization process.

In addition to providing a comprehensive picture of x-ray multiphoton ionization of heavy atoms, this study lays the groundwork for novel spectroscopies of transient atomic species in exotic, multiple-core-hole states that have not been explored previously.

Future Plans: The *ab initio* ionization dynamics calculations accompanying the experimental work described above have predicted an intriguing x-ray pulse-length dependence of the ionization process, which could not be studied in the previous experiment since pulse-duration tunability was not yet available at EuXFEL. Through a collaborative effort led by scientists from EuXFEL, we have recently developed the experimental tools to tune and measure the x-ray pulse durations, and a new beamtime is planned to combine these new capabilities with a measurement of the Xe charge state distributions as a function of x-ray pulse duration in order to test the theoretical predictions. Future expansions to other atomic targets and heavy-atom containing molecules are also planned.

4.2. Channel-selective imaging of nuclear wave packets with x-ray-driven Coulomb explosion

– Rudenko, Rolles

Project Scope: Recent experiments at the EuXFEL ([P22,P24], see also section 3.2.2) demonstrated that intense femtosecond x-ray pulses are a very efficient tool for CEI of polyatomic molecules because they induce rapid multiple ionization of a large fraction of the molecular ensemble. The main goal of this project is to apply XFEL-driven CEI to time-resolved studies of ultrafast molecular processes, and to analyze the interplay between the Coulomb explosion and distance-dependent charge transfer dynamics.

Recent progress: Following up on our previous work on 3D CEI of halomethanes at the EuXFEL [P22], we have recently applied this technique for time-resolved imaging of nuclear wave packets in strong-field-ionized diiodomethane (CH_2I_2). Fig. 14a-c display the experimental 3D Newton plots (see [P22,P39]) obtained for three different charge-state combinations measured with the x-ray pulse arriving 500 fs after the intense NIR pump. They show distinct features which are indicative of different photodynamics: The $C^{2+}/I^{3+}/I^{3+}$ channel (Fig. 14a), where the charges are nearly equalized, favors the contribution from bound molecules and is dominated by I–C–I bending vibrations in the cationic ground state, which can be directly seen in the delay-dependent momentum-space angle shown in Fig. 14d. The $C^{+}/I^{4+}/I^{5+}$ channel (Fig. 14b) with low carbon charge favors the events where the methylene group is detached from the rest of the molecule. By selecting only the dissociating molecules (by choosing the events with low C^{+} energy in Fig. 14e),

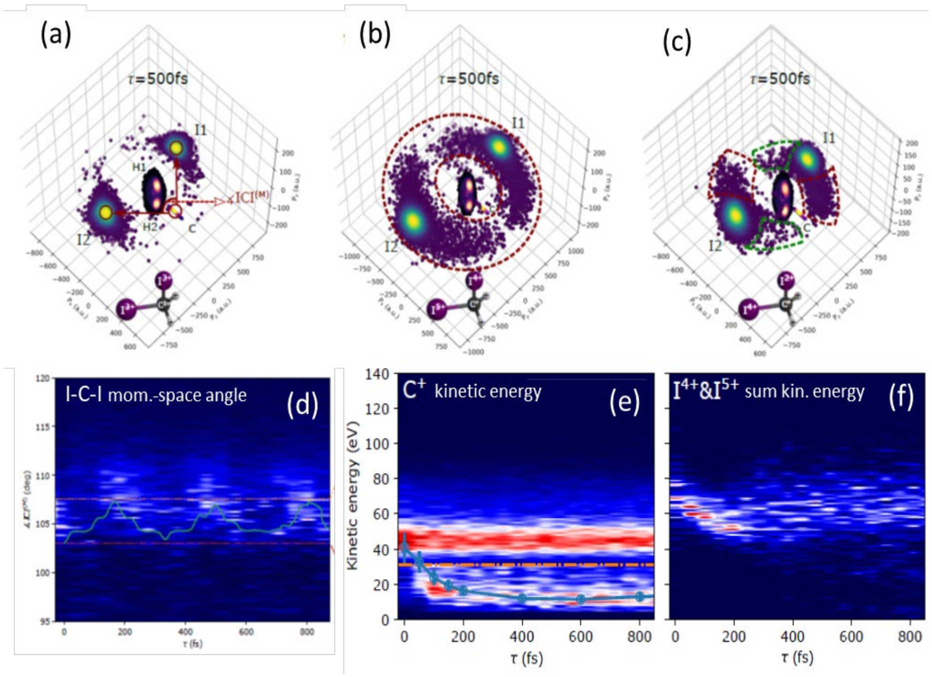


Figure 14. (a-c) Molecular-frame momentum distributions of ion fragments from the ionization of CH_2I_2 molecules by 2 keV XFEL pulses arriving 500 fs after the irradiation by 800-nm, ~10^{14} W/cm^2 NIR laser pulses. The data are shown for $C^{2+}/I^{3+}/I^{3+}$ (a); $C^{+}/I^{4+}/I^{5+}$ (b) and $C^{+}/I^{2+}/I^{4+}$ (c) coincidence channels. For all channels, either one or two H+ ions were detected and are also shown in the plots. (d) The measured momentum-space I-C-I angle for the $C^{2+}/I^{3+}/I^{3+}$ channel as a function of NIR – x-ray delay. The solid line shows the measured average value of the angle. (e) Delay-dependent kinetic energy of C^+ fragments for the $C^{+}/I^{4+}/I^{5+}$ channel. The solid line shows the results of the CE simulation for I_2^+ formation. (f) Delay-dependent sum energy of two iodine ions for the same events as in panel (e) but only for the C^+ energies below the dashed line plotted in (e).

we observe that the corresponding iodine fragments energy stays large at large delays (Fig. 14f), reflecting the formation of molecular iodine. Finally, the analysis of the $C^{+}/I^{2+}/I^{4+}$ channel (Fig. 14c) with asymmetric iodine charge distribution reveals that this channel contains a strong contribution from the evenrs where one of the C-I bonds has bean cleaved by the pump pulse.

Future Plans: Immediate next steps on this project will include a detailed quantitative analysis of the relation between the momentum-space and real-space angles based on the modelling of x-ray ionization developed by Phay Ho (Argonne) and the analysis of the time-dependent CEI observables based on molecular dynamics simulation for I_2 and I_2^+ formation performed by Patricia Vindel-Zandbergen (New York University). More generally, we plan to exploit the observed channel selectivity of x-ray-driven CEI to disentangle mixed reaction pathways and map minor channels in ultrafast photochemical reactions.

4.3 Time-resolved state-specific molecular dissociation with XUV broadband transient-absorption spectroscopy – Thumm

Project Scope: Along with diffraction-based methods and charged-particle imaging and spectroscopy, XUV and x-ray transient absorption is an important novel tool for ultrafast science. The goal of this project is to model transient absorption observables for ultrafast molecular dynamics, focusing on combining FEL-based and HHG-based XUV and soft x-ray light sources.

Recent progress: Recent proof-of-principle DI investigations with O_2 molecules used a unique combination of XUV-FEL-pump and XUV-HHG-probe pulses. They reveal the dissociation dynamics in the FEL-excited O_2^+ (c $^4\Sigma_u^-$ v=0) state by the delay-dependent identification of specific resonances of both ionic O^+ ($^4S^o$) and neutral O (^3P) and O (^1D) fragments in the broad-band HHG absorption spectrum (Fig. 15) [P15,28]. This demonstrated the temporal resolution of competing tunneling dissociation and pre-dissociation, based on the state-specific probing of characteristic absorption resonances in neutral and ionic fragments.

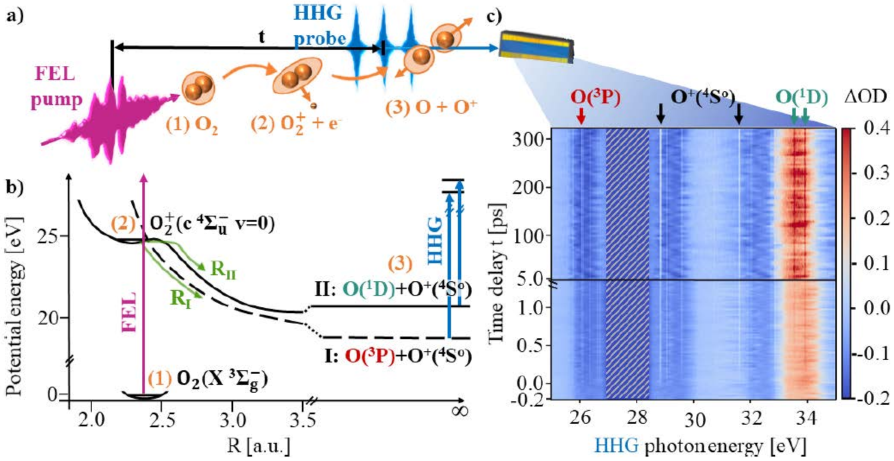


Figure 15. (a) Experimental scheme of all-XUV transient-absorption spectroscopy [P15]. (b) Relevant potential energy curves of O_2^+. (c) Time-resolved absorption spectrum [28].

These results demonstrate an exciting opportunity for nonlinear all-XUV-optical wave mixing, using HHG and FEL pulses [P15,28]. The method benefits from the narrow-band spectral selectivity and tunability and high intensity of the FEL-pump pulse, as well as the broad-band spectral coverage of the HHG probe pulse. The combination of two key advantages of complementary XUV ultrafast light sources enables state-selective time-resolved absorption spectroscopy experiments.

Future plans: Interestingly, this scheme promises the imaging – over a large spectral range – of the electronic-structure evolution in a dissociating molecule, from its initial bound configuration to the dissociation limit. We thus plan to continue this experiment-theory collaboration [P15,28,29] with detailed numerical simulations of the nuclear dynamics in XUV-excited O_2^+ cations. This requires us to extend our recent calculations of the dissociation dynamics of O_2^+ [30,31], most importantly, by including all relevant dipole-allowed XUV pump-pulse excited cationic states.

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

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Project Scope: The AMOS Program at LBNL seeks to answer fundamental questions in atomic, molecular, and chemical sciences that are central to the mission of the Department of Energy's Office of Science. The Program consists of a variety of closely coupled experimental-theory efforts, united by the overarching goal to provide deep insight into the fundamental interactions that drive key chemical processes in simple molecules, complex molecular systems, and molecules in complex environments. Major areas of emphasis include the dynamics of inner-shell excitation, photoionization, multiple-ionization, and dissociation of small molecules as well as time-resolved studies of the flow of charge and energy in atoms and molecules in the gas phase, in the condensed phase, and at interfaces. Experiments apply a broad span of existing and emerging tools based on a combination of laboratory- 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, ultrashort pulse electron beams, 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 coincident momentum imaging, as well as ultrafast X-ray and electron scattering and coherent diffractive imaging. The theory component of the Program focuses on the development of new methods for solving, from first-principles, complex multi-atom and multi-electron processes that play key roles in the dynamics of the systems under investigation. The close coupling between experiment and theory as well as the complementary nature of the different activities within a single program provide a framework to tackle problems across a broad range of timescales, system sizes and, in particular, complexity that are otherwise intractable.

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

1. **Photon- and Electron-Driven Processes in Atoms and Small Molecules**
2. **Photon-Driven Processes in Complex Molecular Systems and Molecules in Complex Environments**
3. **First-Principles Theory of Dynamics and Electronic Structure**

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

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

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

Attosecond Dynamics

The attosecond dynamics subgroup develops new nonlinear spectroscopies that utilize attosecond extreme ultraviolet (XUV) pulses produced by high harmonic generation (HHG) for time-resolving the fastest electronic dynamics in atoms and molecules. The XUV pulse in combination with two noncollinear near-infrared (NIR) pulses generates spatially isolated four-wave mixing (FWM) emission signals by taking advantage of the phase-matching condition. XUV attosecond FWM (as-FWM) spectroscopy disentangles the complex spectral effects in traditional transient absorption and has proven its power in characterizing electronic, vibrational, and vibronic dynamics (Cao et al. **2018**, *Phys. Rev. A* 97, 023401; Warrick et al. **2018**, *Faraday Discuss*. 212, 157; Fidler *et al.* **2020**, *J. Phys. Photonics* 2, 034003). The technique has also allowed ultrafast decaying dynamics measurements directly in the time-domain, such as the few-fs decay lifetimes of vibrational levels of the 3*s* Rydberg inner-valence state of O_2 (Lin et al. **2021**, *Faraday Discuss.* 228, 537) and the core-hole-pair decay in NaCl near the Na^+ $L_{2,3}$ edge (Gaynor et al. **2021**, *Phys. Rev. A* 103, 1). This work yielded insights into the importance of many-electron correlation effects for the respective excitonic decay mechanisms. Furthermore, a collaboration with theorists M. Gaarde and K. Schafer (LSU) refined the understanding of as-FWM signal generation as a time-dependent accumulation of an AC Stark phase grating (Fidler et al. **2019**, *Nat. Commun.* 10, 1384).

Autoionization Lifetimes of Atoms and Molecules Investigated with Attosecond Four Wave Mixing *(Lucchese, McCurdy, Leone, Neumark)*

Recent Progress: Recent work uses the enhanced signal specificity of FWM to understand short-lived, complex electronic dynamics in atoms and small molecules. With FWM, we have successfully investigated the lifetimes of autoionizing inner-valence excited Rydberg states of the isolated polyatomic molecule CO_2 (Fidler et al. **2022**, *Phys. Rev. A* 106, 1). FWM signals were observed to be emitted from the $n = 5 – 8$ states of the Henning sharp *nd* Rydberg series with measured decay times of 38 ± 2 fs, 55 ± 1 fs, 93 ± 3 fs, and 124 ± 4 fs. With collaborators C.W. McCurdy and R. R. Lucchese, calculations suggest that those values are close to the lifetimes of the $n = 6 – 9$ members of the Henning diffuse-character Rydberg series. Calculated oscillator strengths have verified the dominant FWM pathway which is consistent with experimental observation of probing lifetimes of Henning diffuse Rydberg series with emission from Henning sharp Rydberg series. Furthermore, FWM experiments have successfully quantified the autoionization decay lifetimes of 2*s* inner-valence electronic excitations in neon atoms (Puskar et al. **2023**, *Phys. Rev. A* 107, 033117). Experimental lifetimes for the 3*s*, 3*p*, and 3*d* states were measured to be 7 ± 2 fs, 48 ± 8 fs, and 427 ± 40 fs, respectively. Accompanying calculations from our collaborator, L. Argenti (UCF), verified the findings and supported the expected trend that the autoionization lifetime should be longer for states that have a smaller penetration in the radial region of the 2*s* core hole, which is the case for the higher angular momentum Rydberg orbitals in neon.

Recent FWM experiments have probed core-excited state lifetimes in atomic xenon (Puskar et al. **2023**, *in preparation*). An XUV pulse at ~ 65 eV excites a core-level 4*d* electron into the $6p_{5/2}$ and $6p_{3/2}$ spin-orbit split XUV-bright (dipole-allowed) states. Each 6*p* state has two neighboring XUV-dark (dipole-forbidden) states, the 6*s* and 6*d* states, resonantly accessible by NIR pulses. In Fig. 1-1(a), spatially isolated FWM emissions from the $6p_{5/2}$ and $6p_{3/2}$ states are clearly observed at 65.1 eV and 67.0 eV, respectively. Using either a bright- or dark-state pulse delay sequence, we can

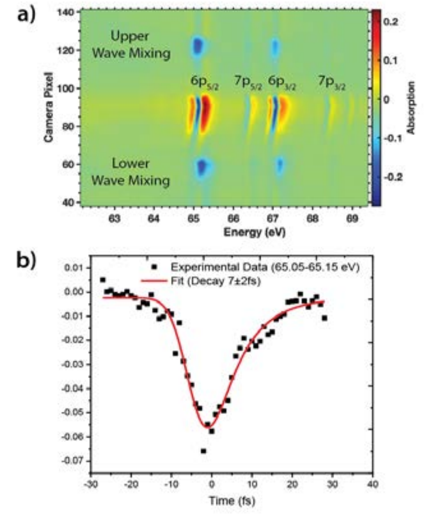

Fig. 1-1: FWM in Xe $4d^{-1}$ core excited states. (a) Full chip image in temporal overlap with the on-axis transient absorption signals and the off-axis four-wave mixing emission signals. (b) Bright-state scan of the $4d_{5/2}^{-1}$ 6p state.

obtain the lifetimes of the bright and dark states of a core-level electron directly in the time-domain. So far, we have conducted a $4d_{5/2}^{-1}$ 6p bright-state scan, resulting in a measured decay lifetime of 7 ± 2 fs [Fig. 1-1(b)]. The literature values for the linewidths in the spectral domain are 109.8 meV, 111.0 meV, and 106.3 meV, which translate to 6 fs, 5.9 fs, and 6.2 fs decay lifetimes, respectively. FWM experiments to characterize dark-state lifetimes in xenon are currently in progress. A direct determination of the core-excited state lifetimes in wave mixing signals promises to refine our understanding of the physical mechanisms governing highly excited atomic decays.

FWM experiments currently in preparation will directly probe doubly excited states in helium. An XUV pulse at ~60 eV will excite both electrons of the $1s^2$ ground state into the $2s2p$ doubly excited state. With the $2p^2$ dark-state within resonance of NIR pulses, not only can we characterize the $2s2p$ bright-state lifetime (literature value 17.5 fs), but also the $2p^2$ dark-state lifetimes (literature value 108.3 fs) directly in the time domain. These states in helium are also prime candidates to probe strong-field effects like Autler-Townes splitting and Rabi cycling. Ott et al. (Ott et al. **2014,** *Nature* 516, 374) showed a clear Autler-Townes splitting of the $2s2p$ resonance with an NIR intensity of $3.5 \cdot 10^{12}$ W/cm^2 using a transient absorption scheme. With our NIR intensity comfortably in the 10^{13} W/cm^2 range, we anticipate seeing strong Autler-Townes-splitting signatures in the FWM emission for the first time. Furthermore, we expect to be able to probe the Rabi cycling between the 2s2p and the $2p^2$ state in real time using the FWM technique. With FWM, we can directly time-resolve the Rabi-cycle-induced population transfer as a periodic signature in the state lifetime's exponential decay. A direct, time-resolved observation of Rabi cycling would deepen our fundamental understanding of strong-field physics in atoms and exquisitely complement our theoretical understanding of the Rabi frequency.

Future Plans: We are currently working on extending the FWM scheme to the soft X-ray (SXR) spectral region. This is highly relevant as core-level FWM measurements are anticipated to disentangle complex electronic and vibrational dynamics in organic molecules in an atomic-site specific manner. From a technical perspective, the SXR photon-energy region will be accessible using longer wavelength (1.3 μm) driving pulses from an existing optical parametric amplifier for the HHG process. Recently, a prototype of the required HHG-cell has been built. On the way towards reaching the chemically-relevant carbon K-edge (around 300 eV), the higher anticipated photon flux at the sulfur $L_{2,3}$ edge (around 180 eV) will allow for characterizing electronic-correlation-affected bright- and dark-state lifetimes of $L_{2,3}$ pre-edge resonances in SF_6: the FWM scheme will be able to directly measure the natural lifetimes of these states and decipher them from vibrational broadening and other mechanisms that contribute to the linewidth in spectral-domain measurement techniques. As a next step, FWM spectroscopy at the argon $L_{2,3}$ edge around 250 eV promises insights into the role of electron-correlation effects such as Auger-Meitner decay on the dynamical evolution of inner valence holes. One of the first experiments when reaching the carbon K-edge will focus on formaldehyde. FWM will enable to experimentally characterize for the first time a theoretically predicted doubly-excited state $[C(1s) + O\ ne^- \rightarrow (\pi^*)^2]$, which is one-photon forbidden. Multidimensional experiments enabled by FWM spectroscopy will access this doubly excited dark state, revealing its energetic location and lifetime. 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 energy- and angle-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, 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 we are able to pursue in small quantum systems with reaction microscopy, a.k.a. COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS). The investigations are performed using XUV synchrotron radiation, 2-color photon absorption schemes with our tabletop intense high harmonic generation laser system, and two soft X-ray photon absorption from single free electron laser pulses. Our studies focus on fundamentally important systems ranging from small and midsize polyatomic molecules (e.g., D_2O, CH_3OH, and HCOOH) to more complex systems (such as H_2O-H_2O and pyrrole-d-H_2O dimers, see Subtask 2) that are within reach of both complete experimental characterization and accurate theoretical treatment and interpretation. This approach enables tight coupling of the experiment and theory thrusts, which directly inform and inspire each other.

Dissociation Dynamics of Water Molecules Induced by Core and Valence Ionization

(Lucchese, McCurdy, Rescigno, Slaughter, Weber)

Recent Progress: In collaboration with the Frankfurt group (T. Jahnke & R. Dörner), DOE BES-AMOS PIs from KSU (D. Rolles, A. Rudenko), and other international partners, we recently studied the dissociation dynamics of single water molecules in rapid charge-up processes upon O(1s) ionization with two X-ray photons within one European XFEL (EuXFEL) pulse (1 keV, 4.4 mJ, < 25 fs, 970 Hz). Focusing solely on the nuclear dynamics, we demonstrated that, on a timescale of a few femtoseconds after core ionization and subsequent Auger decay, water undergoes structural deformation such as asymmetric O-H bond stretching and/or opening of the bond angle all the way up to 180°, eventually leading to rapid 2-body or 3-body fragmentation in asymmetric and/or unbent geometries (Jahnke et al. **2021**, *Phys. Rev. X* 11, 041044). For the same conditions we now investigated the dynamics triggered by oxygen core-shell ionization in three water isotopologues, H_2O, D_2O, and HDO, leading to the 3-body breakup producing O^{2+} + H^+/D^+ (Guillemin et al. **2023**, *accepted for publication in Struct. Dyn.*). We observe similar structural changes such as asymmetric bond elongation and bond-angle-opening mechanisms that occur for all three systems, but with significant differences: (1) Due to the larger mass, dynamical patterns are slower to evolve in D_2O, resulting in narrower angular distributions between the detected fragments [compare Fig. 1-2(a) and b)]. (2) Due to the asymmetric mass distribution in HDO, structural asymmetry arises in the dissociation dynamics, evident in the very different fragment pair angular distributions [see Fig. 1-2(c)]. For this particular isomer we applied the native frame (NF) analysis, in order to find out if the sequential dissociation of the HDO^{2+} dication, resulting in $H^+ + OD^+$ after the absorption of a 1st photon [via photoionization and Auger-Meitner (AM) decay], followed by further fragmentation of $OD^{3+} \rightarrow O^{2+} + D^+$ after the absorption of a 2nd photon (again triggering photoionization and AM decay), reproduces the measured momenta of the $H^+ + D^+ + O^{2+}$ fragmentation channel. The NF-analysis is better suited

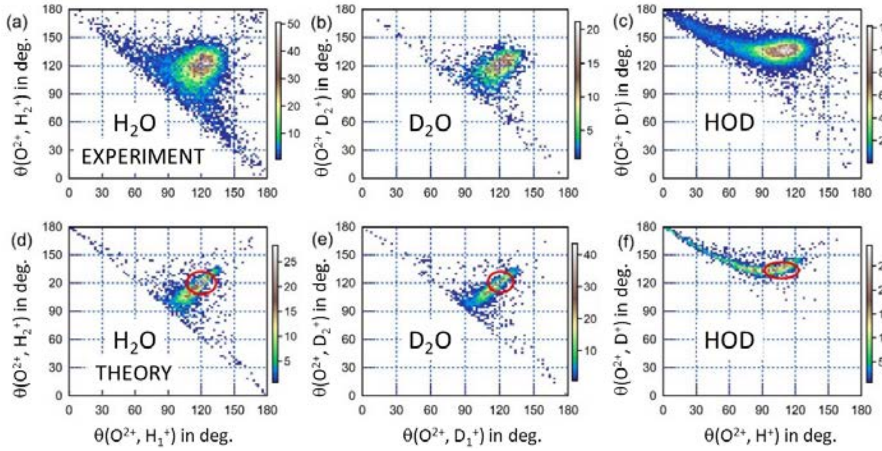

Fig. 1-2: Relative angles between the detected proton (deuteron) and oxygen momentum for different water isomers after two X-ray absorption and AM decay cycles. Top panels (a – c) depict the experimental results, and panels (d – f) represent the simulation. The red ovals in the simulation panels indicate the value ranges for the event of a Coulomb explosion from only the neutral ground-state configuration.

to reveal sequential dissociation processes than Dalitz or Newton plots, because the big mass difference of the O and H/D fragments degrades their resolution markedly. Yet, the NF-analysis failed to unequivocally replicate the experimental particle momentum distribution, which should show that the relative angle between the two dissociation axes of the assumed sequential dissociation is isotropic. The reason for the observed discrepancy lies in the core assumption of the NF-analysis, i.e., the requirement for clearly decoupled dissociation sequences in which the fragments of the two steps do not interact with each other and, hence, do not show any correlation. Any correlations between the fragments are lost when at least one rotational turn of the OD^{3+} intermediate takes place. This condition is apparently not fulfilled in this experiment as the OD^{3+} rotation takes, on average, several 100 fs and is thus markedly slower than the duration of the ionizing X-ray pulse (< 25 fs), which dissociated the OD^{3+} intermediate prematurely. Our advanced theoretical modelling (*ab initio* molecular dynamics simulations in combination with the XMOLECULE electronic structure toolkit) suggests that, instead, the dynamics is dominated by an immediate Coulomb explosion, which produces O^{2+}, H^+, and D^+. We also revealed that the two-step fragmentation processes, which generates O, H^+, and D^+ in the 1st ionization step, followed by a delayed photoionization and AM-decay of the neutral O fragment producing an O^{2+} dication, takes place less often. The sequential two-step fragmentation, yielding H^+ and OD^+ in the 1st step and $O^{2+} + D^+$ in the 2nd step, only contributes to a minor degree.

Future Plans: Understanding the various possible ionization mechanisms and dissociation dynamics of the water molecule, which represents a prototypical triatomic target system of fundamental importance, remains a challenge. As seen in our recent EuXFEL experiments, various ionization and fragmentation mechanisms can be at play, and several electronic states can be involved. Similar challenges exist even when narrow-band XUV and X-ray light sources, such as synchrotrons, are employed. ALS experiments recently enabled our state selective investigations of the valence photo double ionization (vPDI) of water. We were able to identify super-excited radical water cations as a source for long-lived excited oxygen fragments that can form a free radical and initiate secondary reactions (Iskandar et al. **2023**, *Phys. Chem. Chem. Phys.* 25, 21562). Moreover, we tracked the formation, rotational excitation, and kinetic energy release (KER) of dissociating transient OD^+ fragments in the sequential dissociation of water, resulting in the three-body fragmentation channel $D^+ + D^+ + O$ (Severt et al. **2022**, *Nat. Commun.* 13, 5146). In the next step we quantified the branching ratios to produce either $D^+ + D^+ + O$ or $D^+ + O^+ + D$ from the OD^+ intermediate in the sequential dissociation yielding the same low KER(OD^+) (Iskandar et al. **2023**, *J. Chem. Phys.* 159, 094301). Yet, as it turns out, this slow sequential dissociation processes generating $D^+ + O^+ + D$ heavily competes with other fragmentation mechanisms that yield higher KER(OD^+) and are slightly slower/faster than the direct/sequential fragmentation channels. We are currently tracking down the competition between two quasi-direct and one quasi-sequential dissociation scenarios with symmetric and asymmetric OD stretches near the FC region that involve spin orbit coupling state-selectively. Aided by multi-reference configuration-interaction calculations from the LBNL-AMOS theory team, the dissociation dynamics on the potential energy surfaces and their seams will be traced and their ultrafast time scales will be deduced.

Electron Correlation, Particle Migration, and Bond Formation in Polyatomics *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: Electron-electron correlation is still a fundamental challenge for quantum mechanical descriptions of electronic structure and dynamics. It is exquisitely present in the direct vPDI of atomic and molecular targets ejecting two electrons upon interaction with a single photon. Electron-electron correlation is expected to govern the emission patterns of the continuum electrons. For molecules, these observables require the measurement of relative electron-electron emission angles in the molecular frame with respect to the polarization vector of the incoming light, which are very hard to obtain. So far, this was only realized for atoms like He and diatomics like D_2. We now extracted highly differential state-selective cross sections for the direct double ionization of C_2H_4 producing 2 CH_2^+ + 2 e^- after vPDI with 40.5 eV. For the rare but clean case where mainly the S_2 dication state is populated, followed by a transition to S_1 via a conical intersection, we were able to determine recoil frame photoelectron angular distributions (RFPADs). They are governed by a combination of selection rules and Coulomb repulsion effects, as the emission direction of the reference electron changes with respect to the recoil axis of the symmetric breakup (see Fig. 1-3). The analysis in collaboration with the AMOS theory team and F. Yip (Cal-Maritime) is ongoing.

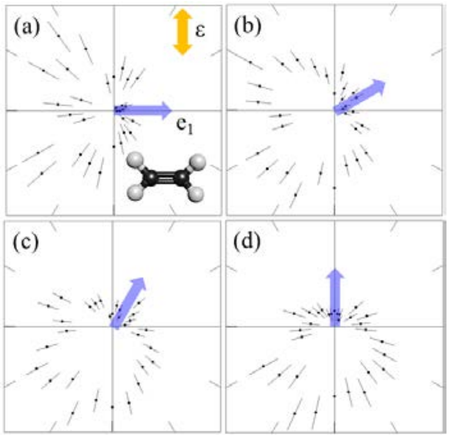

Fig. 1-3: Recoil frame photoelectron angular distributions for equal energy sharing between the two emitted electrons (0.5 ± 0.15) for the vPDI of C_2H_4 with 40.5eV, populating mainly the cation S_2 state. The recoil axis of the symmetric breakup (CH_2^+ + CH_2^+) is orientated horizontal. The polarization vector is vertical (±30°). The reference electron e_1 is emitted toward (a) 0° ± 30°, (b) 30° ± 30°, (c) 60° ± 30°, and (d) 90° ± 30°, as indicated by the purple arrows. Black dots and error bars show the angular distribution of the second electron e_2.

Future Plans: We are currently extending our investigations on state-selective vPDI mechanisms and particle correlations to more complex molecules and their photo-dissociation dynamics. We chose deuterated methanol CH_3OD and its isotopologue CD_3OH as a simple hydrocarbon molecule containing one hydroxyl and one methyl group, because this molecule is known to exhibit ultrafast dynamics such as rapid proton migration and hydrogen elimination as well as CH_3 umbrella vibrational mode excitation. From the twelve vPDI reaction channels we identified so far following 63 eV photon excitation, we started the investigation by comparing the 3-body breakups producing (I) H + CH_2^+ + OD^+ and (II) H^+ + CH_2^+ + OD in which the same fragments are generated but with different electronic charges. For these reaction channels we deduced the momenta of the neutral fragments from momentum conservation. The electron-ion energy correlation maps [see Fig. 1-4(a+d)] tell us that only a small subset of the CH_3OD^{2+} dication states that lead to reaction channel (I) may instead also lead to reaction channel (II). Moreover, channel (II) correlates to only one dissociation limit. This dissociation channel (II) seems to be mostly driven by direct vPDI, while reaction (I) shows mainly autoionization and some minor contributions from direct double ionization at play, as seen from the electron-electron energy correlation maps [islands and diagonals, respectively, in Fig. 1-4(b+e)]. The strongly correlated CH_2^+/H and H/OD^+ fragment pair momenta [see Fig. 1-4(c)] suggest a sequential dissociation to take place, which is starting with the OD^+ + CH_3* breakup, followed by an atomic or molecular autoionization producing $CH_3^* \rightarrow CH_2^+ + H$ in the 2nd step. The vPDI of channel (I) appears to initiate a direct fragmentation, which is supported by the diffuse fragment ion pair momenta of channel (II) [see Fig. 1-4(f)].

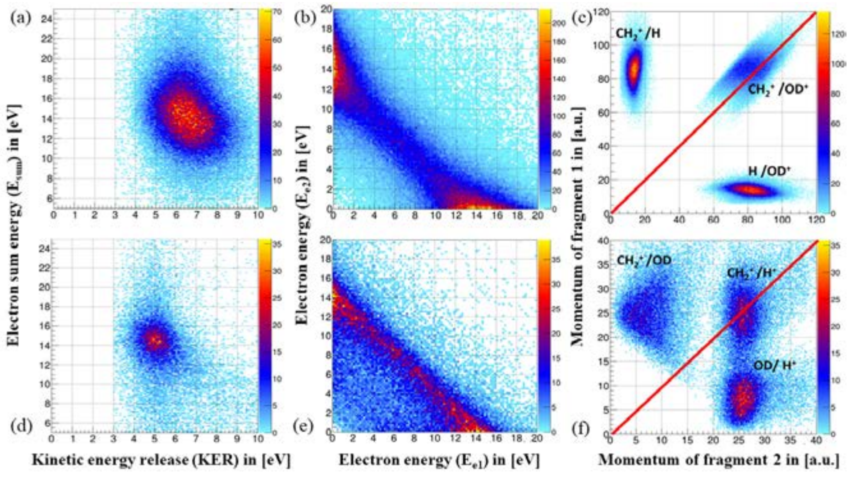

Fig. 1-4: vPDI of CH_3OD with single 63 eV synchrotron photons from the ALS. Top row: channel (I) H + OD^+ + CH_2^+. Bottom row: channel (II) H^+ + OD^+ + CH_2. (a + d) Electron-ion energy maps. The distributions for channels (I) and (II) peak at KER = 6.87 eV, E_{esum} = 14.5 eV and KER = 5.2 eV, E_{esum} = 14.37 eV, respectively. (b + e) Electron-electron energy correlation maps. (c + f) Fragment ion pair momenta maps, as indicated in each panel.

We also observe remarkable signatures of proton migration and autoionization for the 2-body fragmentation channels producing H^+, D^+, HD^+, HD_2^+, and H_2D^+. The latter three reaction pathways, together with the 3-body breakups generating HD^+, are currently being isolated and further analyzed to study hydrogen migration and bond formation via photoelectron angular distributions in the lab and molecular frame.

Hydrogen migration and bond formation also takes place in the vPDI of HCOOH and its isomer HCOOD, which we recently investigated at the ALS with 56 eV photons. The two processes of water formation, $HCOOH^{2+} \rightarrow H_2O^+ + CO^+$, and hydrogen formation, $HCOOH^{2+} \rightarrow H_2^+ + CO_2^+$, are especially interesting because of the complex isomerization and dissociation dynamics required to form the molecular ions. The water formation process is prominent in both isotopologues. Yet, the H_2^+ formation is very rare in HCOOH, and our online analysis reveals that HD creation is even less likely in HCOOD. Comparing electron-ion energy correlation maps and branching ratios will help us to identify favorable molecular structures and quantify favorable conditions for hydrogen migration and bond formation in methanol, formic acid, and their deuterated isotopologues.

Non-Adiabatic Dissociative Dynamics of Small Molecules Upon Two-Color Single Ionization

(Lucchese, McCurdy, Rescigno, Slaughter, Weber)

Recent Progress: Understanding electron-nuclei interactions in bound and continuum states is essential for the control of chemical transformations involving excited states and non-adiabatic transitions. In a 2-color VUV-pump – NIR-probe experiment of single H_2 and D_2 molecules at the ALS, absorption of VUV photons prepared vibrationally excited H_2^+ and D_2^+ molecular ions that are dissociated by the absorption of a single NIR photon. The ongoing very challenging analysis of this difficult experiment revealed that not all vibrational states of D_2^+, which were excited upon VUV absorption and identified via the photoelectron energy spectrum measured in coincidence with parent and fragment ions, were dissociated by the NIR pulse to produce D + D^+ + e^-. This was surprising because the transitions were energetically accessible and symmetry-allowed. At the same time, no such NIR dissociation suppression was found for H_2^+. The calculations of the LBNL-AMOS theory team reproduce the photoelectron spectra of the $D + D^+ + e^-$ and the $H + H^+ + e^-$ dissociation channels well when the transition probability from the neutral ground state to the dissociative continuum is given by the product of the VUV and NIR Franck-Condon factors. Evidently, our interrogation scheme is sensitive to the difference between the products of the continuum nuclear wave functions $H + H^+$ and $D + D^+$ and their respective bound H_2^+ and D_2^+ nuclear wave functions. Specifically, the missing $v = 16$ and 20 peaks in the D_2 experiment are due to minima in the Franck-Condon factors between the bound and continuum vibrational states of D_2^+.

We also found that some vibrational states that are classically forbidden to access geometries that can be dissociated with the 1.2 eV NIR pulse, contributed to the measured fragments. A careful inspection reveals that these geometries are not in reach by tunneling of the nuclear wave packet. Moreover, small time-dependent and time-independent asymmetries were detected in the body-fixed photoelectron emission patterns. The latter two findings are puzzling, given the low laser intensity of $\sim 1 \cdot 10^{11}$ W/cm^2, and we are in the process of analyzing the vibrational state selective dissociation in the energy and time domain in an ongoing collaboration with the LBNL-AMOS theory team. This work is carried out together with G. Laurent (Auburn University).

Future Plans: As seen above, probing the dissociation dynamics of electronically and vibrationally excited small molecular systems via reaction microscopy provides exquisitely detailed insight in the coupled electronic-nuclear dynamics and transition moments of molecular light-matter interaction. To fully exploit this sensitivity and push it into the time domain, pump-probe schemes, employing ultra-short light pulses, are needed. We have recently installed a new Yb-fiber based laser system producing 115 W, 600 fs, 1030 nm light pulses at 55 kHz repetition rate. After compression to ~45 fs using a krypton-filled, stretched hollow core fiber and a chirped mirror array, we achieve >1.5 mJ per pulse. Sum-frequency-generation will be used to convert 1030 nm to 515 nm and 343 nm, which will be focused into a gas cell to efficiently produce VUV photons by HHG. With this new setup, we expect to achieve intensities high enough to absorb two VUV photons (2 × 12 eV or 7.2 + 12 eV) in molecular gas jet targets (O_2, CO, N_2O, and NO_2), enabling the study of state-selective dissociation processes using electron-ion coincidence 3d-momentum imaging. VUV probe photons are necessary to follow the dissociation processes over long internuclear distances, while still producing photoelectrons that have higher energy than any background electrons. Building on our recent progress on atoms and mainly non-dissociative molecules (Larsen et al. **2020**, *Phys. Rev. A* 101, 061402(R); Larsen et al. **2020**, *J. Chem. Phys.* 153, 021103; Larsen et al. **2020**, *Phys. Rev. A* 102, 063118; Larsen et al. **2023**, *J. Chem. Phys.* 158, 024303), we now aim to measure time-resolved MFPADs and electron-ion Energy Correlation Maps (ECOMs) in order to investigate dissociation dynamics after excitation of Rydberg and (dark) molecular valence states.

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 metastable 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. We recently investigated the possible role of Feshbach and shape resonances in the breaking of a model peptide bond (Panelli et al., **2021**, *Phys. Rev. R* 3, 013082) and the simplest organic acid (Griffin et al., **2020**, *J. of Phys.: Conf. Series* 1412; Slaughter et al. **2020**, *Phys. Chem. Chem.*

Phys. 22, 13893) by electrons with low energy near, and even below, the lowest electronic transitions in formamide and formic acid, respectively.

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

Recent Progress: We investigated the influence of methylation on the dynamics of dissociative electron attachment to imidazoles and carboxylic acids. Imidazoles are found in many pharmaceuticals, and they are highly relevant to potential radiopharmaceutical applications through the production of reactive radicals and anions following electron attachment. We recently completed a study of dissociative attachment of resonant electrons to 1-methyl-5-nitroimidazole (1M5NI). We found that electrons with low energies (3-5 eV) interact resonantly with 1M5NI to produce NO_2^- with high abundance, as well as CN^-, CNO^- and heavier fragments remaining after the loss of OH, NO, and CH_3 from the parent anion. We detected no significant production of hydride (H^-) anions. The fragment kinetic energies are consistent with a three-body breakup or a stochastic mechanism in the dissociation of CN^-, whereby the available energy is broadly distributed into any of the available nuclear degrees of freedom, in addition to the CN^- kinetic energy. Clearly, significant motion or rearrangement of the C_3N_3 ring, the NO_2 or the CH_3 moieties is required for the release of CN^-. This contrasts with the dominant NO_2^- dissociation, which may only require stretching of the nitro C–N bond. This work, which was performed in collaboration with M. Centurion (U. Nebraska Lincoln) and G. Garcia (CSIC, Spain), was recently published in *Int. J. Mol. Sci*. (Lozano et al. **2023**, *Int. J. Mol. Sci*. 24, 12182) .

Future Plans: In acetic acid, (CH_3COOH), we will focus on the higher energy attachment resonance at 9.6 eV, which breaks a C-H bond to produce a hydride anion H^-. Fig. 1-5 shows a preliminary measurement of the angular distribution and corresponding momentum image for partially deuterated acetic acid (CH_3COOD). The two rings, each having discrete magnitude of the outgoing H^- fragment momentum, suggest distinct C-H break dynamics. The inner peak may be due to the loss of the deuteron by O-D break or an H-loss by C-H break, followed by a hydride dissociation producing H^- with low kinetic energy from the methyl side. This contrasts with the reaction channel yielding H^- with higher momentum (outer peak), which is most likely due to the H^- + H_2CCOOD two-body dissociation. The sharp structures in the angular distribution of the 2-body breakup channel are consistent with prompt dissociation, with little or no rotation of the dissociation axis following electron attachment. Thus, the angular distribution is expected to be a clear signature of the molecular-frame electron attachment probability. This work is ongoing, in collaboration with M. Centurion (University of Nebraska, Lincoln).

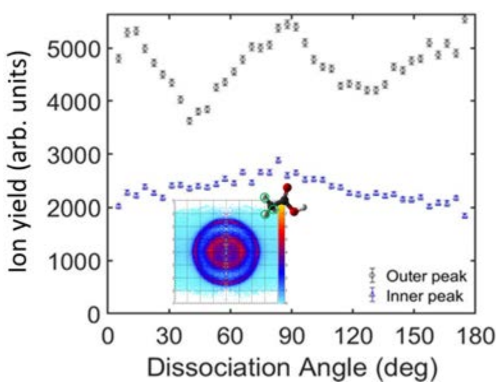

Fig. 1-5: Preliminary anion fragment measurements for electron attachment to deuterated acetic acid CH_3COOD, for H^- loss (C-H break) at 9.6 eV. The incident electron direction is up in the inset momentum image. The magnitude of the H^- momentum and angular distributions for the inner and outer peaks suggest distinct C-H break dynamics, possibly involving dissociation of neutral H or D and two-body breakup, respectively.

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, J. Qian, D. S. Slaughter, Th. Weber

Excited-State Dynamics Probed by Ultrafast Core-to-Valence Transient Absorption Spectroscopy *(Gessner, Head-Gordon, Leone, Neumark)*
In this activity, excited-state molecular dynamics are studied in real-time and from atomic site-specific perspectives using femtosecond time-resolved transient XUV absorption (TXA) spectroscopy. High-order harmonic generation (HHG) based experiments are complemented by high-level *ab initio* electronic structure and molecular dynamics (MD) calculations to disentangle the fundamental underpinnings of photoinduced molecular transformations.

Recent Progress: We performed a combined experimental-theoretical study of 268 nm UV light-induced dynamics in 2-iodothiophene (C_4H_3IS). The dynamics are experimentally monitored with a femtosecond XUV probe that measures iodine N-edge 4d core-to-valence transitions. Experiments are complemented by density functional theory calculations of both the pump-pulse induced valence excitations as well as the XUV probe-induced core-to-valence transitions. Possible intramolecular relaxation dynamics are investigated by *ab initio* molecular dynamics simulations.

The careful comparison of theory and experimental results allows to draw a comprehensive picture of the complex UV photochemistry and reveals a 2-step dissociation mechanism in the aromatic compound (Fig. 2-1). In contrast to the more intensely studied group of small haloalkanes, UV excitation in the aryl halide does not directly access a dissociative σ* state, but instead excitation to a bound ππ* state is identified as the predominant initial product of the molecule-light interaction. Perhaps counterintuitively, this excitation leads to an initial contraction of the C-I bond. This rearrangement allows the molecule to approach a conical intersection between the ππ* state and a πσ* state that is dissociative along the C-I coordinate, ultimately enabling C-I bond fission on the πσ* surface. A relatively narrow bond-length region along the C-I stretch coordinate between 230 and 280 pm is identified, where the transition between the parent molecule and the thienyl radical + iodine atom products becomes prominent in the XUV spectrum due to rapid localization of two singly occupied molecular orbitals on the two fragments. The findings have been published in Toulson et al. **2023**, *J. Chem. Phys.* 159, 034304.

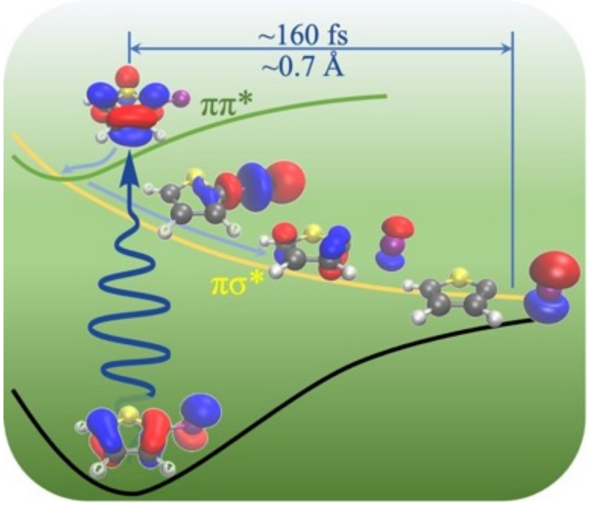

Fig. 2-1: Two-step dissociation mechanism revealed by a combined TXA/DFT experiment/theory study: UV-excitation of 2-iodothiophene with 268 nm radiation populates a bound ππ* state that leads to an initial contraction of the C-I bond. This allows the molecule to approach a conical intersection and access the dissociative πσ* state, leading to C-I bond fission (Toulson et al. 2023, *J. Chem. Phys.* 159, 034304).

Future Plans: Future transient inner-shell absorption studies at LBNL will reach the sulfur $L_{2,3}$-edge (~170 eV) and carbon K-edge (~285 eV). Gaining access to sulfur and carbon as local reporter atoms opens up a plethora of potential systems to study, including aromatic heteroatomic molecules. The assembly of an advanced HHG setup to reach these photon energies, consisting of a combination of a high-power optical parametric amplifier (OPA) and a high-pressure HHG cell is in an advanced stage.

UV-Induced Dissociation Dynamics of Bromoform Probed by Ultrafast Electron Diffraction

(Gessner, Leone, Neumark)

The UV photochemistry of bromoform has been the focus of numerous experimental and theoretical studies with the goal to gain quantitative insight into possible relaxation products and their underlying reaction pathways. Following a previous TXA study of 268 nm induced bromoform dissociation dynamics in our group (Toulson et al. **2019**, Struct. Dyn. 6, 054304), we are currently analyzing the results of a recent mega-electron-volt ultrafast electron diffraction (MeV-UED) experiment at SLAC National Accelerator Laboratory, probing the same dynamics using time dependent scattering patterns of relativistic femtosecond electron pulses.

***Recent Progress*:** In addition to a real-space analysis of the UED patterns after transformation from the momentum domain of the raw data, we have developed an alternative analysis technique that enables the determination of transient molecular structures directly in momentum space. The method circumvents some of the challenges associated with the finite detection range and cutoff toward low momentum transfer, which can potentially lead to artefacts in the real-space reconstruction. The combination of real- and momentum-space analyses provides a significantly higher level of confidence in the resulting trajectories than either technique on their own. Preliminary results indicate a bifurcation of relaxation channels including a fast (≤500 fs) direct dissociation to produce Br radicals and a comparably long lived (≥1.1 ps) structure consistent with theoretically predicted parent molecular isomers.

***Future Plans*:** We will further advance the new data analysis capability with the goal to determine, on a quantitative level, the branching ratio between the observed reaction channels and compare it to both experimentally determined and theoretically estimated yields of possible relaxation pathways.

Interfacial Energy- and Charge-Transfer Processes in Heterogeneous Light-Harvesting Systems Probed by Time-Resolved X-ray Photoelectron Spectroscopy

This effort focuses on the development and application of ultrafast time-resolved X-ray photoelectron spectroscopy (TRXPS) and time-correlation X-ray photoelectron spectroscopy (TCXPS) techniques to gain access to the transient electronic configurations and dynamic changes that drive interfacial charge transfer and photochemistry.

Impact of Water Environment on Interfacial Electron Dynamics in a Nanoplasmonic Photocatalyst *(Gessner, Neumark, Qian)*

Recent Progress: Combinations of metal nanoparticles and transition metal semiconductor substrates are among the most intensely studied hybrid light harvesting systems for photocatalytic applications. We previously demonstrated the exquisite sensitivity of picosecond TRXPS to transient interfacial electron-hole configurations in an archetypical model system for nanoplasmonic light harvesting, consisting of a nanoporous TiO_2 substrate sensitized with 20 nm diameter gold nanospheres (Borgwardt et al. *J. Phys. Chem. Lett.* **2020**, 11, 5476). The TRXPS data give quantitative access to the absolute amount of charge injected with sub-elementary charge sensitivity. During the past year, we managed to extend the studies to ambient pressure conditions in order to take the next step toward monitoring the atomic-scale electronic dynamics underlying chemical reactivity in solar light harvesting systems under conditions of photocatalytic activity. Fig. 2-2 shows (a) the basic concept and (b) first results of picosecond time-resolved ambient-pressure X-ray photoemission (TRAPXPS) measurements of charge injection and recombination dynamics in AuNP-sensitized TiO_2. The measurements were performed at BL 11.0.2 of the ALS. Transient shifts of the Au4f photolines as a function of pump-probe delay for (b) dry and (c) wet conditions at 60 mTorr water pressure demonstrate a significant impact of the water environment on the interfacial electron dynamics that form the basis for photocatalytic activity. The increase in amplitude of the transient shifts by a factor of ~3 and the increase in lifetime of the charge-separated state (i.e., longer signal decay times) in the wet compared to the dry sample indicate that conditions for photocatalytic activity of the interface improve substantially with the introduction of the reactant.

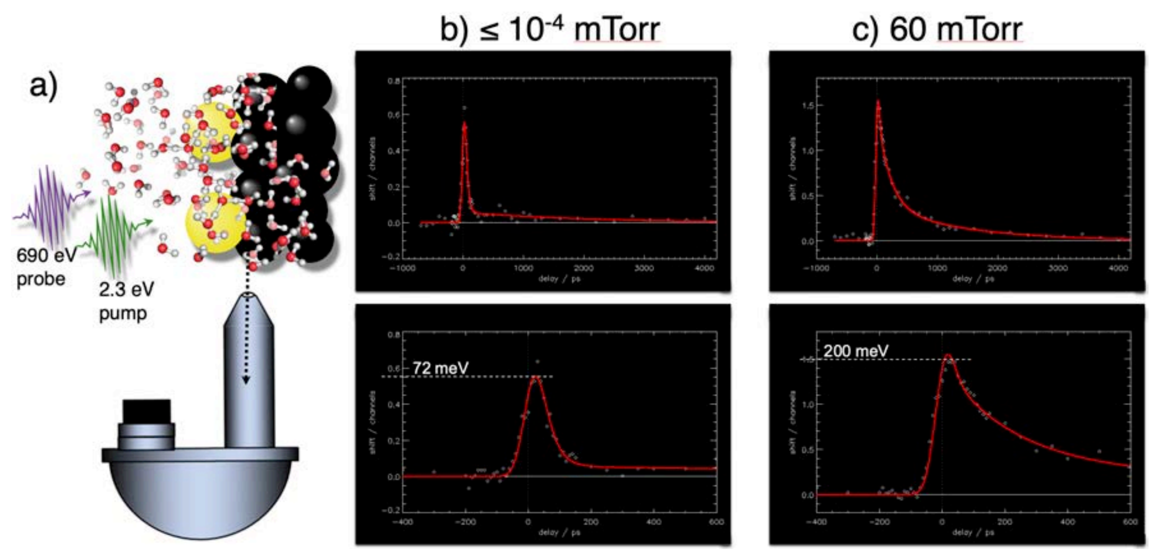

Fig. 2-2: a) Visible-pump / X-ray-probe picosecond time-resolved X-ray photoelectron spectroscopy has been extended to the near-ambient pressure regime for the first time, allowing the real-time probing of interfacial chemical dynamics under environmental conditions. b),c) Preliminary results from a study of photoinduced charge-transfer dynamics in gold nanoparticle sensitized TiO_2. Shown are time-dependent shifts of the Au4f photoline induced by the transient generation of interfacial electron-hole pairs for b) a dry and c) a wet interface. The stark differences between the effect amplitudes and dynamic trends in b) and c) illustrate a significant impact of water exposure on the dynamics of the charge-separated state, which forms the basis for enabling interfacial chemistry, such as solar hydrogen production.

Future Plans: We will perform a detailed analysis of the TRAPXPS measurements on the AuNP-TiO_2 system, performed during two recent ALS beamtimes, and aim to extend the studies toward systems that employ core-shell NPs as chromophores and electron donors. To elucidate the physics underlying the observed phenomena, we collaborate with the Qian group at LBNL and the Pascal group at UC San Diego, employing a combination of *ab initio* electronic structure and dynamics calculations with molecular dynamics-based simulations of the interfacial water coverage (see Subtask 3 and Qian's Early Career Research Program abstract).

Dynamics in Helium Nanodroplets

This effort focuses on a better understanding of fundamental dynamics in neutral ground state, excited state, and ionized helium nanodroplets. The relatively simple electronic structure of He atoms makes the droplets a popular testbed for understanding the emergence of collective electronic properties and dynamics from the atomic constituents of complex systems. Dynamics are probed at XFEL light sources, such as the Linac Coherent Light Source (LCLS) and the European XFEL (EuXFEL), employing combinations of femtosecond X-ray scattering and ion time-of-flight (TOF) mass spectrometry techniques.

Femtosecond X-ray Coherent Diffractive Imaging of Dynamics in Strong-Field Induced Nanoplasmas *(Gessner)*

Recent Progress: A EuXFEL proposal led by our group and submitted in collaboration with the groups of Andrey Vilesov (USC), Paul Scheier (U Innsbruck), Daniela Rupp (ETH Zürich) was awarded beamtime at the Small Quantum Systems (SQS) instrument. The experimental campaign, conducted in June 2023, followed up on our previous LCLS and EuXFEL based studies on imaging the early stages of strong-field induced nanoplasma formation (Bacellar et al. **2022**, *Phys. Rev. Lett.* 129, 073201) and of charge distributions in ionized droplets (Feinberg et al. **2022**, *Phys. Rev. Res.* 4, L022063), respectively. Pristine and Xe-doped neutral droplets, as well as positively and negatively charged droplets were exposed to near-infrared (NIR, λ=800 nm) pulses with intensities up to ~10^{15} W/cm^2. The induced dynamics were monitored by femtosecond X-ray (hν=1 keV) scattering patterns and ion TOF spectra, which were recorded in coincidence on a shot-by-shot basis. The data analysis is ongoing. While the original goal of the campaign to impose a qualitatively new level of control of nanoplasma seeding by few-electron doping was apparently not achieved, the experiments provided a trove of novel data to investigate nanoplasma formation and decay dynamics under a variety of conditions. Preliminary results also indicate that the experiment led to the discovery of a new, intrinsic femtosecond NIR/X-ray cross-correlation timing tool for cluster studies at XFELs. Fig. 2-3 shows the NIR/X-ray pump-probe time delay dependent yield of He$^+$ ions from pristine, neutral droplets containing ~10^9 atoms. NIR pulses arrive before (after) X-ray pulses for positive (negative) delays. The enhanced He$^+$ yield at negative delays is ascribed to an X-ray nanoplasma seeding effect, whereby interaction with X-ray pulses leads to moderately charged droplets (Saladrigas et al. **2021**, *Eur. Phys. J. Spec. Top.* 230, 4011) that contain quasi-free electrons to seed and amplify nanoplasma formation by the subsequent NIR pulse. The falling edge of the ion yield signal provides an intrinsic monitor for spatiotemporal NIR/X-ray overlap, time zero of the delay range, and the temporal resolution of the measurement. A fit of the trend indicates an approximate full width at half maximum (FWHM) of the temporal instrument response function of 40 fs, corresponding to a factor of ~3 improvement in temporal resolution over our previous study.

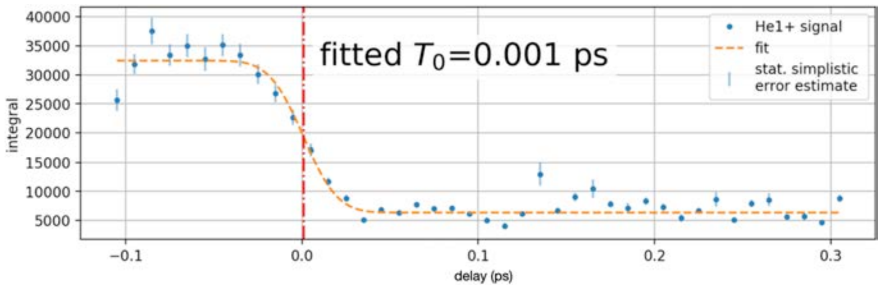

Fig. 2-3: NIR/X-ray pump-probe time-delay dependent He$^+$ ion yield, recorded in coincidence with X-ray scattering patterns, provides an intrinsic temporal cross-correlation tool for *in-situ* monitoring of the spatiotemporal overlap. See text for details.

Future Plans: We are currently classifying thousands of images recorded during the experimental campaign. This time-consuming initial step of the data analysis will be followed by a detailed investigation of femtosecond surface expansion and picosecond droplet/plasma disintegration dynamics, using reconstruction tools developed during previous campaigns.

XUV Ultrafast Transient Polarization Spectroscopy X-UTPS *(Slaughter, Weber)*

We recently established Ultrafast Transient Polarization Spectroscopy (UTPS) (Thurston et al. **2020**, *Rev. Sci. Instrum.* 91, 053101) as a four-wave mixing (FWM) scheme to probe both the real and imaginary parts of the 3$^{\text{rd}}$-order nonlinear response of excited electronic states in molecules. 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, e.g., access to dynamics near conical intersections, even if there is no change in the electronic binding energies. With a particular emphasis on larger molecules and liquids, 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. 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.

Both UTPS and X-UTPS probe the nonlinear response of a system using one excitation pulse and only two probe pulses, instead of three or more probe pulses in other FWM techniques employing, e.g., the BOXCARS geometry. Our recent UTPS experiments in the NIR regime have demonstrated the minimization of temporal and spectral instabilities with such a reduction in technical complexity. Optical Kerr Effect (OKE) phase-matching constrains the signals to be colinear with the probe pulse. While the signal and probe are colinear, the near infrared (NIR) Kerr gate pulse is noncolinear with the probe and signal, like the as-FWM approach in Subtask 1. However, in X-UTPS the FWM signals are separated from the XUV probe by polarization analysis via multilayer XUV mirror technologies.

Recent Progress: The extension of UTPS, which we previously demonstrated using NIR pulses (Thurston et al. **2020**, *J. Phys. Chem. A* 124, 2573), to the XUV demands very high XUV intensities, exceeding 10^{12} W/cm^2. In previous XUV pump-probe ionization studies of small molecules (e.g., Champenois et al. **2019**, *J. Chem. Phys.* 150, 114301) we have found that such intensities require very high XUV pulse energies exceeding 50 nJ per pulse before the XUV focusing mirror, accounting for the limited reflectivity of the latter. To achieve these high intensities, we have adapted the existing tabletop XUV beamline, which is driven by 15 mJ ultrashort (40 fs) NIR (780 nm) pulses in a 3 m focusing geometry, to achieve such high pulse energies by high harmonic generation (HHG) in a newly-designed windowless gas cell. We separate the XUV from the NIR fundamental using a grazing-incidence dichroic mirror and characterize the XUV spectrum using a variable line space grating, also reflecting the XUV at grazing incidence, and an MCP detector. Further characterization, as well as space and time overlap between the XUV and NIR pulses, is achieved using a velocity map imaging (VMI) photoelectron spectrometer, which is inserted and removed from the X-UTPS endstation without any significant impact on the vacuum configuration or upstream optics. The HH intensity (Fig. 2-4) is optimized by varying the gas type (typically argon or krypton), cell pressure, and gas cell path length, which ranges from 5 mm to 35 mm.

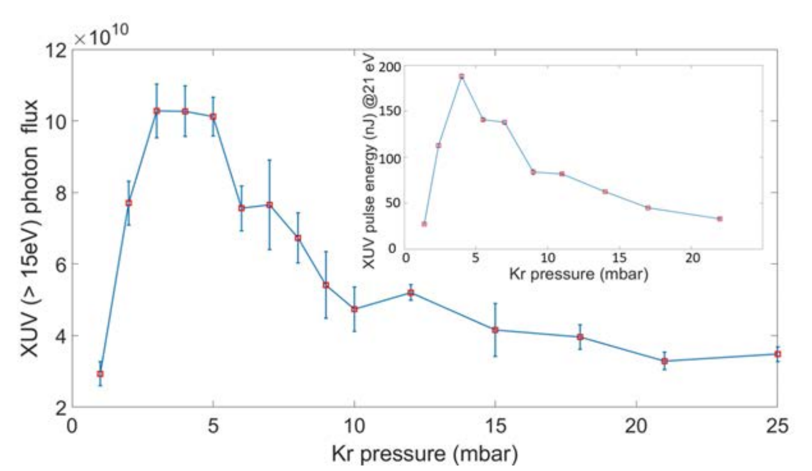

Fig. 2-4: Measured number of XUV photons per pulse and pulse energy at 21 eV photon energy (inset), as a function of the HHG cell pressure, for the present tabletop HHG beamline configuration. The absolute photon yield is determined from the typical quantum efficiency of the MCP detector for this XUV energy range.

Our recent efforts in the development of time-dependent nonlinear spectroscopy theory are performed in collaboration with Dr. Liang Tan (Molecular Foundry, LBNL). We have developed a new numerical method to simulate the time evolution of molecular systems in Liouville space, where we compute the time-dependent nonlinear polarization response of a model molecule to two optical pulses in the density matrix formalism. The polarization response of the molecule is computed by scanning the relative phases of the optical fields in real space to extract the specified frequency components. This approach also allows the time-dependence of both electronic populations and electronic coherences to be computed exactly for a model molecule having three or more electronic states. We compute the energy levels and transition dipole moments using the Multi-Configurational Self-Consistent Field (MCSCF) approach with the aug-cc-pCVDZ basis set. This provides a simple toolset to model a time-resolved 2-color FWM experiment and to understand the evolution of a gaseous or condensed phase molecular system in terms of electronic decay and dephasing rates. Nuclear dynamics are now also included by an electric field-dependent force function, currently implemented to describe librational motion of a rigid molecule in a solvent that is interacting with two pulses having a variable femtosecond delay. We have tested this low computational cost approach by comparison with experimental measurements of FWM for two NIR pulses and one 260 nm UV pulse in liquid nitrobenzene. We find good agreement between the electronic-librational dynamics model and the experiments (not shown here).

Future Plans: The first experiments that apply the new tabletop XUV configuration for XUV nonlinear spectroscopy are now in preparation. Optimization of the HHG spectrum is underway to determine the laser intensities, gas types, and gas pressures, to demonstrate the sensitivity of the new setup to XUV nonlinear signals, including OKE signals arising from XUV and NIR FWM in O_2. For this purpose, we apply the VMI module to characterize the XUV spectrum at the interaction region, as measured by photoelectron imaging of argon or simple molecules such as O_2 or N_2. We then aim to optimize the experiment to enhance nonlinear XUV signals, starting with photoionization by two XUV photons within a single pulse, followed by time-resolved photoelectron imaging experiments employing delayed XUV-pump and XUV-probe pulses. This will guide the X-UTPS experiments targeting the dissociation dynamics of excited electronic states in O_2 and CF_3I.

In case the XUV intensity in the present configuration is still insufficient to produce all-XUV time-resolved nonlinear photoelectron and optical signals, we have prepared the XUV beamline to accommodate a more efficient HHG scheme that is limited to lower XUV photon energies, where the XUV is produced by a 390 nm driving field (second harmonic of 780 nm, generated in a BBO crystal). Even after accounting for the limited efficiency of second harmonic generation, we have measured yields of 9.3, 15.5, and 21.7 eV XUV photons that are higher than the XUV yields generated with 800 nm pulses using similar long-focusing conditions (Larsen et al. **2023**, *J. Chem. Phys.* 158, 024303).

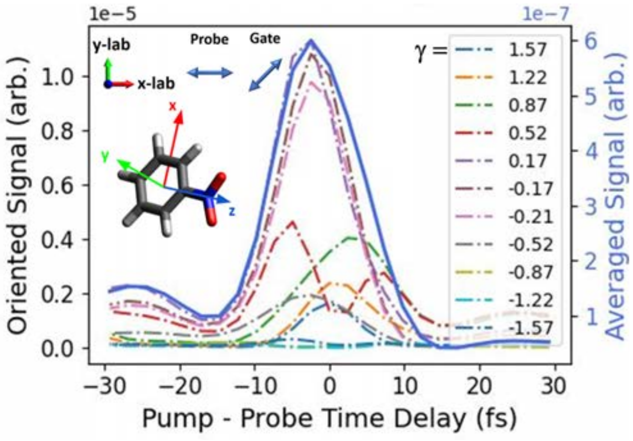

Fig. 2-5: Simulated 3rd-order polarization signal (Oriented Signal) computed in the molecular frame, for several different orientation angles γ (dash-dot curves), compared with the laboratory-frame Averaged Signal (blue solid curve), which is computed as an average of all molecular orientations. Inset: Schematic illustration of the laboratory-frame orientation of nitrobenzene corresponding to the extrinsic Euler angles $\alpha = 0.96$, $\beta = 0.1.27$ $\gamma = -0.21$, in the convention $R_{\text{mol-lab}} = Y(\alpha)Z(\beta)Y(\gamma)$.

To connect the molecular-frame numerical simulations to the laboratory frame that is accessible in the experiments, we will apply time-dependent perturbation theory, which we recently developed to compute the 3rd-order polarization in the laboratory frame. This approach employs orientation-averaging and local field corrections to simulate the third-order polarization and FWM signals in the laboratory frame, which is defined by the polarization of the optical pulses. By projecting the molecular-frame density matrix onto the laboratory-frame coordinates, it may be possible to retrieve the small set of molecular alignments that primarily contribute to the measured 3rd-order polarization signals (Fig. 2-5). This promises to guide molecular-frame simulations to reliably predict experimental signals at a significantly reduced cost compared with orientation-averaging.

Reaction Pathways in Few-Molecule Complexes

Investigating ionization mechanisms and dissociation dynamics of small molecular complexes and solvated biomolecules in the gas phase upon VUV or X-ray absorption is important for our understanding of the fundamental processes that underpin the destructive photochemistry of radiation damage in materials and cells within living organisms. This is a very challenging task, because the cluster targets are very dilute, and the electron and (virtual) photon transfer processes between the cluster components compete with the ionization and dissociation processes of the monomers. In this project, we apply reaction microscopy (a.k.a. COLTRIMS), which is well-established in Subtask 1 to gain highly differential insight into electron-electron correlation and electron-nuclei interaction. With this technique we are able to discern ionization mechanisms and reveal the state-selective coupled electronic and nuclear motion of the dissociation products via observables such as the electron-ion and the electron-electron energy-correlation maps, nuclear conformation maps (depicting the kinetic energy release as a function of the dissociation angle), and the recoil-frame photoelectron angular distributions (RFPADs).

Competition of Ionization Mechanisms and Dissociation Pathways After Valence Photo Double Ionization of Molecular Dimers *(Slaughter, Weber)*

Recent Progress: Interatomic/intermolecular Coulombic Decay (ICD) has proven to be a prominent and important ionization mechanism in small environments, such as weakly bound atomic and molecular clusters. Yet, in water dimers, for example, it competes with direct double ionization and autoionization when valence photo double ionization (vPDI) takes place. This became apparent in vPDI experiments at the ALS employing single photons with 60 eV, where we isolated two new 3-body breakup channels, namely $D_2O^+ + D^+ + OD^*$ and $D_2O^+ + D^* + OD^+$, which are not discussed in the literature. These two channels likely originate from Proton Transfer Mediated Charge Separation (PTMCS) after single ionization via a Zundel type intermediate (D_2O—D^+—OD^*). We investigated the $D_2O^+ + D^+ + OD^*$ channel in the energy domain (see Fig 2-6.). We find that mainly two water dimer dication states contribute, and mostly two dissociation limits are reached [see the main and faint islands in panel (a) and the 1st and 3rd contributions in panel (c)]. The electrons are mostly emitted simultaneously [as evident by the diagonal in panel (b)]. The contribution from autoionization can be separated by gating out the events along the diagonal in the electron-

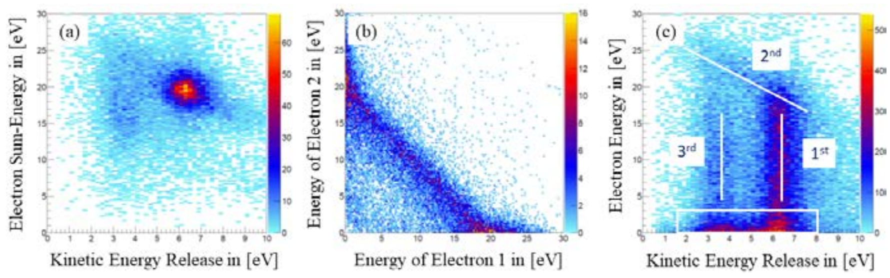

Fig. 2-6: vPDI of water dimers with 60 eV photons from the ALS resulting in the $D_2O^+ + D^+ + OD^*$ fragmentation channel. (a) Electron sum energy as a function of the kinetic energy release, showing mainly one prominent and one faint island corresponding to two dication states and two dissociation limits at play. (b) Electron-electron energy correlation map illustrating contributions from (mainly) direct double ionization and autoionization. (c) Electron-ion energy map showing three contributions: 1st and 3rd stem from the direct double ionization. The second contribution marks the correlated electrons of the autoionization events (upper diagonal and lower white box).

ion energy correlation map [“2^{nd}” contribution in panel (c)]. Investigating the fragmentation channel $D_2O^+ + D^+ + OD^*$ in terms of particle angular distributions might provide direct access to the geometry of the dimer. Further analysis will be performed in collaboration with the group of T. Orlando (Georgia Tech.).

Future Plans: We intend to investigate the relaxation/decay pathways and dynamics in pyrrole-d-water ($C_4H_4NCH_3$ - H_2O) dimers after Resonant Auger Intermolecular Coulombic Decay (RA-ICD) with highly differential insight [similar to our previous studies on N_2 and O_2 dimers (Trinter et al. **2014**, *Nature* 505, 664)]. The goal is to understand, with atomic site-specificity, the intermolecular relaxation mechanisms that are responsible for the first steps in radiation damage of biomolecules, and to determine their relative contributions. Specifically, the competition between ICD and electron transfer mediated decay (ETMD), and the influence of PTMCS in such complex dimers after resonantly driving Auger-Meitner (AM) decay from an initial O(1s) excitation in the water molecule site will be studied using reaction microscopy. We aim to measure the electron-ion energy correlations as well as the lab and recoil frame electron angular distributions. These key observables will allow us to identify the electronic states and ionization mechanisms at play. ADC(2) level calculations from our collaborator L. Cederbaum (U. Heidelberg) predict the electron energy distributions of the competing ICD, ETMD, and AM processes that will be produced after creating the inner-shell vacancies in the RA process. These signatures will form islands in the 2D electron-ion energy correlation maps and enable us to isolate the contributions for further analysis in terms of branching ratios and electron emission angles with respect to the polarization and the recoil frame of the dissociating dimer. Two photon energies will be used as control parameters in order to track the different outcomes and electronic states at play. The project will be carried out in collaboration with T. Orlando (Georgia Tech.).

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

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

Simultaneous Treatment of Electronic and Nuclear Motion in Pump and Ionizing Probe Experiments *(Lucchese, McCurdy, Rescigno)*

To reliably describe ultrafast pump and ionizing probe experiments it is necessary to simultaneously treat nuclear motion and the correlated electron dynamics of photoionization. To predict and interpret the results of such experiments requires a simultaneous treatment of photoionization and nuclear motion, which can be accomplished if all the transition amplitudes between relevant states of the molecule and the photoionization amplitudes of all of those states are known at all the geometries of the target molecule that can occur in the dynamics during the pump/probe sequence of pulses. We have developed a method that can treat electron dynamics and one vibrational degree of freedom, and we are proposing a method to extend this to multiple vibrational dimensions.

Recent Progress: In a recent study (Bello et al. **2023**, *Phys. Rev. A* 108, 033104) we employed the methods we developed earlier for diatomics (Bello et al. **2021**, *Phys. Rev. Res.* 3, 013228). The time-dependent wave function is expanded in an approximately complete set of Born-Oppenheimer product basis functions of electronic and nuclear vibrational states -- including both the electronic (photoionization) continuum states and nuclear (dissociation) continuum states. The electronic continuum states at each internuclear distance are constructed in Schwinger variational calculations based on a numerical representation of the scattering states, using a close-coupling expansion between correlated ionic states.

We applied these methods to pump and ionizing probe processes in LiH with perpendicular polarization that probe the dynamics on the lower pπ and dπ Rydberg states of the molecule, as shown in Fig. 3-1. The electron kinetic energy and nuclear kinetic energy release, taken together, reveal the multiple pathways dissociative ionization that will exist in general because the photon energy of a pulse that can excite Rydberg states will frequently be able to ionize it as well. However, coincidence measurements of those two quantities will generally be necessary to reveal wave packet motion on the intermediate dissociative Rydberg states as a function of time delay. Rydberg states parallel the ion states to which they converge so as shown in Fig. 3-1, the electron kinetic distributions viewed alone are essentially constant as functions of time delay.

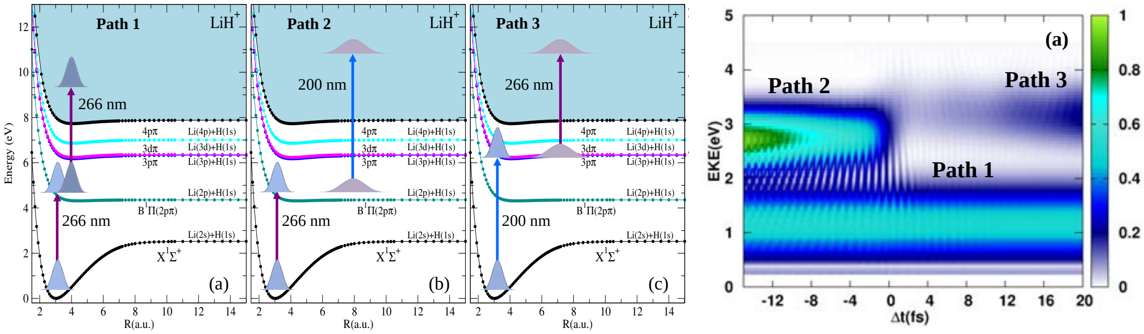

Fig. 3-1: Left panels: three pump and probe paths to the dissociative ionization continuum of LiH^+ for 5 fs pulses at 266 nm and 200 nm. Right panel: predicted electron kinetic energy distributions as a function of time delay.

Future Plans: Even in single-pulse two-photon ionization, as in the LBNL AMOS group's recent study of O_2 (Larsen et al. **2023**, *J. Chem. Phys.* 158, 024303), the nuclei move during the ionization process and the photoelectron distributions record that motion. We are applying these methods to fully describe this experiment and explore the dependence of the photoelectron spectrum and angular dependence on pulse duration. These calculations will employ a new variant of our methods that makes use of the Multiconfiguration Time-Dependent Hartree method (Beck et al. **2000**, *Phys. Reports* 321, 1) to propagate the nuclear wave packets coupled to the ionization continuum. With this variant we plan next to attack a pump and ionizing probe problem in water in full dimension.

Two-Electron Differential Cross Sections for Double Photoionization of Molecules by One Photon *(Lucchese, McCurdy, Rescigno)*

Single-photon double ionization of molecules is a process driven by electron correlation and is particularly sensitive to correlation in the initial state of the neutral molecule. We have studied such double ionization processes of atoms and diatomic molecules. We are currently developing methods that can be applied to non-linear molecules for which experimental data has been obtained in Subtask 1.

Recent Progress: In collaboration with F. Yip (Cal State Maritime, LBNL BLUFF) we have finished a study of the dependence of the double photoionization on initial state correlation of Li_2 by examining the convergence of the cross sections with respect to its natural orbital expansion and submitted a manuscript to the *Physical Review A*. Surprisingly, while in the case of H_2 many terms are required in this expansion to produce even the qualitative shape of the differential cross sections, it converges with very few terms for Li_2, despite its long 5 Bohr bond distance and much stronger left-right correlation.

Future Plans: Also, in collaboration with F. Yip, we are finishing an analysis of the effect of initial state correlation in the case of LiH. In collaboration with Roger Bello, a postdoc in our group until last May and now at the Autonomous University of Madrid, we will report new method developments and complete the TDCS calculations for double ionization of water to produce the three states in which two electrons are removed from one valence orbital.

Double Photoionization of D_2O by One Photon *(Lucchese, McCurdy, Rescigno)*
Experimental studies on double ionization of molecular systems necessarily involve the breakup of the doubly ionized molecules. Molecular frame differential cross section for the photoelectrons, are then obtained using angle resolved coincidence measurements of the emitted photoelectrons and the heavy fragments of the doubly ionized molecules. To connect these measurements to the initial molecular frame quantities and thus to the computed two-electron differential cross sections, one must often know the detailed mechanism of the fragmentation. We have thus studied the dynamics of the fragmentation of doubly ionized molecules.

Recent Progress: Our analysis of the single photon double ionization of D_2O leading to a rare but measurable 3-body breakup into $O^+ + D + D^+$ in the ALS experiment led by Th. Weber is nearing completion. The O^+ ion can be produced by either direct or autoionization processes. In collaboration with A. E. Orel (UC Davis), we found that the direct process is dominated by a sequential mechanism that first produces OD^+ (a^1D, b^1S^+) + D^+; the transient OD^+ then dissociates to $O^+ + D$ through a combination of spin-orbit and non-adiabatic charge transfer transitions. Solving a three-channel time-dependent Schrödinger equation with appropriate off-diagonal spin-orbit or non-adiabatic terms verified the mechanism and reproduced the general trends of the measured relative transition rates (see Fig. 3-2). This work was published in (Iskandar et al. **2023**, *J. Chem. Phys.* 159, 094301).

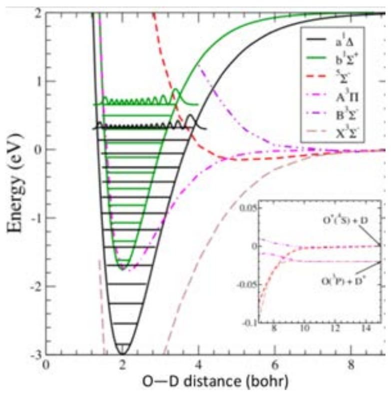

Fig. 3-2: Selected states of OD^+. Spin-orbit transitions from the a and b singlets populate the A^3P near its dissociation limit. Coupling between A, X and B states can result in O^+ production.

For the indirect (autoionization) process, we found that absorption of a single photon with energy well above the double IP can produce a dissociative super-excited mono-cation of D_2O^+ which can decay either directly ($D_2O^+ \rightarrow D + D^+ + O^*$) or sequentially ($D_2O^+ \rightarrow OD^* + D^+ \rightarrow O^* + D + D^+$), followed by autoionization of O^* at large distance. This work has been published in (Iskandar et al. **2023**, *Phys. Chem. Chem. Phys.* 25, 21562).

Time Delay in Molecular Photoemission (*Lucchese*, *McCurdy, Rescigno*)
Measurement of attosecond time delays in photoionization has become a well-established probe of the interaction of the emitted electron with the residual ion. Observations of the delay, $\tau = \hbar \frac{\partial}{\partial E} \arg \left\langle \Phi_k^{(-)} \middle| \sum_i \epsilon \cdot r_i \middle| \Phi_0 \right\rangle$, measure the energy derivative of the relative phase of the photoionization amplitude and can reveal signatures of resonances and their interference with background scattering in the body frame. The energy derivative in this definition implies that this quantity can go beyond the fixed-energy quantities, such as the total cross sections, and molecular frame photoelectron angular distribution, to consider how those quantities change as a function of energy. Additionally, understanding the energy dependence of the phase of the transition matrix element is also key to understanding the shape and position of the photoelectron wave packets that are formed when a system is ionized by an attosecond light pulse.

Recent Progress: In collaboration with the group of H.-J. Wörner (ETH Zurich), we studied photoionization time delays in photoionization of Kr_2 dimers (Heck et al. **2022**, *Phys. Rev. Lett.* 129, 133002). Both the effects of multiple scattering and coherent emission from two centers are seen in the measured and computed time delays. An additional collaboration with Wörner's group was a study on the time delays in the vibrationally resolved photoionization of O_2 leading to the $X\ ^2\Pi_g$ ground state of the O_2^+ ion (Submitted for publication *Phys. Rev. Lett.*). In this system, there was sensitivity of the time delays to the bond length. This sensitivity was found to be due to the effects of inter-channel coupling to a shape resonance in the $b^4\Sigma_g^-$ ionization channel.

Future Plans: We have completed an initial study of time delay in core-level molecular photodetachment, which reveals in detail the interaction of the photoelectron with the residual molecule at low energies that are typically obscured by Coulomb scattering in photoionization of neutral targets. We are focusing on a comparison between C_2^-, where previous theory and experiment (Douguet et al. **2020**, *Phys. Rev. A* 101, 033411) have confirmed the presence of narrow shape resonances in four channels close to threshold, and CN^-, where the residual neutral is polar and has K-edges that are well separated. The comparison shows some similarities due to shape resonances as well as striking differences due to dipole effects in CN^- that are only revealed in the time delay (see Fig. 3-3). The results of this study, done in collaboration with C. Trevisan (Cal State Maritime, LBNL BLUFF), are being prepared for publication. This work will be extended to small polyatomic anions in future studies.

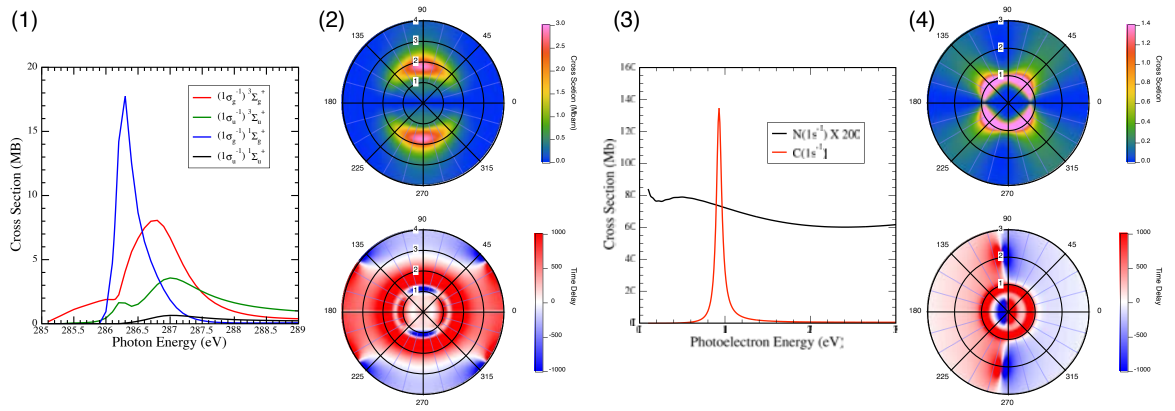

Fig. 3-3: From Left to right: (1) total C_2^- detachment cross sections in four channels, labeled by residual core-neutral state; (2) cross sections and time delays for C_2^- in $^3\Sigma_g^+$ channel for perpendicular photon polarization as a function of photoelectron energy and angle; (3) total CN^- detachment cross sections for C(1s) and N(1s) removal; (4) as in (2), for C(1s) ionization.

Development of Grid-based Electron Polyatomic Molecule Collision Code *(Lucchese, McCurdy)*

The studies proposed above, on the simultaneous treatment of electronic and nuclear motion and on the photoemission time delays, are based on the ability to compute one-photon ionization amplitudes for molecular systems. Our current codes that we use to study such processes have limitations on the types of systems and processes to which they can be applied. One suite of codes, the basis-set complex Kohn code, can be applied to general molecular systems as long as the kinetic energy of the continuum electron is not too high and the molecule is not too large. We also have grid-based methods which are currently limited either to linear molecular systems, or to rather simple single-channel calculations on small to medium-sized polyatomic molecules. Such grid-based methods are not limited to low kinetic energies and can thus study processes such as resonant Auger ionization. We have thus begun a development project to compute electron scattering dynamics on larger molecules based on grids and with the same multichannel capabilities of the basis-set complex Kohn method. This new code will be referred to as the ePolyGrid code.

Recent Progress: We have continued the development of the overset grid program ePolyGrid by including a more efficient method for partitioning functions which have discontinuities at nuclear centers that are not at the origin of the numerical grid used to represent the functions. This approach is based on multiple overlapping spherical grids that are located at each nuclear center. With such a representation, which contains redundancies, one must partition a function into contributions on the central grid, which encompasses the whole molecular system, and the sub-grids around each center. Previously, this partitioning was accomplished using switching functions (Greenman et al. **2017**, *Phys. Rev. A* 96, 052706). The switching function approach worked but was limited by the need to represent the hole created in the central grid in the region of each sub-grid.

We have begun to implement an alternative approach for partitioning functions on the central grids and sub-grids. In this method, a function on the central grid will be replaced in the region of a sub-grid by a smooth low-order polynomial, which can be easily expanded about the origin of the central grid. The cusp behavior of a function will then be represented on the sub-grid. In Fig. 3-4 we show the partitioning applied to the $4a_1$ orbital of O_3, with the cusp behavior on the two terminal O atoms only present on the sub-grid with the remaining function on the central grid being smoother and easily represented by the central grid centered on the central O atom. This partitioning should allow for a much more compact representation of the functions used in the scattering code and thus be more efficient in the computation of the scattering quantities of interest.

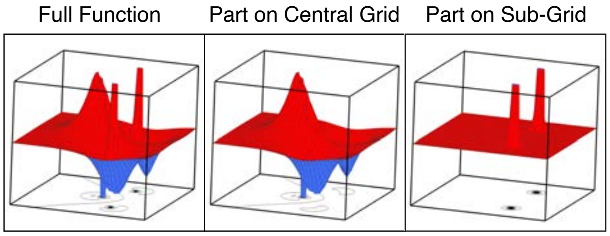

Fig. 3-4: Illustration of the grid partitioning method applied to the $4a_1$ orbital of O_3.

Future Plans: We expect to complete the coding for this approach for one-channel calculations in the near term and will then extend this approach to multichannel calculations needed to treat problems of interest discussed in other parts of Subtask 3 and in Subtask 1.

Unraveling the Femtosecond Jahn-Teller Dynamics of CH_4^+ by Orbital-Optimized DFT Calculations *(Head-Gordon, Leone, Neumark)*

Fig. 3-5: Schematic showing pump-induced dynamics in CH_4^+ and the x-ray probe of those dynamics which is measured and simulated.

Recent Progress: Theoretical calculations (Head-Gordon, under AMOS support), and ultrafast transient XAS experiments (Leone, Neumark, under separate GPCP support) have been used to study CH_4^+ prepared by 800 nm strong-field ionization (Ridente et al. **2023**, *Science* 380, 713). The TrXAS calculations were used to interpret time-resolved measurements at the carbon K-edge (280–300 eV). Comparison of experiment to X-ray spectra computed by orbital-optimized density functional theory (OO-DFT) (Hait et al. **2021**, *J. Phys. Chem. Lett.* 12, 4517), indicates that after ionization, CH_4^+ undergoes symmetry breaking driven by Jahn–Teller distortion away from the initial tetrahedral structure (T_d) within ~10 fs (see Fig. 3-5 for a schematic of the process). This yields direct insight into the energy flow from electronic to vibrational degrees of freedom, and detailed analysis of the simulations shows that oscillations seen in the simulated and experimental signals (Fig. 3-6) at longer times are associated with a 1200 cm^{-1} scissoring mode that closes down one HCH bond angle by more than a factor of two (Fig. 3-5), and at the same time opens up other HCH angles to be considerably larger than tetrahedral. The quality of the OO-DFT calculations, as well as the adequacy of the *ab initio* dynamics simulations that provide the structures for the XAS calculations is evident in the excellent agreement between simulated and experimental signals. The pronounced blue shift in the signal can be understood in terms of a change in SOMO character to take on additional p character as the small HCH bond angle makes mixing with the CH antibonding orbitals energetically unfavorable.

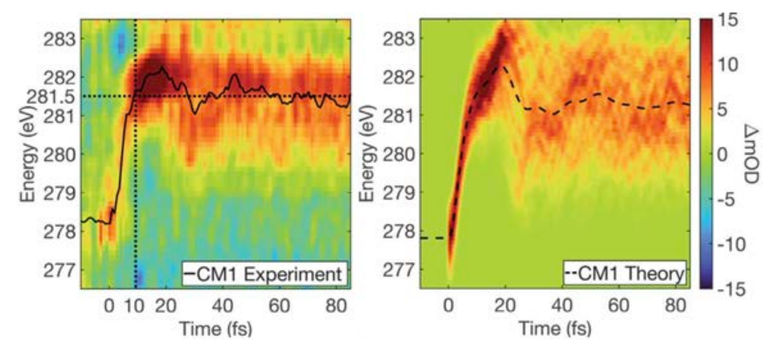

Fig. 3-6: Comparison between simulated TrXAS spectrum (right) associated with the C(1s→ SOMO) core excitation as a function of time (right) and the measured spectrum (left).

Future Plans: The excellent agreement between simulations and experiments suggests that a range of other experiments, where assignments are potentially ambiguous based on experiments alone, can benefit from computations using the OO-DFT approach (and related methods being developed by the Head-Gordon group). Three other joint studies have been published this year. Several more such collaborations are underway/planned between Head-Gordon group and partners including Gessner, Leone and Neumark, and Ramasheshaʼs group at Sandia.

Electron-Affinity TDDFT (EA-TDDFT) (*Head-Gordon*)

Recent Progress: Recently, the Head-Gordon group has reported (Carter-Fenk & Head-Gordon, **2022**, *J. Phys. Chem. Lett.* 13, 9664) a new development that provides a very promising alternative strategy for resolving the limitations of standard TDDFT for core excited states: namely the lack of particle−hole attraction and orbital relaxation that lead to extreme errors in the prediction of K-edge X-ray absorption spectra (XAS). They overcome these problems by deriving a linear-response formalism that uses optimized orbitals of the $(n-1)$-electron system as the reference, building orbital relaxation and a proper hole into the initial density. This approach is therefore fundamentally different than simply using the ion orbitals to perform TDDFT (which does not correct the particle-hole self-interaction error and thus typically increases the already large errors obtained using TDDFT with ground state orbitals. By contrast, the new EA-

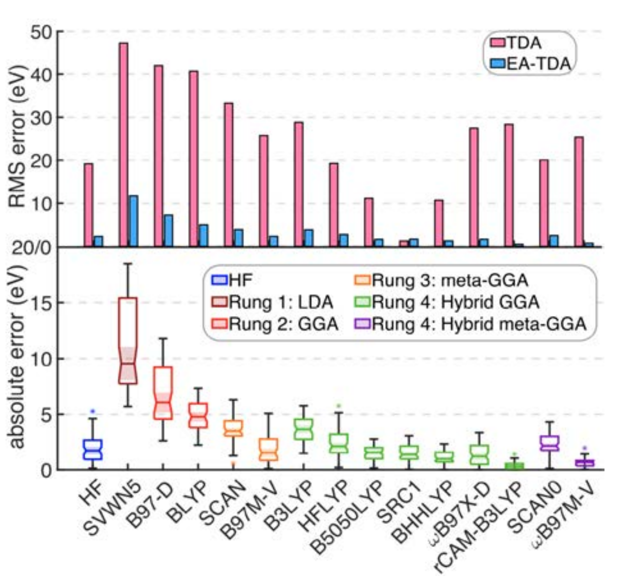

Fig. 3-7: Upper panel shows errors in standard TDDFT vs the new EA-TDDFT method; both in the Tamm-Dancoff approximation (TDA) for 65 K-edge transitions against experiment for 15 functionals. The lower panel shows EA-TDA error statistics: the shaded region is the 95% confidence interval for each functional; the horizontal line at each notch center is the median absolute error.

TDDFT approach is an exact generalization of the venerable static-exchange approximation from wavefunction theory to DFT, which ameliorates the particle−hole interaction error associated with the adiabatic approximation and reduces errors in TDDFT XAS by 1-2 orders of magnitude. With a statistical performance of just 0.5 eV root-mean-square error (for the best performing functional tested) and the same computational scaling as TDDFT under the core−valence separation approximation, it seems possible that EA-TDDFT will be of great utility in XAS calculations of large systems. Fig. 3-7. shows the dramatic improvement that EA-TDDFT yields relative to standard TDDFT. While the accuracy of EA-TDDFT does not exceed that of OO-DFT (it appears comparable, although different functionals are optimal for each approach), EA-TDDFT has the advantage of delivering all relevant core-excited states in a single calculation, rather than requiring state-specific optimization.

Future Plans: It is clearly very desirable to extend EA-TDDFT from core excitations in closed shell molecules in their ground states to include core excitations in open shell molecules. Core excitations in radicals will be the next target, and core excitations in valence-excited states of closed shell molecules will also be of great interest.

Electron-Affinity TDDFT (EA-TDDFT) for the Condensed Phase (*Head-Gordon*)

Recent Progress: Immediately building on the advance represented by EA-TDDFT, the Head-Gordon group has reported condensed phase simulations (Carter-Fenk & Head-Gordon, **2022**, *Phys. Chem. Chem. Phys.* 24, 26170) using this new methodology. In applications to X-ray absorption spectroscopy (XAS), simple methods like CIS and TDDFT that codify only single excitations into the wave function are prone to catastrophic errors in main-edge and post-edge features whose shapes act as a crucial fingerprint in structural analyses of liquids. They showed that these errors manifest primarily due to a lack of orbital relaxation in conventional linear-response theories and that core-ionized references, like those of EA-TDDFT, can eliminate the errors in the spectral profile, even in the highest-energy parts of the post-edge. Crucially, they find that single excitations atop core-ionized references are sufficient to elucidate liquid-phase XAS spectra with semi-quantitative accuracy. The results shown in Fig. 3-8 for XAS of aqueous ammonia illustrate the qualitative improvement that is obtained by using EA-TDDFT (or even EA-CIS) relative to direct use of conventional TDDFT (or CIS), even after shifting to align the pre-edge feature as well as possible. These results, as well as similar ones reported for liquid water and aqueous ammonium ion, open the door for methods like electron-affinity CIS/TDDFT to be used as efficient alternatives to higher-order wave function approaches.

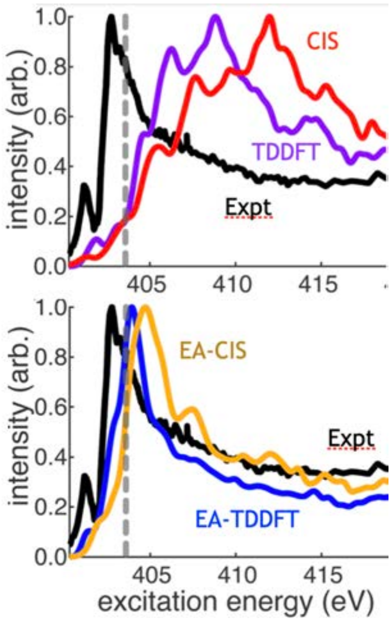

Fig. 3-8: Simulations (colors) versus experiment for XAS spectrum of aqueous ammonia. Use of ion orbitals via EA-TDDFT or EA-CIS (lower panel) greatly improves over use of neutral orbitals (upper panel), even after alignment.

Future Plans: These results reinforce the fact that EA-TDDFT is sufficiently accurate, efficient, and straight-forward to apply to permit applications to a range of complex XAS simulations. Further developments will be needed to go beyond K edges to L and M edges via inclusion of vector relativistic effects.

Elucidating the Earliest Electron Dynamics Underlying Interfacial Charge Transfer Processes

(Qian)

A fundamental understanding of ultrafast charge transfer processes at the heterojunction between two materials (i.e., the donor and the acceptor) is essential to exploit the full potential of novel light harvesting schemes. Take the experimentally studied gold nanoparticle (AuNP)/TiO_2 heterojunctions (Subtask 2) as a prominent example, the complete interfacial charge transfer processes entail three stages of events, that are of vastly different timescales:

- Excited by the continuous visible light or by a laser pulse of ~532 nm, the gold nanoparticles (AuNP) will display an attosecond timescale optical response.
- Subsequently, the gold plasmon will dephase into hot electrons and holes that can be transferred across the metal-semiconductor interfaces for promising photocatalytic and photovoltaic applications. This event is on the order of sub-100 femtosecond timescale.
- The separated holes and electrons will eventually recombine on a timescale of picoseconds to nanoseconds.

All three stages of events (optical response, charge injection, and charge recombination) are of fundamental importance and remain difficult to observe and understand by experiments alone. Our LBNL AMOS core program activities focus on a time-resolved *ab initio* understanding of the earliest attosecond to sub-100 femtosecond dynamics underlying interfacial charge transfer processes. The longer picosecond to nanosecond charge recombination dynamics will be tackled in a separate, yet synergistic Early Career program (see separate Early Career abstract). For validation, we will apply computational XPS modules developed in-house to compare with the time-resolved X-ray photoemission spectroscopy (TRXPS) and time-resolved ambient pressure X-ray photoemission spectroscopy (TRAPXPS) experiments described in Subtask 2.

Recent Progress: One of the pioneering theoretical works (Long et al. **2014**, *J. Am. Chem. Soc.* 136, 4343) employed single-particle based, linear-response time domain density functional theory (LR-TDDFT) with nonadiabatic molecular dynamics (NAMD) to investigate the nonequilibrium, plasmon-driven electron dynamics at the AuNP/TiO_2 semiconductor interface. For AuNP sizes of 20 atoms, the authors concluded that an electron would appear inside TiO_2 instantaneously upon photoexcitation with a high probability of ~50%. The remaining 50% follow the more conventional electron injection picture, where an electron-hole separated state described by a hot electron distribution will be first created on the AuNP, and then the electron will move into the TiO_2 substrate on a sub-100 fs timescale. The theoretically predicted high efficiencies are impressive and variants of the direct injection mechanism have also been proposed based on experimental work (Wu et al. **2015**, *Science* 349, 632). However, the reliability of the NAMD result heavily depends on an accurate prediction of the distribution of excited states prepared by the light, which is a function of both the excited states method that one employs, and the computational setup of the nanoparticles (size, shape, periodicity) used in the simulation. Thus, to gain a comprehensive understanding of the charge transfer process, it is important to investigate the details of the optical coupling between the photo-active material and the light via *ab initio* calculations.

Identification of the most stable structure(s) of a system is a prerequisite for the calculation of any of its properties from first principles. We made strides in this direction by carefully evaluating which input atomic structures are the most representative to study. We began with the thermodynamically most stable anatase TiO_2 (101) surface with a surface energy of 0.61 J/m^2 (Martsinovich et al. **2012**, *Phys. Chem. Chem. Phys.* 14, 13392; Zhang et al. **2015**, *J. Phys. Chem. C* 119, 6094) as our basis. We then sampled the Wulff shape (Barmparis et al. **2015**, *Beilstein J. Nanotechnol.* 6, 361) Au clusters of 19, 43, 79, 135, 201, and 297 atoms in size until a work function convergence is achieved at the Au_{135} cluster. The convergence results are summarized in Fig. 3-9a. Based on these results, it would be most ideal to combine the Au_{135} cluster (or larger) with the TiO_2 (101) surface as the computational proxy of the nanoparticle-semiconductor heterojunction. However, restrictions of the conventional plane-wave based DFT require a compromise, leading to a unit cell size of ~400 atoms (which is considered already massive and computationally challenging!). We note that innovative approaches to enable larger scale DFT calculations are developed within Qian's Early Career Research Program, described in a separate abstract.

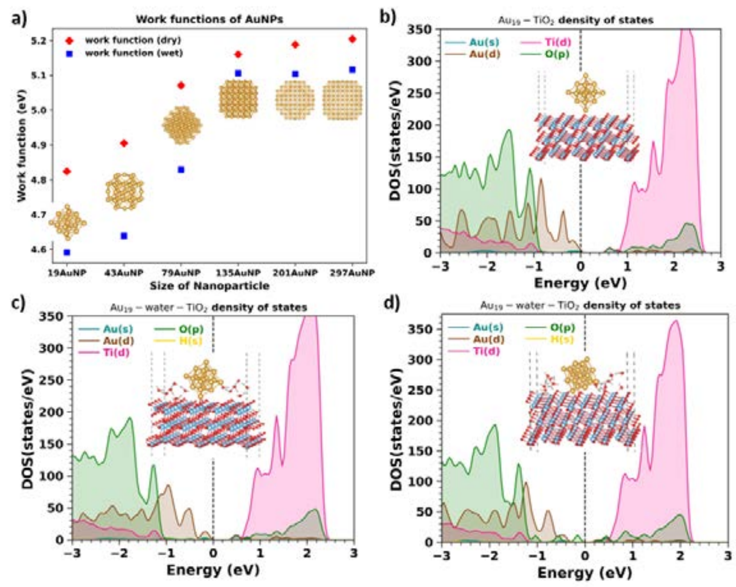

Fig 3-9: a) Work function converges at the Au_{135} cluster by sampling an array of Wulff shape Au nanoparticles. The "wet" datapoints represent monolayer water covered Au clusters. b) Density of states (DOS) of the "dry" Au/TiO_2 interfacial system supports earlier experimental evidence of the site-specific, transient local charge injection from the electron donor (AuNP) to the electron acceptor (TiO_2). c) Density of states (DOS) of a representative "wet" Au/TiO_2 interfacial system. d) Density of states (DOS) of another "wet" Au/TiO_2 interfacial system with a different orientations of water molecules.

Inspired by the most recent TRAPXPS results on H_2O exposed interfaces, described in Subtask 2, we have begun studying the effect of a solvent environment by comparing results for dry vs. wet Au/TiO_2 samples. Different orientations and numbers of water molecules led to strikingly distinct band gaps and electronic density of states (DOS). As shown in Fig. 3-9b, the total DOS resembles a sum of individual peaks from the Au, the TiO_2, and the solvation environment. The maximum contributions in the valence band (VB) edge arise from Au-*d* orbitals, while the conduction band (CB) edge is mostly influenced by Ti-*d* orbitals. The computational observation further supports earlier experimental evidence of the site-specific, transient local charge injection from the electron donor (AuNP) to the electron acceptor (TiO_2) (Borgwardt et al. **2020**, *J. Phys. Chem. Lett.* 11, 5476). Since the plasmon excitation band of the Au cluster (centered around 2.3 eV) lies well inside the TiO_2 conduction band, we can use the density of the TiO_2 acceptor states available at the plasmon excitation energy as an indicator for how efficient the charge injection process is. If the density of acceptor states is high and the overlap between donor and acceptor is significant, we would expect that more channels open and a higher transfer probability will lead to a shorter photoinduced electron transfer timescale, and vice versa.

Future Plans: The band structures obtained from the above plane-wave based DFT can be further used to fit a Slater-Koster file for tight binding (TB) acceleration. Real-time, time-dependent density functional theory (RT-TDDFT) will be employed to predict the optical spectrum of the excited plasmon. An RT-TDDFT tight binding (RT-TDDFTB) scheme will be adopted to further reduce the computational cost, which will allow us to simulate the time-resolved charge injection processes on the order of sub-100 femtoseconds. The charge separated states will generate a unique XPS fingerprint. We will continuously apply and extend our computational XPS modules (Xu et al. **2022**, *J. Chem. Theory Comput.* 18, 5471) to complement the TRXPS and TRAPXPS experiments described in Subtask 2.

Peer-Reviewed Publications Resulting from this Project (2021–2023)

Authors who are PIs of this FWP appear in blue font, students and postdocs who were supported by this FWP appear in green font, and LBNL PIs of other BES-supported research, including those at our DOE User Facilities, appear in red font.

A. Publications that were solely supported by this FWP, and those in collaboration with others that are based on research that is intellectually led by the FWP and advances one or more of the FWP's objectives.

2021

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2021

Bello, R. Y.; Lucchese, R. R.; Rescigno, T. N.; McCurdy, C. W., Correlated Variational Treatment of Ionization Coupled to Nuclear Motion: Ultrafast Pump and Ionizing Probe of Electronic and Nuclear Dynamics in LiH. *Phys. Rev. R* **2021**, *3* (1), 013228, DOI 10.1103/PhysRevResearch.3.013228. *The FWP supported the work performed Lucchese, and Rescigno on this project.*

Britz, A.; Attar, A. R.; Zhang, X.; Chang, H.-T.; Nyby, C.; Krishnamoorthy, A.; Park, S. H.; Kwon, S.; Kim, M.; Nordlund, D.; Sainio, S.; Heinz, T.; Leone, S. R.; Lindenberg, A.; Nakano, A.; Ajayan, P.; Vashishta, P.; Fritz, D.; Lin, M.-F.; Bergmann, U., Carrier-Specific Dynamics in 2H-$MoTe_2$ Observed by Femtosecond Soft X-ray Absorption Spectroscopy using an X-ray Free-Electron Laser. *Struct. Dyn.* **2021**, *8* (1), 014501, DOI 10.1063/4.0000048. *This FWP supported Leone's interpretation of the data.*

Camper, A.; Skantzakis, E.; Géneaux, R.; Risoud, F.; English, E.; Diveki, Z.; Lin, N.; Gruson, V.; Auguste, T.; Carré, B.; Lucchese, R. R.; Maquet, A.; Taïeb, R.; Caillat, J.; Ruchon, T.; Salières, P., Two-Dimensional Phase Cartography for High-Harmonic Spectroscopy. *Optica* **2021**, *8* (3), 308–315, DOI 10.1364/OPTICA.403859. *The FWP supported the computational results reported in this study provided by Lucchese.*

Epifanovsky, E.; Gilbert, A. T. B.; Feng, X.; Lee, J.; Mao, Y.; Mardirossian, N.; Pokhilko, P.; White, A. F.; Head-Gordon, M. et al., Software for the Frontiers of Quantum Chemistry: An Overview of Developments in the Q-Chem 5 Package. *J. Chem. Phys.* **2021**, *155* (8), 084801, DOI 10.1063/5.0055522. *Computational methods developed by the M. Head-Gordon group under AMOS support (OO-DFT for XAS, etc) were included in this large multi-group publication.*

Feinberg, A. J.; Verma, D.; O'Connell-Lopez, S. M. O.; Erukala, S.; Tanyag, R. M. P.; Pang, W.; Saladrigas, C. A.; Toulson, B. W.; Borgwardt, M.; Shivaram, N.; Lin, M.-F.; Al Haddad, A.; Jäger, W.; Bostedt, C.; Walter, P.; Gessner, O.; Vilesov, A. F., Aggregation of Solutes in Bosonic Versus Fermionic Quantum Fluids. *Sci. Adv.* **2021**, *7*, eabk2247. DOI: 10.1126/sciadv.abk2247. *The FWP supported the experiment contributions by Saladrigas, Toulson, Borgwardt, and Gessner, as well as Gessner's contributions to authoring the beamtime proposal and the journal article.*

Holzmeier, F.; Joseph, J.; Houver, J. C.; Lebech, M.; Dowek, D.; Lucchese, R. R., Influence of Shape Resonances on the Angular Dependence of Molecular Photoionization Delays. *Nat. Commun.* **2021**, *12* (1), 7343, DOI 10.1038/s41467-021-27360-y. *The FWP supported the computational results and theoretical interpretation by Lucchese that are reported in this study.*

Jahnke, T.; Guillemin, R.; Inhester, L.; Son, S.-K.; Kastirke, G.; Ilchen, M.; Rist, J.; Trabert, D.; Melzer, N.; Anders, N.; Mazza, T.; Boll, R.; De Fanis, A.; Music, V.; Weber, T.; Weller, M.; Eckart, S.; Fehre, K.; Grundmann, S.; Hartung, A.; Hofmann, M.; Janke, C.; Kircher, M.; Nalin, G.; Pier, A.; Siebert, J.; Strenger, N.; Vela-Perez, I.; Baumann, T. M.; Grychtol, P.; Montano, J.; Ovcharenko, Y.; Rennhack, N.; Rivas, D. E.; Wagner, R.; Ziolkowski, P.; Schmidt, P.; Marchenko, T.; Travnikova, O.; Journel, L.; Ismail, I.; Kukk, E.; Niskanen, J.; Trinter, F.; Vozzi, C.; Devetta, M.; Stagira, S.; Gisselbrecht, M.; Jäger, A. L.; Li, X.; Malakar, Y.; Martins, M.; Feifel, R.; Schmidt, L. P. H.; Czasch, A.; Sansone, G.; Rolles, D.; Rudenko, A.; Ueda, K.; Moshammer, R.; Dörner, R.; Meyer, M.; Pfeifer, T.; Schöffler, M. S.; Santra, R.; Simon, M.; Piancastelli, M. N., Inner-Shell-Ionization-Induced Femtosecond Structural Dynamics of Water Molecules Imaged at an X-ray Free-Electron Laser. *Phys. Rev. X* **2021**, *11* (4), 041044, DOI 10.1103/PhysRevX.11.041044. *The FWP supported Th. Weber in contributing to the experiment, interpreting the data, and writing the publication.*

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Rebholz, M.; Ding, T.; Despré, V.; Aufleger, L.; Harmann, M.; Meyer, K.; Stooß, V.; Magunia, A.; Wachs, D.; Birk, P.; Mi, Y.; Borisova, G. D.; Castanheira, C. C.; Rupprecht, P.; Schmid, F.; Schnorr, K.; Schröter, C. D.; Moshammer, R.; Loh, Z.-H.; Attar, A. R.; Leone, S. R.; Gaumnitz, T.; Wörner, H. J.; Roling, S.; Kuleff, A. I.; Ott, C.; Pfeifer, T., All-XUV Pump-Probe Transient Absorption Spectroscopy of the Structural Molecular Dynamics of Diiodomethane. *Phys. Rev. X* **2021**, *11* (3), 031001, DOI 10.1103/PhysRevX.11.031001. *This FWP supported Leone's interpretation of the data.*

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Bello, R. Y.; Lucchese, R. R.; McCurdy, C. W., Pump and Ionizing-Probe Dynamics in a Simultaneous Treatment of Electronic and Nuclear Motion in LiH. *Phys. Rev. A* **2023**, 108, 033104. DOI 10.1103/PhysRevA.108.033104. *The FWP supported R. Lucchese and C. W. McCurdy who participated in the interpretation of the computed data and in the writing of the manuscript.*

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Troß, J.; Carter-Fenk, K.; Cole-Filipiak, N.C.; Schrader, P.; Word, M.; McCaslin, L.M.; Head-Gordon, M.; Ramasesha, K., Excited State Dynamics During Primary C–I Homolysis in Acetyl Iodide Revealed by Ultrafast Core-Level Spectroscopy. *J. Phys. Chem. A* **2023,** *127, 18*, 4103–4114, DOI 10.1021/acs.jpca.3c01414. *The computational modeling and interpretation by the M. Head-Gordon group was supported by AMOS.*

Early Career: From Molecules to Continuum: Exploring a Universal, Transferable, and Physics-Based Understanding of Chemical Dynamics from ab-initio

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Project Scope Kohn-Sham Density Functional Theory (KS-DFT) (as realized in prevalent computational software like Q-Chem, VASP, Gaussian etc.) is a powerful mathematical model of electronic structures. It is widely utilized to calculate properties of systems with up to a few hundred atoms, whereas difficulties persist for wavefunction methods to scale above tens of atoms. These limitations present a significant challenge for the description of modern-day renewable energy technologies, which mandate electronic structure representations for nanoscale systems consisting of >1,000-10,000 atoms.

In this project, we will focus on the development and application of real-space KS-DFT, which is a promising theoretical method for achieving electronic structure level insight into chemical dynamics in realistically large and complex systems with up to >10,000 atoms. We aim to unveil a fundamentally new set of chemistry-structure-property relationships in heterogeneous systems at the nanoscale, where geometry, confinement, and atomic interactions interplay. Inspired by experiments in the LBNL AMOS Program, we will investigate the electronic structure details of picosecond to nanosecond timescale charge recombination processes at plasmonic nanoparticle (NP) /semiconductor interface. We will use the AuNP/TiO_2 composite as our model system, due to the chemical stability of Au and the ideal band alignment between Au and TiO_2. Our computational findings will be validated by ultrafast X-ray spectroscopy experiments.

Recent Progress We have started the project by developing predictive models of X-ray Photoelectron Spectroscopy (XPS) signatures within the theoretical framework of real-space KS-DFT. Given our overarching goal of explaining and predicting large nanoscale phenomena from a local atomic spectator's perspective, we decided to pursue the pseudopotential ΔSCF strategy (with only double the cost of a normal ground state single point calculation) for the accurate prediction of XPS binding energies.

Future Plans Building upon our previous success with 2nd row elements (Xu et al., **2022**, *J. Chem. Theory. Comput.*, 18, 5471), we will first enable XPS prediction capabilities beyond 1s core excitation. We most recently examined several 3rd row elements, and obtained initial good results for 1s, 2s, and 2p excitation including Si, P, and S with ~0.2 eV accuracy. Our eventual goal will be to build new capabilities for quantitatively predicting the core ionization energies for Au_{4f}, Ti_{2p}.

We will also gradually increase our system size to the desired nanoscale and eventually predict ΔE_b of Au_{4f}, Ti_{2p}, and O_{1s} as site-specific spectators to elucidate ultrafast charge transfer dynamics in plasmonic AuNP/TiO_2 semiconductor interface. We identified the sodium carbonate/bicarbonate nanodroplet system with an intermediate size (~1000 atoms) as a steppingstone, to build expertise and define expectations before we move on to even larger systems

(~10,000 atoms). For this system, high-quality experimental XPS results exist (Lam et al. **2017**, *J. Chem. Phys.*, 146, 094703). The experiment detected a surprisingly high concentration of the doubly-charged carbonate compared to the single-charged bicarbonate species at the gas-liquid interface. In contrast, the traditional picture of classical electrostatic theory predicts a higher likelihood for strongly hydrated ions (i.e., the doubly-charged carbonate) to stay in the bulk. We will obtain the nanodroplet atomic structure via our collaboration with the Pascal group (UCSD). Using the intermediate system as a case study, we will tackle the numerical problems associated with increasing complexity by exploring Pulay, Kerker mixing schemes and an improved initial guess for the rapid and robust convergence of self-consistent field (SCF).

Peer Reviewed Publications Resulting from this Program (Project start date: 08/2023)

No publications to report.

PULSE: Ultrafast Chemical Science at SLAC

P.H. Bucksbaum, D.A. Reis, K. Gaffney, T. Heinz, T. Martinez, T. Wolf, A. Natan, J. Cryan, S. Ghimire, A. Cordones-Hahn, M. Kling, 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.

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 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.

Research themes: 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:

- 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.

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

- 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*

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[1] https://www6.slac.stanford.edu/blog-tags/ultrafast-science

[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/

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.

Key Personnel:

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;
Professor Matthias Kling, Nanoscale Catalysis;
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;

Management Structure: The Ultrafast Chemical Science FWP is directed by Prof. Phil Bucksbaum. The FWP is part of the SLAC Chemical Sciences Division, directed by Dr. Frank Abid-Pedersen, which in turn is part of the SLAC Energy Sciences Directorate, directed by Interim Associate Lab Director Prof. Kelly Gaffney. The intellectual vitality of the program is assisted greatly by its organization within a parallel Stanford University organizational unit, the Stanford PULSE Institute, which directed by Prof. David Reis.

Recent organization changes: The UCS FWP was formerly organized with one subtask for each of its principal investigators. In 2022 we reorganized our subtask structure by reducing the total number of subtasks to encourage synergy among the programs of our PIs. The FWP is now organized into four subtasks plus a proposed fifth subtask awaiting guidance following its review earlier this year:

1. AFAM: Attosecond and Femtosecond Atomic and Molecular Physics (Bucksbaum, Cryan)
2. UEDES: Ultrafast Electron Dynamics in Extended Systems (Reis, Heinz, Ghimire)
3. GPUC: Gas Phase Ultrafast Chemistry (Wolf, Martinez)
4. CDCE: Chemical Dynamics in Complex Environments (Gaffney, Cordones-Hahn, Natan)
5. UDNS (proposed): Ultrafast Dynamics on Nanoscale Surfaces (Kling)

Program highlights: Here are recent examples of research progress:

Enhanced cutoff energies for direct and rescattered strong-field photoelectron emission of plasmonic nanoparticles: In work led by the UDNS subtask we measured strong-field ionization from metal nanoparticles (NPs), and observed almost isotropic electron momenta, rather than the strong anisotropy observed in atoms and small molecules. We also found direct photoemission from metal NPs had cutoff energies that can exceed 300 times the ponderomotive potential, with a strong nonlinear intensity-dependence, thus demonstrating a complete breakdown of the Strong Field Approximation that is the standard description for atoms and

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

molecules under similar irradiation conditions. [Saydanzad E, et al. (2023) Nanophotonics, 12(10):1931–1942]

Rehybridization dynamics into the pericyclic minimum of an electrocyclic reaction imaged in real-time: In work led by the GPUC subtask we combined ultrafast electron diffraction data and AIMS excited state wavepacket simulations to image rehybridization dynamics in photoexcited $\alpha\mathrm{TP}$ near the pericyclic minimum, a critical geometry on its reaction pathway. We observe significant rehybridization and π-bond alternation during relaxation, providing a new perspective on the origin of the stereospecificity of electrocyclic reactions. [Liu et al.(2023), Nature Communications, 14(1):2795]

Real-space inversion and super-resolution of ultrafast scattering: Adi Natan, PI in the CDS subtask, has developed a new approach to directly resolve real-space structural features from x-ray scattering signals, beyond the diffraction limit imposed by the finite scattering momentum transfer. He demonstrated super-resolution of simultaneous motions de novo from data previously collected in experiments performed and modeled by the GPUC subtask. This approach opens the way to directly trace the spatiotemporal shape of coherent wave-packet motions and energy redistribution of different atom-pairs that take place simultaneously, without bias based on traditional modeling constraints. The approach is expected to be useful for high-fidelity scattering signals from future LCLS-II experiments. [Natan A (2023) Physical Review A, 107(2):023105]

These are just three of the advances this year. More summaries of our work are in the five subtask abstracts that follow this overview.

Awards Prizes, and other Honors this year:

Tony Heinz was chosen as a Fellow of the Materials Research Society, 4/2023.

Space allocations: Most of the laboratories, student and staff offices, as well as a theory center, are located in the SLAC Central Laboratory Building 40/40a complex. About 10,000 square feet are allocated to research laboratories and a computer room for this FWP. Additional space exists in the new SLAC Arriaga Science Center, planned for joint LCLS-PULSE research utilization.

Collaborations: In addition to strong links to LCLS, we also have collaborative connections to other outside research labs. An updated list including DESY, the Lawrence Berkeley Laboratory, the Center for Free Electron Lasers (CFEL) in Hamburg, several research groups in the UK and Europe, and other BES-AMOS groups at the University of 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 the LCLS scientific staff to commission instruments and prepare for early science at LCLS-II.
- We continue to assisted in the development of laser and timing tools currently at LCLS.

- Several PULSE scientists have staff positions at LCLS. Dr. James Cryan is AMOS Department Head at LCLS, and Dr. Thomas Wolf is Chemistry Department Head at LCLS. Prof. Matthias Kling is the Director of the Scientific Research Division at LCLS.
- We connect LCLS to the Stanford PULSE Institute by assisting in their student and postdoctoral recruitment and mentorship.

Knowledge transfer to the community: 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. The PIs from this FWP have commonly served as Chair on a rotating basis. The 2023 UXSS in June was held at DESY, and next year's 2024 UXSS will be at SLAC, chaired by UCS PI Shambhu Ghimire.

Attosecond and Femtosecond Atomic and Molecular Physics (AFAM)

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Participants: *Phil Bucksbaum (PI), James Cryan (co-PI), Taran Driver, Siqi Li, Jun Wang, Nick Werby, Emily Thierstein, Ian Gabalski, Erik Isele, David Reis, Todd Martinez, Thomas Wolf*

Collaborators: SLAC: Ruaridh Forbes, Agostino Marinelli, Mike Glownia, Mike Minitti, Peter Walter, Matt Ware,, Nanna Holmgaard, Matthias Kling; Imperial College: Jon Marangos, Oliver, Vitali Averbukh, Marco Ruberti; UAM: Fernando Martin, Alicia Palacios, Gilbert Grell; The Ohio State University: Lou DiMauro, Greg McCracken, Daniel Tuthill; UCL: Carla Faria, Andrew Maxwell (moved to Aarhus), Agapi Emmanouilidou, Miles Mourtney; U. Conn: Nora Berrah, Sandra Beauvarlet; Others: Robert Luccese (LBNL); Peter Weber (Brown), Jordan O'Neal (Tokyo), Anna Wang (Harvard).

Project Scope*:* We study motion of electrons and atoms in molecules on their natural time scales to understand and control the earliest stages of chemical change; and to study fundamental ultrafast and strong-field interactions that reveal their internal dynamics. Significant electron motion occurs in tens of attoseconds to tens of femtoseconds, the scales associated with the spectral shifts and spacings of valence or inner-valence electrons, and so we are pursuing experiments which can probe dynamics on these extreme timescales. These experiments also develop and validate concepts about the response of atomic structure, chemical bonds, inner-shell atomic dynamics, and even in atomic nuclei, to strong laser fields. The field strengths that we employ are typically in the range of $3 - 10\ V/\text{Å}$, but they can range as high as focused X rays at $3kV/\text{Å}$ (several hundred atomic units). These fields can create and probe coherent superpositions of electronic states which evolve in hundreds of attoseconds to hundreds of femtoseconds. New pump and probe opportunities are becoming available at the LCLS and are expected to be standard operations at LCLS-II. We also apply strong ultrafast coherent fields that range from THz to X rays, and pulse durations from picoseconds to attoseconds, thereby covering a dynamical time and frequency scales relevant to atomic physics and to chemistry.

Recent Progress 2023:

Improvements in Spectral Domain Ghost Imaging: This year we continued to develop machine learning (ML) methods applied to the analysis of complex datasets collected with X-ray Free Electron Lasers (XFELs). We have developed an efficient one-step method that combines photon spectrum correlation analysis with the reconstruction of three-dimensional momentum distribution from velocity map images, utilizing spectral-domain ghost imaging in an attempt to improve the spectral resolution. To illustrate the effectiveness of ghost imaging we worked with the beamline staff at the Free-electron LASer in Hamburg free-electron laser (FEL) to apply this method to analyze the photoionization of the 2p-shell of argon. Despite the wide range of ionizing pulse bandwidths generated by the FLASH FEL, our approach successfully resolves distinct spectral features arising from the spin-orbit splitting of $Ar^+(2p^{-1})$ (See figure below). Furthermore, our method allows for the retrieval of binding energy spectrum linewidths that approach the resolution limits imposed by the spectrometers used to collect the data. This breakthrough paves the way for extending spectral-domain ghost imaging to scenarios where the observable photoproduct is high-dimensional, offering exciting possibilities for future research and applications.

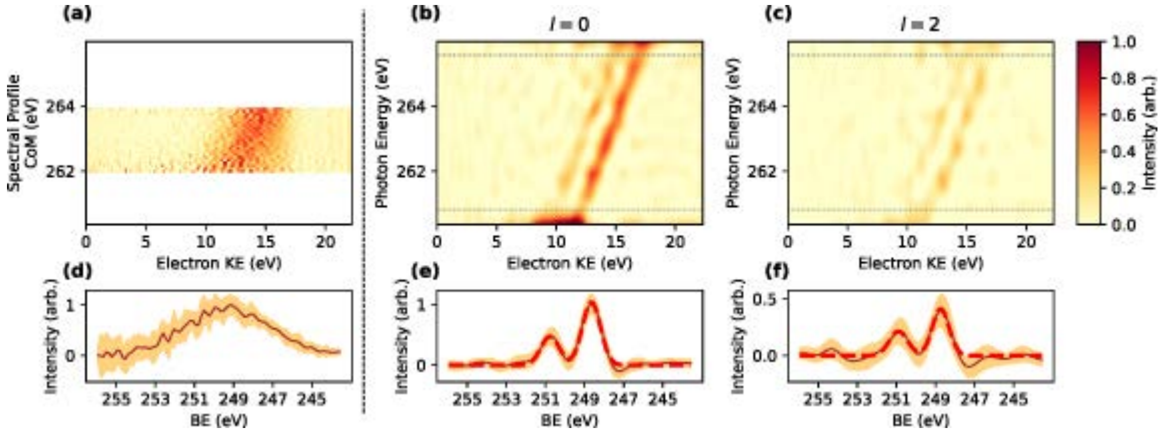

Figure 1 (From [Wang 2023]) Comparison between the conventional binning-and-averaging method (a)(d) and our method (b)(c)(e)(f). (a) Energy distribution obtained with pBasex applied to the cumulative VMI image, with preliminary grouping of shots by the center-of-mass (CoM) of spectral profile. (b), (c) Photon-energy resolved argon 2 p photoelectron KE spectra of the l = 0 and l = 2 Legendre polynomial components of the angular distribution, both being normalized to the maximum intensity in l = 0. The grey dotted lines delineate the photon energy range for (e) and (f). (d)–(f) Binding energy (BE) spectra of (a)–(c) extracted by shifting the KE spectra at each photon energy, see main text. The brown solid lines are the mean over the photon energy range, and the shaded regions represent the standard deviation. The red dashed lines in (e) and (f) are the sum of fitted Gaussians.

Validity of the Standard Streaking Model used to time the arrival of attosecond x-ray pulses: The co-axial streak camera is indispensable today in attosecond XFEL experiments, since it has become the primary means to determine arrival times of attosecond XFEL pulses at a target. Standard streaking models (SSM) rely on the assumption that the strong laser field does not alter the ionization process, but only transfers laser-field momentum to the continuum photo-emitted electrons after they are produced (i.e. the streaking effect). To test the range of validity for SSM, we worked with theory colleagues at the University College London to calculate continuum molecular wavefunctions for the open-shell molecule NO^+ within the Hartree-Fock framework, and simulate the angular distributions of core-ionized photoelectrons in the presence of a strong IR circularly polarized field [Mountney 2023]. Our results show that the SSM assumption depends strongly on the relative value of the photoelectron kinetic energy E and the streaking field ponderomotive potential U_p. The SSM model is valid when E>>U. In the opposite limit of near-threshold ionization so that U_p >>E, the SSM fails, and instead the distribution angle for photoemission can be controlled by the phase of the streaking field at the moment of arrival of the attosecond x-ray pulse.

Ionization by the transient collective field of a relativistic electron bunch: We are also working with Agostino Marinelli's group to investigate the manipulation of the Coulomb field generated by a highly relativistic electron beam. Our goal is to shape this field into a broadband pulse that can effectively drive ultrafast and strong-field physics experiments.This Coulomb field generates a pulse with a cutoff frequency that can be adjusted across a wide range, from terahertz (THz) to extreme ultraviolet (EUV). Importantly, this pulse functions as a "half-cycle" impulse when interacting with target systems. Our theoretical exploration of this technique is detailed in [Cesar, 2023].

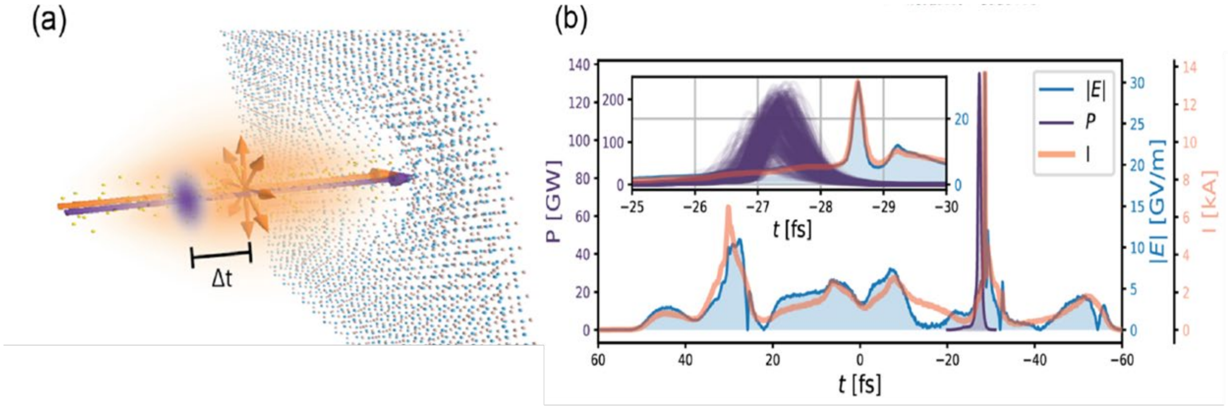

Figure 2: (a) Cartoon of a space-charge pump, x-ray probe experiment. (b) The space-charge field (blue), electron beam current (red) and the power of sample XFEL pulses (purple) from start-to-end simulations of the LCLS-II cuS beamline [Cesar 2023].

Time-resolved x-ray spectra: We have augmented our previous time-resolved x-ray scattering studies of photoexcited CS2 to X-ray photoelectron spectroscopy (TRXPS) in the same system. We find that changes in the nuclear structure following photoexcitation affect the sulfur 2p binding energy, which in turn leads to dissociation into CS and S photoproducts [Gabalski 2023].

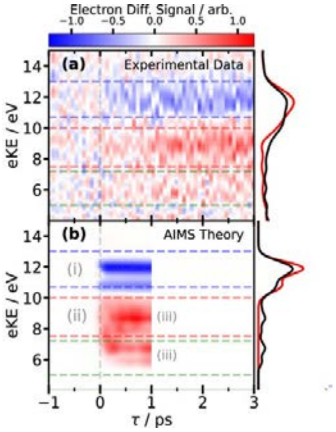

Figure 3 (a) Experimental TRXPS difference signal as afunction of pump−probe delay τ and electron kinetic energy (eKE). Pre-time-zero (red, “τ < −0.25 ps”) and late-time (black, “2 ps < τ <5ps”) spectra are shown beside the time-resolved difference signal. (b) Simulated TRXPS difference signal calculated using an ensemble of singlet AIMS trajectories. Three regions of interest (i–iii) described in the text are indicated. [Gabalski 2023]

<u>Future Plans:</u>

Attosecond campaign progress on analysis: Observations of femtosecond electron motion following x-ray absorption: We continue to analyze attosecond x-ray-pump/x-ray-probe experiments of ultrafast charge motion in aminophenol. The main feature is rapid decay of the signal over a few femtoseconds. Models developed with the Martin (UAM) and Ruberti (Imperial) groups show this is the result of the dephasing of the initial hole state . We see a revival of the absorption signal after ~5 fs as well, due to a partial reformation of the hole near the oxygen-site, as well as evidence for the on-set of proton motion on the 10-fs timescale [Isele 2023]. Additional data were collected on the meta-aminophenol isomer, which is under analysis in cooperation with the Ohio State University group; and x-ray photoemission spectral data were also collected, and are under analysis. ***Time resolved hard x-ray analysis:*** We completed an experiment at SACLA to use TRXS to map intramolecular motion during and following strong-field ionization in polyatomic molecules SF6, CH2I2, and CH2IBr. Analysis on this work is continuing.

New Campaign Experiments: we plan to demonstrate impulsive stimulated Raman scattering employing a pair of identical soft x-ray pulses with variable time delay in para-aminophenol (pAp), the molecule described above. The population of valence-excited neutral molecules produced by the pulse pair will be probed via UV-induced photoionization. This experiment will reveal

Angular streaking: The single-shot spectral fluctuations of XFEL pulses can interfere with attempts to use streaking measurements to determine the time of arrival of the pulse. This is a major source of error in streaking measurements. Covariance analysis of the data in streaking experiments might help to mitigate single-shot phase inference of the streaking field. We are currently analyzing this problem. We also have an upcoming beamtime using shaped x-ray pulses to control the coherence in core-excited states. Finally, much of our effort in the coming year will be devoted to support of Early Science efforts in TMO.

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Background and Significance

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 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. These observations indicate that the non-equilibrium nuclear geometries accessed by electronic excited state trajectories can play a major role in dictating excited state dynamics, not just the strength of the coupling between electronic states. This hypothesis represents a new conceptual framework that could supplant prior conventional wisdom with sufficient evidence. The Chemical Dynamics in Solution (CDS) sub-task aims to connect the investigation of this central hypothesis to the selective and efficient driving of chemical transformations with light. More specifically, we endeavor to:

- Identify how excited state electron and spin density distributions control non-radiative relaxation with an emphasis on metal-ligand molecular orbital hybridization; use this understanding to influence design of photocatalysts for targeted functions.
- Observe the influence of solvation on electronic excited state trajectories with atomic-resolution; use this understanding to influence the design of photocatalysts with desired solute-substrate interactions.

The incisive observation of electronic excited state dynamics is an essential step towards these objectives. To meet these goals, the CDS sub-task focuses on the development and application of ultrafast x-ray scattering and spectroscopy 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. Moving forward, our method development activities will focus on two directions emphasizing the new capabilities of LCLS-II. First, we will use the increase in soft x-ray laser repetition rate to develop resonant inelastic x-ray scattering (RIXS) as a powerful approach to tracking time-dependent changes in electronic excited state metal-ligand covalency. Second, we will use the high-energy extension of the hard x-ray laser wavelength-range to 0.5 Å to develop model-independent methods for inverting the time dependent and anisotropic XSS signal to real space molecular structures in the presence of changes in the solute and solvation structure.

Recent Progress

Controlling metal complex excited state properties with metal-ligand covalency **(Gaffney, 2021; Larsen, 2021; Reinhard, 2021; Jay, 2022; Kunnus, 2022; Reinhard, 2023)**: Long charge transfer (CT) excited state lifetimes prove to be a critical metric for the majority of photosensitizers and photoredox catalysts. Achieving long CT excited state lifetimes has proven very challenging for first row transition metal complexes, with only a limited number possessing nanosecond or longer lifetimes. This reflects the smaller ligand field splittings for 3d, versus 4d and 5d, metal complexes. The smaller ligand-field splittings of 3d metal complexes reduce the energies of the metal centered (MC) electronic excited states and enable them to efficiently quench the optically generated CT excited states. Eliminating this relaxation pathway proves to be a common objective for the development of first row photosensitizers and photoredox catalysts.

Determining how to use metal-ligand orbital hybridization (metal-ligand covalency) to influence the relative energies of CT and MC excited state directs a significant part of our effort in the CDS sub-task. Manipulation of the metal-ligand covalency enables the spatial distribution of the metal 3d orbitals to be modified with the orbital delocalization leading to an increase in the ligand field interactions, a decrease electron exchange interaction, and ultimately the destabilization of MC excited states. Depending on the metal and the ligand, these covalent interactions can predominantly influence the π- or σ-bonding, creating additional means of systematically varying excited state electronic structure.

This new focus is inspired by new Fe carbene complexes being synthesized by Jim McCusker (Michigan State U.) and Fe amido complexes being synthesized by Dave Herbert (U. Manitoba). The mixed polypyridyl-carbene complexes synthesized by the McCusker group combine strongly covalent Fe carbene (Fe-C) σ-bonding carbene ligands with moderately covalent π-bonding polypyridyl ligands. The Fe-amido complexes of the Herbert group use the strongly covalent Fe amido (Fe-N) π-bonding of the Fe amido. Based on optical transient absorption, the mixed polypyridyl-carbene complexes have CT lifetimes of roughly 10 ps and the Fe-amido complexes have CT lifetimes of 3 ns, indicating the these ligand designs provide a promising approach for 1st row metal photosensitizers. The nanosecond lifetime for the Fe-amido complex contradicts conventional wisdom, because the Fe-amido bond emphasizes covalency over ligand field strength.

With the goal of deepening the understanding of the electronic structure and electronic excited state relaxation dynamics of these Fe photosensitizers, we have pursued two parallel approaches. First we have used a combination of Fe L-edge and N K-edge x-ray absorption spectroscopy (XAS) and resonant inelastic x-ray scattering (RIXS) to investigate the influence of metal-ligand orbital hybridization on excited state electronic structure. Secondly, we have used simultaneous ultrafast XSS and Fe 1s3p XES to investigate the electronic excited state relaxation mechanisms (Biasin, 2021; Gaffney, 2021; Reinhard, 2021; Reinhard, 2023).

XAS and RIXS, when applied at the metal L-edge or ligand atom K-edge, can readily identify the metal and ligand contributions to excited state electronic structure, respectively (Larsen, 2021; Jay, 2022; Kunnus, 2022). In our investigations of the Fe-amido complex, we used the N K-edge results to validate the strong mixing of the amido N π and Fe t_{2g} orbitals. The mixing of N 2p character in the HOMO was clearly observed by the appearance of a characteristic absorption peak in the 1-electron oxidized Fe-amido complex and in the appearance of a weak MLCT peak in the RIXS spectrum (Larsen, 2021). Additionally, we used Fe L-edge RIXS to quantify the relative energies of the MC excited states, enabling the extraction of d orbital splitting (10Dq) and electron repulsion scaling factor (β) (Larsen, 2021). The covalent interaction in the Fe-amido complex was found to decrease the electron exchange interaction, offsetting the effects of the weaker ligand field. Overall, the stabilization of MC excited states for the Fe amido complex compared to a polypyridyl complex was significantly less than that expected by the decrease in 10Dq alone, by a factor of 2 (^{3}MC state) to 4 (^{5}MC state). Thus, tuning metal-ligand covalency of the π-symmetry orbitals was found to be a novel tool for the systematic tuning of excited state electronic structure in Fe photosensitizers. Establishing how the strong π-bonding ligands influence excited state dynamics will be explored further in the Proposed Work by extending the RIXS studies to the ultrafast time domain.

Real-space methods for viewing chemical dynamics in complex chemical environments **(Biasin, 2021; Lin, 2021; Natan, 2021; Yang, 2021a; Yang, 2021b; Natan, 2023)**: The CDS sub-task has pursued three parallel developments focused on establishing direct structural probes of complex chemical dynamics in solution. We have:

- Developed and commissioned a new liquid-jet endstation for solution-phase ultrafast electron diffraction measurements in collaboration with Thomas Wolf, Jie Yang, and Xijie Wang.
- Implemented high-energy (18 keV) XSS to effectively separate the solute and solvation response to electronic excitation in solution.
- Established a model-free approach to invert scattering signals to real space images, surpassing the diffraction limit, using scattering kernels and signal priors that naturally arise from the measurement

constraints.

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 (Lin, 2021).

UED has multiple strengths, in particular the high spatial resolution and large elastic scattering cross-section for relativistic electrons. These strengths notwithstanding, as presently implemented, space charge effects, even for MeV electrons, still require a compromise between the time resolution and signal-to-noise. This motivates our continued effort to use the increased photon energy range of LCLS-II to advance ultrafast XSS. We recently led an ultrafast XSS experiment using 18 keV (0.7 Å) x rays that has demonstrated the ability to decompose ultrafast chemical dynamics into specific changes in the solute and 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 directly trace the spatiotemporal shape of coherent vibrational wavepacket motions and energy redistribution of different atom-pairs that take places simultaneously, without bias toward the Franck-Condon active modes or the constraints of normal mode analysis. For an Ir-dimer complex, we clearly see the impact of anharmonicity on the time-dependent width of the metal-metal symmetric stretch vibrational wavepacket directly. This is distinct from a Pt-dimer photocatalyst with similar electronic structure, but a more harmonic electronic excited state potential. For the Pt-dimer, we can clearly see the metal-metal bond length oscillate, but changes in the vibrational wavepacket distribution prove more difficult to resolve. We also directly trace the changes in the solvation structure via changes in the solute-solvent pair distribution function. The measurement clearly shows differences in how H-bonding and polar aprotic solvents solvate the Pt-dimer photocatalysts. Specifically, we see evidence for a narrower distribution of solute-solvent first solvation shell distances for H-bonding solvents than aprotic solvents. We are currently in the process of writing-up the results of this investigation.

The success of this analysis has depended critically on the development of model-free inversion methods, capable of surpassing the diffraction limit, using scattering kernels and signal priors. We have used the approach on simulated and experimental data, recovered the simulated atomic motions at sub-Å resolution, and shown how signal fidelity determines the recovery accuracy and resolution limit \cite{Natan2023}. The approach offers a robust path to high-resolution real-space structural dynamics using time-resolved X-ray and electron scattering sources. This approach may help bridging the established pair-distribution function analysis that requires much higher Q-ranges ($Q > 30$ Å^{-1}) with ultrafast x-ray and electron scattering measurements that only now are achieving high signal-to-noise transient signals to $Q \approx 10$ Å^{-1}. In addition to the application of these inversion methods to XSS measurements, we have also applied them to UED studies of ring opening in photoexcited 1,3-cyclohexadiene. Our results are in excellent agreement with the ab initio multiple spawning (AIMS) simulations conducted by Todd Martinez and co-workers, without further processing the trajectories.

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 *n*d 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.

Obtaining a microscopic view and control of Coherence in Solution Phase: We propose to develop and implement ultra-wide-angle (<100 degrees) high-energy ultrafast x-ray scattering, optical control methods, QM/MM simulations, and advanced imaging approaches, to study the microscopic aspects of quantum mechanical decoherence in solution. The extended *Q*-range and anisotropy in the x-ray scattering will enable the shape of time-dependent vibrational wavepackets to be resolved and the role of substrate-solute structure to be investigated for photocatalytic reactions.

Our studies of vibrational decoherence will focus on metal augmented M-PtPOP (PtPOP = $[Pt_2(P_2O_5H_2)_4]^{4-}$) complexes, where M = Ag^+ or Tl^+. We have chosen this chemical system because metal augmentation has been shown to significantly change the rate of vibrational decoherence. Being able to resolve details beyond the mean bond length, such as the shape of a vibrational wavepacket, is therefore of great importance to studying the microscopic details of decoherence. We would like to develop a modality where the spatio-temporal information encoded in coherently controlled wavepackets can serve as sensitive probes for decoherence and energy redistribution. By choosing the wavepacket's initial excitation energy and delay and resolving their time-dependent shape we can map the potential surfaces landscape and the rate by which they decohere. The anisotropy component in such an experiment also presents the opportunity to study orientational decoherence similar to the way rotational dephasing takes place in gas phase scattering.

Our studies of the role of substrate-solute structure will focus on PtPOP. We have chosen this chemical system because the photocatalytic activity of PtPOP has shown substrate selectivity that has been correlated with H-bonding between the substrate and PtPOP where the substrate can be a hydrogen-bonding solvent. Specific hydrogen bonding between the substrate and the POP ligand has been proposed to explain the reaction selectivity, but has not been directly observed experimentally.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

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Gas phase Ultrafast Chemistry (GPUC)

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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 state-of-the-art experimental and theoretical approaches connected to the unique ultrafast facilities at SLAC.

Recent Progress

We have expanded our studies of electrocyclic photochemistry. Electrocyclic reactions in general are characterized by the concerted formation and cleavage of several single and double bonds. This process requires hybridization changes between sp^2 and sp^3 for some of the involved atoms. The reactions are predicted to proceed through a single critical geometry, a so-called pericyclic geometry, since all involved electron orbitals overlap in this geometry in a cyclic fashion. Electrocyclic reactions can proceed thermally on the electronic ground state potential energy surface or via photoinduced nonadiabatic dynamics involving the potential energy surfaces of several electronic states. In the thermal case, the critical geometry is a pericyclic transition state. In the latter case, it is a minimum of the excited state in the vicinity of a conical intersection with the ground state which provides the photoexcited population access to the photoproduct minima of the ground state potential energy surface.

We have investigated the structural dynamics leading into the pericyclic minimum of a photochemical electrocyclic ring-opening reaction with a combination of megaelectronvolt ultrafast electron diffraction and ab initio multiple spawning (AIMS) simulations. We used a derivative of the prototypical molecule 1,3-cyclohexadiene (CHD), α-terpinene (aTP). It exhibits an isopropyl and a methyl substituent on opposite sides of the carbon ring, whereas 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 carbon-carbon distances and, therefore, additional strong features in the static and time-dependent atomic pair distribution functions. These "reporter" distances are sensitive to details of the relaxation into the pericyclic minimum of the excited state, which could not be observed in CHD. In particular, we observe an out-of-plane bending motion of the methyl substituent prior to ring-opening. With the help of the AIMS simulations, we interpret this motion as the signature of rehybridization dynamics of the two carbon atoms, which are directly involved in the bond dissociation during the ring-opening. The rehybridization largely happens in the excited state and prior to the structural opening of the ring. Therefore, the pericyclic minimum represents an early stage of the ring-opening and a substantially later stage of the hybridization change.

Additionally, we expanded our investigations in the sensitivity of the electron diffraction observable to structural dynamics involving hydrogens and to the character of the electronic state. We performed experiments and AIMS simulations of the photodissociation of ammonia. The resulting experimental time-resolved diffraction patterns show clear signatures of both changes in the character of the populated electronic state of ammonia and of the dissocation reaction. The experimental signatures can only be reproduced by simulations of the experimental observable which go beyond the independent atom model, i.e. explicitly account for the electron distribution in the molecule as well as inelastic scattering processes.

We have also simulated the photodynamics of the chromophore of the Green Fluorescent Protein, in environments ranging from vacuum to solvent to protein. This chromophore, which can undergo both isomerization and proton transfer, is a model system for understanding how to control photochemical mechanisms (either by modification of the chromophore itself or through tuning of steric and electrostatic effects in its environment). These theoretical studies pave the way for future experiments using ultrafast diffraction.

Finally, we have shed further light on the theoretical issues surrounding conical intersections computed with single-reference wavefunction methods. We have shown previously that intersections between the reference state and excited states will have the incorrect topology when using single reference wavefunction methods. However, an open question concerns the topology around intersections of excited states. We have shown previously that these were also suspect and the potential energy can become complex around excited state intersections. We recently showed that this artifact may not always be crippling – if the wavepacket itself stays away from the “defective” region, the induced geometric phase effects will still be properly accounted for. This finding implies that coupled cluster methods could still capture the correct physics in some cases.

Future plans

We plan to continue our studies of the interplay between electronic and nuclear degrees of freedom during ultrafast dynamics in isolated molecules. In this respect, we plan target heteroatom-containing model systems exploiting the new capabilities enabled by the LCLS-II upgrade. We plan a series of combined experimental and theoretical studies focused on tuning the accessibility of photochemical reaction pathways by the structural modification of the reactant. We are also exploring the use of coupled cluster methods for excited state dynamics in nucleobases, to be compared to previous LCLS experiments.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

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Ultrafast Electron Dynamics in Extended Systems

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Scope of the program

This sub-task focuses on fundamental light-matter interaction in extended systems such as bulk crystals, nanoscale 2d crystals, interfaces, and surfaces. We are interested in how strong-field driven dynamics in condensed matter systems compare with their atomic and molecular counterparts and what it can tell us about excited states and strongly driven dynamics [Ghimire2019]. In the strong-field limit, condensed matter systems offer a fascinating platform as the strong-field approximation becomes qualitatively invalid, attributed to the high-density and periodicity of the interacting media. Spectacular examples include the study of driven dynamics in monolayer 2d crystals, where many-body interactions and correlations are known to be ubiquitous [Liu2017]. For excitation, we typically use intense near and mid-infrared laser pulses such that the strong-field limit can be achieved without damaging the sample. We utilize ultrafast nonlinear x-ray-based spectroscopies at the LCLS, either in time and energy-resolved wave mixing geometries or in transient absorption setups. Like their gas-phase counterparts, solid-state HHG has shown the potential to be a novel atomic-scale ultrafast probe of the structure and dynamics of extended systems, which are complex and naturally extend over a wide range of time scales. We also analyze photoelectrons and fluorescence as complementary observables. One of the goals of this subtask is to understand the factors controlling charge transfer, excited states, and dynamics, often in the strong-field regime. Our focus has been on model systems created by stacking the 2d van der Waals monolayers described above into vertical heterostructures. This provides us the opportunity to produce low dimensional systems with varying relative bandgaps and band alignments, as well as precisely formed relative crystallographic orientation. These 2d layers also feature strong electron-hole interactions, with the optically excited states being excitonic in character, allowing the investigation of strongly bound excitonic states and their dynamics.

Recent Progress

Strong field interactions in reduced dimensional materials:

Floquet engineering of strongly driven excitons in monolayer tungsten disulfide: Energy levels of isolated atoms and molecules subjected to intense low frequency laser fields experience significant dynamical stark shifts. In this sub-task we extended these studies to 2d crystals. Using a transient absorption spectroscopy in WS_2, we observed a strong stark shift on the 1*s*-exciton state (in excess of 100 meV) and the emergence of a new absorption feature one photon energy away from the dark 2*p*-exciton state (see figure 1). At moderate *E*-fields (around 0.08 V/nm) we observed a blue shift and broadening of the absorption feature. At higher fields (0.2 V/nm and above), we observe a much stronger Stark shift of the 1*s* exciton, and a new feature emerges about one photon energy below the 2*p* state. We find that this new feature disperses in energy with the photon energy of the driving MIR field, and it is present only during the presence of the MIR field. Therefore, we assign this novel feature to a Floquet replica of the 2*p* state ($2p^{-1}$). We reproduce these energy shifts and the novel feature through TDSE calculations using a model 2d potential. Results are published in a letter in *Nature physics* [Kobayashi2023].

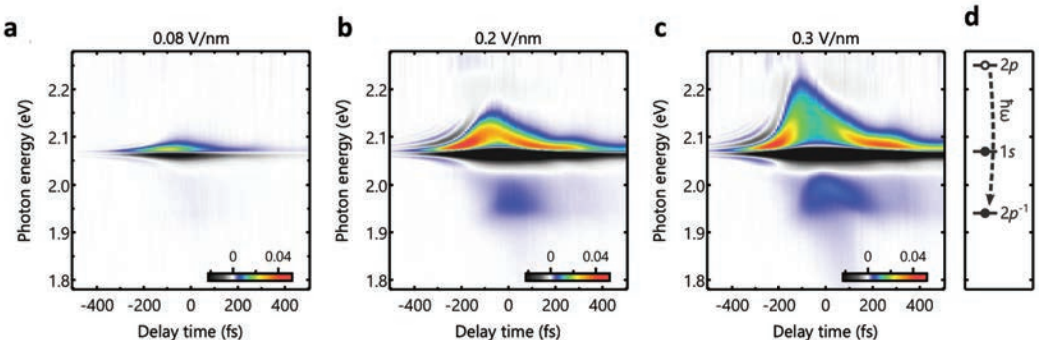

Figure 1: Observation of a Stark shift and Floquet replica of excitonic states in WS_2 via transient absorption spectroscopy. a) shows the change in optical absorption as a function of the pump-probe delay when the MIR pulse has the field strength around 0.08 V/nm. The absorption peak corresponds to the 1*s*-exciton. b) shows the change in absorption for a higher field strength around 0.2 V/nm. In addition to the strong blue shift on 1*s*-peak a new feature is seen at about one photon energy below. c)shows the scan when the MIR pulse has the highest field strength around 0.3 V/nm. Strong shifts and broadenings are seen both on the 1*s*-peak and on the light-field induced $2p^{-1}$ peak. d) shows energy levels in absence of the dressing field.

HHG as a novel probe

Circularly-polarized field-driven HHG: In atomic media the HHG efficiency decreases as a function of the drive laser ellipticity and circularly polarized laser fields do not produce harmonics. This behavior is understood using a semiclassical re-collision model. We discovered that topologically protected surface states exhibit anomalous drive laser ellipticity dependence, where the HHG efficiency is maximum for elliptical fields. Figure 2a shows schematics for HHG using ultra-thin samples in transmission geometry.

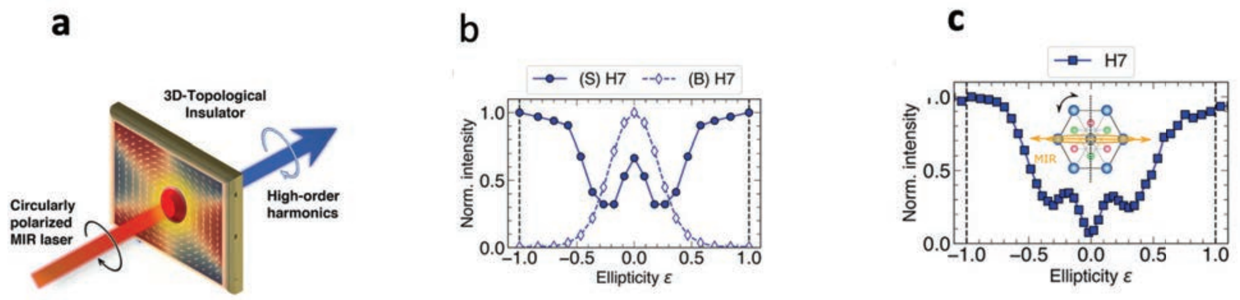

Figure 2: Anomalous laser ellipticity dependent HHG response of topologically protected surface states. a) shows schematics of the experimental setup, b) shows calculation results considering a pair of surface bands and a pair of bulk bands, separately. c) shows the measured results, which closely resembles the behavior of the surface state in calculation results.

In calculations, we solve semiconductor Bloch equations for bulk and surface response separately. For surface response, we consider one valence and conduction band, which form the Dirac cone, and for the bulk band, we pick the highest valence and lowest conduction band. Figure 2 shows the results for 7th order harmonics. It is seen that the response from the bulk bands is very similar to both gaseous and condensed phase argon target [Ndayishimiye 2016]. However, the yield for the surface bands increases with the increase in the laser ellipticity and it becomes maximum for circular polarization. The enhancement of HHG from topological surface states for strongly-elliptical fields, can be attributed to features in the electronic band structure. At relatively low peak intensities, the vortex-like pattern of transition dipole moment between valence and conduction bands are responsible for such behavior. At high peak intensities, the higher-order warping terms of the Hamiltonian are primarily responsible for the enhancement with strongly-elliptical or circularly polarized laser fields. The detailed theoretical results are published in *Phys. Rev. A* [Baykusheva 2021]. In the experiments, we use sub-100 nm thin samples and transmission geometry at normal incidence. The laser ellipticity ϵ is changed from -1 to +1 through 0 by a combination of a half and a quarter waveplate. The optic axis of the quarter waveplate is fixed perpendicular to the mirror plane as shown in the inset in figure 2c. The measured yield of 7th harmonic shows maxima for both left and right circular polarizations. The detailed experimental results are published in *ACS Nano letters* [Baykusheva 2021a].

Probing topological phase transitions: It has been shown previously through angle-resolved photoelectron spectroscopy that the pristine Bi_2Se_3 has the non-trivial topological surface state as marked by the measured Dirac cone. In $(Bi_{1-x}In_x)_2Se_3$ alloys, at x=0.2 the Dirac cone is fully destroyed, making the sample topologically trivial band insulator. We used this material to scrutinize the capability of HHG as an optical probe of the topologically protected surface states.

For linearly polarized laser fields of peak field strengths around 0.2 Vnm^{-1} and wavelength ~4 μm, we found that the pristine samples are about 8 times more efficient than the alloy samples. The difference gets further enhanced for elliptically polarized laser fields. Figure 3 shows the intensity of a representative harmonic (HO5) for various MIR ellipticities, from right-circularly polarized through linear to left-circularly polarized in small increments. For the alloy sample, the generation efficiency for HO 5 is maximum for $\epsilon = 0$ (linear polarization), it drops monotonically as the ellipticity increases to $\epsilon = \pm 1$ (circular polarization). For circular polarization, we did not detect a signal. In contrast, the pristine sample exhibits a strikingly different behavior (blue line): higher absolute yield (~10), which grows with increasing laser ellipticity. For $\epsilon = \pm 1$ the HHG yield is about twice as high as for $\epsilon = 0$. Our results show that a high-harmonic generation process can be a sensitive non-linear probe of the surface states. The detailed results are published in a letter in *Nature Photonics* [Heide2022]

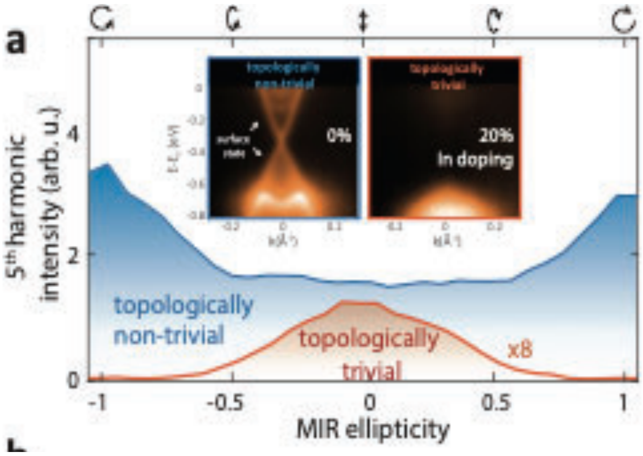

Figure 3: Application of HHG as an all-optical method to probe the topologically protected surface states. Anomalous ellipticity dependence disappears as the samples are doped with impurity concentration that is enough to destroy the surface bands, as seen through angle-resolved photoemission spectroscopy in the inset.

Probes of heterostructures of 2D materials and their dynamics: We have continued our research to understand the electronic properties and ultrafast electron dynamics in model interfaces created by 2d semiconductor monolayers. We have examined heterostructures formed from two different monolayers in the transition metal dichalcogenide family that exhibit type-II (staggered) band alignment. These materials support interlayer optically excited states in which the electron resides in one material and the hole in the other. Since strong electron-hole correlations persist for these states (as well established for intralayer states), these excited states have excitonic character and are termed interlayer excitons (ILXs).

During the past fiscal year, we made use of our recent advances in two new experimental techniques to investigate these ILX states. Our time- and angle-resolved photoemission spectroscopy (tr-ARPES) results are published in *Nature* [Karni 2022]. Results of electromodulation technique, which measures directly the relatively weak ILX absorption, are published in *Science* [Barre 2022]. The tr-ARPES measurements were made in collaboration with the group of K. Dani at the Okinawa Institute of Science and Technology in Japan, which allowed us to image both the electron and hole components associated with interlayer excitons. In particular, we were able to characterize in momentum space the electron and hole distributions. This immediately presented an experimental signature of the valley character of the interlayer exciton. More uniquely, by establishing the widths of the electron and hole momentum distributions, we were able to deduce the size of the exciton, i.e., the electron-hole correlation length. In addition, the combination of separately determined electron and hole distributions also yielded information on the degree of localization of the center-of-mass motion of the interlayer exciton, which was induced by the development of a moiré potential between the two slightly lattice mismatched layers. During the past year, we performed measurements exploring the dynamics of interlayer exciton formation through the usual ultrafast pump-probe methodology.

Regarding the absorption studies of the interlayer exciton, we made use of an electromodulation technique to identify the weak absorption of this charge-separated species. The basis of the method is the large linear Stark effect of the interlayer exciton under a perpendicular electric field. By applying an oscillating perpendicular (quasi-static) electric field, we induce a modulation in the sample reflectivity. This modulation technique helps both with the detection of the weak response (fraction of a percent) and in discriminating against other possible absorption features not arising from the ILX. In our initial research [Barre 2022], we demonstrated the effectiveness of this approach to determine the contribution to the dielectric function of the interlayer absorption in the $WSe_2/MoSe_2$ heterostructure. This study yielded new information about the intrinsic radiative rate of the ILX states and showed by a comparison with photoluminescence measurements that the lowest lying ILX, visible in photoluminescence measurements, could be indirect in the moment, as well as spatially indirect.

During the past fiscal year, we have also extended this measurement technique to examine the influence of resident carriers, i.e., those introduced in the structure by electrostatic gating. We have investigated this effect in transition metal dichalcogenide heterostructures as before. In samples prepared with monolayers having aligned crystallographic structures, we anticipate the emergence of moiré effects. In particular, we observe well defined signatures of electron correlation effects in the system of resident carriers for particular filling factors (doping levels). The influence of correlated electron states was seen in slight, but easily discernible jumps in the energies of the ILX resonances. We are examining the use of the ILX as a sensitive probe of electron-correlation effects and their dynamics in these model systems.

Higher-order x-ray optical mixing: We have recently measured for the first time the ångström-scale microscopic nonlinear response of electrons driven by near-infrared radiation using higher order x-ray optical wavemixing. The concept of measuring linear optically induced charges on the atomic-scale was proposed independently by Freund and Levine [Freund1970] and Eisenberger and McCall [McCall 1971] in the early 1970s. It wasn't until the LCLS x-ray free-electron laser before we were able to perform the first successful experiment, in collaboration with E. Glover (then at LBNL) [Glover2012]. In those experiments we measured a single Fourier component of the induced charge density in diamond irradiated by 1.55 eV light, showing up as an energy and momentum side-band (sum frequency generation) to the 111 Bragg peak of an 8 keV x-ray beam. The experiments can be thought of as nonlinear diffraction from the time-dependent charge density within the unit cell, or equivalently as stimulated inelastic x-ray scattering (anti-Stokes for the sum-frequency) from the optical excitations induced by the laser, and immediately brings to mind the idea of nonlinear crystallography of the excited electronic structure with atomic resolution. Our primary interest is in imaging the nonlinear optical, and even strong-field driven-electronic response in matter, for example during the HHG process (see e.g. [Gorelova2018]). As a first step to this process, we recently measured the first-order sum and difference frequency mixing signal as well as the second-order sum frequency mixing from the 220 diffraction peak in thin single crystal silicon, using a custom designed dispersive monochromator and analyzer pair. Even though silicon is centrosymmetric, the induced charge density can still oscillate at the second harmonic of the laser, due to the lack of inversion symmetry in local bonding environment, while the (non-dipolar) x-ray probe further breaks symmetry in the scattering geometry (this previously allowed us for example to observe the first x-ray second harmonic generation in diamond [Shwartz2014]). At an intensity of $\sim 10^{12}$ W/cm^2 we measure the relative efficiency between the second to first order to be 10^{-3} when the applied field is parallel to the 110 direction. As shown in

Figure 4, the second order charge density shows nontrival polarization dependence.

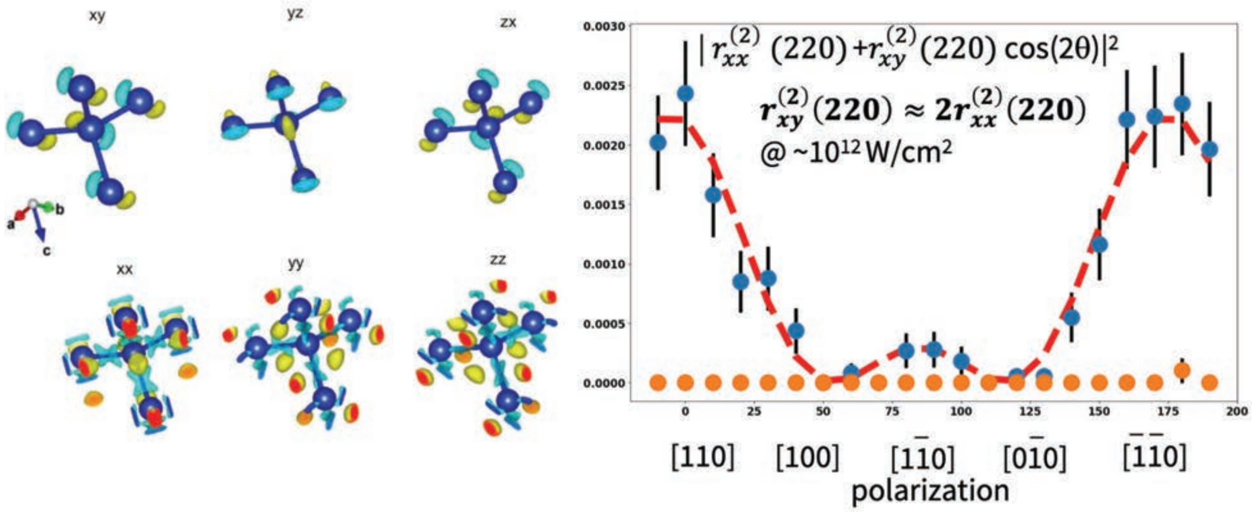

Figure 4. *Polarization dependence of the second order XSFG signal in silicon.* ***(Left)****. The calculated tensor components of the divergence of the real-space microscopic 2nd order susceptibility tensor,* $r_{jk}{}^{(2)}(\vec{r}) = \delta_i \chi^{(2)}{}_{ijk}(\vec{r})$*.* ***(Right)****. The maximum signal strength is about 2.5* 10^{-3} *photons/shot compared to about ~2x10* ^{6} *Photons/Shot (and about 2/shot for the first order side-band). The polarization was varied in the (001) plane parallel to the surface. The dashed line is based on a fit to the expected form of the second order Fourier component of the 220 charge density,* $\rho^{(2)}(220) = r_{jk}{}^{(2)}(220)E_jE_k$.

Planned Research

Element specific ultrafast probing has driven many body dynamics: Recently the LCLS had a spectacular success in generation of attosecond x-ray pulses and their characterization using angular streaking method [Li2022]. Much of the attosecond experiments are being conducted in dilute gas phase samples. We plan to extend those capabilities to periodically driven condensed matter systems, where nonequilibrium dynamics are expected to occur on the time scale of the periodicity present in the carrier of the driving MIR laser pulse [Dejean 2018]. These dynamics are expected to be qualitatively different to their atomic and molecular counterparts because of the extended nature of optical media (high-density and periodicity). We will compare the strongly correlated electron system NiO with other wide band-gap dielectrics, where strong correlations are not expected but contain ample amounts of sub-cycle dynamics as indicated from their HHG response. Our recent collaborative beamtime with Hermann Dürr at the LCLS in standard configuration (≥50 fs x-ray pulses) shows changes in the O-K-edge [Grånäs2022] as opposed to the expected changes in the Ni-L-edge according to the theory from the Rubio group [Dejean2018]. The theory considers the expected role of many-body interactions for example in the form of Ni-*d*-electrons repulsion. Shorter x-ray pulses are required to resolve this discrepancy.

Charge transfer across interfaces: We will continue our investigations of model interfacial systems provided by 2D semiconductor heterostructures to elucidate the dynamics of electron motion at well-defined boundaries. In addition to the already established experimental tools based purely on optical methods (pump-probe and time-resolved photoluminescence) and time-resolved ARPES, we will prepare for measurements using the capabilities of the new high repetition rate LCLS-II free electron laser. By exploiting core-level atomic transitions (through x-ray absorption and emission measurements), we will be able to add element specificity to our probe methodology, as well as having a possible route to extend the measurements down into the sub-femtosecond time regime.

Nonlinear x-ray scattering-based spectroscopy: We are preparing a manuscript from our recent beamtime at the LCLS, where we observed second-order x-ray optical mixing signals in silicon. We plan to continue the development of this measurement in Si and GaAs for multiple spatial and temporal Fourier components of the microscopic charge density, as a function polarization direction to reconstruct all the symmetry inequivalent components of the microscopic nonlinear susceptibility, and its intensity dependence, including a novel interferometric method for retrieving the phase. Furthermore, we were awarded beamtime on the PAL-XFEL to extend the method to the strong-field regime in MgO. Eventually we plan on leveraging new capabilities on LCLS for attosecond all-time-domain measurements and two color soft plus hard x-ray pulses. We will also explore other promising nonlinear x-ray optical methods such as multiphoton x-ray resonant x-ray Raman scattering [Haber] to allow us to access information about excited-state electronic structure, dynamics and correlation.

Peer-reviewed publication resulting from this project (2021-2023)

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9. C. Heide, Y. Kobayashi, A. Johnson, F. Liu, T. F. Heinz, D. A. Reis, and S. Ghimire, "*Probing Electron-Hole Coherence in Strongly Driven 2D Materials using High-Harmonic Generation*" Optica 9, 512-516 (2022).

10. S. Ghimire, "*Probing attosecond phenomena in solids*", Nature Photonics 16,1,7-9 (2022)

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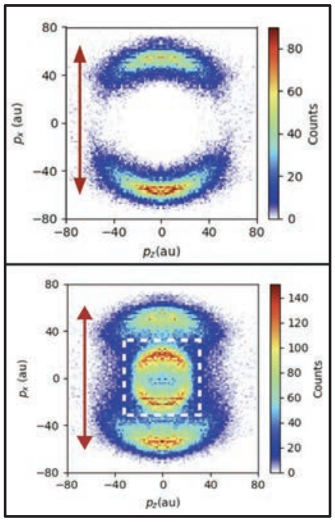

Figure 1. Orientation-averaged proton momentum distribution (in the plane of polarization) for spherical versus cubic nanoparticles.

to provide more catalytic active sites due to their high number of low-coordinated atoms [10]. Figure 1 shows the experimental ion momentum distribution (in the plane of polarization) for spherical versus faceted (cubic) nanoparticles. A majority of the signal observed in the momentum distribution corresponds to H^+, which stems from dissociative ionization of terminal -OH and -OR groups on the nanosurface. Observing the dissociative ionization of H^+ and the catalytic formation of other elementary products (e.g., H_2^+ or H_3^+, where H_3^+ formation requires a complex bimolecular roaming reaction involving neutral and singly ionized H_2) provides a strong indication that the irradiated nanosurface can substantially enhance more advanced catalytic processes. Divergent from previously observed results, cubic NPs exhibit prominent additional features in their ion momentum distribution and a larger enhancement of the H_3^+ channel compared to spherical particles, which is indicative of their effect in enhancing catalytic reaction channels. However, due to the nature of this orientation-averaged measurement, single-shot studies need to be performed to understand these results.

Quantum Chemical Simulations

Recent work has explored the generation of free charges and resultant chemistry on SiO_2 NPs through strong field ionization, however the resulting chemical dynamics leading to surface bond dissociation are still not understood. While not inherently catalytic, SiO_2 becomes rapidly populated with free charges upon photoionization, which mimics aspects of other catalysts. In this work, we performed non-adiabatic quantum molecular dynamics [11-13] (NAQMD) simulations on a hydrated SiO_2 surfaces with field boundary conditions to match that of an ionized NP. We considered both ionized electrons and bound hot electron hole pairs that can form due to local Coulomb trapping. We found that disassociation of silanol groups can occur within tens of fs (see top part of Fig. 2) and is driven by localization of holes [14,15] (see bottom part of Fig. 2). We also investigated chemical dynamics of free water molecules adsorbed to the surface and found that free holes generated in silica could transfer to the water molecules, inducing water splitting reactions that form H_3O^+ and OH^+ ions. Overall, the simulation framework developed illustrates that

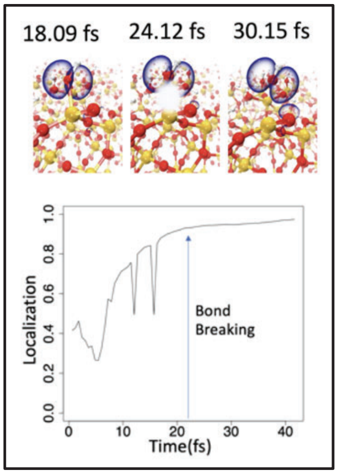

Figure 2. Top: Frames from NAQMD simulation illustrating disassociation of Silanol groups on silica surface within 30 fs. Bottom: Disassociation is driven via hole localization which is quantified through maximum Mulliken contribution of any atom to the hole wave function.

photoinduced surface chemistry on SiO_2 NPs is driven by localization of holes, as well as charge transfer from the surface to free molecular species.

X-ray Driven Chemical Reactions on Nanosurfaces

Building upon our prior optical investigation [16], we recently conducted an experiment at the Eu-XFEL facility where we examined the catalytic formation of H_3^+ on the surface of hydrated SiO_2 NPs ionized by intense, femtosecond X-ray pulses. For the first time, we performed a trimodal spectroscopy and imaging measurement to simultaneously obtain 1) 3D ion momentum distributions (mass-resolved), 2) photoelectron energy spectra, and 3) far-field coherent diffractive images (CDI) of isolated NPs. Fig. 3(a) shows the ion time-of-flight spectrum (filtered for NP hits) for three different sized SiO_2 NPs, compared to the background spectrum. Clearly evident is a large enhancement of the yield of H^+ and H_2^+ fragments. Data analysis on the H_3^+ channel is ongoing. As this experiment was conducted in a single-pulse, fully coincident fashion we are also able to examine the photoelectron spectra directly associated with the selected ion hits. Fig. 3(b) shows the VMI spectrum filtered on just the proton region of the time-of-flight. Finally, Fig. 3 (c) shows the single-shot CDI pattern from an isolated NP indicating the ability to retrieve structural information in this type of experiment.

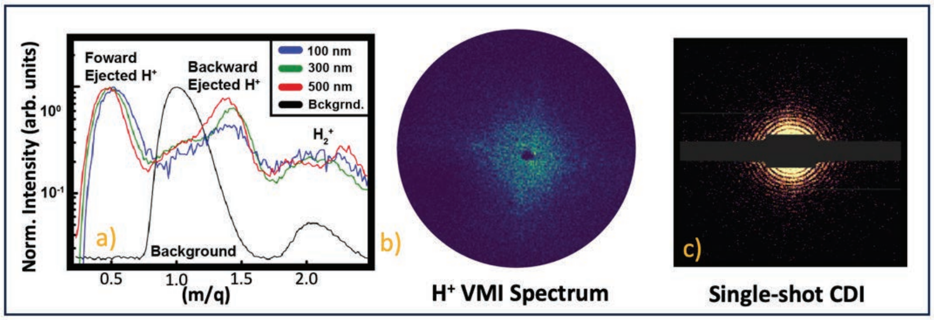

Figure 3. Results from EU-XFEL experiment showing ion-time-of-flight (a) for H+ and H2+ ions emitted from the surface of 100 nm, 300 nm, and 500 nm, SiO2 NPs. (b) Retrieved transverse momenta (VMI image) from the H^+ channel. (c) Single-shot CDI pattern obtained from 500 nm silica particles.

Future Plans

X-ray Spectroscopy and Imaging of Faceted Nanosystems

In this work package, we aim to establish the relationship between nanoscale composition/morphology and site-specific catalytic surface activity. We have submitted a proposal to the Swiss-FEL facility to perform such an experiment, where we plan to employ momentum-resolved photo-ion imaging with tandem X-ray coherent diffractive imaging measurements. We intend to conduct these experiments in a time-resolved fashion; an 800 nm optical pump will serve to create a localized charge on the nanoparticles, inducing elementary photocatalytic reactions, while a 1 keV X-ray probe will induce dissociation from the surface, allowing one to infer site-specific catalytic activity. Fig. 4(a) shows our unpublished results utilizing momentum resolved ion imaging to track surface charge generation and migration on SiO2 NPs with a high degree of spatial resolution. Fig. 4(b) shows a measurement from [17] where X-ray CDI and a 3D phase retrieval algorithm was employed to retrieve the morphology from faceted NPs on a single shot basis. Combining both techniques will allow us to uniquely tag chemical reaction dynamics to the nanoparticle morphology with nanometer resolution.

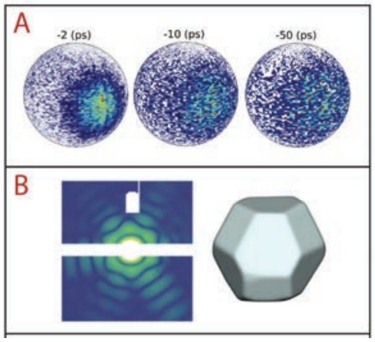

Figure 4. (A): Unpublished results tracking surface charge generation and migration on isolated NPs. (B): Diffraction pattern and 3D image reconstruction of faceted nanoparticles from [17].

Chemical Dynamics on Functionalized Nanosurfaces

Finally, we plan to interrogate ultrafast processes on nanosystems with surface functionalization. Functionalized nanoparticles exhibit numerous unique properties when irradiated with optical fields, leading to several applications within nanoscale device engineering. Advancing nanoscale devices requires an increased understanding of optically photo-driven processes on functionalized NPs, including electronic charge transfer to ligands bound to the NP surface [18], and the dynamics of their photo-detachment [19]. In this work package, we aim to probe the dynamics of photoelectron emission and ligand photo-detachment from the surface of individual, thiol-functionalized gold (Au) NPs using time-resolved X-ray photoelectron spectroscopy (XPS). This work builds on our recently published results on strong-field photoelectron emission from plasmonic AuNPs [20]. Under optical excitation, fast electron emission and surface charge creation in the AuNP will lead to a change in the local bonding environment at the interface, inducing thiolate photo-detachment. The charge-induced chemical shift will be used to track ligand detachment at the sulfur 2p edge. Our results will provide critical insight into how photoelectron emission and the creation and migration of surface charges on plasmonic NPs can induce (or control) molecular photo-detachment, which is paramount for the fabrication of next generation nanotechnology.

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Peer-Reviewed Publications Resulting from this Project (2021-2023)

A. Zhang *et al.*, Optica **9**, 551, (2022).
B. Rosenberger *et al.*, Nanopho. **12**, 1823, (2023).
C. Saydanzad *et al.*, Nanopho. **12,** 1931, (2023).

Ultrafast Dynamics on Nanoscale Surfaces (UDNS)

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Project Scope

Nanoscale physics sits at the boundary between the atomic/molecular regime and that of bulk condensed matter, giving rise to unique phenomena not observed in any other areas of physical science [1]. Such characteristics have led to many nanomaterials being employed in catalysis, as they offer a promising avenue toward achieving efficient light-to-chemical energy conversion [2-5]. While catalysis can occur in the absence of an incident electric field, the optical (plasmonic) response of nanoparticles (NPs) can substantially enhance catalytic reactions by electric field localization and amplification on/near the NP surface [6]. Additionally, surface charge generation and migration are known to play a large role in catalytic enhancement [7].

To provide fundamental insight into photocatalytic processes on the surface of individual, isolated nanoparticles (NPs), we employ a multimodal, operando approach. Here, colloidal NPs are aerosolized, and interfacial reactions are initiated and probed with ultrafast optical and/or X-ray pulses. Tracking photocatalytic reaction dynamics at the interface requires a high degree of spatiotemporal resolution and chemical specificity, which can be achieved through our momenta-resolved charged particle imaging technique. Here, upon photoionization, the nanosurface becomes rapidly populated with free charges. Due to the strong incident fields and resulting charge buildup, dissociative ionization of molecular fragments occurs. The momenta of the emitted positively charged fragments are measured with a time- and position-sensitive detector. Practically, this establishes a one-to-one mapping from the measured momentum to real space on the nanoparticle surface, as we have shown with our recent results with solid nanoparticles [8] and liquid droplets [9]. In this program we aim to extend this method, along with other powerful spectroscopic measurements to provide insight into the primary photocatalytic reaction channels that occur on the nanoscale.

Recent Progress

Photocatalytic Activity on Faceted Nanoparticles

Recently, we extended spatiotemporal imaging to investigate faceted nanosystems (see Fig. 1). The reactivity of a nanoparticle is largely determined by the particle's crystal structure, including any terminating defects or facets, which are thought

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

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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, 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 program, 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 is 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:

Initial studies in this research program have focused on both the excited state relaxation processes and the 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. Previous work presumed that protonation of the ligand pyridyl N atom results in its partial dechelation, creating a five-coordinate species that subsequently accepts electrons from a photosensitizer.[1–4] However, this active species was not isolated or characterized experimentally.

Using a combination of in situ Ni K-edge and S K-edge x-ray absorption spectroscopy (XAS) we probed changes in the coordination structure and ligand protonation state to resolve the protonation mechanism of the catalyst (Ledbetter, 2022). We identified that protonation of the pyS ligand N atoms results in total decoordination of the pyS ligand, which is exchanged for two solvent ligands. Thus the previously reported five-coordinate active species was rejected. This newly realized mechanism results in two possible electron-accepting active species: a solvated Ni(II) species or a protonated pySH ligand. 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 addressed in this program extends this same combination of the metal and ligand atom spectroscopy to investigate the electronic excited states of first row transition metal hydrogen evolving photocatalysts with redox-active ligands. This work has focused on Ni- and Cu-bis(dithiolene) and related complexes that are characterized by large metal-ligand hybridization or covalency in their valence orbitals.[5–7] While 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 are developing S K-edge resonance inelastic x-ray scattering (RIXS) as a probe of both the energy and ligand contributions to the valence electronic excited states. While S K-edge RIXS has gone previously unreported, recent developments in tender x-ray emission spectrometers[8] enabled our measurement of a series of Cu and Ni maleonitriledithiolate (mnt) anionic and dianionic complexes, $[M(mnt)_2]^{x-}$. Strong RIXS features corresponding to the HOMO-to-LUMO excited states are observed. Although these states have been traditionally referred to as ligand field or dd excited states, their strong intensity in the S K-edge RIXS spectra reflect significant ligand contributions to both the occupied and unoccupied frontier orbitals. The excited state charge distribution is therefore inferred from the RIXS spectra, as are the excited state energies, which reflect the changing relative contributions of σ- and π- metal-ligand interactions across the series.

While the RIXS measurements characterize the valence excited states in the ground state geometry, we have also performed transient Ni K-edge and S K-edge XAS to characterize the ultrafast dynamics and relaxation pathways for a series of Ni(bisdithiolene) like complexes. Using $Ni(mpo)_2$ (mpo = 2-pyridinethiolate-N-oxide) as an illustrative example, we observe two prominent electronic excited state species, as well as a long-lived photoproduct. From the Ni K-edge XAS, we identify that the initially excited ligand-to-metal charge transfer state is short-lived and the lowest energy ligand field excited state is formed within ~0.2 ps, with large planar-to-tetrahedral structural reorganization observed to follow over the next several picoseconds. Although the longer-lived nominal 'ligand field' ^3LF state looks very much like a high-spin Ni(II) species from the Ni perspective, we find that the S K-edge XAS reflects significant ligand character in LUMO vacancy. Thus, our results indicate that the nominal ligand field or metal centered excited states are better described as having ligand-to-metal charge transfer character. These results resolve the effects of the strong metal-ligand orbital hybridization of dithiolene type complexes on their excited state electronic structure for the first time.

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 continued analysis of the SwissFEL and LCLS datasets already measured. 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):

Ledbetter, K.; Larsen, C. B.; Lim, H.; Zoric, M. R.; Koroidov, S.; Pemmaraju, C. D.; Gaffney, K. J.; Cordones, A. A. Dissociation of Pyridinethiolate Ligands during Hydrogen Evolution Reactions of Ni-Based Catalysts: Evidence from X-Ray Absorption Spectroscopy. *Inorg. Chem.* **2022**, *61* (26), 9868–9876. https://doi.org/10.1021/acs.inorgchem.2c00167.

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

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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 exciton into separated, independent triplet excitons. The plan for this project was to 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 soon. 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. While we have not gotten to these experiments yet, we have made substantial progress on other experiments in inorganic semiconductors and also advancing the instrumentation, which we detail below.

Recent Progress

We have completed substantial additional analysis requested by reviewers and published our results on valley polarization dynamics in monolayer WS_2 in *Physical Review Letters* [1]. This work was also featured in a DOE Office of Science Highlight.

We have completed several major hardware upgrades to the system. First, we have installed the new sample preparation chamber discussed in last year's abstract. A picture of the new chamber connected to the ARPES endstation is shown in figure 1a). Second, we have fully integrated the new cryo-cooled hexapod manipulator (purchased with DOE supplmental funding) into the data acquisition software system. This makes finding small exfoliated flake samples at the focus of the photoemission electron microscope (PEEM) much faster. Third, we have completed the installation of an Er:fiber comb (purchased with DOE funding) as the front end for our high-power Yb:fiber amplifier chain. The $\lambda = 1.55$ μm Er:fiber comb is shifted to 1 μm using an all-fiber nonlinear Er-doped fiber amplifier (EDFA) + highly nonlinear fiber (HNLF) assembly similar to Maser et al. [2]. A photograph of the setup is shown in figure 1b). This scheme will enable us to produce tunable pump pulses with arbitrary repetition rate using the overall scheme shown in figure 2. So far the upper branch of this setup is installed and working and the fiber components of the lower branch are also installed and working. We are preparing a publication regarding the pulse pattern modulation scheme [3] and proceeding with the construction of the optical parameteric amplifiers (OPA). This tunable pump setup is in some ways the last piece of the instrument puzzle,

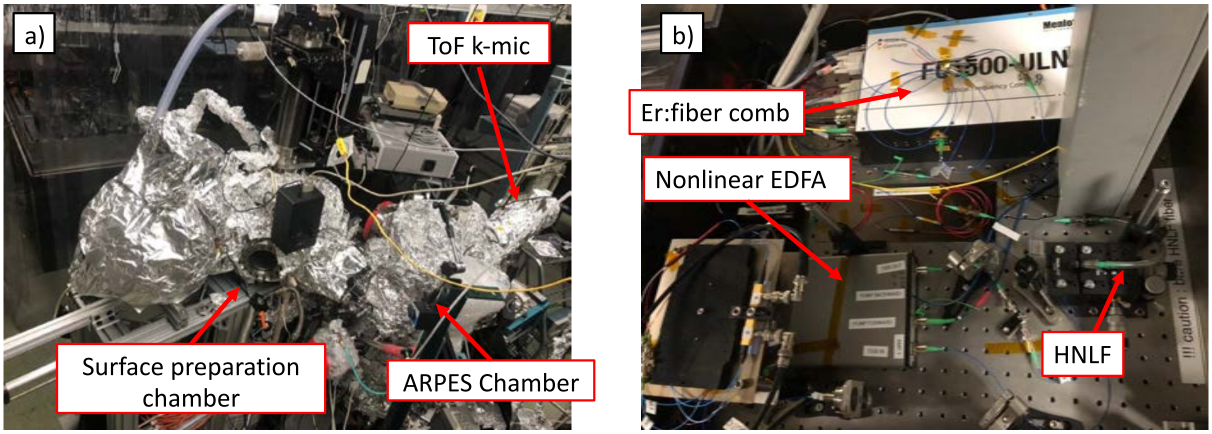

Figure 1: **Major Hardware Installations.** a) Photograph of new surface preparation chamber connected to the ARPES endstation. For characterizing surfaces, the chamber is equipped with an x-ray photoelectron spectrometer (XPS), low-energy electron diffractometer (LEED), and a mass spectrometer for temperature-programmed desorption (TPD). b) New Er:fiber front-end for the ARPES laser consisting of a commercial Er:fiber oscillator, home-built nonlinear Er-doped fiber amplifier, and highly nonlinear fiber for dispersive wave generation at $\lambda = 1$ µm.

as it will allow us to address specific exciton resonances in materials as opposed to our current (somewhat indescriminate) 517 nm pumping.

We have concluded a campaign to record non-thermal electron dynamics and pseudo-spin relaxation dynamics in monolayer graphene. Some example momentum-space snapshots of the photoelectron distributions are shown in figure 3. These dynamics, and their fluence dependence, are highly relevant to the performance of graphene saturable absorbers in mode-locked lasers and other optoelectronic devices based on graphene [5]. Performing quantitative measurements that access the relative competition between electron-electron scattering and electron-phonon scattering has been exceptionally challenging, and pushes the limit of what can be done with momentum microscopy. In particular, very careful control of systematics regarding non-uniform detector aging at high count rates is necessary to properly normalize the distributions. We have now a complete set of data varying the fluence from 45 µJ/cm^2 to 210 µJ/cm^2 and a paper regarding this work is in draft stage. Although there have been many previous ultrafast spectroscopy and time-resolved ARPES studies on graphene, this is actually the first study on neutral (i.e. undoped) graphene with zero density of states at the Fermi level, and also the first study with excitation fluences in the regime where electron-phonon scattering rates are expected to be comparable to electron-electron scattering rates [6].

We continue to participate in the LCLS momentum microscope collaboration and postdoc Sergii Chernov participated in a beam time for commissioning the instrument at PETRA III this fall. Dr. Chernov has now moved to PETRA III as a beamline scientist and continues to work on momentum microscopy.

We have recorded time-resolved ARPES signals from $MoSe_S$/WS_2 heterostructures at several twist angles. Analysis of this data is ongoing but we expect it to result in several publications. Postdoc Alice Kunin presented some of this work at the 15th International Conference on Electronic Spectroscopy and Structure in Oulu, Finland and the 2023 SSRL/LCLS Users' Meeting in Menlo Park, CA.

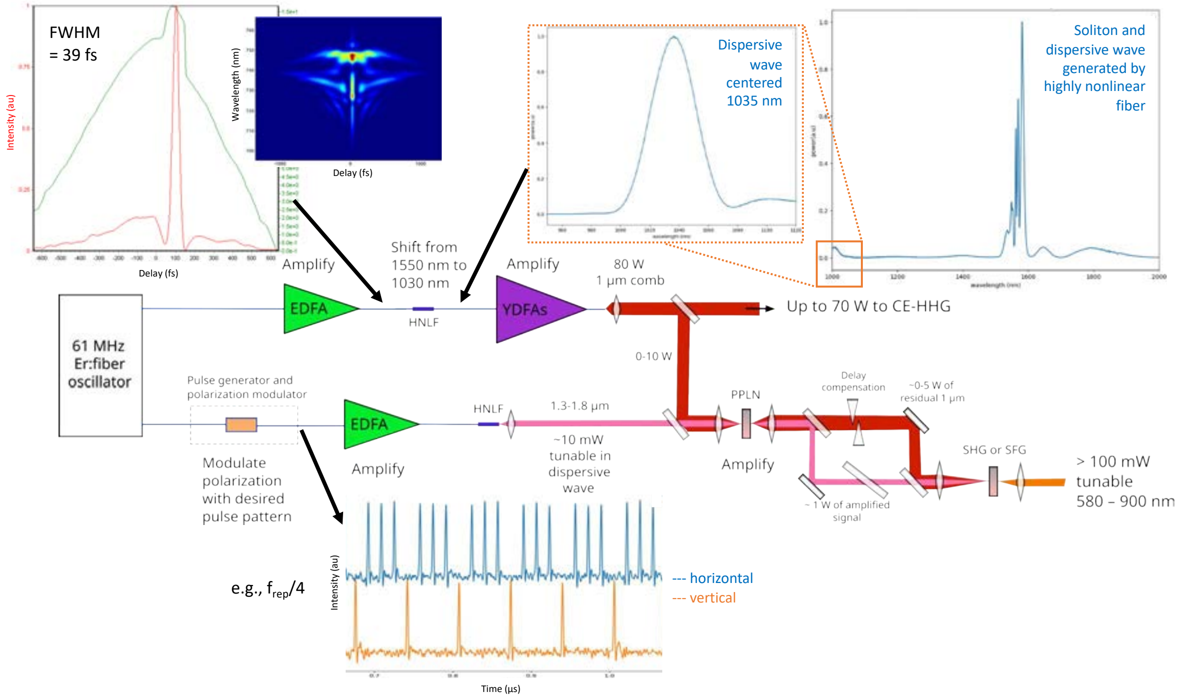

Figure 2: **Scheme for tunable pump pulse generation at arbitrary repetition rate.** Pulses at $\lambda = 1.55$ µm are amplified and shifted in wavelength using nonlinear Er-doped fiber amplifiers (EDFA) combined with highly-nonlinear fibers (HNLF) in two branches. The upper branch is shifted to $\lambda = 1$ µm for seeding our high-power Yb-doped fiber amplifier system [4]. The lower branch is shifted between $\lambda = 1.3$ µm and $\lambda = 1.8$ µm for seeding an optical parameteric amplifier based on periodically-poled lithium niobate (PPLN). The polarization modulation scheme illustrated in the lower branch allows us to optimize the repetition rate of the experiment for the sample physics under study.

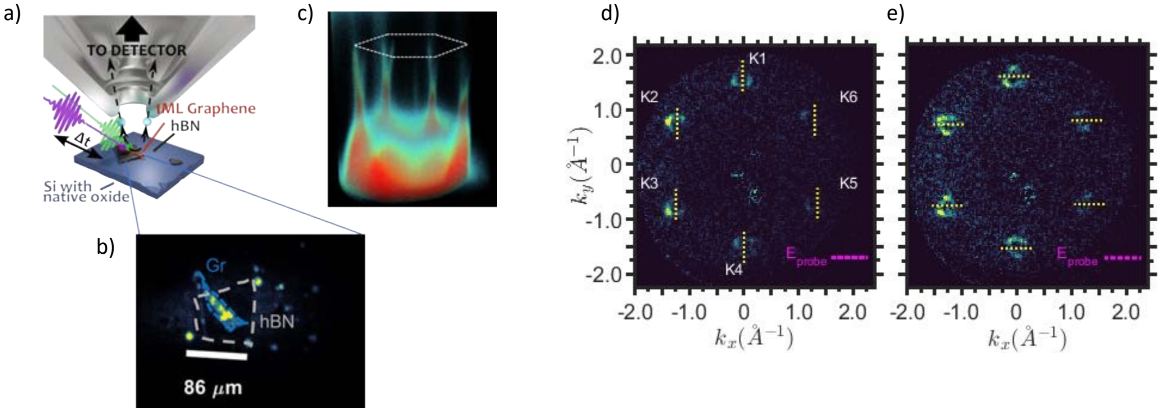

Figure 3: **Snapshots of excited electrons in graphene.** a) Illustration of time-resolved momentum microscopy of an exfoliated graphene flake. b) Real-spaced photoemission electron microscope (PEEM) image of an exfoliated monolayer graphene flake (Gr) on hexagonal boron nitride (hBN). c) 3D data representation showing excited electrons above the Fermi level (Dirac point). d) and e) Momentum-space images of excited electrons recorded after excitation with the in-plane electric field of the pump pulses polarized in the x and y directions, respectively. Nodes in the photoelectron distributions, are clearly seen along the polarization direction, as expected based on the pseudo-spin selection rules [7]

Future Plans

We will continue work on tr-ARPES experiments in 2D materials. Specifically, we plan to conclude our studies of hybridized excitons in $MoSe_2$/WS_2 bilayers and publish the results. We also have several other heterostructures we would like to study. The machine is currently "oversubscribed" in this regard, with samples coming in from many collaborators. We also do plan to do the experiments on tetracene, pentacene, and eventually hexacene, as outlined in our proposal. A recent report from our competitors at the Fritz Haber institute show the promise for tr-ARPES in this regard [8]. We view these as "preliminary results" as the ARPES images are quite non-descript compared to what we believe is achievable with our system.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

- A. Kunin, S. Chernov, J. Bakalis, Z. Li, S. Cheng, Z. H. Withers, M. G. White, G. Schönhense, X. Du, R. K. Kawakami, T. K. Allison. "Momentum-resolved Exciton Coupling and Valley Polarization Dynamics in Monolayer WS_2." *Phys. Rev. Lett.* **130**, 046202 (2023).

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[1] Alice Kunin et al. "Momentum-Resolved Exciton Coupling and Valley Polarization Dynamics in Monolayer WS_2". *Phys. Rev. Lett.* 130 (4 2023), p. 046202. DOI: `10.1103/PhysRevLett.130.046202`. URL: `https://link.aps.org/doi/10.1103/PhysRevLett.130.046202`.

[2] Daniel L. Maser et al. "Coherent frequency combs for spectroscopy across the 3–5 micron region". *Applied Physics B* 123.5 (2017), p. 142. ISSN: 1432-0649. DOI: `10.1007/s00340-017-6714-y`. URL: `http://dx.doi.org/10.1007/s00340-017-6714-y`.

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[5] Xi Peng and Yixin Yan. "Graphene saturable absorbers applications in fiber lasers". *Journal of the European Optical Society-Rapid Publications* 17.1 (2021), p. 16. DOI: `10.1186/s41476-021-00163-w`. URL: `https://doi.org/10.1186/s41476-021-00163-w`.

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[7] Ermin Malic et al. "Microscopic theory of absorption and ultrafast many-particle kinetics in graphene". *Phys. Rev. B* 84 (20 2011), p. 205406. DOI: `10.1103/PhysRevB.84.205406`. URL: `https://link.aps.org/doi/10.1103/PhysRevB.84.205406`.

[8] Alexander Neef et al. "Orbital-resolved observation of singlet fission". *Nature* 616.7956 (2023), pp. 275–279. DOI: `10.1038/s41586-023-05814-1`. URL: `https://doi.org/10.1038/s41586-023-05814-1`.

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

DOE Grant No. DE-FG02-01ER15213

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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 the theory of ultrafast processes in strong optical fields in finite systems: nanopatches of two-dimensional materials of hexagonal symmetry and hexagonal polycyclic molecules.

2. Recent Progress

The recent progress covers the period of 2021-2023 and is illustrated by publications [1-15].

2.1 High harmonic generation in graphene quantum dots [13]

A unique property of graphene quantum dots (QDs) is their zero dimensionality, which results in dimensional quantization of electron states and discrete energy spectra. Such energy spectra have a finite band gap, which strongly affects electron dynamics in graphene QDs placed in the field of a short and strong optical pulse. We examined such dynamics numerically for a graphene QD consisting of 16 atoms. We obtained that the electron dynamics can be reversible or irreversible depending on the pulse frequency. If the pulse frequency is much less than the band gap of the quantum dot, then the electron dynamics is almost reversible, i.e., after the pulse, the electron system returns to its initial state. But if the pulse frequency is comparable to the band gap, then the electron dynamics become highly irreversible, i.e., the final populations of the excited quantum dot states are almost the same as their maximum populations during the pulse. The reversibility of electron dynamics also strongly depends on the dephasing processes. We found that the dephasing processes make the electron dynamics incoherent and more irreversible. Since the electron dynamics determines the nonlinear optical response of the system, such as high harmonic generation, then the nonlinear optics of graphene QDs strongly depend on the dephasing processes.

The dephasing is introduced through the relaxation of the nondiagonal elements of the density matrix. We found that it affects both the intensities of the high harmonics and the harmonic cutoff. The intensities of high harmonics increase with the relaxation time, i.e., when the electron dynamics become more coherent; this can be attributed to the fact that for the coherent dynamics, more paths can contribute to the formation of high harmonics coherently, resulting in more significant intensity.

The effect of relaxation on the harmonic cutoff is also related to the reversibility of electron dynamics. Namely, with increasing the relaxation time, the electron dynamics become more reversible with less population of the highly excited QD levels. As a result, the harmonic cutoff decreases with increasing the relaxation time. As a function of the field amplitude, the harmonic cutoff shows almost linear dependence at small pulse frequencies when the corresponding energy cutoff is less than the energy range introduced by the QD's lowest and highest energy levels. When this energy range becomes comparable to the energy cutoff, which happens at large pulse frequencies, the cutoff shows a saturated behavior as a function of the pulse amplitude.

2.2 Nonlinear electron dynamics in graphene quantum dots with edge states [14]

We study theoretically interaction of short optical pulses with triangular graphene quantum dots (TQDGs). The radiation spectra of TGQDs placed in the field of an optical pulse depend on the size of the system and also on the parameters of the optical pulse, its amplitude, and frequency. Another characteristic of graphene QDs that can control the radiation spectrum and the corresponding generation of high harmonics is an initial electron population of QD edge states. Such edge states exist in graphene QDs with zigzag edges. Since the edge states in such systems are in-gap states, they can strongly affect the generation of high harmonics. Namely, the generation of high harmonics depends on the number of initially occupied edge states.

The strongest effect is observed for the systems, i.e., TGQDs with zigzag edges, which have an even number of edge states. In this case, if half of the edge states with the same spin component are initially populated then even high harmonics in the radiation spectra are suppressed. The level of suppression strongly depends on the frequency of the pulse. If the frequency of the pulse is close to the resonant condition, i.e., to the energy difference between the edge states and the conduction band states, then the even harmonics are weakly suppressed and the corresponding peaks in the emission spectra are clearly visible. But if the frequency of the pulse is small and far from the resonant condition, then suppression of even harmonics is strong with almost no peaks visible in radiation spectra at even frequencies.

The suppression of even harmonics at half-filled edge states is almost the same for different polarizations of the incident pulse, i.e., for x and y linearly polarized pulses. Strong suppression of even harmonics in radiation spectra of TGQDs at a specific filling of TGQD edge states opens a possibility of control of the intensity of high harmonics by variation of the gate voltage.

2.3 Ultrafast nonlinear electron dynamics in circular graphene quantum dots.

Generation of high harmonics in low dimensional systems, such as quantum dots (QDs), interacting with a short optical pulse opens a possibility of controlling the nonlinear optical response of such systems by changing their size and shape. We addressed the problem of high harmonic generation in graphene QDs, which have the shape of a disk. The unique property of such QDs is that the band gap is entirely due to dimensional quantization without any bulk contribution, i.e., the graphene monolayer does not have any band gap. Thus, the band gap strongly depends on the QD size and correspondingly the nonlinear optical response of graphene QDs is determined by their dimensions. The QDs are described within an effective model of the Dirac type and the length gauge was used to describe the interaction of QDs with an optical pulse. The advantage of using the effective model is that it allows to consider QDs of large size, at the same time it limits the intensity of the applied pulse. We consider the amplitude of a pulse less than 0.2 V/A.

There are two main characteristics of the radiation spectra of QDs. The first one is the intensity of generated high harmonics and the second one is the cutoff frequency. Both of these characteristics can be controlled by the QD radius. The intensities of the lowest generated harmonics are mainly decreases with the QD size achieving their largest values for small QDs. At the same time, under some parameters of the pulse, the maximum intensities of high harmonics are realized at the intermediate QD sizes.

The cutoff frequency of radiation spectrum has more universal behavior. It monotonically increases with the QD size, which is related to the fact that for larger quantum dots, there are more energy levels within the dot, which results in more dynamical trajectories that contribute to generation of high harmonics.

We considered the QDs that have a special disk shape. We expect that the obtained results that are related to the dependencies of the intensities of high harmonics and the cutoff frequency on the QD size will be similar for other shapes of graphene QDs.

3. Future Plans

We plan to develop a theory of ultrafast nonlinear optical response of nanoscale topological systems. The nonlinear response can be controlled by applying periodic potential to 2d materials, such as graphene or transition metal dichalcogenides. We will analyze the effect of such periodic potential on the generation of high harmonics in the systems.

4. Peer-Reviewed Publications Resulting from this Project (2021-2023)

[1] P. Kumar, T. M Herath, and V. Apalkov, "*Bilayer graphene in strong ultrafast laser fields*", J. Phys.: Condens. Matter 33 335305 (2021).

[2] S. A. O. Motlagh and V. Apalkov, "*Absorption properties of graphene quantum dots under ultrashort optical pulses*", Phys. Rev. B 104 (4), 045421 (2021).

[3] S. A. O. Motlagh and V. Apalkov, "*Anomalous ultrafast all-optical Hall effect in gapped graphene*", Nanophotonics (2021), https://doi.org/10.1515/nanoph-2021-0227.

[4] 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).

[5] 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).

[6] P. Kumar, T.M. Herath, V. Apalkov, "*Ultrafast valley polarization in bilayer graphene*", Journal of Applied Physics **130** (16), 164301 (2021).

[7] S. Gnawali, R. Ghimire, K.R. Magar, S.J. Hossaini, V. Apalkov, "*Ultrafast electron dynamics of graphene quantum dots: High harmonic generation*", Physical Review B **106** (7), 075149 (2022).

[8] K.R. Magar, S.A.O. Motlagh, V. Apalkov, "*Topological resonance in graphene-like materials*", Journal of Physics: Condensed Matter **34** (37), 375301 (2022).

[9] P. Hewageegana and V. Apalkov, "*Circularly-polarized-pulse-driven ultrafast optical currents in monolayer hexagonal Boron Nitride (h-BN)*", Solid State Communications, 350, 114774 (2022).

[10] P. Kumar, T.M. Herath, S.A.O. Motlagh, V. Apalkov, "*Control of valley polarization in gapped graphene by linearly polarized ultrashort optical pulse*", Physica E: Low-dimensional Systems and Nanostructures **140**, 115145 (2022).

[11] S.J. Hossaini, R. Ghimire, V. Apalkov, "*Ultrafast nonlinear absorption of TMDC quantum dots*", Physica E: Low-dimensional Systems and Nanostructures, 115239 (2022).

[12] Ahmal Jawad Zafar, Aranyo Mitra, and Vadym Apalkov, "*Ultrafast valley polarization of graphene nanorings*", Physical Review **B 106**, 155147 (2022).

[13] S. Gnawali, R. Ghimire, K.R. Magar, S.J. Hossaini, V. Apalkov, "*Ultrafast electron dynamics of graphene quantum dots: High harmonic generation*", Physical Review **B 106** (7), 075149 (2022).

[14] S Gnawali, V Apalkov, "*High harmonic generation governed by edge states in triangular graphene quantum dots*", Physical Review **B 108** (11), 115434 (2023).

[15] Dalton C Hunley, S Azar Oliaei Motlagh, Rupesh Ghimire, Vadym Apalkov, "*Ultrafast pulse pumping of topological nanospaser*", Journal of Physics: Condensed Matter, **35** (31), 315302 (2023).

Early Career, grant N° DE-SC0020311

New correlated numerical methods for attosecond molecular single and double ionization

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Project Scope

Continuous advances in the XUV and soft-x-ray ultrafast technologies, pursued at large free-electron-laser facilities 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) We have developed a modified version of Becke's scheme [Becke1988] that applies to molecular photoionization, with atomic weights switched off outside the molecular region. A central master grid covers the complementary smooth weight in the interstitial and long-range region. **[Ref. 1]**

ii) We have extended LUCIA code [Olsen1988] to generate one-, two-, and three-body transition density matrices (TDM) between ionic states with arbitrary symmetry and multiplicity, using the formalism of string-based determinant expansions of wave functions **[Ref. 8]**.

iii) We interfaced the TDMs data from LUCIA, as well as the hybrid integrals from the SCATCI library of UKRmol+ [Masin2020], with ASTRA **[Ref. 8]**.

iv) We have derived and tested the formulas for one- and two-body operators between spin-coupled single-ionization states in terms of reduced ionic transition density matrices **[Ref. 8]**.

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 generates the close coupling blocks for overlap, Hamiltonian, and dipole operators. The code, takes into account group symmetry, multiplicity, close-coupling-space composition **[Ref. 8]**.

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 **[Ref. 8]**.

vii) The XCHEM code, of which the PI is a co-developer, is a benchmark for ASTRA modules. In collaboration with V. Borrás, we have rewritten the modules on scattering-states, the diagonalization of the Hamiltonian, 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, Ref. 5]**.

viii) We have tested the ASTRA CC code to compute bound-states observables in the N2 molecule, with both uncorrelated and correlated ions, and resonance parameters in neon **[Ref. 7]**.

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.

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) We have implemented the calculation of the total photoionization (PI) cross section of molecules, based on the optical theorem, and ascertain excellent agreement with reference data for the N_2, and H_2CO (formaldehyde) molecules, and for the boron atom. We have explored the scalability of the code to larger molecule, such as Mg-Py ($MgH_{12}C_{20}N_4$) **[Ref. 8]**.

xiii) We have implemented the calculation of the transient-absorption spectrum (TAS) in fixed-nuclei approximation, and started testing it on the O_2 and CO molecules *[under development]*.

xiv) J. M. Randazzo (CONICET) was postdoc in this project from Jan 2020 to Jan 2021. In July 2021, two postdocs, Carlos Marante and Siddhartha Chattopadhyay, joined the group, focusing on the development of the single- and double-ionization sectors of ASTRA.

xv) The project involved three undergraduate (D. Perkowski, F. Kalluf Faria, C. Klatt), one high-school student (Suchita Vennam), and now three graduate students (A. Short, N. Lewis, F. Kalluf Faria) in the group, who will use ASTRA to compute pump-probe TAS and photoelectron spectra.

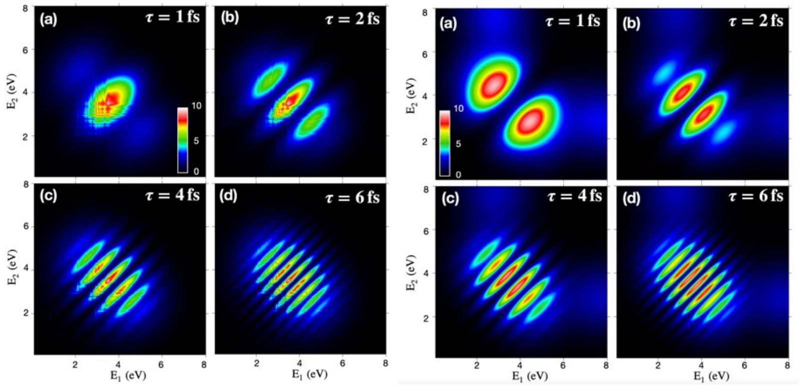

Fig. 1: Joint photoelectron distribution of the pump-probe TPDI of neon, in the Ne^{2+} $2p^4$ (^1S) (left panels) and the Ne^{2+} $2p^4$ (^3P) (right panels) channels, at four delays. The two-particle interference [Palacios2009] has opposite parity for the two parent-ion multiplicities, which reflects the different exchange symmetry of the photoelectron pair.

xvi) We have implemented a two-photon double-ionization (TPDI) virtual-sequential model to reproduce the pump-probe double ionization of atoms and molecules. The method, benchmarked in helium **[Ref. 6]** has been extended to neon. Results are being prepared for submission.

xvii) We have implemented the calculation of multichannel scattering states in ASTRA. This is a major development that allows us to compute partial photoionization cross sections, molecular-frame photoelectron angular distributions (MFPADs) and, in the next cycle, the fully differential photoelectron angular distributions for pump-probe processes. The results are in exceptionally good agreement with benchmark calculations with XCHEM.

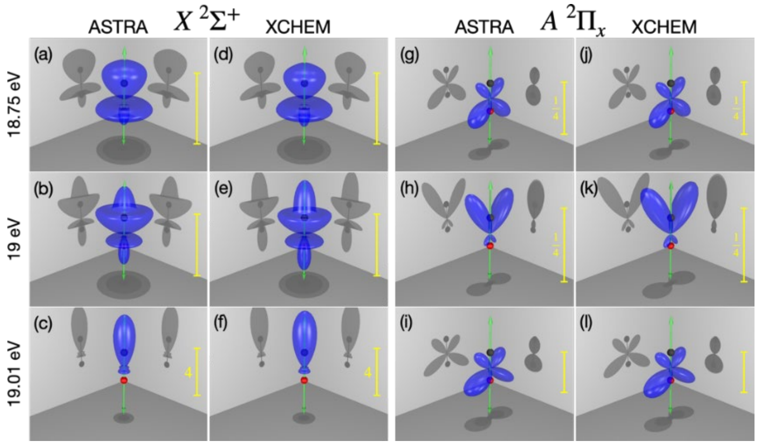

Fig. 2: Comparison between MFPADs for the single ionization of the CO molecule in two different ionic channels, computed for three energies across an autoionizing state using both ASTRA and XCHEM. A similarly good agreement is found for the integral partial cross sections and for the laboratory-frame photoelectron angular distributions. Good agreement with experiment is found for the partial ionization cross section of formaldehyde.

xviii) These results have been presented at conferences (DAMOP and ATTO VIII), and the associated manuscripts are either submitted or in preparation. The contribution J. M. Randazzo, C. Marante, S. Chattopadhyay, H. Gharibnejad, B. I. Schneider, J. Olsen, L. Argenti, *ASTRA, A Transition Density Matrix Approach to the Interaction of Attosecond Radiation with Atoms and Molecules*, Proceedings of the ATTO VIII Conference, is due to be published by Springer-Nature.

Future Plans

Finalize the benchmarking of the TDSE solver in an essential-state basis to reproduce attosecond optical observables (ATAS, 4WM). Complete manuscripts on the MFPADs, ATAS, TPDI of neon, valence ionization of CH4, and photoionization of Mg-Py. Write TDSE solver in the full close-coupling basis, and projector on scattering states, to reproduce pump-probe photoelectron spectra. Progress with the extension of LUCIA to RAS-CI and GAS-CI. Implement the finite-pulse TPDI method in molecules and test it against existing experimental results.

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Peer-Reviewed Publications Resulting from this Project (2021-2023)

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Ultrafast Atomic and Molecular Dynamics Driven by Ultrashort Intense Laser Pulses

(Award No. DE-SC0001771)

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Project Scope

The quest of studying the dynamics of matter at ultrashort time scales has driven the development of a variety of ultrafast laser technologies. Nowadays, laser pulses with a duration of a few tens of attoseconds (1 as = 10^{-18} s) have been generated in research laboratories. 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.

This progress has made it possible to probe, steer and control electrons in atoms, molecules, and solids. Measurements on the attosecond timescale have been under ongoing rapid development for more than a decade. Recently, the application range of these laser pulses has been even further extended by the capability to control the polarization of the laser light. Stimulated by this development there is an upsurge in activities toward an understanding of the interaction of matter with complex laser light fields which vary in pulse duration, polarization, or spatial configuration.

With the work in our projects, we aim to provide theoretical support related to the application of ultrafast optical techniques, the understanding of the temporal resolution of ultrafast dynamics in matter, and the analysis of processes driven by complex light fields. A current focus is on the study of phenomena that are driven and controlled via the polarization of the light field. We address fundamental questions concerning the interaction of atoms and molecules with intense laser pulses as well as provide support for ongoing experimental work in the research area.

Recent Progress

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

A. Ionization with short circularly and elliptically polarized laser pulses

In this project we analyzed the dependence of the laser induced ionization probability of atoms on the magnitude and sign of the magnetic quantum number of the initial state, previously observed in experiment [1,2]. The selectivity in ionization is a key element for the generation of ultrashort spin-polarized electron pulses, which are sources to probe chiral systems and magnetic properties of materials on ultrafast timescales. In our calculations we showed that doorway states that are exclusively accessible from the initial state for counter-rotating electrons provide a mechanism for this selectivity in ionization in the multiphoton and tunneling regime and that an even larger ionization ratio of about 1:10 can be achieved in the widely unexplored few-photon ionization regime [DOE3,DOE4].

We have now extended these studies by obtaining photoelectron energy and angular distributions for the interaction of a rare gas atom with circularly and elliptically polarized laser pulses [3]. More specifically, we have analyzed the following recently reported observations and theoretical predictions. First, it has been observed that in circularly polarized laser fields the energy spectra of photoelectrons emitted from initial states with opposite helicity differ [1,2]. For counter-rotating electrons the maximum of emission occurs at lower energies than for co-rotating electrons, which was related to the difference in azimuthal velocities at the tunneling exit. Next, for ionization in elliptically polarized laser fields it has been observed that the most probable emission angle increases with the energy of the emitted photoelectron [4]. This observation contrasts with theoretical predictions based on classical Monte-Carlo calculations due to which the Coulomb interaction of the photoelectron with the residual ion should lead to a decrease in the photoemission. Furthermore, the emission angle was found to be larger for the counter-rotating electrons than for the co-rotating ones [5].

In our studies we showed that the differences in the photoelectron energy spectra and the shifts in the emission angles can be understood based on quantum selection rules for photon absorption and the above-mentioned additional pathways for counter-rotating electrons. Since the pathways are characterized by certain sets of quantum numbers, we were able to separate the probabilities for the pathways in the numerical calculations to support our interpretation. Furthermore, we developed a simple model based on the interference and relative phase difference between just three continuum states which provides remarkable agreement with the full numerical results and once again emphasizes the importance of the additional ionization pathways available for the counter-rotating electrons.

B. Analytical calculations of ionization rates

Ab-initio numerical solutions of the time-dependent Schrodinger equation, even for the single-electron atomic case are time-consuming. A popular alternative method is based on the so-called strong-field approximation, in which calculations are often performed using the saddle point approximation [6]. While applications of this approximation method have been successful, especially in the tunnel ionization regime, less is known about the limits of the application range of the technique. We have developed an alternative approach of calculating the Keldysh amplitude, i.e., the length-gauge form of the ionization amplitude in the strong-field approximation. In our approach the amplitude is evaluated exactly by expanding it in Fourier components and partial waves [7]. Comparisons of the semi-analytic model predictions with results of ab-initio numerical simulations of the time-dependent Schrodinger equation for the interaction of electrons in short-range potentials with intense laser light yield excellent agreement, for wavelengths from the single-photon to the multiphoton to the tunneling regime. Specifically, for ionization from initial states with higher angular momentum quantum number, e.g., *p*-states, a significant improvement over predictions based on the popular saddle-point approximation is found. Furthermore, the current model rate allows for interpretation of the strong-field ionization process in terms of multiphoton absorption pathways and angular momentum selection rules.

C. High harmonic generation in bichromatic laser fields

Enabling elliptically polarized high-order harmonics overcomes a historical limitation in the generation of this highly nonlinear process in atomic, molecular and optical physics with applications in other branches. Perhaps, one of the simplest configurations to implement for the generation is the use of two linearly polarized laser pulses at frequencies ω and 2ω in a geometry in which the polarization vectors are orthogonal to each other. Yet, generation of high harmonics in this configuration entails an important open question. A recent experiment has shown that in such bichromatic cross-polarized laser fields interacting with noble gas atoms high-order harmonics with a surprisingly large ellipticity can be generated [8]. However, this observation is counterintuitive and in disagreement with earlier theoretical predictions but attempts of theoretical analysis of the mechanism behind the surprising experimental result are sparse [9].

The development of our numerical TDSE solver in 3D puts us in the position to perform a systematic study of high harmonic generation in such fields. So far, we were able to shed new light on this controversy between experimental observations and theoretical predictions [DOE5]. Results of numerical calculations confirm the previous experimental data that in short laser pulses even harmonics with large ellipticity can be obtained for the interaction of such cross-polarized laser pulses with atoms initially in a *s*- or *p*-state, while odd harmonics have low ellipticity. The amount of the ellipticity can be controlled via the relative carrier-envelope phase of the pulses, their intensity ratio and the duration of the pulses.

D. Single-active-electron potentials for molecules

The long-term goal of our studies of the laser-driven excitation and ionization with structured light of various polarization stages remains the interaction of such laser pulses with molecules. We therefore develop single-active-electron potentials for diatomic molecules. The method is based on concept of the linear combination of atomic orbitals (LCAO) but requires additional potential terms to find good agreement with potentials from time-dependent density functional calculations, as shown in preliminary results in a different project [9]. We are in the process of studying which kind of additional potential terms are useful and how those can be justified.

Future Plans

We will continue to focus on the interaction of atoms with circularly and elliptically polarized lased light in view of recent experimental work. For example, we plan to further analyze the observation of a flip of the asymmetry in the forward-backward emission of photoelectrons in few-cycle circularly polarized pulses as a function of electron energy [11]. Furthermore, we plan to continue our work on high harmonic generation in bichromatic laser fields, in order to further deepen our understanding of how the ellipticity of the harmonic signals can be controlled. Finally, we plan to develop single-active-electron potentials for homonuclear diatomic molecules and then extend the work to heteronuclear molecules.

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Peer-Reviewed Publications Resulting from this Project (2021-2023)

[DOE1] 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).

[DOE2] J. Venzke, A. Becker, and A. Jaron-Becker, *Imaging attosecond ring current dynamics in helium atom,* Physical Review A **103**, 042808 (2021).

[DOE3] S. Walker, L. Kolanz, J. Venzke, and A. Becker, *Enhanced ionization of counterrotating electrons via doorway states in ultrashort circularly polarized laser pulses*, Physical Review A **103**, L061101 (2021).

[DOE4] S. Walker, L. Kolanz, J. Venzke, and A. Becker, *Selectivity in electron emission induced by ultrashort circularly polarized laser pulses,* Physical Review Research **3**, 043051 (2021)

[DOE5] B. Ghomashi, S. Walker, and A. Becker, *Enabling elliptically polarized high harmonic generation with short cross polarized laser pulses,* Scientific Reports **13**, 012843 (2023)

Nonlinear X-ray Optics for Transition Metal Chemistry and Coherent X-ray Spectroscopy

Award # DE-SC0023270

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I. Project Scope

This project focuses on developing X-ray free-electron laser (XFEL)-based nonlinear hard x-ray optics to probe the dynamics of electrons that control chemical bonding and reactivity. Our approach exploits the phenomenon of stimulated X-ray emission spectroscopy (S-XES) from Kα and Kβ lines of 3d transition metal systems and aims at developing fundamentally new X-ray spectroscopy tools based on these phenomena. The research focuses on two thrusts:

Thrust 1: Develop S-XES into a New Ultrafast X-ray Spectroscopy Probe of Electronic Structure and Dynamics with Enhanced Sensitivity. The chemical sensitivity of Kα and Kβ X-ray emission is provided by the energies and intensities of multiplet (final state) lines that comprise each spectrum. In Thrust 1, we will first determine the optimal range of XFEL pump and seed pulse parameters to achieve Kα and Kβ S-XES in Mn compounds. Based on these findings, we will control the enhancement of individual multiplet lines by appropriate tuning of the seed and pump pulse parameters. We pump and seed Kα and Kβ S-XES in chemically and spectroscopically important Mn model compounds using two-color XFEL pulses. We establish the concentration limits for seeded S-XES and investigate if this approach can be extended to metalloproteins. The last aim is to observe stimulated resonant inelastic X-ray scattering (S-RIXS), which might further enhance the spectral sensitivity of our new approach.

Thrust 2: Develop Phase-Stable Femtosecond X-ray Pulse Pairs for Application to Coherent Spectroscopies. We exploit the phenomenon of S-XES to develop phase-stable femtosecond X-ray pulse pairs for application to coherent spectroscopies. Our first aim is to determine the correlation of XFEL pulse parameters and phase-stable X-ray fs pulse pairs by implementing new diagnostics that show under which conditions phase-stable X-ray pulse pairs can be best generated. Using this information, we optimize the parameters for the XFEL pump pulse compression to ensure the required pump pulse intensity and duration for creating phase-stable X-ray pulse pairs the maximal intensity and range of temporal spacing. The last aim is to demonstrate the application of phase-stable X-ray pulse pairs for nonlinear X-ray spectroscopy by conducting a proof-of-principle transient absorption experiment. Here we measure a sample in an excited state and follow how its decay affects each of the two transient X-ray pulses as a function of pulse spacings in the 2-10 fs time window.

II. Recent Progress

During our previous studies of S-XES of various Mn compounds, the stimulated emission displayed large spatial inhomogeneities and spectral broadening in single-shot spectra, beyond what would be expected for any multiplet splitting or spectator core-hole generation [1]. We are now understanding the observed phenomena by implementation of 3D Maxwell-Bloch theory recently developed by our collaborators [2]. We find that the inhomogeneous spectra arise from emitted hard X-rays behaving like an optical laser that filaments and forms a supercontinuum (generates white light) [3]. The spatial distribution arises form formation of hotspots during gain guiding driven focusing and filamentation in the transition from spontaneous to amplified emission [4,5]. During this process large energetic broadening analogous to super-continuum generation is driven through Rabi flopping [6], i.e., the periodic modulation of populations in two-level systems within a time-varying field. Rabi flops/cycles are ubiquitous in nature and seen in many applications from photonics [7] to quantum computing [8] but have not yet been observed in the hard X-ray regime. In general, despite numerous efforts [9–12] to extend nonlinear optics to X-rays, many phenomena such as filamentation that is often associated with nonlinear optical regime have previously not been observed or investigated with hard X-rays. This is due to the physical origin for these phenomena in the optical regime come from sample nonlinearities predominately arising from the Kerr effect and plasma generation that modify the refractive index [3], which in hard X-rays is anticipated to be close to unity. Our results demonstrate that many aspects of strong lasing physics associated with the optical regime can occur in hard X-rays paving the way for new nonlinear hard X-ray lasing based optics. To elucidate the filamentation process we focus on the response of Mn to single strong spike representative of the strongest spike in a self-amplified spontaneous emission (SASE) pump pulse, as previous studies have suggested a temporal spike only creates super-fluorescent emission if the intensity is high enough for sufficient population inversion [1]. Fig. 1a shows time domain of a gaussian pump pulse to

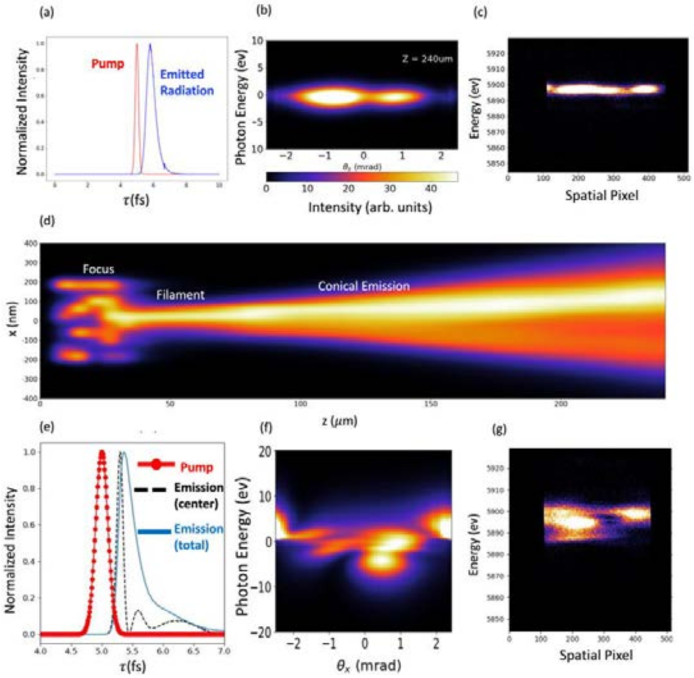

Figure 1 Rabi Flopping and Filamentation. (a) Example of simulated SASE spike and emitted light. (b) and (c) Simulated and experimental observed 2D spectral-spatial spectra. (d) Simulation of focusing, filamenting and conical emission of hard X-rays resulting in observed hotspots. (e) Rabi Cycles at increased pump intensity. (f) Simulated 2D spatial spectral distribution where Rabi cycles occurred. (g) Analogous observed S-XES single-shot spectrum.

represent a single SASE spike (10 μJ pulse energy, 150 nm diameter beam size, 100 attoseconds pulse length) and the time domain emitted radiation at the end of propagation through the sample. The energy-angular dispersion for the one of the transverse axes (z axis is designated as the propagation axis) of the emitted light is plotted in Fig. 1b. The two hotspot spectra observed in Fig. 1b is analogous to many of the observed spectra with example plotted in Fig. 1c. We find that during the beginning of the propagation the emission process is dominated by spontaneous emission so there is a wide and random distribution of the emitted light in space. When transitioning to the region of amplified spontaneous emission the light focuses towards the center experiencing a gain guiding effect [4] as the population inversion centers towards the pump focus. Upon entering strong lasing/fluorescent regime the population inversion decreases resulting in gain saturation that is uneven in space. This results in a conical emission regime, spreading out the light and diffracting any hotspots seeded from the transition from spontaneous to amplified emission. This total process is captured in Fig. 3d which shows the transverse distribution of the light for one of the transverse axes as function of propagation axis where the focusing, filamenting, and diffracting of the hot spots can clearly be seen. When increasing the intensity of the pump pulse, we find that Rabi oscillations could occur in the emitted radiation near the pump focus which is illustrated in Fig. 1e. Due to inhomogeneities of the Rabi flopping in space and tradeoffs between different possible decay channels during the Kα stimulated emission process, the total emitted radiation exhibits a strong trailing edge resulting in a redshift that is consistent with previous study near the strong lasing regime [13]. An example of output 2D spectra with large spatial/spectral clumps that form the induced Rabi oscillations combined with filamentation and the corresponding observed experimental spectra are plotted in Fig. 3f and Fig. 3g, respectively.

With newly implemented 3D maxwell Bloch theory [2] we can now illustrate how hard X-rays can behave like optical lasers during filamentation resulting spatially inhomogeneous and energetically broad spectra that are observed in stimulated emission experiments. The physical processes of gain guiding [4] and Rabi-flopping [6] drive these effects and are demonstrated concretely in hard X-rays for the first time. Further understanding and harnessing of such effects will be critical for next generation nonlinear X-ray science. This research is currently in preparation for a manuscript.

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III. Future Plans

- We have received two beam times at SACLA to carry out the research for the two thrusts, respectively. The first beam time will be in November 2023 focusing on Kα S-XES for various Mn compounds with different oxidation states. Learning from our data published recently, we will adjust the seed pulse to the lowest possible intensity levels for gaining more control of seeding the various multiplet lines. The second beam time will in March 2024 focusing on X-ray pulse pair generation. Here we will employ a new setup that allows us to simultaneously measure the pump pulse, seed pulse, and S-XES fringe spectra.
- Finishing the writeup of two manuscripts on the seeding of multiplet lines in Mn S-XES, and on the spectral phenomena discussed in the Recent Progress section. We will also Explore potential applications of the recently spectral phenomena (filamentation, Rabi oscillations).
- Analysis of existing data, preparation for the November 2023 and March 2024 beam times, analysis of the data taken at these beam times.
- Dissemination of results at conferences, meetings, and in peer-reviewed journals

IV. Peer-Reviewed Publications resulting from this Project (2021-2023)

Doyle, MD; Halavanau, A; Zhang, Y; Michine, Y; Everts, J; Fuller, F; Alonso-Mori, R; Yabashi, M; Inoue, I; Osaka, T; Yamada, J; Inubushi, Y; Hara, T; Kern, J; Yano, J; Yachandra, VK; Rohringer, N; Yoneda, H; Kroll, T; Pellegrini, C; Bergmann, U; **Seeded stimulated X-ray emission at 5.9 keV**, *Optica* **10**, 513-519 (2023) https://doi.org/10.1364/OPTICA.485989.

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

Award Number: DE-SC0012376

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Project Scope

The goal of our research program is to investigate *fundamental interactions between ultrafast photons and molecular systems* to advance quantitative understanding of electron correlations, charge transfer and proton transfer. Our research investigations focus on probing, on femtosecond and attosecond time-scales, 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 where we were awarded beamtimes. **2)** The investigations of electron dynamics in molecules at the attosecond timescale with the XLEAP capability at LCLS-II. **3)** Time-resolved molecular dynamics using the MeV-UED instrument at SLAC Nat. Lab.

We use IR/UV table-top lasers with our COLTRIMS at our UConn-based lab to prepare our FELs experiments and train our students. We present below results completed this past year and plans for the immediate future.

Recent Progress

1. Probing ultrafast roaming mechanisms in ethanol: electron transfer versus proton transfer

A topic of great interest in molecules is roaming mediated proton transfer (PT) [a] and the "inverse" harpoon mechanism, which is electron transfer (ET) from the neutral moiety to the dicationic cofragment [b]. Recent work includes pump-probe studies with both FELs and table-top optical lasers. During roaming, the molecule dissociates and the fragments transiently move in each other's proximity, albeit at larger internuclear distances, in contrast to directly following the path predicted by conventional transition-state theory. Specifically, roaming chemistry has been observed in neutral hydrogen and hydrogen molecule elimination [c]. For example, roaming-mediated proton transfer (PT) was observed in several alcohol dications created by a strong pump pulse and probed by a weak pulse. At the end of the roaming process in the dication, the charges of the system are separated by PT-mediated charge transfer, which plays an important role, e.g., in chemistry, biochemistry and astrochemistry. Theoretical calculations show that the time scale of PT is typically on the order of tens of femtoseconds, similar to some electronic decay channels. Recently, direct evidence for an ultrafast competition between ET and PT was observed by Gope et al., [b] in the dissociative ionization of methanol.

We have combined an experimental and theoretical study of the competition between ultrafast ET and PT in the dissociative ionization of ethanol. We used pump-probe spectroscopy with the FLASH-II XUV FEL and measured the fragment ions using Coulomb explosion imaging with a COLTRIMS. The experiment was performed for three different photon energies, 28, 32, and 70 eV, in order to gain a better understanding of the molecular dynamics. The ethanol dication was created by the pump XUV pulse, and neutral H_2 is formed by an ultrafast isomerization process. Due to the induced-dipole interaction between the charged and the neutral moieties, H_2 is weakly bonded to $C_2H_4O_2^+$ and undergoes a long-range, prolonged roaming. The second FEL XUV pulse acts as a disruptive probe that can interrupt the roaming process before the subsequent PT or ET occurs. If the probe pulse arrives early enough, it “disrupts” (i.e., dissociates or ionizes) the dicationic $(H_2{-}C_2H_4O)^{2+}$ precursor, leading to a depletion of the H_2^+ and H_3^+ channels. For longer time delays, the probe pulse is less likely to disrupt the roaming, thus the yield of both H_2^+ and H_3^+ increases until reaching saturation. H_3^+ formation occurs when H_2 abstracts one proton from either the methyl or the hydroxyl site, while H_2^+ is formed via ET from H_2 to the dication. Since the formation can occur with slightly different time scales, the ratio of H_2^+ to H_3^+ will vary, depending on when the roaming process is disrupted. We used for our experiment ion momentum imaging to identify those H_2^+ and H_3^+ ions that are produced via roaming, by investigating the yields and yield ratios as a function of pump-probe delay. The analysis of our data allowed us to observe dynamics as a function of time delay; i.e. a change in the yield ratio of H_2^+ to H_3^+ as a function of time delay. Through the use of ab initio molecular dynamics simulations, we were able to attribute this behavior to a competition between electron transfer from H_2 to $C_2H_4O_2^+$ and proton transfer from $C_2H_4O_2^+$ to H_2 [1].

2. Machine-learning calibration of intense X-ray free-electron-laser pulses using Bayesian 2 optimization

X-ray free-electron lasers (XFELs) have brought new ways to probe and manipulate atomic and molecular dynamics with unprecedented spatial and temporal resolutions. A quantitative comparison of experimental results with their simulated theoretical counterpart, however, generally requires a precise characterization of the spatial and temporal X-ray pulse profile, providing a nonuniform photon distribution. The determination of the pulse profile constitutes a major, yet inevitable, challenge. A calibration scheme was developed by the Santra group for intense XFEL pulses utilizing a set of experimental charge-state distributions of light noble gas atoms at a series of pulse energies. Our experimental data published in the case of the resonance-enhanced multiphoton ionization in the X-ray regime project [7] were used in combination with first-principles simulations of the underlying atomic X-ray multiphoton ionization dynamics to develop the model. The calibration builds on Bayesian optimization, which is a powerful, machine-learning-based tool particularly well suited for computationally expensive numerical optimization. The model successfully demonstrated the calibration of the pulse duration as well as the spatial fluence distribution profile of XFEL pulses. Our method will serve as a comprehensive tool for characterizing ultraintense and ultrafast X-ray pulses [2].

Future Plans.

Our goal is to complete and start new ultrafast molecular dynamics projects using FELs. The principal areas of investigation planned for the coming year are: **1)** Finish the draft and submit the manuscript regarding our successful time-resolved UED experiment conducted at SLAC National lab. The work investigated the competition of molecular dissociation and ring opening in 2-bromothiophene (C_4H_3BrS). **2)** Finish the draft and submit the manuscript for the time-resolved ultrafast dynamics experiment, subsequent to the ionization of C_{60} near a giant resonance (surface plasmon) in the XUV regime using the FLASH-II FEL. This resonance consists of strongly correlated electrons. **3)** Finish the analysis of the time-resolved experiment we conducted during our granted FEL beamtime at the FERMI FEL. The experiment consisted to investigate intermolecular interactions of molecular iodine solvated in small water clusters. **4)** Carry out the experiment that will map out the UV-induced dissociation of water molecules and will measure the hydroxyl radical formation in real time using a COLTRIMS at the EUXFEL in the spring of 2024. Our beamtime proposal was accepted and this experiment will prepare us to use the future high rep rate and the COLTRIMS named DREAM at LCLS-II.

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

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Program Scope or Definition

This project, which started on August 15, 2019, is in collaboration with the groups of Daniel Rolles and Artem Rudenko at Kansas State University, Peter Weber 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 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 focused 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. The second two-year cycle, which just concluded, added an investigation of the wavelength dependence of the reaction dynamics to the scope of the project and also included a new target molecule: cyclopentadiene. 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.

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 in the project 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 and FLASH in Hamburg, and the FERMI FEL in Trieste.

Recent Progress

I. Interconversion between quadricyclane and norbornadiene

The UV-induced ultrafast interconversion between quadricyclane (QD) and norbornadiene (NB) can store and release a significant amount of chemical energy in a reversible manner, which makes this isomerization reaction an interesting candidate, e.g., for solar energy storage. Following up on our initial work on this reaction, we have continued the data analysis of our time-resolved photoelectron spectroscopy (TRPES) measurements at FERMI and the ultrafast electron diffraction (UED) experiment at SLAC and have made significant progress in the first-principles simulations, as described in more detail in the following. Furthermore, we performed high-resolution UV/XUV absorption measurements for QD and NB at the synchrotron SOLEIL and ultrafast X-ray scattering (UXS) experiments on both molecules at the LCLS. Combining these complementary data sets and our extensive electronic structure and molecular dynamics calculations, we have developed a comprehensive understanding of the UV absorption spectra of QD and NB and the ensuing electronic relaxation and structural interconversion dynamics when starting the reaction from QD.

I.1 Ultrafast electronic relaxation. Combining the experimental TRPES data recorded at FERMI with our electronic structure calculations (performed using RMS-CASPT2 based on SA(9)-CASSCF(2,6)) and molecular dynamics simulations using the surface-hopping method, we have identified the contribution of two dominant and competing electron relaxation channels after excitation of QD at 200 nm, which had not been identified in prior work on this molecule: (i) A "slow" relaxation proceeding via the 3p Rydberg state on a timescale of several hundred femtoseconds, visible in Fig. 1 at 2.1 eV binding energy; and (ii) an extremely fast (< 100 fs) relaxation via strong Rydberg-valence coupling that appears as a nearly vertical structure at small delays. Both relaxation pathways can lead to interconversion from QD to NB as well as to the formation of hot ground-state QD, both of which appear at ~7 eV binding energy in Fig.1. Our calculations are able to clearly distinguish both pathways.

We have also performed Rydberg fingerprint spectroscopy (RFS) measurements at Brown at variable pump wavelengths between 195 and 220 nm, which are currently still under analysis. The preliminary results show a clear dependence of the relative population of the 3p and 3s Rydberg states on the excitation wavelength.

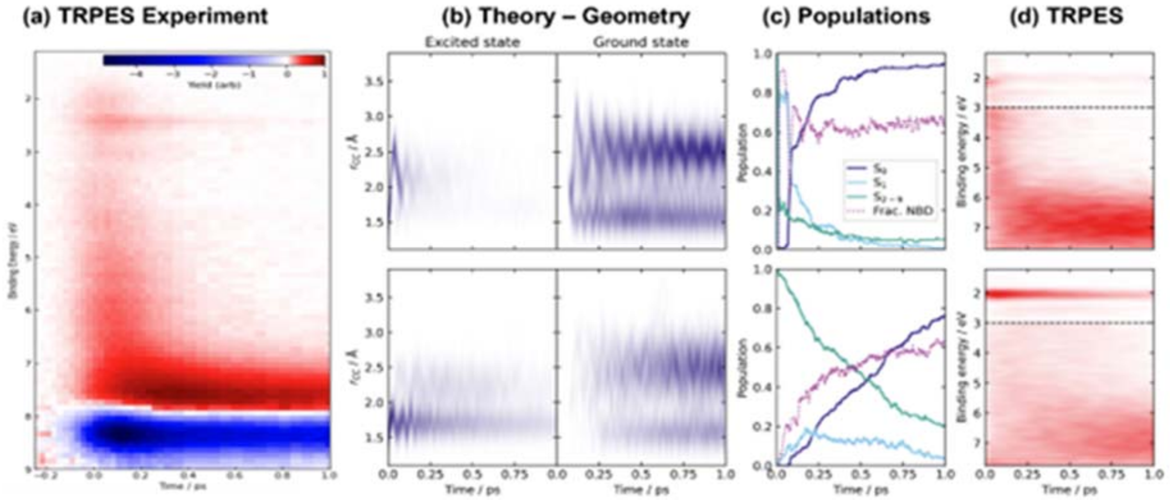

Figure 1: (a) Experimentally measured photoelectron binding energy spectra of QD after 200-nm excitation as a function pump-probe delay time between UV and XUV pulse, plotted as the electron yield *difference* between spectra taken with and without the UV-excitation pulse. (b, c, d) Simulated dynamics, separated into the two mechanisms (top and bottom row). The top row shows the *fast* mechanism corresponding to trajectories originating on S_2 ($3p_x$/V mixed valence state) and the bottom row the *slow* mechanism with trajectories originating on the $S_{3/4}$ ($3p_{y/z}$ Rydberg states). (b) Heat maps for average carbon-carbon distance r_{cc}. The left-hand panel shows the dynamics for the excited states, while the right-hand panel shows the S_0 ground state. (c) Populations of the electronic states as a function of time, where $S_{2\text{-}9}$ shows the cumulative population on all excited states above S_1. (d) Simulated TRPES signal, convoluted by a Gaussian of FWHM 0.1 eV and 94 fs. Signals with binding energy above 3 eV have been scaled 300% (the two regions separated by a horizontal dashed line).

I.2 Nuclear dynamics captured with UED. While the TRPES experiment is ideally suited to investigate the electronic relaxation dynamics, it cannot capture the nuclear motions or distinguish the QD and NB reaction products since their ionization potentials are rather similar and their spectral signatures are strongly overlapping. We have therefore studied the same interconversion reaction using MeV-UED and X-ray scattering at LCLS using the same excitation wavelength of 200 nm.

Figure 2 shows a false color plot of the UED 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, along with the calculated signal from the trajectory simulations. There is good qualitative agreement between the experiment and theory, except for the positive signal appearing around t = 0 and s < 1 Å-1, which we attribute to changes in the electronic density after excitation to the Rydberg state. The theoretical diffraction signal was calculated using the independent atom model, which does not capture changes in electronic density, thus we are now performing ab-initio scattering calculations that should reproduce this feature as well. The time dependence shows that the low-s signal rises first, and the signals at larger s start to increase significantly when the low-s feature decays. Given that the low-s feature indicates the molecule is in the Rydberg state and the higher s feature represents structural changes, this suggests that large changes in structure are delayed with respect to excitation. While the analysis is still ongoing, our preliminary interpretation is that the slow channel is dominant, and the large changes in structure are generated after the molecule crosses the conical intersection and reaches the ground state.

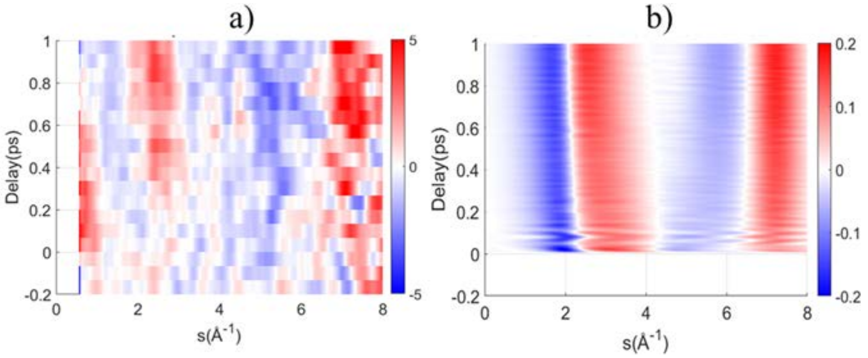

Figure 2: a) Experimental difference-diffraction signal. b) Calculated signal based on the trajectory simulations.

Furthermore, once the UV-excited QD and NB molecules have returned to the electronic ground state, the dynamics are far from over, and the molecules can continue to interconvert and, eventually, break up into smaller fragments, e.g., by emission of a hydrogen or a C_2H_2. We can see consistent signatures of these ground-state dynamics in the data TRPES, UED and XRS data (not shown here). These data are currently still under analysis and interpretation.

II.2. Structural dynamics of cyclooctadiene measured by UED

Photoexcitation of the eight-membered ring cis-cycloocta-1,3-diene (cis-COD) can lead to the formation of multiple products, including trans-COD and the four-membered ring bicyclo [4.2.0]oct-7-ene (BCO). Previous studies using femtosecond high-intensity photoionization mass spectrometry by Fuss and collaborators concluded that the main reaction products on the femtosecond scale to be trans-COD and hot cis-COD, with BCO accounting for only 1% of the products(1). On the other hand, it is known that BCO can be formed thermally or by sequential excitation from cis COD to trans-COD and then from trans-COD to BCO. Time resolved photoelectron spectroscopy measurements (TRPES) measurement of the same molecule have found the relaxation to the ground to take place in approximately 100 fs after excitation with a photon energy of 4.75 eV (2). We have carried out UED measurements, supported by theory, on the dynamics of COD excited by 6.2 eV photon energy (Fig. 3). The experiments and data analysis were carried out in collaboration with Thomas Weinacht and Yusong Liu, and the theory was performed in the group of Spiridoula

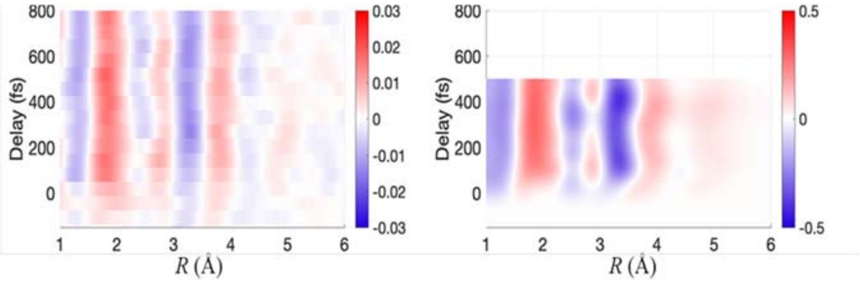

Figure 3. Experimental and theoretical difference pair distribution function (ΔPDF) for photoexcited COD. Left panel: Experiment. Right panel: Theoretical signal constructed based on the simulated trajectories.

Matsika. We see clear evidence for the prompt (within 150 fs) formation hot cis-COD, trans-COD and BCO. The UED observable was calculated from the trajectory simulations, and shows good agreement with the experimental data. The excited molecules go through a transition geometry at the conical intersection, before returning to the ground state. We have identified a new reaction channel that involves a distortion of the ring, in which the ring becomes more elliptical. Along this coordinate, the wavepacket moves compactly from the Franck-Condon region to the conical intersection, after which it spreads rapidly as it reaches the ground state and multiple products are formed. We are currently preparing a manuscript on these results. Further experiments using time-resolved photoelectron spectroscopy are planned to experimentally verify the transition to the ground state and the timing of formation of the different products.

III. Cyclopentadiene and methylated cyclopentadienes

Organic ring systems are ubiquitous molecular structures. They occur in many biological systems where they have important functions, they are part of numerous synthetic materials, and they are commonly found in pharmaceuticals. The creation of, and interconversion between, organic ring systems is of central importance to synthetic chemistry.

Organic three-membered and four-membered rings are well known but are more difficult to create in comparison to larger rings. This is because small rings have significant strain on the carbon bonds as their bond angles are far below the preferred sp^3, sp^2 or sp hybridization angles. Photochemical pathways afford an elegant access to such strained rings, since the non-thermal photon energy can be efficiently converted to chemical energy in coherent reaction pathways. Yet their reaction mechanisms are poorly understood, and their dependence on the excitation wavelength is completely unknown. Based on literature reports, we chose the cyclopentadiene (CP) system for our investigations. Upon UV excitation, the molecule undergoes reactions to bicyclo[2,1,0]pentene (BP)(3; 4) and tricyclo[2,1,0,02,5]pentane (TP)(5).

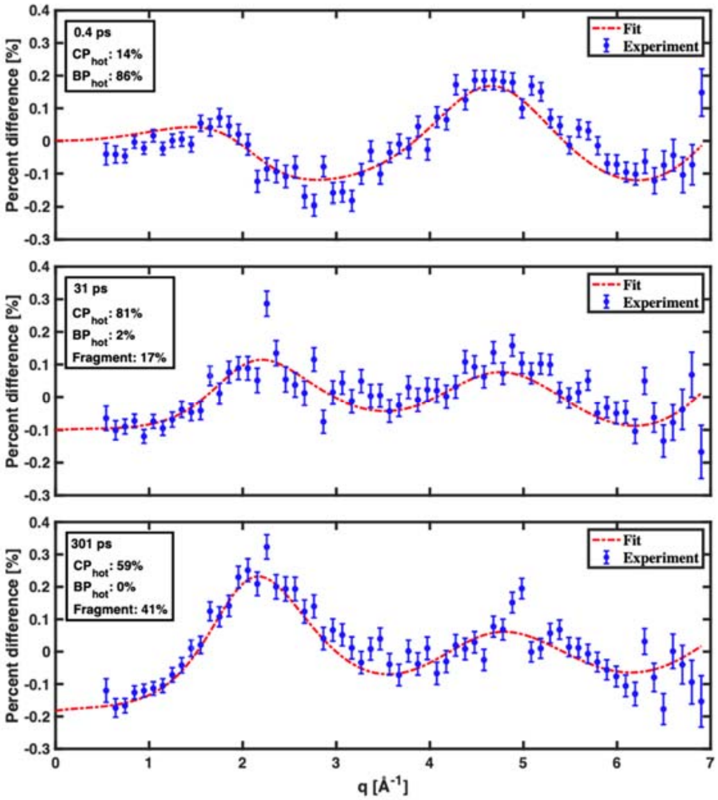

Figure 4: Pump-probe x-ray scattering signals of CP after excitation at 243 nm at 400 fs (top), 31 ps (middle) and 301 ps (bottom). The photochemical reaction initially yields the strained molecule BP with high yield. At longer decay time, the hot molecules decay into fragments.

III.1. Ultrafast X-ray scattering of CP. In June 2022 (LX65), we performed gas-phase x-ray scattering experiments at the CXI endstation of LCLS using three different pump wavelengths (243 nm, 252 nm, and 257 nm) to investigate the time-dependent structural changes of the molecule as it evolves along its reaction pathway. The experiment provided the first directly structural experimental evidence for the formation of the bicyclic, strained ring. In addition, we also found evidence for a back-reaction to form hot CP from BP on a time scale of many picoseconds and a fragmentation to form C_4H_x and CH_{6-x}. Figure 4 illustrates the percent difference scattering pattern of CP upon excitation with a 243 nm pulse across different time delays, together with preliminary fits. At extended delays, the fraction of BP decreases, which is caused either by a back-reaction to hot CP or by fragmentation. Comparison between the different wavelengths in Figure 5 shows a noticeable difference in final product formation, suggesting a wavelength-dependent branching ratio. The full set of data from LX65 is still being analyzed and merged with the theory results. To support the X-ray scattering experiments, we are performing time-resolved mass spectrometry measurements at KSU at the same pump wavelengths as used at LCLS. While the analysis is still ongoing, the mass spectra also show different levels of product formation at different wavelengths. Although difficult to interpret on their own, we hope that the combination of the mass spec results with the X-ray scattering experiment and the dynamics calculations will allow us to obtain a complete picture of this fascinating reaction.

<u>III.2. Methylated cyclopentadienes</u>. We have carried out UED and TRPES experiments on methylated derivatives of CP to determine how the addition of methyl groups affects the dynamics and the yield of different products. These experiments, combined with theory, will help us determine the key nuclear motions and electronic changes that drive the reaction. We have carried out UED measurements on penta-methylated CP excited at a wavelength of 266 nm at UNL. The absorption band of the methylated derivatives is shifted with respect to CP so we used a different wavelength. In the UED measurements, we see clear evidence of significant structural changes taking place over the first few hundred femtoseconds. The data analysis and interpretation for this experiment is still in the early stages.

The TRPES measurements on tetramethyl-CP and pentamethyl-CP were performed at the FLASH FEL facility in Hamburg at two different excitation wavelengths, 266 and 257 nm, as shown in Figure 6, complemented by time-resolved mass spectrometry at 266 nm at KSU. Our preliminary analysis of the FLASH and KSU data shows different de-excitation timescales for tetramethyl-CPD and pentamethyl-CPD as well as a clear dependence on the excitation wavelength. We plan to confirm and complement these observations by further UED

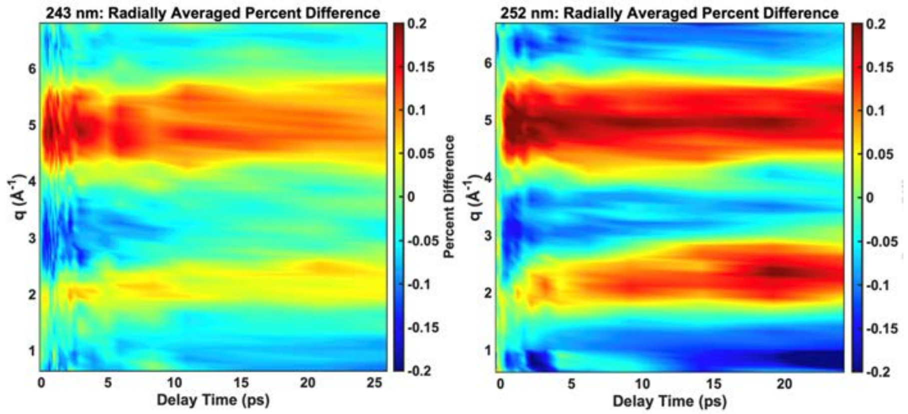

Figure 5: At LX65, we measured the reaction dynamics of CP upon optical excitation at different wavelengths. Shown is the radially averaged percent difference scattering signal as a function of pump-probe delay time for excitation at 243 nm (left) and 252 nm (right). While a detailed analysis is ongoing, a visual comparison suggests that the signals depend on the excitation energy. (Note in particular the deep blue signal at very low q for 252 nm).

experiments at UNL and via ultrafast X-ray scattering at LCLS, as well as by comparison with electronic structure calculations and molecular dynamics simulations that are currently in progress.

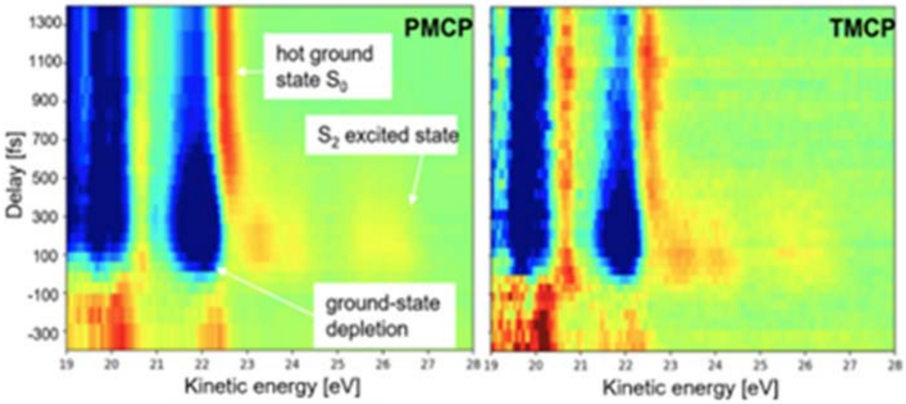

Figure 6. Time-resolved photoelectron spectra of PCMP (left) and TMCP (right) after 266-nm excitation measured at FLASH with 29-eV photons, plotted as the electron yield *difference* between spectra taken with and without the UV-excitation pulse. The residual positive difference before time zero is an artifact due to insufficient background subtraction and will be corrected for in the final analysis. While the overall dynamics in PMCP and TMCP look rather similar, we observe differences in the time constants and the relative yields of the different spectral contributions.

IV. Distinguishing 3D molecular structures with Coulomb explosion imaging

Besides our efforts relying on ultrafast X-ray diffraction, UED and TRPES described above, we have continued to develop the Coulomb explosion imaging (CEI) approach as a complementary tool for studying ring-conversion reactions. Following up on a recent breakthrough experiment at the European XFEL (EuXFEL), which demonstrated that this technique can visualize the position of each individual atom in ring molecules with an iodine marker(6), within this project we have shown that XFEL-based CEI can be efficiently applied to distinguish "ring" and "chain" isomers of C_7H_8 molecules without any marker atoms. During the last year, we have worked on adapting this approach to three-dimensional imaging of non-planar molecules using table-top near-infrared lasers. As illustrated in Figure 7 for three molecules with

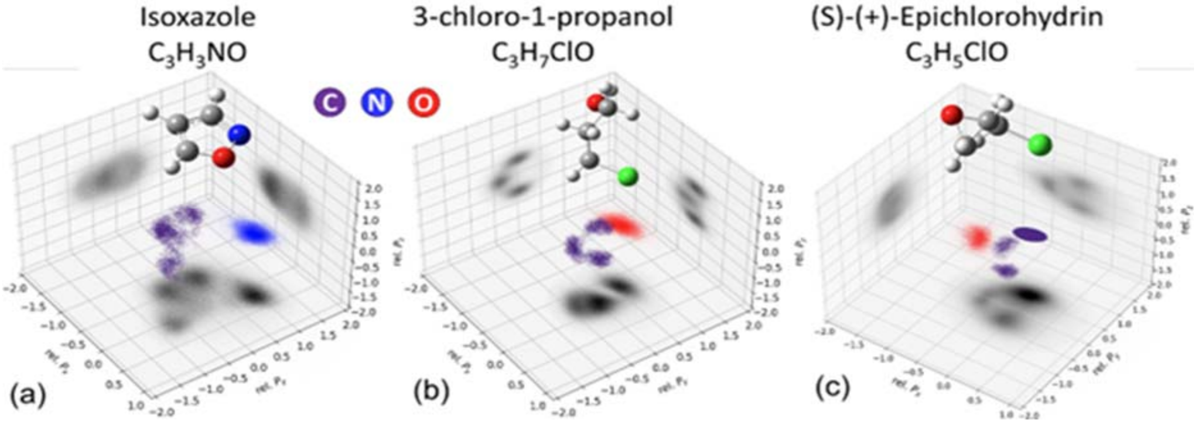

Figure 7: 3-D CEI images (3-D Newton plots of the normalized fragment momenta) of (a) isoxazole, (b) 3-chloro-1-propanol, and (c) epichlorohydrin (corresponding ball-and-stick models of the molecular structures shown above), which serve as model systems for the geometries of the possible products expected to be formed in various ring-conversion reactions.

different geometries, to represent such 3D data, we utilize the modified 3D Newton diagrams that we introduced earlier for smaller molecules(7; 8). As can be seen from these data, each molecule exhibits a well-localized and distinctive pattern in 3D momentum space. A comparison with simple Coulomb explosion simulations shows that these patterns carry a unique signature of the 3D molecular geometry(9).

V. Attosecond X-ray scattering

In the past year, we continued our efforts towards simulating attosecond ring currents, and how they can be probed with hard X-ray scattering. These simulations are a compliment to the ring-opening studies in the collaboration, and these findings are expected to form the basis for potential XFEL measurements of currents in ring-shaped molecules via hard X-ray pump/probe. Building on our previously reported study of ring currents in oxazole(10), which relied on the ensatz that the scattering is proportional to the time-derivative of the density (11), we further determined how molecular shape dictates currents and scattering. We used real-time time-dependent density functional theory (RT-TDDFT) with hybrid functionals, and the time-evolving densities and currents were computed on-the-fly in parallel in the NWChem software package.

We previously observed that the scattering exhibits complex modulations related to short and long-range currents in the molecule. To further quantify this, we completed studies of currents in a range of molecules, for the case of UV as well as soft X-ray pumped dynamics. Hard X-ray pumps, which are the most likely modality for experiments, are currently a work-in-progress. Figure 8 shows the scattering modulations in UV-pumped carbon monoxide, roughly corresponding to a coherent superposition of π and π* states. At times of low current (0.28 fs, 0.40 fs), there is a broad weak scattering signal at 2.0 A^{-1}, arising from a distribution of weak short-range currents centered around each atom. As the electron flow increases, long-range curved currents appear (0.33 fs) which shifts the scattering peak to 1.5 A^{-1} and increases the magnitude by a factor of ~4. The shifts, intensity modulations, and time-varying widths of scattering peaks all contain information about the electron dynamics, making interpretation challenging even for simple case like carbon monoxide. Similar results for currents in homocyclic rings (benzene) and heterocyclic rings (aminophenol, oxazole) suggest these interpretations are general. This is being confirmed for a broader range of molecules and excitation types. Additionally, an improved description of coherent

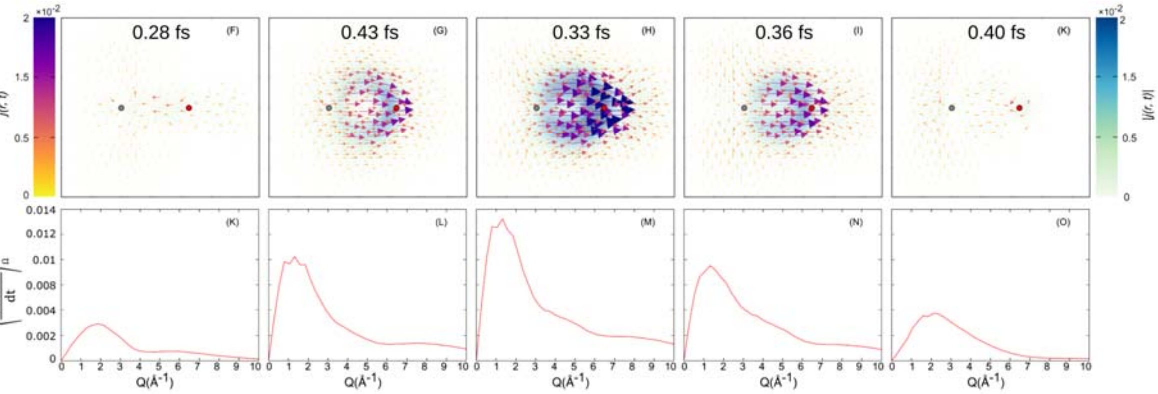

Figure 8. (top) Simulated attosecond currents in carbon monoxide following UV pumping to a π/π* superposition. (bottom) The corresponding X-ray scattering signal shifts from weak and high Q, when the currents are weak and local around atoms, to strong and lower Q when there is flow across the molecule.

scattering beyond the time-derivative ansatz is being developed by the Kirrander and Lopata groups.

We have investigated the role of Compton ionization in ultrafast non-resonant x-ray scattering(12). Figure 9 shows how elastic, bound-bound, and bound-continuum scattering contributes to the total scattering signal. It is evident that a significant portion of the total scattering stems from transitions to the continuum, shown as $S_{in}^{[1]}(q)$. This is an important observation which emphasizes that, for energy-integrating detectors, it is imperative that signals are predicted and interpreted using total scattering calculations which account for the full spectrum of transitions. In the context of electron dynamics, the effect is particularly striking and truncating the signal early is shown to lead to spurious and erroneous values. We have also investigated the role of electron correlation in scattering signals, finding the x-ray scattering signal is quite sensitive to correlation effects(13).

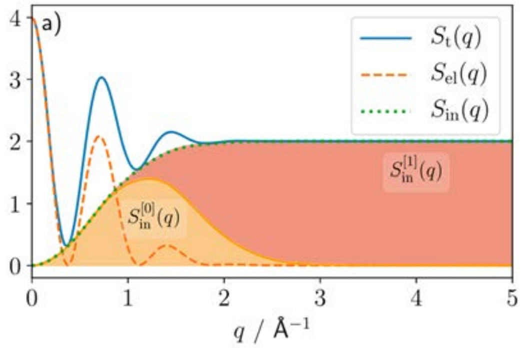

Figure 9. Total x-ray scattering signal, $S_t(q)$, from the asymmetric Shin–Metiu ground state, with the elastic $S_{el}(q)$ and inelastic components $S_{in}(q)$. The colored areas display the decomposition of the inelastic signal into the bound-bound $S_{in}^{[0]}(q)$ and the bound-continuum $S_{in}^{[1]}(q)$ inelastic contributions.

Future Plans

We will finalize the interpretation of the QD experiments and theory and submit these results for publication, similarly for the UED results on COD.

We have a beamtime scheduled for November of this year at the SLAC MeV-UED instrument. Here we will carry out experiments with CP and methylated derivatives. At the present time, we are optimistic that our LCLS beamtime application L10150 will get the green light for Run 22, which will happen in the first half of 2024. The experiments will build and expand our studies of the cyclopentadiene system. In particular, we hope to attain a better signal to noise ratio and a better time resolution than in the UXS beamtimes in the last user run, and we aim to study the methylated compounds during that beam time. We are also planning on repeating the time-resolved mass spectrometry experiments at KSU on CP and methylated CP to confirm and better quantify the observed differences between different excitation wavelengths and between the penta- and tetra-methylated species. The experimental results with be combined with the existing theoretical simulations on CP and new simulations for the methylated derivatives, which are currently in progress. We will then extract the relevant electronic relaxation pathways and nuclear motions, and compare CP with its derivatives.

These concrete scientific plans will be accompanied by further technical developments: At Brown University, we continue our development of a new photoelectron spectrometer that interfaces with a new ultrafast laser system. Using hollow core fiber compression, our target is to obtain a time resolution of <10 fs. First experiments will target the systems we are studying with the other methods, in particular cyclopentadiene and its methylated derivatives. At KSU, a new 100-kHz laser system will be installed this fall, which we hope to be a game changing step for our time-resolved Coulomb explosion imaging experiments. The new laser will also have a dedicated HHG source that we plan to use for TRPES experiments with superior temporal resolution. At UNL, we will upgrade the buncher cavity in our UED system, which we expect will result in better time resolution and long-term stability of the setup.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

Lauren Bertram, Peter M. Weber and Adam Kirrander, “Mapping the photochemistry of cyclopentadiene: From theory to ultrafast x-ray scattering,” Faraday Discussions (2023), Advance Article, 10.1039/d2fd00176d.

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Kyle Acheson and Adam Kirrander, "Automatic Clustering of Excited-State Trajectories: Application to Photoexcited Dynamics", J. Chemical Theory and Computations (2023), DOI: 10.1021/acs.jctc.3c00776

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

Award Number DE-SC0014170

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Program Scope or Definition

This project aims to investigate photochemical reactions at the molecular level by observing how the molecular structure changes upon light absorption. The project relies on ultrafast electron 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, which reveals the nuclear motions triggered by the laser excitation and the reaction products.

Introduction

In photo-induced molecular reactions light can be converted into chemical and kinetic energy on femtosecond time scales. The capability to observe 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 UED systems will be used in this project. The first is the MeV-UED instrument 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 1 kHz. This setup includes an optical system to deliver laser pulses with a tilted intensity front on the sample at multiple wavelengths. The tilted laser pulses compensate the velocity mismatch of laser and electrons through the sample to reach femtosecond resolution. We will also carry out X-ray scattering experiments at the CXI endstation at LCLS, which will be complementary to the UED measurements.

Recent Progress

Over the last year of this project, we have carried out UED experiments at UNL on two molecules: iodobenzene and trifluoroiodomethane (CF_3I). We have also improved our data analysis toolbox by developing a genetic algorithm structure retrieval code. The code was tested with simulated and experimental diffraction data. We successfully tested a new heated sample delivery system with liquid samples up to 150 C and are currently upgrading it to reach 300 C, which will allow us to work with solid samples that have very low vapor pressure. We have also continued the data analysis of three prior experiments on the dynamics of o-nitrophenol, stilbene and bromocyclopropane.

UED experiment on iodobenzene: We have captured the UV photodissociation of iodobenzene following excitation by a UV femtosecond laser pulse using our UED instrument at UNL. Prior measurements have observed that the dissociation proceeds with two different time constants, both on the order of hundreds of femtoseconds. Our experiments aim to verify these findings by looking at the dissociation time, and to determine the structural deformation of the ring during and after the dissociation. These experiments are carried out in collaboration with Daniel Slaughter of LBNL and with theory support from the group of Loren Greenman of Kansas State. We are currently at the stage of data analysis and interpretation. Preliminary analysis of the different diffraction signal (Figure 1) shows a dissociation time of several hundred femtoseconds.

Structure retrieval: We are developing a genetic algorithm for direct retrieval of time-varying molecular structures from diffraction measurements. Previously, genetic algorithms have been used to retrieve static molecular structures, or the structure of reaction products. Here we want to extend this method to the case of multiple reaction products and time-dependent products. We first characterized the performance of the genetic algorithm with simulated diffraction patterns, where the algorithm was able to retrieve structures consistently with errors below 1%. We then tested the algorithm with experimental UED data on the photodissociation of CF_3I, where a UV femtosecond laser pulse produces a C-I bond break. We have used the genetic algorithm to accurately capture the change in the F-C-F angle of the CF_3 fragment after dissociation. We are currently testing how fast vibrations that cannot be time-resolved affect the accuracy of the retrieval. We will also apply the algorithm to determine the relative yields for the cases where there are multiple reaction products, and investigate the effect of large amplitude vibration on the retrieval.

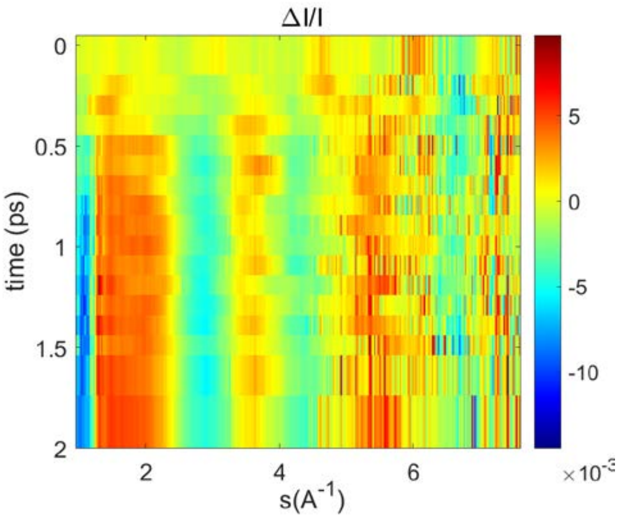

Figure 1. Diffraction difference signal for photoexcited iodobenzene. The diffraction signal matches a calculated signal of photodissociation of the iodine atom.

UED data analysis of UV excited bromocyclopropane (BCP): Organobromides are important in atmospheric chemistry because they can absorb UV light to generate highly reactive fragments that contribute to the depletion of ozone. Multiple pathways have been proposed in the photodissociation of BCP, producing a bromine atom and a cyclopropyl radical or an allyl radical, where an intermediate step might produce a transient allyl-Br radical. We have carried out UED measurements at the SLAC MeV-UED instrument to determine the product branching ratio and the presence of the intermediate state. The experiments were led by Pedro Nunes (formerly at UNL, now at Diamond Light Source in the UK) and the simulations were carried out by Conor Rankine (University of York). Based on the analysis of the diffraction patterns, we have observed no evidence of the intermediate state and a product yield consisting mostly of ring-closed molecules on the femtosecond and few picosecond time scale. We are currently in the process of drafting a manuscript.

UED data analysis of photoexcited cis-stilbene. The excited state dynamics of cis-stilbene leading to the formation of trans-stilbene and dihydrophenanthrene (DHP) has been extensively investigated both experimentally and theoretically. Much less is known about the dynamics triggered by ionization of cis-stilbene. We have investigated the ultrafast dynamics of stilbene using the MeV-UED instrument at SLAC in the Fall of 2020. Data was collected to at two different powers of the excitation UV laser pulses. We have identified that at the lower power, the excitation is a combination of a 1-photon valence excitation and 2-photon ionization. At the higher power, we observe almost exclusively ionization. We have identified the structure of the cis-stilbene cation and the timescale for structural changes. The experiments are in good agreement with simulations carried out by the group of Todd Martinez at Stanford. We are currently drafting a manuscript based on these results.

UED data analysis of proton transfer in UV excited o-nitrophenol. The photolysis of nitroaromatic hydrocarbons, such as o-nitrophenol, has sparked significant scientific interest as a possible anthropogenic source of atmospheric nitrous acid. The electronic structure and product yield of photoexcited o-nitrophenol have been investigated extensively, however, the ultrafast nuclear dynamics accompanying the non-radiative relaxation remains largely unexplored. Interestingly, at longer wavelengths the photodissociation is preceded by proton transfer, while at shorter wavelengths it is predicted that dissociation takes place without proton transfer. We have investigated the dynamics of o-nitrophenol at two different wavelengths: 330 nm and 300 nm. At the longer wavelength we see clear evidence of proton transfer, followed in time by a torsion of the nitro group, and no evidence of dissociation over the first 2 ps. This indicates a sequential process started by proton transfer and that dissociation takes place over a longer time scale. We are analyzing the results at 300 nm excitation and are in the process of submitting a manuscript on the results at 330 nm with theory support from the group of Todd Martinez. We will continue the analysis of the data at 300 nm to determine the sequence of events and the yield of photodissociation on the picosecond time scale.

Future plans

We will continue with the analysis and interpretation of the experiments with iodobenzene. We will continue the analysis of o-nitrophenol at the second wavelength where we already have acquired data and carry out experiments at 266 nm where different dynamics are expected. We will complete the analysis of BCP and stilbene and submit manuscripts for publication. We will continue investigating the application of the GA to the retrieval of dynamical structures. Our proposal for an X-ray scattering experiment at LCLS (LX 74 "Imaging roaming mediated dynamics in halogenated alkanes by ultrafast X-ray scattering" PI: Martin Centurion) was accepted and originally scheduled for beam time in May 2022. However, due to facility issues it has been postponed to 2024. If successful, this would be the first time that a roaming reaction is spatially resolved. A UED experiment on Thymine for which were awarded beam time at the SLAC MeV-UED instrument for the Fall of 2022 (U115: “Isolated nucleobase UED studies for understanding photoprotection” PI: Markus Guehr) has been postponed until 2024 due to issues at the facility. We will continue with the development of our heated sample delivery system at UNL and carry out UED experiments at UNL. We plan to submit a new proposal to carry out further X-ray experiments at LCLS and MeV-UED experiments at SLAC after carrying out the planned experiments.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

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"Multichannel photodissociation dynamics in CS2 studied by ultrafast electron diffraction"

Phys. Chem. Chem. Phys. 24, 15416 (2022). DOI: https://doi.org/10.1039/D2CP01268E

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

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Program Scope

The ability to measure and control ultrafast dynamics in excited states of atoms and molecules 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 drive strong-field excitation of bound electronic coherences in gas-phase atoms and molecules using a novel source of single-cycle optical field transients, to reconstruct the time-dependent wave packets and probe their decoherence using attosecond interferometry, and to control the dynamic evolution of the system on attosecond to few-femtosecond (1 femtosecond = 10^{-15} seconds) timescales.

Recent Progress

In the proposed experiments, coherent wave packet dynamics in excited electronic states of atoms and molecules will be triggered using strong-field near-infrared light transients, with durations close to a single optical cycle, and the dynamics will be tracked using a variant of attosecond interferometry[1,2], in which the spectrally-resolved interference of the coherence emission (extreme ultraviolet free-induction decay, XFID) with an isolated attosecond pulse produced via high-order harmonic generation will be measured as a function of the time delay between the two pulses. Unlike previous demonstrations of attosecond interferometry, which measured the interference between two attosecond pulse trains generated by multi-cycle laser pulses, the experiments proposed here require intense, single-cycle field transients, both to trigger an excited electronic wave packet with a high degree of coherence[3] and to generate an isolated attosecond pulse which can act as a local oscillator to interfere against XFID emission with arbitrary spectral content. Furthermore, due to the low intensity of the XFID emission in comparison to HHG, it is necessary to perform the experiments at high repetition rates.

The proposed experiments are to be supported by a source of near-single-cycle field transients, generated from a moderately high-power (20 W) ytterbium-doped laser amplifier with 50 kHz repetition rate, and their application to generating high-order harmonics. Generating few-cycle pulses from such a laser is technically challenging due to the relatively long laser pulse duration of 280 fs (approximately 80 optical cycles), which necessitates a high compression factor. In 2020, we demonstrated (simultaneously with groups from INRS and Vienna) a new approach to pulse compression of such long laser pulses, which is based on an enhancement of spectral broadening due to rotational alignment of molecular gases[4]. Through experiments and simulations, we showed that, for sufficiently long driving laser pulses, the instantaneous Kerr nonlinearity and the delayed rotational nonlinearity can combine to drive strong, red-shifted spectral broadening.

For the pulse duration of our laser (280 fs), we identified N_2O as the optimal gas for achieving broad spectral bandwidths, and we demonstrated the generation of a supercontinuum spectrum covering two optical octaves from 500 to 2100 nm with well-behaved spectral phase suitable for compression. Pulses compressed using chirped mirrors (with spectrum covering 700-1400 nm) to a duration of 1.6 optical cycles were shown to be suitable for driving high-order harmonic generation in argon gas, and the XUV harmonic spectrum was observed to merge into an apparent supercontinuum in carrier-envelope phase-integrated measurements.

The rotational enhancement of the nonlinearity additionally leads to a natural spatial and temporal confinement of the pulse, which was discovered by the INRS group and dubbed multi-dimensional solitary states (MDSS)[5]. Using MDSS, that group compressed few-cycle pulses generated from a stretched Ti:Sapphire laser using only material dispersion. However, the spectral coverage of the supercontinuum we generate from the Yb-doped laser amplifier, which contains most of its energy in the 1-2 μm spectral range and thus crosses the zero-dispersion wavelength of most glasses, presents significant challenges for compressing the entire bandwidth using MDSS. We circumvented this challenge by developing a simple, low-cost light field synthesizer[6], in which the output spectrum from the hollow-core fiber was split into two channels covering 1.0-1.5 μm and 1.5-2.0 μm, respectively using a dichroic mirror. The short-wavelength region was compressed by propagating through materials with normal dispersion: two dichroic mirrors and CaF_2 glass, while the long-wavelength region was compressed using the negative dispersion of fused silica. The pulses were then recombined using a second dichroic mirror and characterized using frequency-resolved optical gating (FROG). The retrieved pulse had 7.5 fs FWHM pulse duration, which is only 1.6 optical cycles at the center wavelength of 1.4 μm. The synthesized pulses based on MDSS have several advantages over conventional self-phase modulation. First, the spectrum is red-shifted from 1.03 to 1.4 μm, which should allow us to take advantage of the ponderomotive scaling of high-order harmonic generation to generate higher-energy harmonic cutoffs. Second, the pulses are compressed without the use of chirped mirrors, resulting in an inexpensive, stable, and compact setup.

While FROG provides a robust metric for the pulse duration, we have found that it is unreliable for characterizing the complex temporal profile of pulses compressed using MDSS. Furthermore, the proposed experiments would benefit from a direct measurement of the sub-cycle electric field waveform, rather than only the pulse envelope. Recently, our group showed that the TIPTOE technique (tunnel ionization with a perturbation for time-domain observation of electric fields)[6] can be adapted to a solid-state target[7] and single-shot geometry[8] for few-cycle mid-infrared fields. Using the MDSS pulses, we have recently the technique to near-infrared wavelengths and demonstrated the first single-shot measurement of electric field waveforms in this important spectral region. In the experiments, we combine an intense "fundamental" pulse and a weak "perturbation" pulse on a thin ZnO crystal with a small noncollinear angle. The fundamental pulse induces nonlinear excitation in the crystal, which can be monitored by measuring the yield of band fluorescence emission, and which is modulated by the field of the perturbing pulse. The noncollinear geometry allows us to map the time-delay axis onto one of the spatial axes of the crystal plane, thus encoding the full electric field waveform of the perturbing pulse on the spatial dependence of the band fluorescence emission. The band fluorescence is collected using a lens, spectrally filtered, and imaged onto a CMOS camera detector. Comparison of the measured electric field waveform with the pulse envelope retrieved from FROG shows excellent agreement between the two methods. The single-shot field sampling technique is a valuable addition to the proposed attosecond interferometry measurements, as the combination of the two techniques will provide a direct measurement of the carrier-envelope phase of the pulses, while also allowing us to simultaneously measure both the electronic and vibrational coherences excited in molecular gases by the strong near-infrared fields. The technique is now being further extended to the near-infrared through the use of an AlGaN nonlinear medium.

Pulse compression with MDSS works well at low repetition rates: the few-cycle pulses referenced above were all obtained at low repetition rates below 1 kHz, whereas our laser is capable of operating at 50 kHz repetition rate with the full pulse energy of 400 μJ. At higher powers, we have observed a drop in the fiber throughput and a narrowing of the supercontinuum spectrum. These effects can be attributed to rotational heating[9], which reduces the degree of molecular alignment and thus the spectral broadening, and thermal lensing, which prevents efficient coupling into the fiber. Operating the fiber in a pressure-gradient geometry can eliminate the worst effects of thermal lensing[10], but leads to turbulent gas flow and instability in the spatial profile and pulse energy of the pulses exiting the fiber. Furthermore, since the gas flow remains too low to provide a fresh gas sample for the laser to interact with, differential pumping does not mitigate the effects of thermal excitation on the spectral broadening. We have identified two promising approaches to power scaling. First, by filling the fiber with a mixed gas of N_2O and helium, we find that thermal excitation effects are suppressed. We attribute this behavior to collisions between N_2O molecules and helium atoms, which can efficiently carry energy away from N_2O and eventually couple it of the fiber through collisions with the fiber walls. Second, by placing the in- and out-coupling windows of the fiber very close to the fiber tip, we strongly suppress the effects of thermal lensing. Work is ongoing to explore the peak- and average-power limits for MDSS compression in mixed gases.

In addition to near-single-cycle durations, the proposed experiments demand pulses with stable carrier-envelope phase (CEP). During the last year, we have demonstrated the stabilization and control of the CEP of few-cycle pulses, and the use of such pulses to generate CEP-dependent harmonic spectra in the vicinity of the harmonic cutoff. The observed carrier-envelope phase dependence is evidence of attosecond gating of the cutoff harmonics and is a major step towards the realization of the proposed experiments. Since the proposed experiments require isolated attosecond pulses that cover the low-energy region of the harmonic plateau, we have planned to extend the supercontinuum spectra to lower energies through the use of polarization gating.

Future Plans

In the final year of the project, we aim to generate carrier-envelope phase dependent XUV supercontinuum spectra that cover overlap with the XFID emission of bound and autoionizing states of Ar and N_2 (~10-30 eV). We will then demonstrate the attosecond interferometry setup using two isolated attosecond pulses, with the goal of measuring the recombination phases for comparison with the measurements in Ref. 1. The recombination phases for HHG with linearly-polarized and polarization-gated attosecond emission will be compared. Finally, we will perform attosecond interferometry measurements of excited state dynamics in Ar and N_2 gases.

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9. Y. Liu, et al. “Single-shot measurement of few-cycle optical waveforms on a chip,” Nature Photon. 16, 109-112 (2022).
10. J. E. Beetar, et al. “Thermal effects in molecular gas-filled hollow-core fibers,” Opt. Lett. 46, 2437-2440 (2021).
11. L. Arias, et al. “Few-cycle Yb laser source at 20 kHz using multidimensional solitary states in hollow-core fibers,” Opt. Lett. 47, 3612-3615 (2022).

Peer-Reviewed Publications Resulting from this Project (2021-2023)

1. D. Dempsey, et al. “Comparative study of optical nonlinearities of CO_2 and N_2O via single-shot spatio-temporally-resolved visualization,” Opt. Commun. 545, 129669 (2023).
2. Truong, T.-C., et al. “Light-field synthesizer based on multidimensional solitary states in hollow-core fibers,” Opt. Lett. 48, 2397-2400 (2023).
3. J. E. Beetar, et al. “Thermal effects in molecular gas-filled hollow-core fibers,” Opt. Lett. 46, 2437-2440 (2021).
4. Y. Liu, et al. “All-optical sampling of few-cycle infrared pulses using tunneling in a solid,” Photon. Res. 9, 929-936 (2021).

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

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October 6, 2023

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.

Recent Progress: This project started in August of 2020, i.e., in the height of the pandemic. Naturally progress has been significantly impacted by the pandemic. Initially access restrictions to the labs were the primary impediment. While their impact did not last long, supply chain issues have had a significant impact, and continue to do so.

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 worked for approximately two years, although with fairly low usage due to other supply chain hold ups, and then failed due to damage to the nonlinear crystals in June 2023. Due to delays in obtaining replacement crystals from Lithuania by way of Austria, the system was not fully functional again until mid-September. The lack of an operating system for the last 3 months prevented progress on this project at the most important time.

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, however issues with fabrication has resulted in the use of a slightly longer cell of 1 mm at a low vapor density, which is controlled by the temperature.

Once the cell was received, we developed an approach to reliably heat it to the required temperature while keeping the windows hotter than the side arm to prevent condensation of liquid iodine on the windows. We found that a rather simple approach of wrapping nichrome wire around the cell body close to each window worked best. Measurements of the absorption spectrum, as shown in Fig. 1 verify that we can achieve an optical density in the desired range near 0.3 at a cell temperature of approximately 200 C. The optical density can be tuned by cell temperature.

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 frequency-doubled Nd:YAG laser to provide the reference beam.

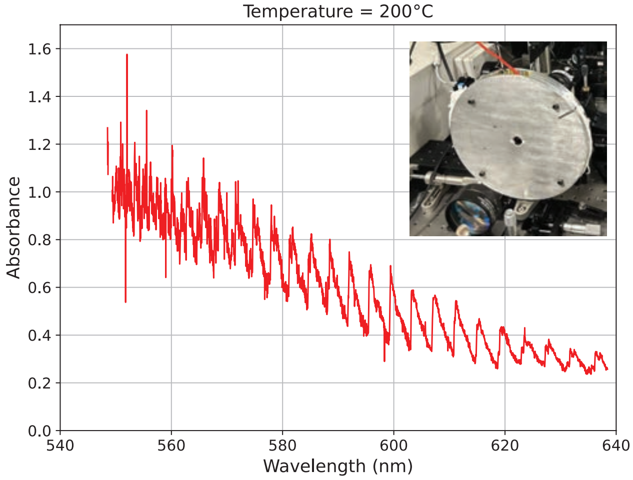

Figure 1: Absorption spectrum of the iodine cell at a temperature of 200 C. Inset shows custom oven for holding the cell.

To achieve short pulses at the sample requires additional dispersion compensation, beyond that built into the NOPA. We have explored several options. We tried a commercially available pulse compressor, however at large enough levels of dispersion compensation, the amount of spatial chirp became unacceptable. We plan to return this unit to the vendor. Using a home built prism compressor is providing reasonably well compressed pulses at the sample, however there is still an issue with spatial chirp, we are currently trying to diagnose and fix this issue, we believe it is arising from small alignment issues in the compressor.

We have made a initial attempts to observe a 3-pulse four-wave-mixing signal from the iodine cell. The challenge is to separate the signal from scatter of the incident pump beams. The spectrum of the light traveling in the direction of the signal, $\mathbf{k}_s = -\mathbf{k}_A + \mathbf{k}_B + \mathbf{k}_B$. To estimate the scattered light, the beam in direction $\mathbf{k}_C$ is blocked (it has the least scatter) to obtain a spectrum of the scatter from the other two pulses, which is then subtracted. The resultant spectrum is a combination of the four-wave-mixing signal, due to the interaction of all three pulses, with cross terms that arise because the final measurement is of intensity. We are currently working to minimize the scatter and optimize the four-wave-mixing to generate a signal that is sufficient strength and purity to be usable for generation multidimensional coherent spectra.

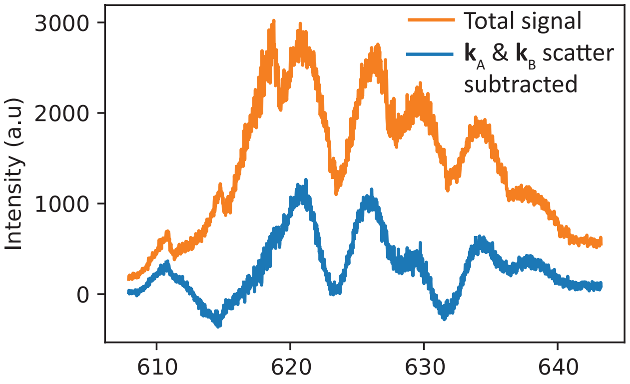

Figure 2: Measured spectrum in the direction of the 3-pulse four-wave-mixing signal, which is contaminated with scatter from the pump beams. The orange curve is the as-measured signal. The blue curve is after subtraction of the scattered light from beams $\mathbf{k}_A$ and $\mathbf{k}_B$

Future plans: Our goals for the next project period are now largely focused on solving technical issues to yield a sufficiently strong signal for producing multidimensional coherent spectra. Once we solve these issues, we can pivot to science goals. We have identified the following issues, and list their solutions, that are degrading the quality of the signals and preventing the measurement of a multidimensional spectrum:

- Due to the additional path length through the compressor, the beam is expanding such that the focal spot is smaller than designed, hindering optimization of the overlap. Solution: install a telescope to reduce the transverse beam size and recollimate it (in progress).

- There is still residual spatial chirp, which is attributed to the pulse compressor. Solution: optimize the alignment of the compressor.
- The pulsewidth at the sample still longer than transform limited. Solution: Use a FROG apparatus to characterize the residual chirp and compensate using additional steps such as chirped mirrors.

Once these technical issues are addressed, we will pivot to addressing science goals. The science goals for the next year of the project will focus on answering the following questions, which have been descoped given the technical issues that have impeded progress:

- 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?

The goal of the first phase of the project is to use MDCS to provide a complete and detailed map of 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.

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.

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.

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.

Peer-Reviewed Publications resulting from this project (2019-2022): 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

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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) Femtosecond intramolecular rearrangement of the CH_3NCS radical cation

Jacob Stamm, Shuai Li, Stephen H. Yuwono, Swati S. Priyadarsini, Piotr Piecuch and Marcos Dantus, *J. Chem. Phys.* **157**, 214304 (2022).

Strong-field ionization, involving tunnel ionization and electron rescattering, enables femtosecond time-resolved dynamics measurements of chemical reactions involving radical cations. Here, we compare the formation of CH_3S^+ following the strong-field ionization of the isomers CH_3SCN and CH_3NCS. The former involves the release of neutral CN, while the latter involves an intramolecular rearrangement. We find the intramolecular rearrangement takes place on the single picosecond timescale and exhibits vibrational coherence. Density functional theory and coupled-cluster calculations on the neutral and singly ionized species help us determine the driving force responsible for intramolecular rearrangement in CH_3NCS.

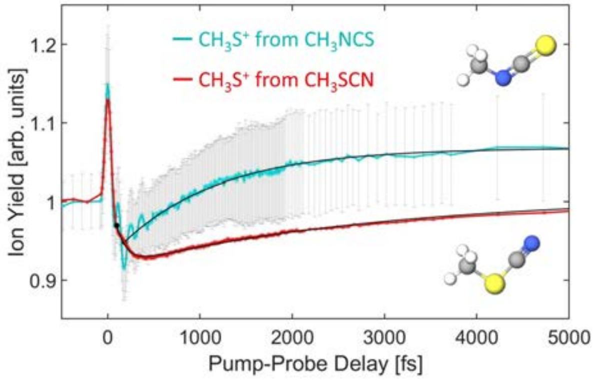
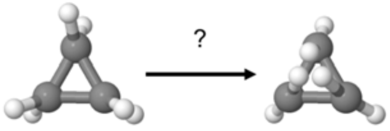


Figure 3. *The time-resolved yield of CH_3S^+ from CH_3NCS (blue) and CH_3SCN (red) following ultrafast ionization. Both ion yield traces are normalized such that the yield at long negative time delays is unity. Error bars for the CH_3S^+ yield from CH_3NCS show +/- 1 standard deviation.*

Our findings illustrate the complexity that accompanies radical cation chemistry following electron ionization and demonstrate a useful tool for understanding the cation dynamics after ionization.

(b) What is the Mechanism of H_3^+ Formation from Cyclopropane?

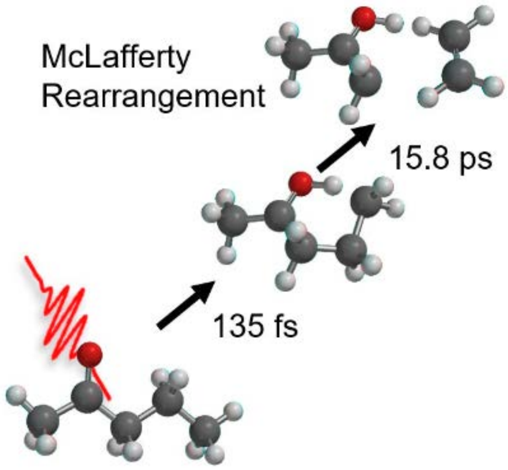
S. Kwon, S. Sandhu, M. Shaik, J. Stamm, J. Sandhu, R. Das, C. V. Hetherington, B. G. Levine, M. Dantus. *J. Phys. Chem. A*, *Accepted for publication.*



We completed an experimental and theoretical study to determine the mechanism of H_3^+ formation from cyclopropane. We examined a recently proposed mechanism in which three hydrogen atoms in one plane of the cyclopropane dication come together in a concerted 'ring-closing' mechanism to form H_3^+. TREIMS measurements indicate the formation time is 249 ± 16 fs. This timescale is not consistent with the concerted formation. Measurements on propene, an isomer of cyclopropane, reveal an H_3^+ formation time of 225 ± 13 fs, a timescale similar to the formation time in cyclopropane. *Ab initio* molecular dynamics simulations and the fact that both dications share a common potential energy surface support the ring-opening mechanism. The reaction mechanism following double ionization of cyclopropane involves ring opening, then H-migration, and roaming of a neutral H_2 molecule, which then abstracts a proton to form H_3^+. These results further our understanding of complex interstellar chemical reactions and gas-phase reaction dynamics relevant to electron ionization mass spectrometry.

(c) The Surprising Dynamics of the McLafferty Rearrangement

J. Stam, S. Kwon, S. Sandhu, M. Shaik, J. Sandhu, R. Das, J. Sandhu, B. Curenton, C. Wicka, B. G. Levine, L. Sun, M. Dantus. *J. Phys. Chem. Letters, Accepted for publication.*



One of the better-known fragmentation mechanisms in mass spectrometry is the McLafferty rearrangement. It occurs in radical cations and is characterized by a γ-hydrogen transfer to a double-bonded atom through a six-membered transition state, with beta-bond cleavage to produce a neutral olefin. We measured the timescales of the McLafferty rearrangement reaction (Scheme 1) in 2-pentanone, 4-methyl-2-pentanone, and 4,4-dimethyl-2-pentanone. The pump-probe dependent yields of the McLafferty product ion were fit to a biexponential function. For 2-pentanone the fit revealed a fast 135-fs and a slow 15.8-ps time constant. It is the long τ_2 timescale that we find to be surprising. If this step required exclusively electronic motion, it would be completed a few orders of magnitude faster. Instead, we find experimentally and through examination of AIMD trajectories that this step requires significant exploration of multiple internal degrees of freedom to reach the molecular geometry that enables the π-electron rearrangement. In other words, the molecular wavefunction explores the multidimensional potential energy surface until it finds the transition state responsible for π-electron rearrangement and dis- sociation into an enol and olefin. This vibrational control of an ostensibly pure electronic motion parallels the Marcus picture of electron transfer.

(d) H_3^+ Formation from Methyl Halogens and Pseudohalogens

J. Stamm, S. Sandhu, S. Kwon, A. Chakraborty, S. S. Priyadarsini, J. Shen, J. Sandhu, M. Shaik, C. Wicka, A. Mehmood, B. B. Levine, P. Piecuch, M. Dantus, In preparation for *Nat. Comm*.

Currently, there is no cohesive model explaining what determines H_3^+ formation following the double ionization of small organic compounds. The recently elucidated roaming mechanism of H_3^+ production involves the formation of a neutral H_2 which then abstracts a proton. Despite multiple reports of this mechanism, a detailed explanation for the formation of H_2, the yield of H_3^+, and the timescale of this unimolecular reaction, remains unknown. We performed yield and femtosecond time-resolved measurements following strong-field double ionization of precursor CH_3X molecules, where X = Cl, I, OH, CN, NO_2, NCS, and SCN. We find that the timescale of H_3^+ formation from these compounds ranges from ∼100 fs in CH_3OH to ~650 fs in CH_3Cl, while the normalized H_3^+ yield is negligible for CH_3I, CH_3SCN, CH_3NO_2, and CH_3CN and increases as $CH_3NCS < CH_3Cl < CH_3OH$. High-level computational chemistry methods were used to determine the dication electronic structure, which informs the H_2 formation patterns across all the compounds studied. We find the HOMO of the dication, in all cases other than CH_3SCN and CH_3NO_2, has bonding character between two hydrogen atoms and anti-bonding character to the rest of the dication, thus favoring the formation of neutral H_2. *Ab initio* molecular dynamics (AIMD) simulations were performed to gain insight into the timescales and yields of H_3^+ formation. The adiabatic relaxation energy following double ionization enhances the process, while competing reactions suppress H_2 formation. These complementary experimental and theoretical findings provide predictive guidelines for H_3^+ formation, an important aspect to assess alternative sources of this important ion in the universe.

(e) Initial-site characterization of hydrogen migration following strong-field double-ionization of ethanol

T. Severt, E. Weckwerth, B. Kaderiya, P. Feizollah, B. Jochim, *et al. Nat. Commun. in review.*

Collaborated with primary authors E. Wells, and I. Ben-Itzhak on this project with the aim of using coincidence ion-imaging measurements of a few deuterium-tagged isotopologues of ethanol to determine the contribution of each initial-site composition to hydrogen- rich fragments H_3^+, H_2O^+, H_3O^+, and CH_4^+ following strong-field double ionization.

(f) Insights into ultrafast H_3^+ formation provide a glimpse into primordial chemistry

M. Dantus, *Nat. Chem*. **15**, 1202-1203 (2023).

I was invited to write a News & Views about two recent publications in Nat. Chem. on the formation of D_3^+ following the ionization of D_2-D_2 van der Waals clusters.

Future Plans

i. I was invited to write a review article for Accounts of Chemical Research on the use of tunnel ionization and disruptive probing to study the reactions of radical cations with femtosecond time resolution.

ii. I was invited to write a review article for Science on chemical reactions that are difficult or have yet to be studied with femtosecond time resolution.

iii. The Keldysh parameter is used to differentiate between multiphoton ionization and tunnel ionization based on the atomic ionization potential, the wavelength, and peak intensity of the laser pulse. Recent theories have moved beyond the free-atom approximation to provide a more refined picture of tunnel ionization in atoms. However, the different geometric and electronic structures of molecules complicate the distinction between multiphoton and tunnel ionization. We plan to perform a number of experiments on polyatomic molecules to arrive at guidelines that can be used to determine the prevalent ionization process given a type of molecules and the laser pulse parameters.

iv. We plan to explore the dynamics and control of two types of systems. For 2-mercaptoethanol ($HS\text{-}CH_2CH_2\text{-}OD$), 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.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

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).

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

AWARD NUMBER: DE-FG-04ER15614

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1.1 PROJECT SCOPE

The primary focus is to explore the realm of ultrafast electron and molecular dynamics using different but complementary tools. In one thrust, we explore and exploit fundamental aspects of generation and measurement of high harmonic and attosecond pulses to assess fundamental atomic and molecular processes. In recent years, our attention has turned to using attosecond pulses to extend the realm of strong field studies using a new method dubbed Quantum Trajectory Selector. 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, which continues to date, between OSU and KSU groups. A third thrust is the implementation of an AMO science program using the ultrafast, 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. The program's ultimate objective is advancing these methods as robust tools for imaging and probing electron dynamics thus producing the complete molecular movie.

Progress over the past year includes: (1) application of our "quantum trajectory simulator" concept for exploring XUV-seeded recollision physics, (2) progress in the study of high harmonic generation from liquids and (3) investigations utilizing the attosecond capabilities of the XLEAP mode of the LCLS.

1.2 PROGRESS IN FY2023

The Quantum Trajectory Simulator concept. A major thrust of our laboratory during this funding period was to develop and utilize a new capability for selecting and controlling quantum trajectories, we dubbed this method the Quantum Trajectory Simulator (QTS). The concept is based on Feynman's principle that the outcome of a quantum process is dictated by the sum over all the quantum trajectories that contribute to it. Naturally, when analyzing experiments, we often refer to these individual trajectories even though they have not been measured individually. Over the past two years, we have demonstrated a fully functioning QTS which allows us to directly measure and time the outcome of selected trajectories that summed together make up a quantum process. Our QTS operates in the strong field domain, where a simple semiclassical model is ubiquitously used to describe individual quantum trajectories. Here we benchmark the QTS against the semiclassical model and show that we can directly clock the recollision events once a simple calibration procedure based on streaking of direct electrons is applied. As we show, no theory is needed to extract the timing.

In a typical strong field ionization experiment, a single high-intensity near-infrared (NIR) laser promotes bound electrons into the continuum by tunnel ionization and the strong electric field drives the trajectory of the "freed" electron wave packet (EWP). As the field changes sign, a sub-class of electron trajectories can return to interact with the parent ion. These are of particular interest due to the many physical phenomena attributed to them: elastic (LIED) and inelastic (NSDI, RESI) scattering, and dipole recombination (HHG). This is the basis of the semi-classical rescattering or three-step description. In this QTS study, we are interested in simulating these processes in helium and argon, and other atomic and molecular systems.

In the semi-classical view, tunnel ionization and wave packet propagation are directly coupled by the same low-frequency intense field. In addition, the exponential dependence of the tunneling rate confines the birth phases near the field extrema. This significantly constrains the initial conditions and thus the ability to control the abovementioned processes. The QTS approach decouples the ionization from the EWP propagation by using a XUV attosecond pulse to drive single photon ionization in the presence of a phase-locked intense mid-infrared (MIR) field. The MIR field is strong enough to quiver the electron but not ionize the ground state. The decoupling of ionization and propagation allows trajectory selection at any initial phase by controlling the time delay between the XUV pulse and the strong MIR field. Now the experimentalist can independently tune the properties of the XUV and MIR pulse, opening new avenues for strong field investigation.

The recently constructed QTS apparatus consists of an optimized beamline for delivering bright, shaped XUV attosecond pulses and an end-station equipped with an electron and ion spectrometer. The beamline was designed to deliver the maximum number of XUV photons within a prescribed energy and bandwidth (~ 5 eV). In our experiments so far, the central photon energy is sculpted either at 16 eV or 26 eV which is determine by two different multilayer mirrors and metal filters. We use two-color generation schemes that deliver high photon numbers using argon or krypton gases. The current studies use a fundamental field from 1.7-2.4 μm. The QTS apparatus also has an optimized mechanical and optical design for good interferometric stability between the XUV and MIR pulses of approximately 50 *as*.

During the past year, we studied the delay dependence for both the electron and ion yield under different experimental conditions, *i.e.* MIR intensity & wavelength, XUV central photon energy. Our initial studies are focused on helium and argon atoms. For both the double ions and the electrons, a clear dependence on the XUV-MIR delay is observed (see Fig. 1[a] & [c]). Both the ions and electrons oscillate at $2\omega_{\mathrm{MIR}}$ in the spectrogram. This strongly supports that the QTS observables are being produced by XUV-seeded recollision. Furthermore, the MIR or XUV fields alone produce little or no double ion, respectively.

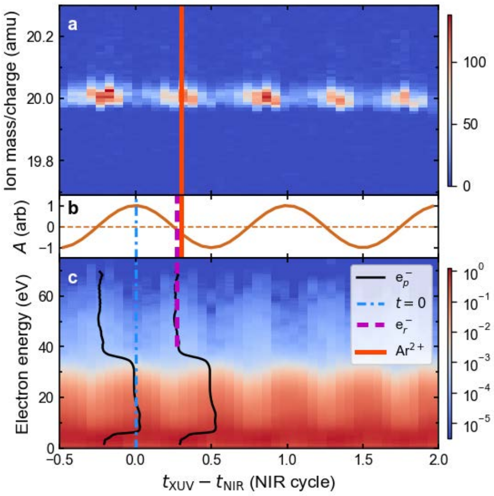

Figure 1: The delay spectrogram for argon atoms. (a) Ar^{2+} ion production and (c) photoelectron yield for argon using the QTS approach. (b) Plot of the fundamental field vector potential calibrated by the streaking of direct electrons. The experiment uses 13 TW/cm^2, 2.4 μm pulses and a XUV pulse with a central photon energy of 16 eV near the argon threshold (15.7 eV).

Strong field non-sequential double ionization (NSDI) in the semi-classical model results when the field-driven EWP returns to the core with sufficient energy to free a bound electron via (*e,2e*) inelastic scattering. In other words, the return energy ($3U_p$ maximum) must exceed the binding energy of the Ar^+ (27.63 eV). The MIR parameters in Fig. 1 is such that $3U_p = 20.6$ eV $< I_p(Ar^+)$, so direct (*e,2e*) impact ionization is not possible. However, impact excitation followed by MIR ionization is possible, *i.e.* RESI. Based on these observations we have developed a model that incorporates both impact ionization from direct and excitation mechanisms, yielding excellent agreement with the measurement. The theory work is a collaboration between Ken Schafer (LSU) and Abraham Camacho (OSU).

Once the experimental XUV-MIR recollision signature for NSDI was established, the next and important step in the QTS experiments is to directly clock the elastic and the (*e,2e*) recollision processes. Figure 1 is illustrative of this measurement, here the data collection is performed by an interleaved method for the (a) doubly charged argon ion and (c) electrons at each delay step. The spectrogram is the result of varying the delay between the XUV and MIR fields which oscillate at $2\omega_{\mathrm{MIR}}$.

Our QTS approach explicitly recognizes that a timing calibration can be defined by measuring the phase of the maximum streaking energy for the direct electrons which corresponds to an ionization time at the zero of the electric field (alternatively, the maximum of the vector potential). This calibration of the **A** field is illustrated by the blue dot-dash line in Fig. 1. Once the zero E-field (alternately the max **A**) is defined, the electrons and ions can be clocked against it. The purple dash and solid red vertical lines Fig. 1(a) and (c) illustrate the retrieved phases of the double ion and rescattered electrons, respectively. The extracted times are 0.30 and 0.27 MIR cycles, respectively. The small difference in time (~200 *as*) is consistent with the classical ionization phases leading to $10U_p$ electrons and $3.17U_p$ return energies. Additionally, the extracted times for the rescattered electrons increases with increasing intensity, *i.e.,* U_p, while the double ionization times remains relatively constant.

We are currently investigating this behavior in greater depth, among other observations, but the viability of the QTS approach is clearly demonstrated. We are currently preparing a manuscript for *Nature Physics*.

High Harmonic Spectroscopy (HHS) in liquid sheets. HHS has been a very powerful tool in ultrafast physics allowing access to electron dynamics and structure in various media. The HHG mechanism is well understood in gases and has been extensively studied in solids, but in liquids, the mechanism is still unclear since there is relatively little experimental and theoretical investigations. The main goal of this project is to understand the physical mechanism of high harmonic generation in liquid phase. Key questions are the role that intermolecular structure plays in the liquid mechanism and can one extract ultrafast solvation dynamics. To this end, we have studied HHG in different solvent classes and in varying binary mixtures. We have also tuned the fundamental wavelength and intensity used for generation.

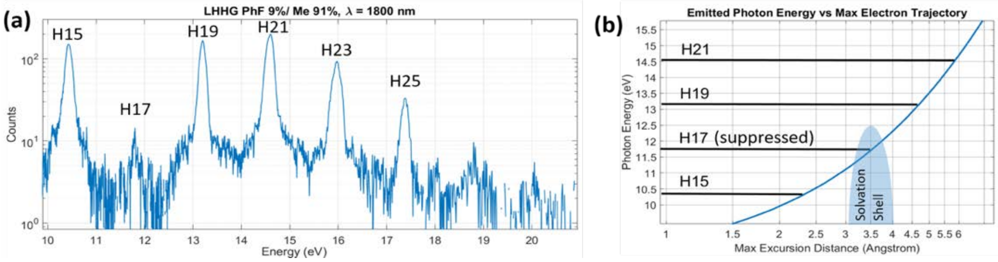

Figure 2: Results and calculations behind solvation study: (a) The measured harmonic spectrum of a 9% molar fluorobenzene solution shows a suppression of the 17th-order harmonic using a 17 TW/cm^2, 1.8 μm fundamental wavelength and (b) shows the mapping of the harmonic photon energy onto to the corresponding maximum electron trajectory. The plot shows that the 17th-order corresponds to a maximum trajectory displacement of ~3.5 A.

Our most recent experimental studies have been performed to further explore HHG spectroscopy as a probe of solvation dynamics. Over the last year we obtained evidence that HHG is sensitive to solvation structure formed in certain solutions. In low molar concentrations (9-15%) of fluorobenzene solvated in methanol, we observe a suppression of the harmonic yield for specific localized orders that varies with field parameters and concentration. The suppression for the 17th-order is evident in Fig. 2(a). We find that this suppression may be correlated with the resulting solvation structure. Note, there is no suppression for the pure liquids.

The evidence suggests that the propagating electron wave packets (EWP) are sensitive to the newly formed solvation structures. Furthermore, the EWP that has an excursion distance that is equal to the newly formed solvation shell distance will have a high probability to scatter since the instantaneous energy at the turning point will be near zero. Consequently, minimizing the contributions of these trajectories to harmonic generation at specific orders. Thus, there is a correlation between the suppressed harmonic order and propagation distance, *i.e.,* solvation shell distance. This correlation is illustrated in Fig. 2(b).

To further test this model, we measured the HHG in fluorobenzene/methanol solutions as a function of the fluorobenzene concentration. We observe that as the concentration is changed from 9% to 15%, the suppression moves to higher photon energy, *i.e.,* switches to the next highest order. In our model this implies that a solvation structure is moving to a larger intermolecular distance which is then being probed by the low energy electrons involved in the HHG process and mapped onto the harmonic spectra. Recently, we have established collaboration with two theory groups, John Herbert (OSU) and Mette Gaarde and Ken Lopata (LSU). We believe that computational chemistry is an essential element for making progress on the subject.

Investigations at the LCLS. Our recent efforts at the LCLS are described in the abstract for AMOS project DE-SC0012462.

1.3 FUTURE PLANS

Quantum trajectory simulator: Over the past year, we have firmly established that the QTS method is a robust and new tool for studying attosecond dynamics. Over the next year, we will (i) continue to explore the clocking of recollision events as we finely control the initial QTS conditions. (ii) Our recent development of bright harmonic sources allows the pursuit of our primary goal of extending these QTS studies to the ionization of helium, where more precise calculations can model the role of electron correlation in strong field processes. (iii) Survey QTS control of molecular ionization as a prelude of enhanced LIED. Our preliminary results on CO_2 ionization show clear evidence of QTS phase dependence for the fragments and double ion. We will now extend the QTS method towards molecular frame measurements. Ken Schafer (LSU) and Abraham Camacho (OSU postdoc) will continue to provide theory support for this program.

HHG from liquid sheets. We will continue to study binary mixtures. To date, all evidence suggests that the length scale is an important metric in the strong field dynamics in liquids. Future experiments will examine the wavelength dependence at higher concentrations of fluorobenzene to determine how the suppression behaves and if a change in solvation structure can be extracted. The results will be compared to calculated radial distribution functions of the solution structure. In addition, different solutes will be used to further explore the fluorobenzene solution result. Hexafluorobenzene and 1,3,5-trifluorobenzene solutions will be studied in an attempt to distinguish the role of the fluorine atoms and the benzene ring in the context of solution HHG. The wavelength scaling of the harmonic yield in liquid phase has not been measured. We will study this scaling and compare to gas phase results. However, although our experiments are providing interesting results, we believe that a detailed understanding needs a strong computational chemistry component, hopefully our collaborations will bear fruit over the next year.

LCLS: The group will continue participation in the LCLS Directors Charge Migration Campaign. We also have a proposal pending for studying x-ray strong field physics using the XLEAP LCLS capabilities.

LIED: We continue to collaborate with the Kansas State University group (Cosmin Blaga and C. D. Lin) for investigating the sensitivity of LIED to geometric factors, such as isomerization and size.

1.4 PEER-REVIEWED PUBLICATION RESULTING FROM THIS PROJECT (2021-2023)

1A. "Clocking Auger electrons", D. C. Haynes *et al.*, Nat. Phys. **17**, 512 (2021). doi: 10.1038/s41567-020-01111-0.

2A. "Attosecond metrology", P. Agostini, A. Piper and L. F. DiMauro, in Handbook of Laser Technology and Applications (CRC Press) p. 307-320 (2021).

3A. "Two-dimensional retrieval methods for ultrafast imaging of molecular structure using laser-induced electron diffraction", Su-Ju Wang *et al.*, J. Chem. Phys. **155**, 164104 (2022). doi: https://doi.org/10.1063/5.0064761.

4A. "Attosecond coherent electron motion in Auger-Meitner decay", Siqi Li *et al.*, Science **375**, 285 (2022). doi: 10.1126/science.abj2096.

5A. "Controlling fragmentation of the Acetylene cation in the vacuum ultraviolet via transient molecular alignment", L. Varvarezos *et al.*, J. Phys. Chem. Lett. **14**, 24 (2022) doi: https://doi.org/10.1021/acs.jpclett.2c03354.

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Electron Quantum Dynamics in Strong-Field Irradiation

Grant No. DE–FG02-05ER15713

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Project Scope

We have built upon the virtual detector method [1, 2, 3, 4, 5] of Feuerstein and Thumm [6], in which the time-dependent Schrödinger equation (TDSE) is integrated while encoding outward-bound photoelectron waves into classically-evolving "virtual" particles. The theory is closely related to the Bohmian and Feynman path-integral formulations of quantum theory. It has undergone incremental advances over the years, such as to account for the quantum phase accumulated by photoelectrons en route to observation [1]. This has led to better agreement with experimental measurements and the full TDSE-based numerical solution. A key result is that in the single-active-electron scenario, the virtual-particle momentum distribution displays interference rings separated energetically by the laser frequency, which signifies the above-threshold ionization mechanism.

Additionally, we are investigating non-perturbative ionization using our implementation of the numerical scheme developed by Patchkovskii and Muller [7]. This technique differs from space-time integration employed in our virtual detector studies—based on our development of the model soft-core Coulomb potential [8] with its approximate eigenstates [8, 9]—in that it enables a numerically exact solution for hydrogen in full dimensionality. We have analyzed the consequences of resonant field-excitation of atomic states [10, 11] and the resulting energy-level splitting—the so-called Autler-Townes effect [12]. Our study has attracted recent attention from researchers interested in understanding further the characteristics of Autler-Townes doublets arising in different contexts. See Bayer *et al.* [13] and Olofsson and Dahlström [14].

Recent Progress

Our recent focus has been atomic systems with two active electrons and, specifically, their nonsequential ionization dynamics. This year, we published a first-ever application of the extended virtual detector method to a multi-electron system.

We are currently engaged in a followup investigation based on the familiar polarization-aligned two-electron model Hamiltonian. Our previous work has led us to consider nonsequential ionization in the single- to few-cycle regime. The purpose is to gain a better understanding of correlated electron emission with a field profile that causes at most a few principal *e*-*e* collisions to occur, and for that reason it provides a theoretically clean scenario to analyze. A calculation of the ionization probability of He^+ and He^{++}, shown in Fig. 1, indicates that the "knee" structure of nonsequential double ionization (NSDI) [15, 16] is present in this regime as well. Additionally, as panel (b) of Fig. 1 shows, the Schmidt weight measure of entanglement (eigenvalues of the single-particle density matrix [17]) displays a similar variation with intensity. This connection between entanglement and the $2e$ correlation-enhanced ionization yield was first established in our earlier works [17].

We are performing time-resolved calculations of the sub-cycle dynamics of the Schmidt

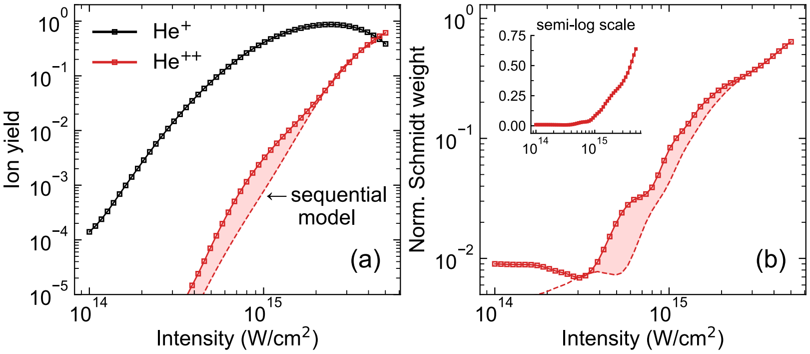

Figure 1: Model helium atom interacting with a single-cycle 780 nm wavelength field. (a) Singly- and doubly-ionized yields vs. laser intensity. (b) Two-electron entanglement (Schmidt weight) vs. laser intensity. Inset: Semi-log scale.

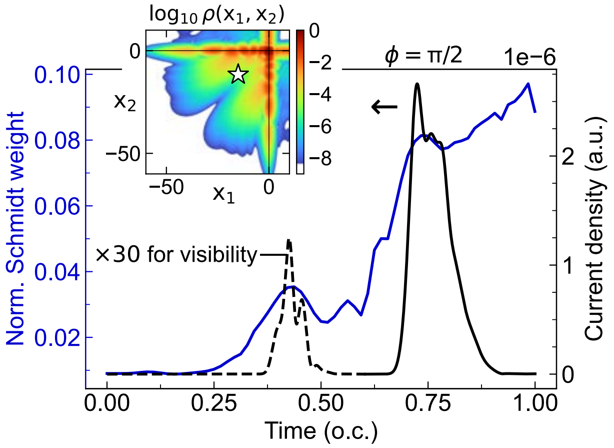

Figure 2: Schmidt weight (blue) vs. time (in optical cycles, o.c.) overlaid with the current density (black) measured at the points $(x_1, x_2) = \pm(15, 11.6)$ a.u. (dashed/solid). Inset: Snapshot of the two-electron probability density $\log_{10}\rho(x_1, x_2)$ at the time instant of the second current density signal (the star indicates the virtual detector location).

weight entanglement measure. This task is quite involved as the full wavefunction must be retained (an absorbing boundary condition cannot be employed) and the corresponding density matrix must be diagonalized for each data point. A key finding is that sharp increases in $2e$ entanglement are linked to the emission of double-ionization jets. In Fig. 2, for a single-cycle sine-squared pulse irradiating a model helium atom, the Schmidt weight and current density signals, measured in the path of double ionization jets, are plotted. The coincidence between signals holds generally as the field profile is altered to vary the momentum gain of the first liberated electron before it undergoes a collision with the second, still bound, electron.

Future Plans

We are planning to conclude and submit for publication before the end of this year the results of our study of $2e$ entanglement and single-cycle NSDI.

We are planning to extend the virtual detector method to 3 dimensions for the first time. This will allow us to investigate 3 one-dimensional electrons and their nonsequential triple ionization dynamics. In this case, TDSE integration coupled with the numerical detection procedure poses a significant computational challenge that will require efficient utilization of the latest parallel computing architectures and features available.

A subject of investigation for which we are developing interest concerns the transfer of orbital angular momentum from an external field to photoelectrons. Accordingly, we seek to extend the work of Patchkovskii and Muller [7] to carry the numerical scheme beyond the dipole approximation and make use of a spatially-structured field.

Peer-Reviewed Publications Resulting from this Project (2021-23)

1. D. Younis and J. H. Eberly, "Strong-field nonsequential double photoionization using virtual-detector theory with path summation", *Phys. Rev. A* **107**, 053117 (2023).

2. D. Younis and J. H. Eberly, "Benchmark of few-level quantum theory vs *ab initio* numerical solutions for the strong-field Autler-Townes effect in photoionization of hydrogen", (invited) *J. Phys. B* **55**, 164001 (2022).

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

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[3] *** Xu Wang, Justin Tian and J.H. Eberly, (invited) "Virtual Detector Theory for Strong-Field Atomic Ionization", *J. Phys. B* **51**, 084002 (2018).

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Robert Moshammer, J. H. Eberly and Jens Biegert, "Transition from nonsequential to sequential double ionization in many-electron systems", *Phys. Rev. A* **96**, 033401 (2017). DOI: 10.1103/PhysRevA.96.033401.

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Probing ultrafast XUV/x-ray induced electron correlation in the molecular frame

Award number: DE-SC0021336

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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.

Recent Progress:

The amplifier of our 1μm high-average-power high-repetition-rate laser system had a broken diode and the problem has been fixed. The construction of the high harmonic generation vacuum line has been completed and the pump-probe beam line has been set up; currently waiting for a nano piezo translation stage to be delivered (abnormally long lead-time). Target chamber for the COLTRIMS has been installed and spectrometer parts are being assembled (currently we are dealing with contamination of some high purity copper parts). COLTRIMS coils assembly have been designed and built; currently we are waiting for custom copper conductor to be delivered (abnormally long lead-time). One graduate student and one postdoc researcher have participated in this project and received instrumental simulation and hands-on training.

Future Plans:

We expect to receive the custom parts for the COLTRIMS and the beamline by the end of 2023 and plan to complete the buildup by February 2024. We plan to carry out the commissioning of the spectrometer in March – April 2023, installation of the gas source by May 2024 and the commissioning of the pump-probe beamline (including XUV beam generation /diagnostics and experiments on noble atomic gases) in May – June. We aim to bring the experimental line to operation by July 2024 and carry out experiments on autoionization of N_2 and/or C_2H_2 in summer 2024. Attosecond streaking measurement will be performed. The phase measurement apparatus will be set up and commission in summer 2024. The milestones to achieve include (1) demonstrating operation of REMI spectrometer by the end of summer 2024; (2) demonstrating generation of attosecond XUV pulses with energy streaking; (3) demonstrating CEP tagging at high repetition rate (200kHz); (4) taking preliminary data on N_2 molecule.

We plan to submit an LCLS beamtime proposal in 2023 for run 23 (beamtime is expected to start in Fall 2024). It is uncertain that the DREAM endstation for simultaneous measurement of electron and ion will be available in run 23. We are planning on proposing experiments using MRCO spectrometer, which is planned for run 22 already, for experiments with electron measurement only. Discussion with theorists is in progress and test theoretical calculation was performed (certain LCLS parameters turned out to be short and we are searching for other suitable atomic/molecular systems).

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

Transient Absorption and Reshaping of Ultrafast Radiation

DE-SC0010431

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October 2023

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 attosecond science groups [R1-R4], [1–4]. We use 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) and through propagation of the emitted radiation in the non-linear medium via the Maxwell wave equation (MWE) [1,5].

Recent Progress

In this abstract we will focus on recent work aimed at the study of temporal, spectral, and spatial reshaping of attosecond XUV and X-ray pulses in gas media, as well as the use of attosecond XUV radiation to study strong field processes. The work is performed in collaboration with experimental groups in the US and Europe [R1-R4], [2–4].

(i) Linear and nonlinear reshaping of intense XFEL pulses in rare gases: We have studied the spectral, temporal, and spatial reshaping of intense ultra-short X-ray pulses as they propagate through a neon gas at atmospheric density or above. We study the case in which the X-ray energy is resonant with a core-to-valence transition in the neutral atom, and where transitions between the highly excited core-hole state and several valence-excited states leads to both X-ray stimulated Raman scattering (XSRS) and X-ray lasing (XRL), along with the resonant free-induction decay (FID). This work is done in collaboration with the Young experimental group at Argonne National Lab [1, 2]. At the theory level, we couple our 3D, cylindrical-symmetry MWE solver to a calculation of the microscopic laser-matter interaction described in terms of coupled few-level systems [1]. A recent experimental campaign was carried out at the Eu-XFEL, studying this type of reshaping of self-amplified spontaneous emission (SASE) pulses. By varying the XFEL central photon energy below and above the K-alpha ionization threshold, both XSRS and XRL were observed, and can be distinguished from each other by, for example, covariance mapping [6]. This is illustrated in Fig. 1(a), which shows our calculated covariance map of the transmitted radiation near 870 eV with that near 850 eV. The narrow Raman transitions between the $1s^{-1}3p$ (and 4p) and the $2p^{-1}3p$ (and 4p) lines are very clear for the lower pump photon energies but largely disappear above 870 eV where the XRL process takes over. The ability to perform high-precision spectroscopy with the chaotic SASE XFEL pulses is one of the highlights of an upcoming paper [2].

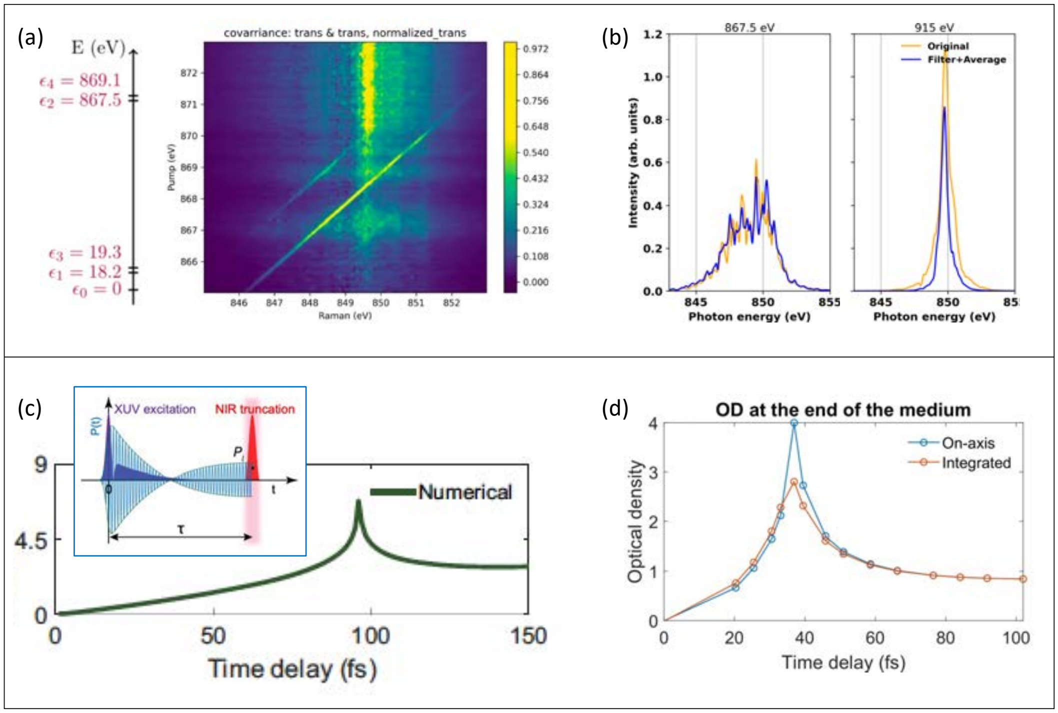

Figure 1: (a) Covariance map for 4,000 SASE pulse calculations with intensity and pulse duration 2×10^{17} W/cm^2 and 40 fs, respectively, propagating through 3 cm neon gas at 2 bar. (b) Radiation near 850 eV for 1×10^{18} W/cm^2 and 15 fs driving pulses with different central energies, with/without 2 fs running average of time-dependent ionization. (c) Inset demonstrates principle of resonant perfect absorption, and the graph shows the delay-dependent optical density (OD), calculated using a few-level model system (adapted from [R3]), exhibiting a sharp spike when the pulse reaches zero area. (d) OD from full TDSE-MWE calculations, both in the on-axis and the radially integrated transmitted signal. The resonance lifetime used in the TDSE-MWE calculation was shorter than in the model calculation in (c).

(ii) Resonant perfect absorption of XUV zero-area pulses: In collaboration with the Ott/Pfeifer experimental group at the Max Plack Institute (MPI) in Heidelberg, Germany, we have studied so-called resonant perfect absorption (RPA) of XUV light on resonance [R3] [4]. This scheme combines the macroscopic temporal reshaping of a propagating, resonant pulse, in which FID leads to a long tail of radiation that is out of phase with the incoming light, and an NIR pulse which abruptly depletes (ionizes) the excited state and therefore terminates the emission in the long tail. This concept is illustrated in the inset of Fig. 1(c). If the IR pulse is timed right, a zero-area pulse can be formed at the resonance frequency, in which the emitted light in the tail exactly cancels the incoming light leading to an enhancement of the absorption by several orders of magnitude. Fig. 1(c) illustrates a model calculation of how the perfect absorption builds up from zero delay where the two pulses overlap, and the ionization of the excited state means there is no absorption on resonance.

As the IR pulse is delayed relative to the FID initiation, more and more of the FID tail being included in the spectrum leads to increased absorption. The full TDSE-MWE calculation in panel (d) shows that RPA is still clearly recognizable within a more realistic laser-matter description. An upcoming publication explores this concept in more detail, showing how the RPA can be controlled in both the frequency domain, and in the longitudinal and transverse spatial domain [4].

(iii) Characterization of temporal structure of XUV FEL pulses: The seeded FEL facility FERMI in Trieste, 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 [R1,R2]. Most recently we have been involved in a study of attosecond coherent control of electronic wave packets in two-color photoionization [R4], verifying that the phase of a specific quantum path can be modified by selectively acting on the phase of a single XUV harmonic.

(iv) Quantum trajectory selection: In collaboration with the DiMauro group at the Ohio State University we have investigated quantum trajectory selection (QTS) [7] applied to non-sequential double ionization in Ar [3]. By using laser fields with a wavelength 1.7- 2.4 μm, intensities can be used that produce large U_p for energetic recollision while minimizing ionization from the NIR field alone. This has resulted in the first experimental demonstration of QTS control of the production of Ar^{2+} via non-sequential double ionization [3].

Future Plans

Several projects are in progress or planned for the near future:

(i) Propagation and reshaping of intense X-ray pulses: This work is ongoing. We are in particular investigating the broad spectral background on the XRL line that is visible in Fig. 1(a), and which is absent in experimental results. We believe this is caused by our approximation for the time-dependent ionization probability, and we are investigating how to go beyond this approximation and/or mitigate its effects, as illustrated in Fig. 1(b).

(ii) Resonant propagation of XUV pulses: We are continuing our collaboration with the Pfeifer group, we are in particular interested in the evolution of absorption lineshapes at very high pressure.

(iii) Complex XFEL waveforms: We are pursuing calculations and (planned) experiments using a single XUV harmonic that launches an electron wave packet close to threshold in a rare gas atom. TDSE calculations show that there is a notable difference in the photoelectron spectra of different atomic targets when an NIR field is present. This difference is not found at very low intensities, but becomes pronounced at intermediate intensities of a few $\mathrm{TW/cm}^2$.

(iv) Quantum trajectory selection: We will extend our modeling of QTS applied to non-sequential double ionization. Two promising avenues are the study of very far below threshold double ionization (*i.e.*, when the returning electron has very little energy) in a variety of atomic systems, and the use of QTS with simple diatomic molecules.

(v) Condensed-phase ATA: We are currently implementing a solution of the semi-conductor Bloch equations into a one-dimensional MWE solver. We are in the process of benchmarking the linear propagation (absorption and dispersion) of IR and UV pulses through such a macroscopic condensed-phase system.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

R1 P. Maroju *et al.*, *Analysis of two-color photoelectron spectroscopy for attosecond metrology at seeded free-electron lasers*, New J. Phys. **23**, 043046 (2021).

R2 P. Maroju *et al.*, *Complex attosecond waveform synthesis at FEL Fermi*, Appl. Sci. **11**, 9791 (2021).

R3 Y. He, Z. Liu, C. Ott, A. N. Pfeiffer, S. Sun, M. B. Gaarde, T. Pfeifer, B. Hu, *Resonant Perfect Absorption Yielded by Zero-Area Pulses*, Phys. Rev. Lett. **129**, 273201 (2022).

R4 P. K. Maroju, *et al.* (36 authors including Li and Schafer from LSU), *Attosecond coherent control of electronic wave packets in two-colour photoionization using a novel timing tool for seeded free-electron laser*, Nat. Phot. **17**, 200 (2023)

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Unraveling ultrafast electron-nuclear dynamics in molecules

Award Number: DE-SC0024182

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I. Project Scope

This project focuses on developing both exact and approximate computationally efficient quantum dynamics methods capable of simulating the laser-induced electron-nuclear dynamics in polyatomic molecules which take into account non-adiabatic effects and proceeds on the multitude of electronic states. Our approach will combine semiclassical description of nuclear motion with on-the-fly *ab initio* evaluation of the electronic structure. Motivated by the current experimental capabilities, a particular emphasize will be given to the development of a predictive general quantum theory and the corresponding computational methods for the description of the ultrafast charge dynamics following molecular ionization. While the main focus will be method development, all new methods will be applied to describe properties and behavior of realistic molecules, interpret recent experimental measurements and guide future experimental efforts.

II. Recent Progress

Quantum dynamics simulations are now established as an indispensable tool for interpreting experiments that probe matter at the microscopic level and on fundamental timescales. Although much has been achieved in the understanding of fundamental physics lying behind the correlated electron-nuclear motion, the accurate numerical simulations of light-induced quantum dynamics in polyatomic molecules remain a formidable challenge.

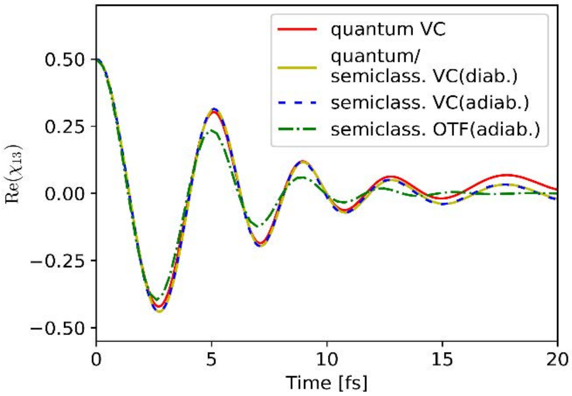

Figure 1: Comparison of electronic coherences in the propiolic acid computed by various quantum and semiclassical methods. Taken from Ref. [1].

Despite the success of fully quantum techniques in calculating the electron-nuclear dynamics resulting from the interaction of a molecule with an external laser field, the existing techniques are still rather expensive computationally, and thus can be applied to simulations of relatively small molecules only. Recently, we demonstrated that a simple, single-trajectory semiclassical scheme can evaluate the electronic coherence time in polyatomic molecules accurately by demonstrating an excellent agreement with full-dimensional quantum calculations (see Fig. 1). In contrast to numerical quantum approaches, the semiclassical one reveals the physical mechanism of decoherence beyond the general blame on nuclear motion. Furthermore, the developed scheme avoids the "curse of dimensionality" appearing in the quantum treatment of large molecules and thus can help to shed light on the continuing debates on the role of quantum coherence in realistic biological systems.

III. Future Plans

Encouraged by the unique computational efficiency and surprising accuracy of the semiclassical technique mentioned in the previous section, we will develop a new family of theoretical approaches that will address the situations when many electronic states are involved in the dynamics and where the non-adiabatic effects play an essential role.

Explicit description of both the electronic and nuclear dynamics requires simultaneous coordinated development of advanced *ab initio* electronic structure methods and computationally efficient techniques for solving the equations of motion for nuclear subsystem. Therefore, we intend to extend the existing and develop new electronic structure methods and semiclassical nuclear dynamics techniques which exploit strong points from both sides and eventually complement each other.

A required prerequisite that makes the usage of semiclassical approaches possible is to have access not only to the electronic energies of the corresponding electronic states but also to the properties such as nuclear gradients and non-adiabatic couplings. While these quantities are readily available for the electronic structure approaches dealing with bound electrons, the implementation of the corresponding algorithms for computing the gradients and non-adiabatic couplings in techniques designed to deal with the electronic continuum has not been reported so far. Therefore, we will extend the existing computational approaches by implementing the required formalism permitting the computations of properties of the involved electronic states.

Since the number of intermediate highly excited electronic states required for accurate simulations of the ionization can be huge, the treatment of electron-nuclear dynamics using standard techniques based on the Born-Oppenheimer-Huang representation of the molecular wavefunction are beyond the current computational capabilities. We, therefore, will focus on developing alternative techniques utilizing the averaging over multiple electronic states.

Although extremely challenging and important by itself, the development of necessary theoretical and computational methodologies is also a prerequisite for a successful realization of the second major goal of the present project, namely the application of the developed techniques for simulating systems of physical, chemical, and biological interest. Starting with calculations of the laser-driven electron-nuclear dynamics in small molecules, we hope to reach the goal of simulating realistic systems such as nucleobases and small peptides.

IV. References

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V. Peer-Reviewed Publications Resulting from this Project (Project start date: 07/2023)

No publications to report.

Physics of Correlated Systems, Award DE-SC0010545

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Project Scope

Our project is developing theoretical methods to handle strong coupling between two or more key degrees of freedom in a broad range of atomic, molecular, and optical systems. Such strong coupling is also referred to as correlations or entanglement in some contexts. The reason it is the focus of much theoretical and experimental interest in this field derives from the fact that the simplest and most common theoretical models, such as the independent-electron model and its improved variants, struggle in many cases to provide an adequate theoretical description. Our group applies a somewhat unconventional theoretical toolkit, including elements such as R-matrix theory and multichannel quantum defect theory, hyperspherical coordinate formulations, or newly developed time-propagation algorithms for ultrafast processes, to treat increasingly complex dynamical and spectral observations. That work is solidly rooted in quantum mechanical theory. In atomic and molecular physics, the word *correlations* has historically been used primarily to treat electron-electron correlation phenomena in atoms and molecules, but we interpret this word more broadly because there is a far more extensive collection of phenomena where multiple degrees of freedom are strongly coupled. Therefore, we treat not only electron-electron correlations, but also electron-nuclear correlations which can interconvert energy between electronic and vibrational or even dissociative degrees of freedom, and external-field or ultrafast laser photon coupling to either electronic or nuclear motion degrees of freedom. The work ranges from ultrafast ionization and/or dissociation processes in simple molecules to coherent multiphoton excitation and ionization processes in atoms with two valence electrons.

Some of our group's research is aimed at developing new ideas for learning about new types of quantum mechanical states and phenomena, breaking bottlenecks that are limiting progress, and in some cases, developing interpretations of experimental results that have not yet been fully or even partially interpreted.

Recent Progress

(i) Multiphoton ionization of strongly correlated atoms

In recent years we have been engaged in a collaborative effort with Arvinder Sandhu's experimental group, in a collaboration between theory and experiment working towards developing an understanding and then extending coherent control of ionization processes triggered by pump-probe short pulse absorption and ionization processes in atomic argon and other rare gas atoms. Two or three ultrafast laser pulses cause time-dependent quantum beats between the alternative pathways, and striking regularities have emerged in this system and have been observed experimentally. Continuing to push towards first article[3] on those joint efforts was published during the past year. We have extended our multichannel quantum defect toolkit to describe time-dependent behavior in the presence of laser field pulses, and the extension has proven to be well-suited to describing the phenomena observed by the Arizona group.[1,3] One finding published last year [8] is that through observation of time-dependent quantum beats arising from coherent pathways that pass through decaying autoionizing *nf* states of argon, higher energy resolution can be achieved than is available from frequency-dependent measurements alone. During the past year, our collaboration described a more challenging (from both a theoretical and experimental standpoint) process involving 3 photon absorption, again in a pump-probe scenario that is sensitive to phases acquired during the photoionization process.[1,3]

Most of our research carried out in the current funding period has treated multiphoton ionization processes in atoms containing two or more valence electrons. A publication last year [6] , carried out with Niranjan Shivaram's group at Purdue University, proposes a way to create entangled photon pairs in the VUV or XUV frequency range with attosecond time correlation when implemented for the helium atom two-photon decay from the 1s2s ^{1}S state to the ground state, although potentially zeptosecond time correlation could be achieved if this idea is eventually implemented for heavier atoms or ions in the periodic table. The idea is to use a single atom as a source of such photons, making use of the fact that an atom in certain states can behave analogously to existing spontaneous parametric down-conversion (SPDC) sources that are common in the visible or infrared frequency spectrum. This would extend the capability for making SPDC time- and energy-correlated photon pairs to much higher frequencies and shorter time scales, beyond the limitations of current sources.

A second major development in the area of multiphoton ionization was also spearheaded by a talented PhD student in our group, Dr. Yimeng Wang, who has since received a Humboldt Foundation Postdoctoral Fellowship and joined a research group in Berlin. Dr. Wang applied our toolkit consisting of variational R-matrix theory and multichannel quantum defect theory in an effort to understand the phase lag measurement involving interfering one- and two-photon processes in the barium atom, which was carried out more than a decade ago by Dan Elliott's group, and had not previously been understood theoretically. Our treatment[7] achieved good agreement with that complicated experiment, and was one of the first detailed calculations to fully account for the phase lag between competing fragmentation channels in any nontrivial system, going well beyond previous theory attempts. Her work also extended the barium treatment to make analogous predictions for this type of process in highly-correlated atomic strontium, in a subsequent article [4], which has not yet received experimental exploration.

Dr. Wang was also part of a collaboration with the groups of Thomas Pfeifer and Christian Ott at the Max-Planck Institute for Nuclear Physics in Heidelberg, which led to an ambitious combined theoretical and experimental study of the simplest above-threshold ionization process in atomic helium, where they completed a set of impressive measurements at the Hamburg free-electron laser facility that quantitatively tested our theory predictions. That work was published as a Physical Review Letter, article [5] in the list below.

That project just described built on our efforts [9,10] to understand the possibility of using interference between two or more photon sources to control the electron ejection process. That goal led to our 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. Such an experiment is of fundamental interest because the final photoelectron state has broken the parity as a good quantum number. Our publication [10] treats that case, again for the prototype system of atomic helium in the vicinity of doubly-excited final state energies. The calculations predict 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. It also suggests 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) Time delay in photoionization

Working with a new graduate student in the group, Karim Elghazawy, we looked into a controversial claim by a Berlin theory group who published an arXiv preprint stating that photoionization time delay cannot experimentally probe the Wigner-Smith time delay. We were skeptical about their claim, and initiated a careful study for a simple one-dimensional Hamiltonian, and our publication [2] decisively disproves their contention. Our study shows clearly that one gets half of the usual Wigner-Smith time delay in photofragmentation compared to the amount of time delay in a scattering event.

Future Plans

Further multiphoton ionization and coherent control studies are underway and should be completed within the coming year. A graduate student, Miguel Alarcon, continues to spearhead our collaboration with the group of Arvinder Sandhu on a class of pump-probe experiments in atomic argon and krypton. That effort is a major jump in complexity, as it involves describing the combination of autoionizing intermediate and final states, whose decay is mediated by the interplay of electron-electron interaction and spin-orbit coupling. We are also continuing our collaboration with the groups of Thomas Pfeifer and Christian Ott at the Max-Planck Institute for Nuclear Physics in Heidelberg, where they have been allotted beam time at Hamburg to more thoroughly investigate interfering one-photon and two-photon processes in helium.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

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[11] *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

Early Career: Theory of the femtosecond and attosecond dynamics of molecules in complex regions of their potential landscapes

DE-SC0022105

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Project scope

This project seeks to apply the tools of quantum optimal control theory to small molecules. It seeks to understand and control the dynamics of molecules in highly excited states. The probing of these states through techniques like photoionization and coincidence momentum imaging will be refined so that the observation techniques optimally observe the excited dynamics. The tools employed are grid-based quantum chemistry and scattering theory codes that are being actively developed and also used to understand molecular and electronic dynamics.

Recent progress

The time-dependent perturbation theory (TDPT) code that is the backbone of our electronic dynamics calculations has been extended and improved so that it is applicable for broader experiments. This work has largely been driven by attempts to reproduce the experimental observation of photoelectron circular dichroism (PECD) in the group of Hans Jakob Wörner. In this work, chiral molecules are probed after ionization which leaves the molecules in ground and excited ionic states. The ions are than detected in a COLTRIMS setup, giving access to the photoelectron dynamics. Crucially, circularly polarized XUV pulses [1, 2] allow access to interferometric measurements using the RABBITT technique [3], and the resulting phases ("attosecond time delays") can be determined for multiple ionization pathways. These phases depend sensitively on the ability of the electronic structure and the scattering theory to reproduce the features of the involved neutral and ionic states. The detailed information from multiple ionization pathways allows us to test our methods for different states, which adds both difficulty and also testability to our calculations. The postdoc driving these experiments and circularly polarized XUV generation, Meng Han, has been hired as an Assistant Professor by Kansas State University and the James R. Macdonald Laboratory. This will allow close collaboration on this and related projects in the future.

The RABBITT experiments probe interference in the continuum states. We model this interference not between continuum states, but between intermediate states in a time-dependent perturbation theory expansion. The accuracy of this approximation relies on whether the basis used in the perturbation expansion is sufficient to model these intermediate states. For instance, the second-order term $\hat{\mu}e^{-iH_0t_2}\hat{\mu}e^{-iH_0t_1}|\psi_0\rangle$ has to remain in the space spanned by the basis for t_1 and t_2 long enough to capture all relevant dynamics within the pulse length. We have engaged in a systematic exploration of basis effects using standard quantum chemistry basis sets augmented with diffuse functions. It should be noted that these calculations still require grid-based scattering calculations in order to project on the correct continuum states when calculating the final photoionization angular distributions.

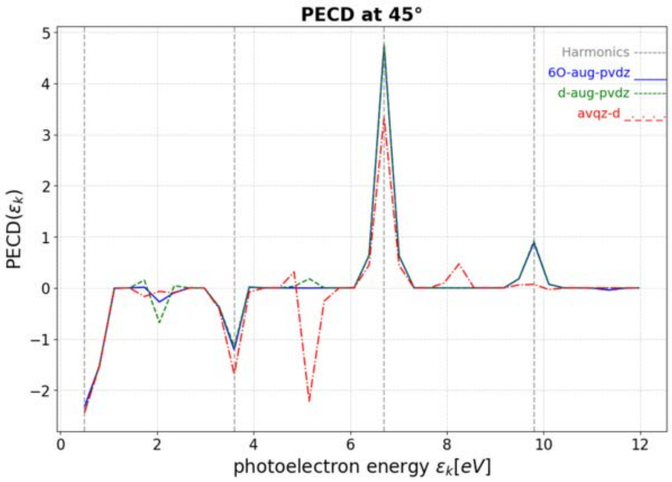

Figure 1: The effect of adding addition diffuse functions to the Gaussian basis used to approximate intermediate states.

We have yet to reach convergence with respect to all basis set parameters, as can be seen in Fig. 1. However, we have determined some behaviors important to understand for photoionization calculations. There are two axes of convergence we have explored, basis $\zeta-$quality and diffuse character. The double-ζ basis set does not capture as many sidebands as the higher quality set, although the figure is shown at a sparse energy grid so some peaks may be missed. The addition of multiple diffuse functions does have differences compared to the tighter basis, although not as much as expected. As we are attempting to capture intermediate states with significant continuum character, we expect that the diffuse functions will make the greatest differences. We are currently exploring this further in the higher ζ basis sets.

Another aspect of the method we are exploring is the sensitivity to the various parameters like the energy levels and dipole matrix elements calculated by quantum chemistry. The RABBITT phase information may be very sensitive to small errors in the theory. The discretized levels that approximate continuum states in the Gaussian basis are spaced unevenly, and they do not follow the expected quadratic behavior even for discretizations of the continuum. This leads to pseudoresonances appearing in the calculated photoelectron spectra, and variability in the phase information. We have explored multiple ways to get around the appearance of pseudoresonances, including adjusting the energies to a regular spacing and adding imaginary components to the energies to broaden pseudoresonance widths. We have performed systematic studies of the behavior of the photoelectron spectra, and RABBITT phases, with respect to these parameters.

We have determined that for many regions in the space of quantum chemistry results the calculated expansion coefficients β in a spherical harmonic expansion of the lab-frame photoelectron angular distribution are robust. Small drifts of the β values can be seen, but for large regions of the space of parameters they are unchanged. These parameters include linear and quadratic fit coefficients to the virtual orbital energies to model Gaussian continuum states, and imaginary components added to these energies. The imaginary components suppress peaks as expected and they also smooth out pseudoresonances. For certain combinations of linear and quadratic fit parameters, some of the β coefficients can be enhanced in a resonance-like manner. These regions illustrate the sensitivity of the calculated RABBITT phases to the quantum chemistry calculations.

In addition to these explorations of the parameter space, we have used the TDPT code

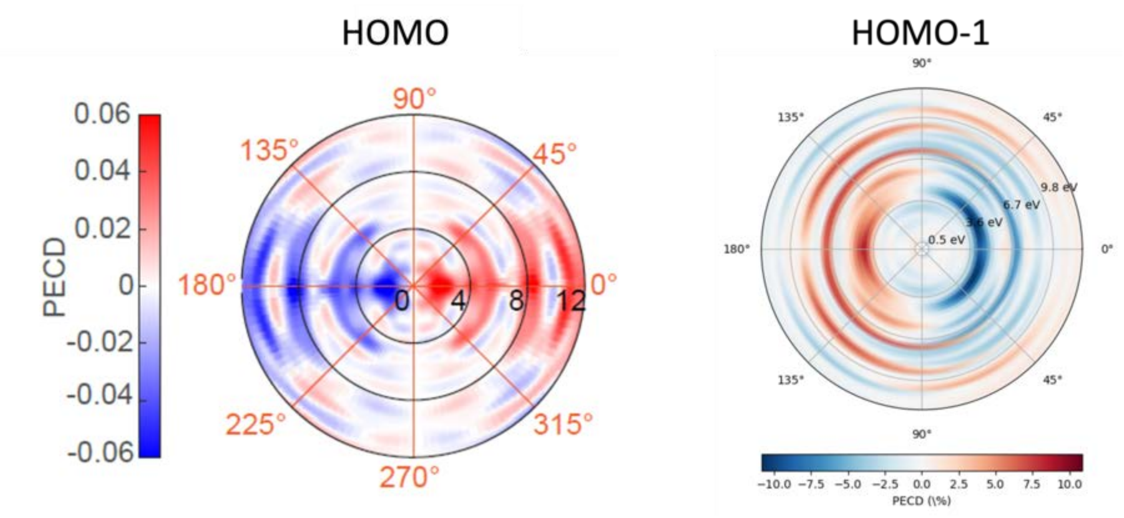

Figure 2: Calculations of the photoelectron circular dichroism of methyl oxirane for ionization from the HOMO and HOMO-1.

to attempt to predict the outcome of RABBITT-PECD experiments on methyl oxirane resulting from ionization from both the HOMO and HOMO-1 orbitals. By modifying the energy spacing in the Gaussian orbitals approximating the continuum, we are able to match the RABBITT phases for the HOMO over multiple side bands.

Future plans

We have studied Gaussian basis sets of different ζ-quality and we have added series of diffuse functions. While we have not yet determined if these bases converge, it seems likely that alternative techniques will be required, especially if we want to look at higher-order processes. We aim to study two such techniques in the medium- to long-term. The first technique is specialized Gaussian basis sets fit for the intermediate states. We will use the GTOBAS program [4], available as part of the UK-RMol package, to fit Gaussians to continuum wave functions within a boundary.

Eventually, we would like to reduce our use of Gaussians and use the grids we use to solve the scattering problem to also hold the intermediate states. We plan to explore techniques like Dalgarno-Lewis summation in order to sum intermediate states on the grid directly [5, 6]. In this technique, inhomogeneous differential equations are solved leading to auxiliary functions that may be used to calculate expectation values that are equivalent to the relevant sum over states. We believe that combining grid-based molecular methods with such techniques to accurately perform equivalent operations to sum-over-states methods may also lead to more accurate calculations of molecular properties like hyperpolarizabilities.

A large part of the future for this project includes further development of molecular grid techniques. We have been exploring the application of the multicenter "overset" grids to molecules using standard quantum chemistry techniques as well as models for highly excited states. We are still developing the code base that will allow us to extend these techniques. A preliminary step of optimizing the photoionization calculation speed is currently underway.

There are two methods that we are exploring, in collaboration with the theoretical group at Lawrence Berkeley National Lab. The first is modifying the procedure for operating on the subgrids associated with atomic centers. Currently, we use interpolation between grids, which is expensive. An alternative using direct calculation of a set of simple basis functions is under exploration. The other method is by code optimization through profiling and adapting to hardware available at the National Energy Research Supercomputing Center. The Perlmutter supercomputer relies heavily on GPUs to accelerate computation, and we are exploring optimization of the overset grid code using GPUs.

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Peer-reviewed publications resulting from this project (Project start date: 08/2021)

No publications to report.

Connecting Molecular Electronic Structure and Electron Spin Decoherence Mechanisms for Quantum Information Science

Award Number DE-SC0022920

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Project Scope

The next generation of information processing devices will rely upon detailed understanding of quantum phenomena at the single atom and molecule level. While the electron spin relaxation processes inherently important for applications in quantum information science have been rationalized on the basis of the Debye model, the assumptions behind this model are incompatible with the structure of molecular materials and, thus, this approach does not yield meaningful insights or predictions for slowly-relaxing, highly coherent molecules.[1] A new approach rooted in molecular structure is therefore required to fully understand high temperature decoherence mechanisms. Our lack of current understanding further stems from a dearth of experimental studies and approaches aimed at probing the key spin-phonon coupling and chemical bonding contributions to decoherence mechanisms. To address these issues, this research will employ and develop new lines of spectroscopic inquiry to quantitatively evaluate the critical spin-phonon coupling processes that control high temperature quantum coherence/decoherence in molecular systems, thus integrating advances in spectroscopy with an impactful scientific research directive. The research will provide firm experimental grounding for theoretical models of spin relaxation, enabling a rational path to high temperature, highly coherent molecular quantum technologies. More generally, this research will tie together new experimental and theoretical approaches to study the structural and dynamic electronic properties of molecular systems, as the models developed here can be translated directly to other critical molecular processes such as intersystem crossing and single ion magnetism. As in high temperature decoherence mechanisms, these dynamical processes are governed by the coupling between electronic spin states and ultrafast atomic motions.

Recent Progress

1.1. Using temperature and matrix effects in pulsed electron paramagnetic resonance (EPR) to illuminate contributions to molecular qubit spin relaxation.

Previous work in the Hadt lab has established T_1 anisotropy measurements as a novel technique for probing electronic structure contributions to spin relaxation in molecular qubits. Across a range of Cu(II) and V(IV) compounds measured at 100 K and a 1:1000 doping ratio, the T_1 orientation dependence displayed a characteristic $\sin^2\theta$ functional form and an average value near 2.5, which points to the role of minority spin wavefunction components induced by spin-orbit coupling. However, additional spin relaxation mechanistic insights may be obtained through the variation of T_1 anisotropy with experimental conditions. We have studied the effect of paramagnetic doping concentration and temperature on T_1 anisotropy in $Cu(acac)_2$ doped into $Pd(acac)_2$ (Figure 1). Across a range of concentrations spanning 2.5 orders of magnitude, the functional form of the T_1 anisotropy does not appreciably change. This shows that the $\sin^2\theta$ T_1 pattern in $Cu(acac)_2$ arises from single-molecular electronic structure interactions and not intermolecular interactions through electron spin-spin dipole coupling. This is consistent with our previous analysis of T_1 anisotropy arising from spin-orbit coupling on a single paramagnetic center. However, when moving from the

1:100 doping to the 1:30 doping level, the relaxation rate increases by about 20% (Figure 1A). This suggests that the electron dipole-dipole couplings do become important for the spin relaxation rate at high doping concentrations, but are either isotropic or only weakly anisotropic. Thus, concentration-dependent T_1 anisotropy studies establish the Hamiltonian components responsible for molecular qubit spin relaxation under different experimental conditions.

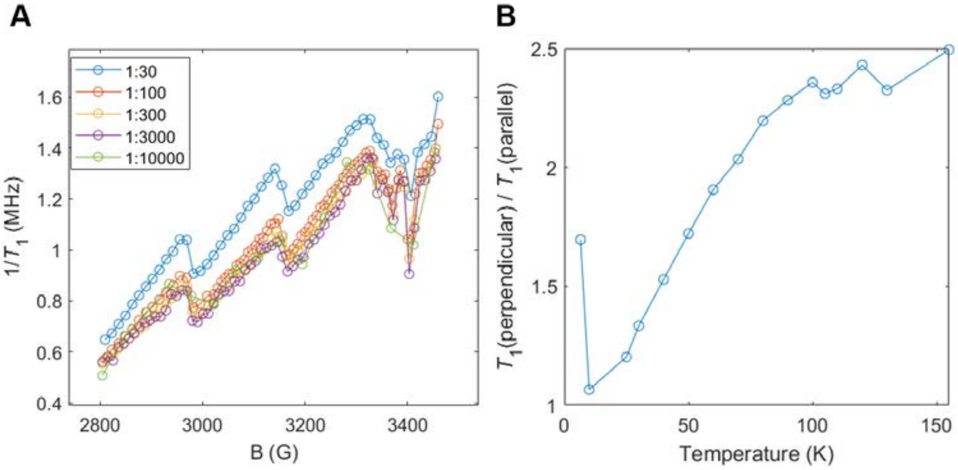

Figure 1. Effects of experimental conditions on T_1 anisotropy for Cu(acac)$_2$ doped into Pd(acac)$_2$. (A) Variation in paramagnetic doping concentration at 100 K. (B) Variation in temperature at the 1:1000 doping level.

Interrogation of the Cu(acac)$_2$ temperature-dependent T_1 anisotropy reveals that almost no anisotropy is present at 10 K, but a monotonic increase in anisotropy occurs above 25 K (Figure 1B). Crucially, spin relaxation above 25 K is thought to be controlled by totally symmetric molecular vibrational modes, while relaxation below 20 K arises from acoustic or pseudoacoustic phonons. This validates that molecular vibrations and not delocalized phonons give rise to $\sin^2\theta$ T_1 anisotropy, indicating the key value of a molecular electronic structure approach to understanding spin relaxation in molecular qubits.

1.2 Using Time-resolved Faraday rotation for all-optical detection of T_1.

Pulsed EPR provides a powerful technique for measuring spin relaxation, but it carries an intrinsic time resolution limit of ~100 ns. Many molecules of interest to molecular quantum information science possess faster spin relaxation than 100 ns under ambient conditions. Such compounds have been traditionally considered "not room-temperature coherent", but coherence/non-coherence is entirely relative to the speed of the instrumental technique employed. Ultrafast optical methods have a sub-picosecond time resolution and so allow for measurement of room temperature spin relaxation dynamics in "non-room-temperature coherent" molecules. To this end, we have built a setup to measure time-resolved Faraday rotation and ellipticity. Intense, wavelength-tunable "pump" pulses are circularly polarized by a photoelastic modulator and used to generate a transient spin polarization in the sample. After some time delay, a weaker, white-light "probe" pulse passes through the sample, and the polarization of a narrow wavelength range is detected by a pair of bridged photodiodes. The spin polarization induced by the pump in the sample interacts with the probe pulse through spin-orbit coupling, rotating its plane of polarization. By varying the time delay between pump and probe pulses, the spin relaxation dynamics are measured through the dynamics of this optical polarization change. Two magnet setups enable temperature dependence and coherent control of the spin polarization from 0 to 7 T. We have conducted preliminary measurements on lead-halide perovskite films, detecting T_1 of ~1.6 ps, significantly below the detection limits of pulsed EPR.

1.3 Interrogating molecular qubit electronic structure via variable-temperature, variable-field magnetic circular dichroism (VTVH MCD)

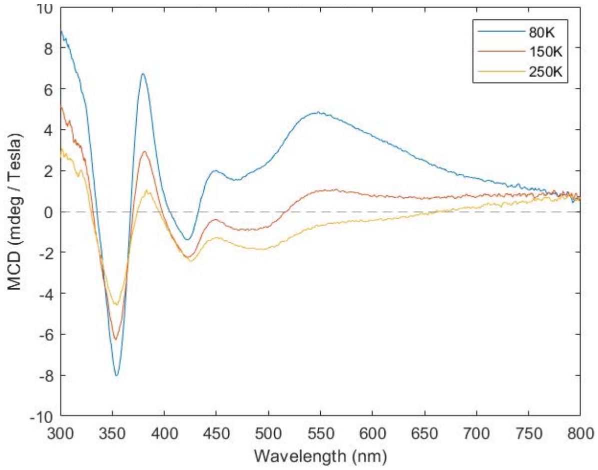

Figure 2. Variable-temperature MCD of (PPh$_4$)$_2$[Cu(mnt)$_2$] in a PMMA film, collected over a range of +/– 4 Tesla.

Ligand field theory derivations of molecular qubit spin relaxation rates predict that the energetic position of the d-d transitions should play an important role. However, these energies cannot be easily obtained from conventional UV-vis absorption spectroscopy, as the covalent, conjugated ligands used for molecular qubits facilitate intense charge transfer transitions, which cover nearly all of the ligand field bands in the absorption spectrum. We are developing variable temperature, variable field magnetic circular dichroism (VTVH MCD) capabilities to identify the position of the d-d bands in molecular qubits. These transitions are selectively enhanced at low temperature due to the role of spin-orbit coupling in the C-term intensity mechanisms. Preliminary experiments on (PPh$_4$)$_2$[Cu(mnt)$_2$] show that the MCD intensity increases as temperature decreases while the spectral shape remains similar, indicating reliable measurement of C-term intensities (Figure 2).

Future Plans

Building on the successes described above, we will continue to develop these three spectroscopic techniques for studying spin relaxation in molecular qubits. Our near-term efforts will focus in two areas: (1) further extension of the T_1 anisotropy temperature and matrix effects to a broader scope of molecular qubits, (2) time-resolved Faraday rotation to directly measure the spin relaxation of fast-relaxing molecules, and (3) application of MCD to a broader compound scope and at lower temperatures.

2.1. Temperature and matrix effects on T_1 anisotropy. While the above temperature-dependent T_1 anisotropy data on Cu(acac)$_2$ in Pd(acac)$_2$ indicate that acoustic phonons do not drive T_1 anisotropy, the influence of the crystal lattice on optical phonon (i.e., molecular vibrations) spin relaxation has not been characterized. To do so, we will compare T_1 anisotropy for [Cu(mnt)$_2$]$^{2-}$ crystallized with a series of counterions: HPy$^+$, AsPh$_4^+$, NEt$_4^+$, and NBu$_4^+$. Each of these counterions enables crystallization of [Cu(mnt)$_2$]$^{2-}$ with an identical complex anion geometry, but with altered lattice symmetry and intermolecular contacts. Thus, the uniquely molecular portion of optical phonon spin relaxation will remain unaltered, while the lattice portion will vary. We will acquire T_1 anisotropy measurements across this series to disambiguate these contributions. We will additionally compare T_1 anisotropy measurements to frozen solution glasses, which possess no phonon structure. Finally, we will extended the temperature-dependent T_1 anisotropy measurements to a range of molecular qubits, characterizing the critical temperatures at which anisotropic spin relaxation occurs.

2.2. Time-resolved Faraday rotation. With the aforementioned setup, we aim to probe structure-function relationships in spin dynamics over a different parameter space than is accessible via EPR. Compounds with higher spin-orbit coupling are expected to provide a larger TRFR signal, albeit at the cost of shorter T_1 times. To maximize signal-to-noise, we will initially focus on inorganic complexes with late transition metal ions. With the cryostat enabling temperature control, we also aim to measure the temperature dependence of T_1 in these systems.

2.3. MCD spectroscopy. We will extend our preliminary measurements to several other molecular qubits for comparative investigations of electronic structure. The results will also be correlated to T_1 anisotropy, for which relative energies of ligand field transitions have been especially implicated. Our experimental setup includes the ability to acquire MCD down to sub-liquid He temperatures for maximum sensitivity to ligand field band positions.

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Peer-Reviewed Publications Resulting from the Project (Project start date: 07/2022)

Kazmierczak, N. P.; Hadt, R. G. "Illuminating Ligand Field Contributions to Molecular Qubit Spin Relaxation via T_1 Anisotropy," *J. Am. Chem. Soc.* **2022**, *144*(45), 20804 – 20814.

On-Chip Attosecond Metrology of Solid-State High-Harmonic Generation

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1 Project Scope

This project will use time-domain spectroscopy in the visible to near-infrared to investigate the generation mechanisms of high harmonic radiation emitted from solid-state systems. Our work aims to resolve open questions regarding the time-domain properties of solid-state high-harmonic field waveforms, as well as the underlying electron dynamics and interplay between different extreme nonlinear light generation mechanisms within solids.

High harmonic generation (HHG) is a non-perturbative process where strong electromagnetic fields excite electrons in matter resulting in the emission of high-order photons. While HHG from atomic and molecular systems has been investigated extensively, many open questions remain about the fundamental emission mechanisms and corresponding electron dynamics responsible for HHG in solids. In particular, questions remain concerning: (1) the complex dynamical interplay between the various emission mechanisms, both intra- and interband, responsible for the higher-order harmonic radiation; (2) how these emission mechanisms depend on the underlying material properties; and (3) the precise temporal structure of the electronic dynamics within the material and resulting harmonic radiation. We aim to address these open questions through sub-cycle, time-domain sampling of the HHG radiation from solids.

Sub-cycle, time-domain characterization of the harmonic radiation would provide a window into the excited electronic dynamics as it evolves in time. By providing both amplitude and phase information about the generation process, it will also provide a link between both the temporal and spectral properties of the radiation, providing needed information for studying material-dependent emission mechanisms, and the precise relationship between intra- and interband dynamics.

While experimental time-domain characterization of HHG in the near- to-mid-infrared driven by terahertz sources has been demonstrated, limitations in the ability to sample weak fields with adequate time resolution have prevented the time-domain characterization of HHG driven by shorter wavelengths in the near- to mid-infrared. This is unfortunate as in this shorter wavelength regime the microscopic electron interactions become more complicated, and there is outstanding debate surrounding the interpretation of experimental data in this region.

To overcome the sensitivity and resolution limits hindering the sub-cycle sampling of high harmonic radiation from solids, we will leverage recent developments by our team of on-chip petahertz electronics for sub-femtosecond sampling of optical fields. We will use these nanoscale, petahertz-electronic devices to provide full polarization and time-domain electric field waveform characterization of high-harmonic radiation driven from a variety of solid state systems spanning the visible to near-infrared.

To compliment our experimental efforts, we will also use extensive comparison to theory and computational models to understand the underlying physics. We will build off of our recent collaboration with Prof. Lars Madsen's group at Aarhaus University using time-dependent density functional theory to explore how time-domain, field-resolved analysis can be leveraged to uncover extreme nonlinear electron dynamics responsible for high-harmonic generation within solids (Phys. Rev. B 107, 054302, 2023).

Unlike past work, our approach will not require spectral characterization or phase retrieval, but will rather be direct oscilloscope-like measurements of the radiation in time. Apart from having direct scientific impact, we anticipate that our work will further the development of highly-sensitive on-chip metrology methods for field-resolved electromagnetic waveform characterization with attosecond resolution. We feel these methods will have impact beyond the studides of HHG in solids by enabling the general study of attosecond- to femtosecond-scale electron dynamics in complex media.

2 Recent Progress

This program was selected for funding in 2023 and work has just recently commenced.

3 Future Plans

In the first year, our experimental efforts will focus on the construct our optical test bed and initial experiments in high harmonic sampling. This effort will include optimization of our near- to mid-infrared laser source and the development of the modified delay lines for testing high harmonic radiation from solid samples. In parallel, we will continue the development and fabrication of the nanoantenna sampling devices tailored for the sampling of mid-infrared harmonic radiation. Initial experiments will start with the generation and spectral characterization of high harmonics before transitioning to our initial sampling experiments. These experimental efforts will be complimented by ongoing development and improvement of our theoretical analysis methods using time-domain harmonic field information using accurate models of HHG from solids, with a particular focus on the extension to models of three-dimensional systems and vectorial harmonic fields.

4 Peer-Reviewed Publications Resulting from This Project (**Project start date: 08/2023**)

No publications to report.

Attosecond Physics with XFEL sources

Award number: DE-SC0022093

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PROJECT SCOPE

In the past few years, the very first attosecond X-ray pulses have been produced at LCLS [1], with additional LCLS experiments planned in the near future [2]. 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.

However, current state-of-the-art attosecond pulse experiments, both from LCLS and tabletop sources, rely on single photon ionization, where an electron absorbs a single photon from a high frequency attosecond pulse, and subsequently leaves the atom, where it is streaked in the continuum by the circularly or linearly polarized infrared light [1-4]. To interpret these experiments, theoretical tools need to be further developed to address the ionization of inner-shell electrons in molecules, including electron correlations and subsequent charge migration. From a practical viewpoint, innovative theoretical approaches are needed 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 high frequency attosecond sources.*

2. *Explore strong field interactions in the high intensity regime.*

To address these aims, we will develop theoretical descriptions of both strong field ionization and single photon ionization relying on semiclassical approaches. Wherever possible, we plan to compare the recently developed theory to existing methods, such as Relativistic Random Phase Approximation (RRPA). Broadly speaking, our key goal is to expand the number of theoretical tools that one can tap into to interpret ionization experiments using both existing tabletop laser sources and the newly available attosecond XFEL sources.

As part of broader experimental campaigns, 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.

RECENT PROGRESS

This past year, I have worked in parallel to address both of the key goals of the project: *attosecond ionization delays in atoms/molecules* and theory of *strong field interactions*. Of the peer-reviewed publications resulting so far from the grant, the first two focus on the latter, while the other two focus on the former. Below we describe these contributions in two separate sub-sections. Note that the Quantum Trajectory Monte Carlo (QTMC) simulations that we recently developed are part of an effort to develop a comprehensive semiclassical description for all ionization phenomena, from single photon to strong field ionization regime, and therefore overlaps with both of these topics.

Strong field interactions:

We recently developed Quantum Trajectory Monte Carlo simulations for strong field ionization of atoms and molecules, see [i,ii] of the publications resulting from this project section. Below we describe the results of these two publications involving strong field ionization and their significance. We applied our QTMC simulations to establish the ionization site of a diatomic molecule by comparing QTMC with previously published experimental data [5]. In a follow-up work [ii], we showed that the carrier-envelope phase does not significantly impact the ratio of upfield vs. downfield ionization events in a molecule. This supports the idea that upfield ionization is a non-adiabatic effect, which is determined primarily by the Keldysh parameter, $\gamma = \omega\sqrt{2I_p}/F$, which depends on laser frequency and field strength (given by ω and F, respectively), but not on the carrier envelope phase. This work on molecules is an extension of my prior work on non-adiabatic effects in strong field ionization, which focused on atoms [6]. It is significant because while non-adiabatic effects in atoms have been a lively area of research over the last 5-10 years, relatively little is understood of non-adiabatic effects in strong field ionization of molecules. Hence commonly used theoretical models, such as Molecular-ADK (MO-ADK) typically assume downfield ionization only. By comparing QTMC with experimental data in [i], we showed that upfield ionization (and hence non-adiabatic effects) are significant in typical strong field experimental regimes.

Note that the QTMC simulations developed and used in [i,ii] are part of a broader efforts to develop semiclassical description of ionization in the attosecond regime, spanning both single photon and non-perturbative strong field ionization regimes. More detail on the QTMC method is to be published in the Springer Proceedings of the 8th International ATTO Conference.

Attosecond Ionization Delays in Atoms and Molecules:

In publications [iii,iv] that appeared this year, we focused on ionization delays in atoms. In particular, [iv] is a detailed tutorial that breaks down the different delays that are contained in the experimentally measured streaking delay. We explain how the Coulomb-Laser coupling contributes to the total streaking delays and show why it is highly dependent on the period of the laser field. We also explain some unsupported assumptions in the prior treatments of the streaking delay (see appendix section of the tutorial). Overall, this tutorial is a self-contained work that explains how the Wigner and the Coulomb-Laser Coupling delay contribute to the total experimentally measured streaking delay.

In publication [iii], we aim to get a better understanding of Wigner delay, which is considered a key short-range potential part of the delay that contains specific information about the target. To this end, we used Relativistic Random Phase Approximation (RRPA) to obtain the Wigner delays of negatively charged halogens (F-, Cl-, Br-,I-) and compare them to Wigner delays of Noble gas ions with the same electronic structure. We found a surprising difference in Wigner delays at low electron energies, with Noble gas ions trending strongly positive, while all halogens trending strongly negative. This was surprising, since Wigner time should be independent of the long-range 1/r potential, which was present in the Noble gas ions, but not in the negatively charged halogens. Rather, the 1/r potential is commonly believed to be contained within the Coulomb-Laser coupling term and not contribute to the Wigner time [iv]. By that logic, streaking experiments on negatively charged ions should contain pure Wigner time. Our results show however that one must be cautious of this paradigm at low electron energies. Indeed, in our tutorial in [iv], we show that the usual separation between Wigner and Coulomb-Laser coupling time breaks down for low electron energies.

Another useful conclusion from our work in [iii] is that although there are strong differences in Wigner delays between negatively charged halogens and the corresponding Noble gas atoms at low electron energies, there is a good agreement at higher energies and this agreement gets better for heavier atoms. This indeed suggests that Xenon, for instance, may be a good approximation for the ionization delays of electrons coming from Iodine. This is useful, since Iodine containing molecules are frequently used in attosecond molecular ionization experiments. Hence, Xenon can be used as a reference gas in such experiments to help determine the role of the molecular environment on ionization delays.

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 high frequency 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 (6,7).

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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PEER REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (Project start date: 08/2021)

[i] L. Ortmann, A. AlShafey, A. Staudte, A.S. Landsman, “Tracking the Ionization Site in Neutral Molecules", *Phys. Rev. Letters* 127, 213201, (2021)

[ii] A. Schimmoller, H. Pasquinilli, A.S. Landsman, “Does Carrier Envelope Phase Affect the Ionization Site in a Neutral Diatomic Molecule?" *Atoms* 11(4), 67, (2023)

[iii] B. Grafstrom, A.S. Landsman, “Attosecond Time Delay Trends across the Isoelectronic Noble Gas Sequence" *Atoms* 11(5), 84, (2023)

[iv] L. Ortmann, A.S. Landsman, “Understanding Attosecond Streaking" tutorial to appear in the Special Issue of *Photonics* (2023)

Tracking multi-electron dynamics in molecules at the attosecond timescale

Award Number: DE-SC0024383

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Project Scope:

After two decades of continuous development, attosecond science has reached a level of maturity and sophistication which allows for investigating multi-electron dynamics in matter at the attosecond timescale. Attosecond pulses with photons energy ranging from ten to hundred electron-volts are now routinely produced and controlled in the laboratory, which allows to probe multi-electronic processes like double-excitation or double-ionization in most atomic and molecular species from absorption of a single photon. In this project, we proposed to explore the correlated electron dynamics as well as the coupled electron-nuclear motion in diatomic molecules, by combining a recently built ultra-stable attosecond beamline and a COLTRIMS-type multi-particle imaging system. 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. Finally, we expect that this new capability will offer promising possibilities to enhance our fundamental understanding of multielectron dynamics in molecular species, and ultimately to identify ways to control them, which will open a new path toward laser-controlled chemistry at the attosecond timescale.

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). The experimental system has been installed in a state-of-the-art laboratory, which offers high-stability and temperature-controlled conditions suitable for the long-term experiments. The system combines a commercial Ti:Sapphire laser system, an attosecond beamline, which is itself composed of an attosecond source, and a stabilized EUV-IR Mach-Zehnder interferometer, an electron momentum spectrometer, and an EUV photon spectrometer. To allow for precise measurements at the attosecond timescale, we have developed a stabilization system for our Mach-Zehnder-type XUV/IR interferometer [1]. It is based on a CW laser propagating coaxially with the pump and probe beams in the interferometer. At the exit of the interferometer, an optical system is used to align coaxially the CW beams in order to produce an on-axis interference pattern that can be captured with a fast photodiode. Such a design presents several advantages over other methods. First, it offers a large stabilization bandwidth, which is mainly limited by the resonance frequency of the piezoelectric transducer used to adjust the interferometer path length. And, more importantly, it allows for a high stability as the relative phase between the two CW waves is directly measured from the photodiode signal without the need of any retrieval procedure. With such a design, we obtained a time delay jitter in the interferometer of the order of 10-as rms over several hours and a feedback frequency close to 300 Hz.

Another major development has been the completion of the multi-particle imaging system (COLTRIMS). Coincidence measurements of the 3D-momentum distribution of all the emitted charged particles will be carried out with a reaction microscope (also known as COLTRIMS for COLd Target Recoil Ion Momentum Spectrometer) [2, 3]. The system has been custom-designed by us, and recently assembled and tested. It combines a modulable charged-particles spectrometer and a multi-hit detector, which is itself composed of an 80-mm microchannel plate and a hexagonal delay-line anode. The geometry of the spectrometer (length of both the extraction and field-free regions) can be adjusted to optimize the detection conditions for a given measurement. By using both a static electric field and a (few Gauss) magnetic field, photoelectrons are confined on helical trajectories toward the detector, ensuring a (quasi) 4π solid angle collection for kinetic energies up to 100 eV. From both the time of flight and the impact position, the complete momentum vector of each photoelectrons is reconstructed and its energy deduced with a resolution ($\Delta E/E$) of about 5%.

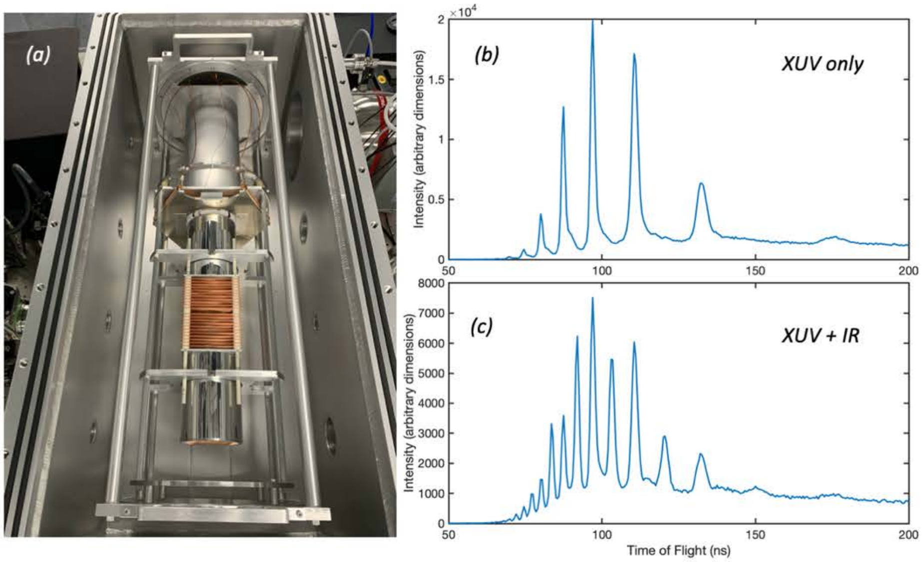

Figure 1: (a) Picture of the COLTRIMS spectrometer. (b) and (c) Photoelectrons Time-of-Flight of photo-electrons generated by absorption of an attosecond pulse trains (APT) and by absorption of an APT and IR field temporally locked, respectively.

The COLTRIMS spectrometer is now routinely used in our laboratory, and we currently are performing our first time-resolved measurements in atoms at the attosecond timescale. As an example, Figures 1(b,c) show the time-of-flight of photoelectrons generated from argon by absorption of an attosecond pulse train (APT) made of odd harmonics and by absorption of an APT and a phase-locked infrared field. In order to perform a complete measurement of the coupled electronic and nuclear dynamics in molecules proposed in this project, we would add a second multi-hit detector for the detection of ions and molecular fragments. No technical development would be necessary to add this second detector to our current system, though, as the spectrometer was designed to allow for such an upgrade in our particles' detection capabilities.

Future Plans

In this project, we propose to employ such experimental capabilities to investigate in details the correlated electron dynamics in molecules. The range of possible experiments we could perform with our experimental system is quite broad. Basically, the entire subset of molecular systems studied previously with COLTRIMS using synchrotron radiation could be revisited in time-resolved experiments. In this project, we would focus our study on two particular benchmark systems. The first system that we would study would be the double ionization of helium, which will serve as a point of departure for a set of experiments dedicated to the study of the correlated electron dynamics in molecules. Helium is the simplest specie exhibiting electron correlation, and such a three-body problem can be fully studied in kinematically complete experiment. The measurement of the individual momenta of the three particles will allow us to extract the information regarding the electron correlation from the triply differential cross sections as a function of the emission angles of both ionized electrons (also referred as final joint momentum distribution), and the photoelectron energy correlation spectra.

We will then follow our comprehensive study by investigating correlated electron dynamics in molecular systems, in particular in hydrogen molecules. Compared to helium, molecular hydrogen possesses an additional degree of freedom. Molecular hydrogen is then a good benchmark system for our study as it is the simplest molecule that exhibits both electron correlation and coupled electron-nuclear dynamics. In addition, it offers the possibility to study electron and nuclear dynamics in regimes where the Born-Oppenheimer approximation is no longer valid. Even in such a simple diatomic molecule, the complexity of the coupled electron and nuclear wave packet motion usually prevents a full theoretical treatment. A systematic and detailed experimental study is then necessary to shed light on the dynamics [4, 5]. Electronic states lie in the EUV region of the spectrum covered by conventional attosecond pulse (from 15 up to 60 eV), while dynamics occurs on the attosecond-to-few-femtosecond time scales. We will then study this system using attosecond pulse trains (APTs) as a pump and a synchronized short femtosecond IR pulse as a probe. APTs are particularly well-suited for such studies as they retain a useful degree of spectral resolution, making the selection of particular set of electronic states controllable energetically.

The number of parameters which could be varied to unravel the electron dynamics is rather large. First, we plan to investigate the dependence of the electron dynamics on the time delay between the attosecond pulse and the IR field. This first experimental approach is motivated by various ab-initio calculations which have shown that the delay between the attosecond pulse and the IR laser sensitively influences the photoelectron momentum distributions and can therefore be adjusted to control the photoelectrons emission. Then, we plan to investigate the role of the attosecond pulse duration. By varying the pulse duration, we expect to measure the strength of the electron correlation in the ionization process. If successful, this experiment would eventually offer an opportunity to control the correlation in the exit channel. Finally, in order to explore how strongly correlated photoelectrons behave after absorbing a few photons, we also plan to carry out a systematic study of the dependence of the process on the number of IR photons involved by varying the intensity of the IR field.

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[5] A. Palacios et al., *Molecular interferometer to decode attosecond electron-nuclear dynamics*, Proceedings of the National Academy of Sciences 111, 3973 (2014)

Peer-Reviewed Publications Resulting from this Project (Project start date: 08/2023)

N/A

Towards imaging time-resolved non-equilibrium molecular structures with ultrafast intense laser pulses

Award number: DE-SC0023192
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I. Project Scope

The purpose of this project is to theoretically and computationally study the dynamics of small molecules, which undergo chemical transformations in femtosecond timescales, by using a combination of different strong-field techniques. These techniques include laser-induced electron diffraction (LIED), high-order harmonic generation spectroscopy (HHS), and coincident photoelectron and photoion fragments energy/momentum distribution measurement. By using single laser pulses, previous applications of LIED and HHS have been largely limited to molecules at or near equilibrium geometries. Furthermore, in the molecular retrieval procedure, used in these techniques, nuclei have typically been treated as classical particles. This project aims to overcome these limitations and extend the current capabilities of the strong-field techniques to image ultrafast changes in molecular structures within the pump-probe scheme. The success of this project would make these strong-field molecular imaging techniques applicable to a much broader class of problems. It would also make these techniques more reliable and potentially applicable to larger molecules. The methods and tools developed in this project should also be relevant to other time-resolved spectroscopic techniques such as attosecond transient absorption spectroscopy and time-resolved photoelectron spectroscopy. In all these methods, the electron-nuclear dynamics is at the heart of all the processes involved.

II. Recent Progress

1. Development of a new method for simulation of the LIED

Together with our graduate student, Mr. Phi-Hung Tran, we started our development of a new semiclassical method that combines Herman-Kluk propagator with strong-field formalism for atoms or molecules in intense lasers. Quite recently we were able to show that our newly developed method, the strong-field Herman-Kluk (SFHK), provides very accurate results for two-dimensional (2D) photoelectron momentum distribution (PMD), see Fig. 1. Due to its semiclassical nature, with this method we were able to provide insightful interpretations for various effects found in rescatteing physics. In contrast to the common belief that there are two paths, so-called long and short trajectories, we found that there are typically multiple trajectories that lead to a given final momentum in the high-energy region. This leads to much richer

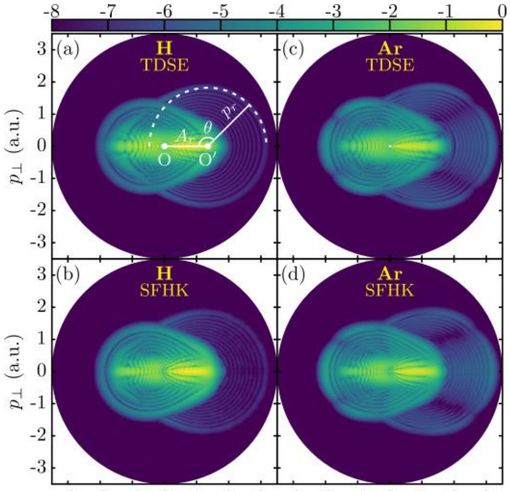

Fig. 1. Comparison of PMD for H (left) and Ar (right) obtained from the TDSE (top) and our semiclassical SFHK method (bottom)

interference patterns than previously thought. We also showed that our method is more accurate and has a larger range of validity than the quantitative rescattering theory (QRS), which has served as the basis for the laser-induced electron diffraction (LIED) and high-harmonic spectroscopy (HHS). Our method can therefore be used to extend current capabilities of these and other ultrafast imaging and strong-field spectroscopic techniques. A major advantage of our method is that it is based on classical trajectories that can be calculated independently. In other words, a primitive parallelization can be used to accelerate the calculations. These results were reported at the DAMOP 2023 meeting, and we have submitted a paper to Phys. Rev. Lett. [1].

2. Three-dimensional (3D) photoelectron momentum distribution at low energies

Together with Mr. Phi-Hung Tran, we have also been collaborating with Prof. C. Trallero and Prof. G. Gibson experimental groups (both at University of Connecticut) on 3D photoelectron momentum distributions (PMDs) from atoms in intense elliptically polarized laser pulse. With experimentally available high-quality 3D PMDs for Xenon, our goal in this project is to understand the ellipticity dependence of the PMD in full 3D at low energies (of the first few above-threshold ionization peaks). There are two most interesting features seen in new experimental data from Trallero's and Gibson's groups. First, there are significant changes of the PMD along the direction of the laser's propagation that have never been observed. Second, in addition to the strong shifts of the offset angle from one ATI ring to the next one that has been observed by Trabert *et al* [2] for the case of hydrogen atom, there is the strong shift of the offset angle even within the first ATI ring that has not been observed before. Overall, we found very good agreement between our numerical solution of the time-dependent Schrodinger equation (TDSE) with experimental data in reproducing both features. To understand the origin of these features, we have also carried out numerical simulations with our SFHK method. We found that the main features of the TDSE and experiments can be reproduced by using nonadiabatic ionization from the SFA within the SFHK method, but they cannot be obtained by using the adiabatic ionization within the SFHK. These results were reported at the DAMOP meeting this June. We plan to finish this project in the next two months.

3. Dynamics of the hole in XUV-assisted high-harmonic generation

Together with our postdoc, Dr. Esteban Goetz, we have started our investigation of the hole dynamics in XUV-assisted high-harmonic generation (HHG). In this scheme, a resonant XUV is used to transfer the hole to a lower level after it was created by tunneling ionization by an intense IR laser. When the emitted electron revisits the parent ion, it has a chance to recombine with the new hole (in the lower level) so that HHG with higher photon energy can be emitted. This scheme was proposed earlier by Buth *et al* [3,4] based on the strong-field approximation. However, this scheme has never been confirmed by more accurate methods or experiments. In fact, the recent experiment carried out at FLASH by Tross *et al* [5] found no evidence of the extended cutoff, as predicted by the model. By using the time-dependent configuration interaction singles (TDCIS), we were able to show clear evidence of this process. We have studied properties for this HHG as the IR and XUV parameters vary. Furthermore, we have analyzed the case when the XUV pulse is partially coherent as it was used in Tross *et al* [5]. We found that the HHG yields in the extended cutoff are significantly suppressed. We speculate that macroscopic propagation can further reduce the HHG yields in the extended cutoff. Our result therefore provides possible explanation for the failure in Tross *et al* experiment [5] to observe any harmonics beyond the regular cutoff. These results were reported at the DAMOP meeting, June 2023, and at the ISWAMP meeting, July 2023. We plan to submit a paper to Physical Review A within a month to report these results [6].

4. Interferometric transient absorption spectroscopy (ITAS)

We have also been collaborating with C. Trallero's and G. Gibson's groups in a project on interferometric transient absorption spectroscopy (ITAS). Experimentally, their groups managed to generate two spatially separated XUV pulses that are phase locked with a temporal jitter of a few zeptosecond (zs). We have carried out simulations of the interference between the HHG from the two arms to compare with their measurements. A joint paper was submitted to Nature Photonics [7].

5. Probing charge migration in carbon-chain molecule with HHG

Together with our postdoc, Dr. E. Goetz, we had also collaborated with a research group in Wuhan, China, headed by Prof. P. Lu and Prof. P. Lan. We calculated photoionization dipole (both magnitude and phase) for a few polyatomic molecules in a range of photon energy. These data were then used in our QRS theory to calculate HHG spectra and compare with their experiments. This collaboration results in two papers, one was published to Advanced Photonics, the other one was submitted to Science Advances [8].

6. Probing nuclear wave-packet dynamics with TRPES

Together with our former postdoc, Dr. Van-Hung Hoang, we have collaborated with Professor H. J. Worner group (ETH, Zurich) on the time-resolved photoelectron spectroscopy (TRPES) in N_2. We showed the evidence of the effect of autoionizing resonances in the observed spectra. In the experiment, the coherent excitation of N_2 by ∼14.15 eV extreme-ultraviolet photons prepares a superposition of three dominant adjacent vibrational levels (with vibrational quantum numbers *v*'= 14–16) in the valence *b*' state. The coherent nuclear wave-packet is then probed by the absorption of two or three near-infrared photons (800 nm), resulting in oscillations in the measured photoelectron spectra. Our calculations confirm that two autoionizing Rydberg states converging to the excited A and B states of the N_2^+ are accessed by the resonant absorption of near-infrared photons. We show that these resonances apply different filters to the observation of the vibrational wave packet, which results in different phases and amplitudes of the oscillating photoelectron signal depending on the nature of the autoionizing resonance. This work clarifies the importance of resonances in time-resolved photoelectron spectroscopy and particularly reveals the phase of vibrational quantum beats as a powerful observable for characterizing the properties of such resonances. Our results were published in Phys. Rev. Lett. (2023).

III. Future Plans

Based on the progress we have made recently, we plan to further develop our semiclassical method, the SFHK, for applications in strong-field processes. The main effort will be the extension to molecules. One of the important features is that this method involves calculation with classical trajectories that can be done independently on different computers. Therefore, we expect that our method can be extended to larger systems in a straightforward manner. So, we intend to test our method on simple molecules and compare the results with the TDSE. We also plan to accelerate the method by using the GPU. We further plan to extend our method for HHG process.

We plan to study LIED and HHS within the pump-probe scheme for dissociating molecules. In the first step in the simulation, the time-dependent nuclear wave packet during and after the pump pulse is obtained from the solution of the coupled channel equations, as well as the surface hopping method that we developed recently. In the second step, high-energy photoelectron momentum spectra induced by the probe pulse at each time delay are calculated by either the SFHK or the Quantitative Rescattering (QRS) theory. We further plan to develop retrieval method based on machine learning (ML). We expect consultation and possible collaboration with Prof. Caiwen Ding group (Dept. of Computer Science & Engineering, University of Connecticut).

Many theoretical and computational tools developed in this project are also relevant to other time-resolved spectroscopic techniques such as attosecond transient absorption spectroscopy (ATAS) and time-resolved photoelectron spectroscopy (TRPES). In particular, the electron-nuclear dynamics is at the heart of all these processes. We therefore plan to perform simulations for other related techniques of current interest to the research community, including the ATAS and TRPES. Together with the LIED and HHS, these techniques provide complementary information about the molecular structure.

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V. Peer-Reviewed Publications Resulting from this Project (start date: 08/2022)

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Beating electronic decoherence (DE-SC0020994)

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Program Scope

This project 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 time-domain. (2) devising atomistic schemes that can suppress decoherence and produce long-lived electronic coherence in molecular system.

Recent Progress

1. Strong field pump-probe of electronic and nuclear wave packets in atoms and molecules

Attosecond measurements have been carried out using attosecond pulses or by exploiting the coherent nature of electron recollision in high harmonic generation. In the past, strong field pump-probe method has been employed to study nuclear wave packets or slow electronic wave packets. The approach was not considered viable for probing dynamics on a few-femtosecond scale. Recently, the Li group showed that by using few-cycle pulses (<5fs), strong field pump-probe can capture electronic dynamics with a period of 6 fs in both atoms (krypton) and molecules (methyl iodide). Multiple vibrational wave packets on different electronic states of the methyl iodide cations were also observed. The method is general and offers a powerful alternative to implement attosecond measurements and will be applied to study electronic decoherence dynamics and the interaction between electronic and nuclear degrees of freedoms. Theoretical modeling on this experiment is currently on-going by the Schlegel group.

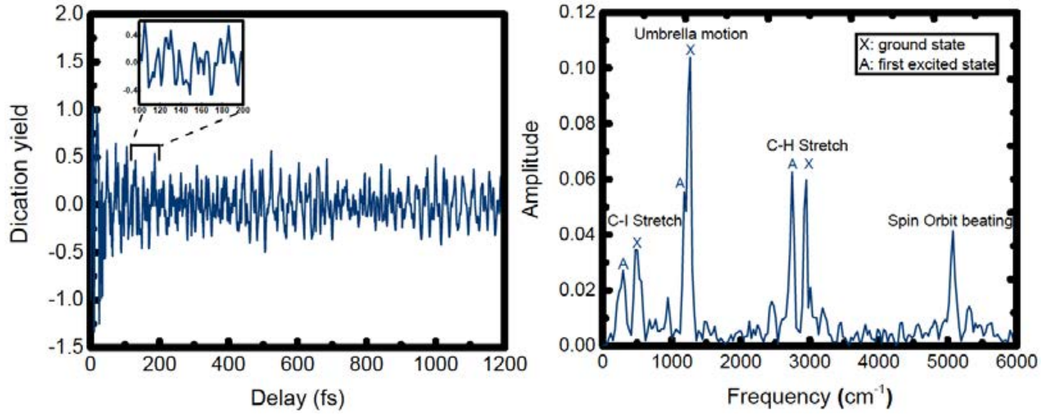


Figure 1. (a) The time-dependent non-dissociative double ionization yield of CH_3I. Inset shows the clear modulation of quantum beatings. (b) Frequency Fourier transform (FFT) of (a) shows the spin-orbit beating along with all symmetric vibrational frequencies in X and A states of methyl iodide cations.

2. Attosecond imaging of electronic wave packets

How to capture the spatial evolution of electrons at their native time scale (attoseconds to a few femtoseconds) is a grand challenge. The ultrafast temporal evolution has been addressed over the past two decades by developing attosecond spectroscopy to produce and probe electronic wave packets with various techniques. However, these techniques do not directly measure the spatial distributions/evolution of the electronic wave packets. In a combined experimental and theoretical study, the Li and Schlegel groups demonstrated a new attosecond technique that can achieve spatial imaging of ultrafast spin-orbit wave packet in the xenon cation for the first time. The method is based on two-electron-angular-streaking (*2eAS*). The results show the initial peanut-shaped hole was quickly filled at half of the spin-orbit period (1.5 fs) in the xenon cation while the shape remains largely the same at this time delay in krypton due to slower dynamics and smaller energy splitting. The result was published in *Physical Review Letters* and was featured in Physics Magazine.

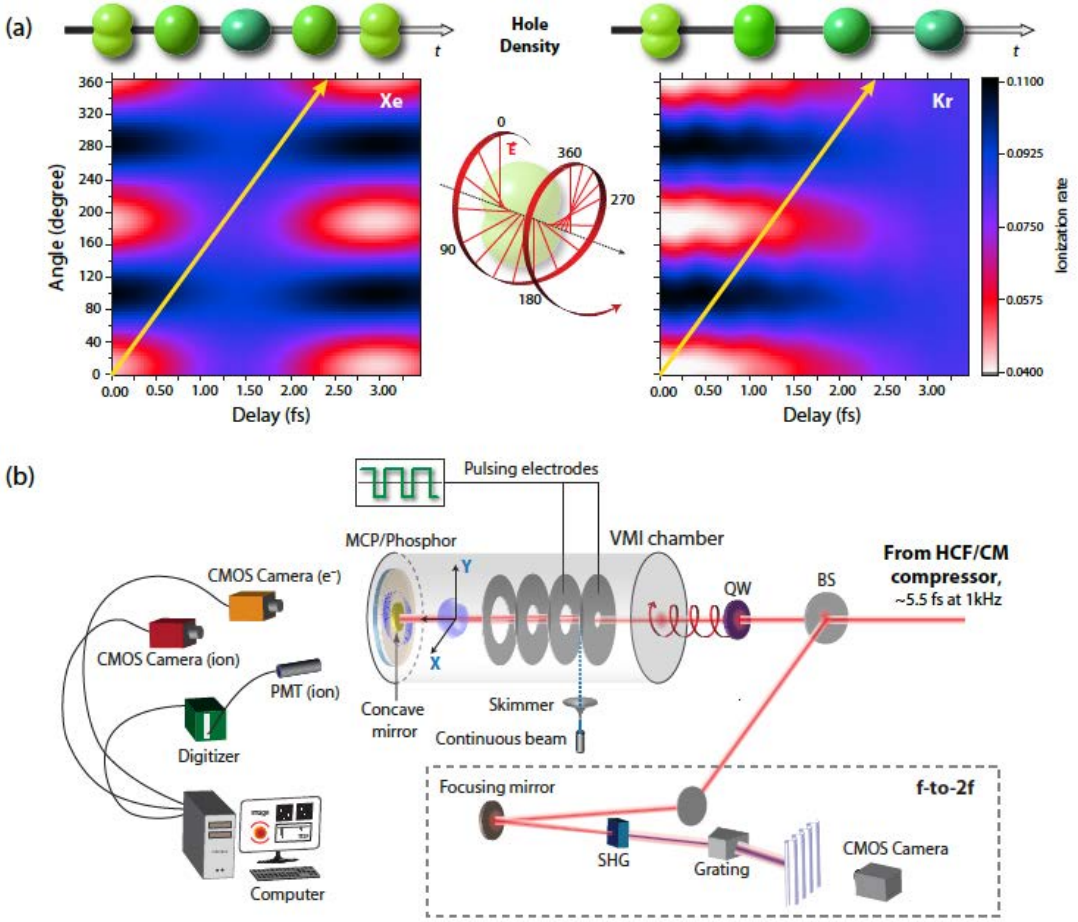
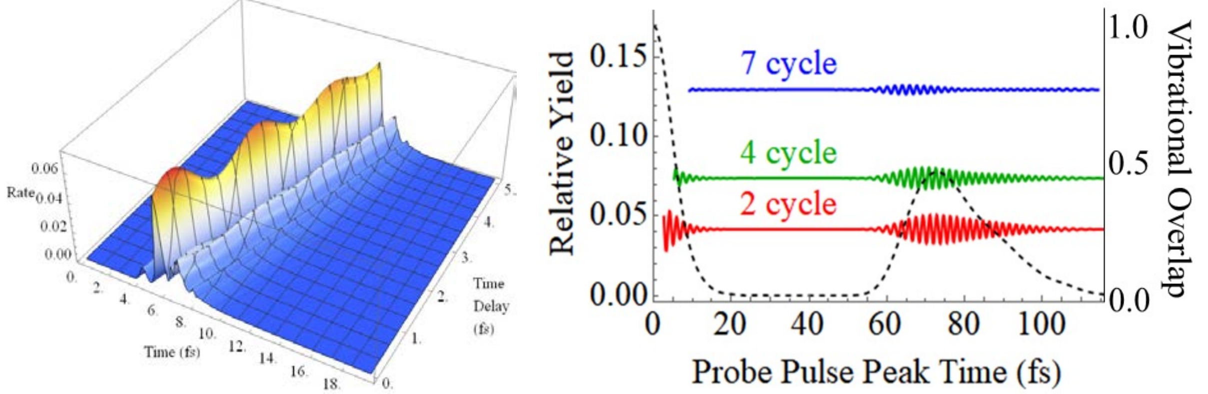


Figure 2. Attosecond imaging of electronic wave packets. (a) Top: the temporal evolution of electronic wave packets in the form of hole density in the xenon cation (left) and krypton cation (right). Bottom: the calculated time- and angle- dependent ionization rates of an electronic wave packet with an initial phase of 0 degree. The yellow lines represent the rotating electric field probing at different directions and time delays. The inset between the two plots illustrates how the rotating electric field of circularly polarized light can map the shape of electron (hole) density. (b) The experimental set-up for achieving phase-resolved *2eAS*.

3. Modeling strong field probe of electronic decoherence and revival by vibrational motions

The dynamics of $HCCI^+$ have been studied extensively by both experimental and theoretical methods. The coherent superposition of the X and A states of $HCCI^+$ results in charge migration between the C≡C π orbital and the iodine π-type lone pair. The Schlegel group showed that the charge migration dynamics can be probed with strong field ionization. Time-dependent configuration interaction (TD-CI) with a complex absorbing potential has been used to simulate the electronic dynamics and strong field ionization. Nuclear motion was modelled by vibrational packets moving on quadratic approximations to the potential energy surfaces for the X and A states of $HCCI^+$. The total ionization rate is given by the electronic component (interactions with the absorbing potential) multiplied by the vibrational component (overlap of the vibrational wavepackets on the X and A surfaces). The vibrational wavepackets on the two surfaces initially move away from each other and their overlap decays to zero in about 15-20 fs. Consequently, the oscillations in the strong field ionization decay at the same rate. Charge migration and oscillations in the ionization yield can be monitored by strong field ionization with intense 2 and 4 cycle linearly polarized 800 nm probe pulses for delay times of up to 10 and 5 fs, respectively. A revival of the vibrational overlap is seen between 60 – 110 fs when the vibrational wavepackets on the X and A surfaces both return to the Franck-Condon region. TD-CI simulations show that the charge migration during this revival can be seen by strong field ionization with intense 2, 4 and 7 cycle probe pulses. This work was published in Journal of Physical Chemistry A.



(a) (b)

Figure 3. (a) Ionization rate of $HCCI^+$ as a function of time and probe pulse delay for a 4 cycle 800 nm pulse. (b) Decay and revival of the ionization yield for $HCCI^+$ for 2, 4 and 7 cycle 800 nm pulses.

4. Developing a new multi-hit 3D momentum imaging system

The Li group has developed novel three-dimension (3D) momentum imaging systems with great performance. The system has enabled new attosecond measurements capable of tracking ultrafast electronic motions. One remaining issue with these systems is the limited number of events per laser shot (typically less than 5). This puts a constraint on non-coincidence measurements and extends acquisition time. Recently, the Li group showed with a simple two-camera imaging system, 3D momentum ion imaging can be achieved with massive multi-hit capability (thousands of events per laser sot). The technique exploits the luminescence decay of the phosphor activated by ion impacts and employs two cameras to time the decay and to extract the time-of-flight (TOF) of each event. Because the camera has no dead time in detecting multiple events, the multi-hit capability is greatly enhanced. The technique will be useful in ion imaging and covariance measurements. Further implementation with electron imaging is also possible. This work was published as a communication in Journal of Chemical Physics.

5. Future Plans

The Li group will continue to study the electronic decoherence/revival dynamics in various iodine-containing compounds using both the *2eAS* method and strong field pump-probe method. The Schlegel group will develop theoretical approaches to model electronic decoherence dynamics on multi-dimensional potential energy surfaces in methyl iodide, which is prohibitively expensive with current methods.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

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Triggering and Probing Attosecond Dynamics with X-rays

Award number: DE-SC0024484

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Project Scope

Driven by advances in ultrafast science, observing the motion of electrons in molecules and solids has become the focus of intense interest. These dynamics, which occur at the sub 5 femtosecond time scale, generally result from a coherent superposition of states and can occur at time scales faster than nuclear motion. These processes are predicted to underpin a wide range of important applications such as energy conversion/storage, optical breakdown, and photochemistry. Soft X-ray transient absorption is one especially promising technique for measuring these processes, due to its suitability for a range of molecular and solid systems, potential for attosecond time resolution, and elemental specificity. Interpretation, however, can be challenging as it generally requires relating the intensity and frequency modulations of a spectrum to the underlying dynamics. Moreover, the dynamics induced by a soft X-ray pumps (e.g., in a soft X-ray pump/probe configuration) remain poorly studied.

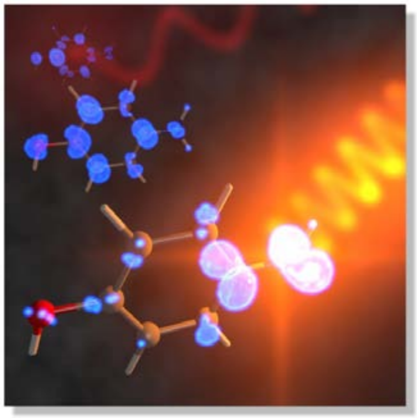

Figure 1: Simulated electron density during an attosecond UV pump/X-ray probe experiment in aminophenol. First-principles methods are critical for interpreting these types of experiments. Simulation data taken from [Chen2020].

To address this challenge, this project uses quantum chemistry simulations to shed light on a few of the fundamental questions related to triggering probing coherent dynamics with soft X-rays. The first objective is to determine general relationships between time-evolving electron density and the corresponding transient inner-shell absorption spectra for a wide range of molecular systems. A density-based picture is a useful compliment to state-based interpretations, and is expected to form a first step towards reversing from time delay to real-time, allowing one to determine what electron dynamics underlie an observed transient spectra. The second objective is to develop a systematic understanding how core-holes created via soft X-ray pulses can be used to induce valence electron dynamics, and how various different heteroatoms influence them. Finally, the third objective is to elucidate the initial mechanisms of band dynamics and materials damage in solids, and to ascertain how band population and polarization effects manifest in transient spectra. The emphasis is on purely electronic sub-10 femtosecond dynamics, and how these can be probed with X-ray transient absorption.

Recent Progress

No progress to report.

Future Plans

In the first year of this project, work will begin on using time-dependent density functional theory (TDDFT) to simulate soft X-ray pump/soft X-ray probe attosecond processes in molecules with heteroatoms (N, O, P, S), for the case of the pump and probe potentially tuned to different K-edges. Initially, this will use a sudden-ionization approximate initial state with a time-delayed broadband probe [Chen2020], before moving on to explicitly treated pump fields. The focus in the coming year will be on validating our techniques against molecules previously reported to exhibit inner-shell triggered electron dynamics at time scales faster than 5 fs. These include aminophenol (currently a work in progress), pyrizine [Ruberti2021], and carboxylic acids [Golubev2021].

In parallel, we will begin simulations of how XUV and X-ray transient absorption can be used to probe the attosecond dynamics during strong-field induced metallization of silicon, and to validate our results against experiment [Schultze2014]. This will use a bulk-mimicking finite cluster TDDFT approach [Darapaneni2020] to allow for all-electron tuned ranged-separated hybrids, which we have reported previously for transient absorption in SiO_2 [Yang2023] and diamond. The pump intensity-dependence of the response will studied, from just below breakdown voltage to just above, to determine how the initial attosecond steps of dielectric breakdown appear in the transient spectra.

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Peer-Reviewed Publications Resulting from this Project (Project start date: 09/2023)

No publications to report.

Complexity and Correlated Motion of Electrons in Free and Confined Atomic Systems

Award number: DE-FG02-03ER15428

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Project Scope

The goals of the research program: 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. Calculations are performed using and upgrading state-of-the-art theoretical methods to understand the essential physics of the experimental results; to suggest future experimental investigations; seek out new phenomenology, especially in the areas of attosecond time delay in photoemission (including photodetachment), outer-shell photoemission in the vicinity of inner-shell thresholds and confined systems. The primary areas of programmatic focus: correlated and relativistic dynamics of photoionization; dynamical properties of atoms endrohedrally confined, primarily in 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

Various aspects of the attosecond dynamics of electrons in the photoemission process, as revealed by Wigner time delay [1-3], have been 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, showing 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.

Studies are continuing of attosecond time delay relativistically in quadrupole channels and spin-flip channels, near Cooper minima, where the dipole cross section is small, and at photoemission angles near 90 degrees (with respect to the polarization of the incident photon) where the dipole photoemission for spin-up photoelectrons vanishes for ns states of closed-shell atoms. The calculations show significant effects of the transition from dipole to quadrupole and spin-flip dynamics in the vicinity of photoemission at 90 degrees with respect to the photon polarization [10], thereby providing a "laboratory" to study the attosecond dynamics of such transitions.

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

In addition, there has been some speculation that Wigner time delay cannot be measured in a photoemission experiment [15]. In response, we have shown that this is simply not true [16]. A formal theory was developed, including a Hermitian operator for the time delay, showing that it is, in fact, a measurable quantity. From a general point of view, the study of Wigner time delay provides information on the phases of transition matrix elements [1-3], which is difficult to otherwise obtain. That, combined with the magnitudes, which are obtained much more easily from cross sections, represents the maximum and most fundamental information we can obtain about transitions, according to our understanding of quantum mechanics.

Our program on confined atoms aims at mapping out their properties 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} [16] and Mg@C_{60} [17]. Confinement resonances [18], 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 [14]. The photoionization of endohedral atoms in nested fullerenes makes the confinement resonances considerably more complicated [19]. These effects carry over to the photodetachment of fullerene (and nested fullerene) cations which exhibit large resonances and a variety of unexpected properties [20]. And calculations taking full account of the molecular symmetry [21] have revealed a wealth of detail on valence and core photoionization of C_{60} and are the most accurate calculations to date.

In response to experiment, a survey of the branching ratios of spin-orbit doublets of the noble gases, Ne, Ar, Kr and Xe has been conducted over a broad range of photon energies well above their thresholds [22], where it was found that the overall branching ratios do not approach the nonrelativistic limit, but all decrease with energy, as predicted theoretically many years ago and confirmed experimentally in a few cases recently [23]. We also demonstrated that the falloff of the branching ratio with energy increases with Z since the relativistic effects cause the ratio of probability densities of the ($j=l-1$)/($j=l+1$) wave functions for a to go as Z^2/r^2 for small r. Also, it was demonstrated that the branching ratios are strongly affected in the vicinity of inner-shell thresholds *via* correlation in the final-state wave functions known as interchannel coupling; this showed that the interchannel coupling was different for the two members of a spin-orbit doublet, i.e., it was affected by relativistic interactions. This will be tested experimentally in late 2023.

Since high-Z atoms are excellent laboratories to study the combination of relativistic and many-electron correlation effects dynamics, the properties of superheavy elements, has been continued [24,25]. 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 because the subshell cross sections are dominated by relativistic and correlated dynamics. Also, a study of Cooper minima of *ns* states of high-Z atoms has found that relativistic effects can be huge and lead to rather different phenomenology from nonrelativistic predictions [26]. Of importance is that experimental studies are now possible [27,28].

Future Plans

We will continue studying attosecond time delay in photoemission, including many-body effects, photodetachment, and nondipole effects and 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) and work on ways to enhance the time-dependent local-density approximation to make it more accurate and to include relativistic interactions to be able to deal with heavy endohedrals accurately. And we shall respond to new experimental capabilities and results as they occur.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

- "Inner-Shell Photodetachment of Na^- using R-matrix Methods," T. W. Gorczyca, H.-L. Zhou, A. Hibbert, M. F. Hasoglu, and S. T. Manson, Atoms **8**, 60-1-9 (2020).

"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. **230**, 4151-4164 (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).
- "K-Shell Photoabsorption in Si^{11+}: Relativistic Contributions via Breit-Pauli R-matrix Calculations," M F Hasoglu, T W Gorczyca, and S T Manson, Physica Scr, 96, 124024-1-5 (2021).
- "Photoionization of endohedral molecules: $N_2@C_{60}$," P. Decleva and S. T. Manson, Physica Scr. **96**, 124005-1-7 (2021).
- "Electron vacancy-level dependent hybrid photoionization of $F^-@C_{60}^+$ molecule," Esam Ali, Taylor O'Brien, Andrew Dennis, Mohamed El-Amine Madjet, Steven T. Manson and Himadri S. Chakraborty, J. Phys. B **55**, 045101-1-9 (2022).
- "Inner-Shell Photoionization of Free and Confined Mg in the Region of the 2p Thresholds," P. Padukka, H.-L. Zhou, T. W. Gorczyca and S. T. Manson, J. Phys. B **54**, 195201-1-12 (2021).
- "Unusual behavior of Cooper minima of ns subshells in high-Z atoms," S. Baral, S. Saha, K. A. Dubey, J. Jose, P. C. Deshmukh, A. K. Razavi and S. T. Manson, Phys. Rev. A **105**, 062819-1-9 (2022).
- "Photoionization Branching Ratios of Spin-Orbit Doublets Far Above Thresholds: Interchannel and Relativistic Effects in the Noble Gases," C. Rasadi Munasinghe, Pranawa C. Deshmukh and Steven T. Manson, Phys. Rev. A **106**, 013102-1-16 (2022).
- "Perspectives on UV and x-ray photoelectron spectroscopy," Stephen H. Southworth and Steven T. Manson, J. Vac. Sci. Tech. A **40**, 043003-1-8 (2022).
- "Photoionization of Atomic Systems using the Random-Phase Approximation Including Relativistic Interactions," Pranawa C. Deshmukh and Steven T. Manson, ATOMS **10**, 71-1-36 (2022).

- “A Glimpse into Photodetachment Spectra of Giant and Nested Fullerene Anions,” Valeriy K. Dolmatov and Steven T. Manson, ATOMS **10**, 99-1-11 (2022).
- “Dramatic Relativistic Effects on the *ns* Dipole Angular Distribution Asymmetry Parameter, β_{ns}, of Heavy and Superheavy Elements,” S. Baral, S. Saha, K. A. Dubey, J. Jose, P. C. Deshmukh, A. K. Razavi and S. T. Manson, J. Phys. B **56**, 055003-1-15 (2023).
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- “Photoionization of C_{60} at High Energies,” Aurora Ponzi Steven T. Manson, and Piero Decleva, Chem. Phys. **572**, 111968-1-10 (2023).
- “The Spin-Orbit Interaction: A Small Force with Large Implications,” Steven T. Manson, ATOMS **11**, 90-1-6 (2023).

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Combining High Level *Ab Initio* Calculations with Laser Control of Molecular Dynamics (DE-FG02-08ER15983 & DE-FG02-08ER15984)

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1 Project Scope

We use intense, shaped, ultrafast laser pulses to follow and control molecular dynamics and high level *ab initio* calculations to interpret the dynamics and guide the control.

2 Recent Progress

A summary of some of our main accomplishments during the past year are summarized below.

2.1 Multimodal Measurements of Excited State Dynamics

A major focus of the work is combining theory with experiment, where the theory simulates the observables directly and compares to the measurements. This approach allows us to focus on the quality of the dynamics calculations in comparing the two. We are currently focusing on comparisons between electronic and structural probes, with time resolved photoelectron spectroscopy (TRPES) being the electronic probe and Ultrafast Electron Diffraction (UED) being the structural probe. The experiments are compared to simulations of the experimental signal obtained from the same set of trajectory surface hopping (TSH) calculations.

We have studied TRPES for several molecules, and were able to interpret their dynamics and get important insights about the molecules and the techniques. The most important insights have been compiled in a feature article.

We have started a comparison of observables using 1,3-cyclooctadiene (COD) as our test molecule. We have already published the TRPES and compared with simulated spectra obtained from the TSH calculations. The same set of calculations are being used to calculate the UED signal using the independent atom model (IAM). We have collaborated with the group of Martin Centurion on the analysis of UED measurements after excitation of COD at 200 nm, deriving significant insights into the dynamics from comparison with the calculations. Specifically, a stretching motion has been identified as a significant reaction coordinate in the motion from the Franck-Condon region to the CI which has a clear signature in the UED signal. There is very good agreement between theory and experiment by comparing the experimental diffraction signal with a calculated diffraction signal based on the trajectory simulations, which validates the product yields predicted by the simulations.

In addition to our work on COD, we were involved in a UED beamtime and the subsequent analysis of both UED and TRPES measurements for 2-Dihydrofuran (DHF) excited at 200 nm. The analysis has yielded intriguing results that connect to the COD work, indicating that one has to be careful in fitting the measured pair distribution function to calculations based on specific structures, because the fits are not unique. This comparison serves as further encouragement to pursue direct comparisons of the measured time dependent pair distribution function with the one simulated based on TSH calculations.

2.2 Strong Field Ionization and Coulomb Explosion Imaging

We have carried out trajectory surface hopping calculations for CD_2O^{4+} in order to determine how the fragmentation of highly charged molecular cations depends on the potential energy surfaces of low lying states, and whether it is reasonable to consider the repulsion forces as Coulombic. The

TSH calculations show very different dissociation dynamics from the classical Coulomb calculations, illustrating that one charge per atom is not a sufficient criteria for treating the dissociation Coulombically. Using only Coulombic forces is inadequate since it does not capture the formation of metastable CO^{2+}. TSH calculations capture the correct bifurcation of 4 vs 3 body dissociation, as can be seen in Figure 1.

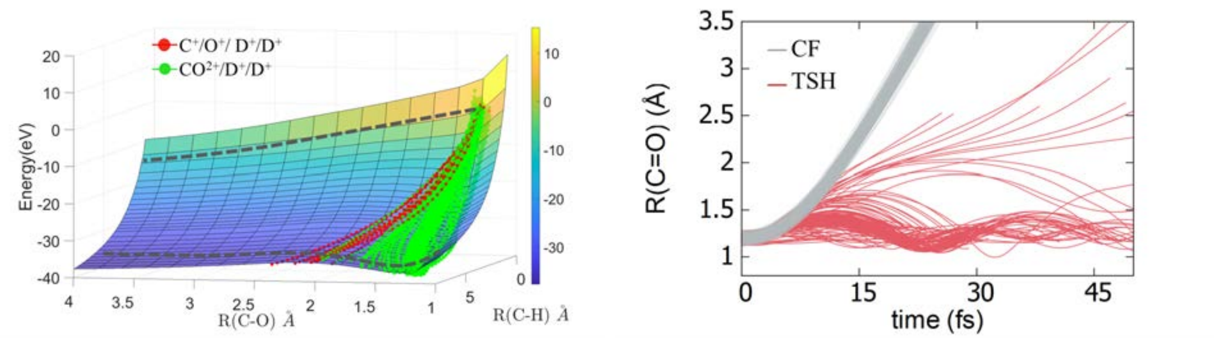

Figure 1: Dissociation dynamics of the CD_2O^{4+} cation. (Left:) Bifurcation of trajectories on S_0 into formation of the products $CO^{2+}/D^+/D^+$ (green) and $C^+/O^+/D^+/D^+$ (red). (Right:) C-O bond length plotted vs time for the dynamics performed on S_0 state of CD_2O^{4+} using simple classical Coulombic forces (CF) and trajectory surface hopping (TSH).

2.3 Technical Developments

Two important technical developments that we undertook were the development of three dimensional velocity map imaging (3D VMI) for electrons and the use of covariance for understanding multiparticle correlations. While we had made use of the Timepix camera to measure the 3D momentum of ions in the past (since $\sim$ 2017), the timing resolution of the camera pixels is only about 1.6 ns, which is not fast enough to provide sufficient sampling of the electron distribution for 3D measurements of electrons. However, we upgraded our Timepix camera in order to add a second TDC channel, which has 240 ps timing resolution. By slowing down the electrons we measured, spreading their arrival time distribution to about 10 ns, and capacitively coupling our MCP detector to the fast TDC, we are now able to carry out 3D VMI measurements of the electrons all within the data stream of the Timepix camera. This capability is highlighted in Figure 2, which shows 3D VMI measurements of electrons from strong field ionization of Xenon.

The other major development was to make use of covariance or cumulants for multiparticle imaging. Covariance measurements of two or three particles provide a high data acquisition rate alternative to coincidence measurements with the same information content. However, the simple

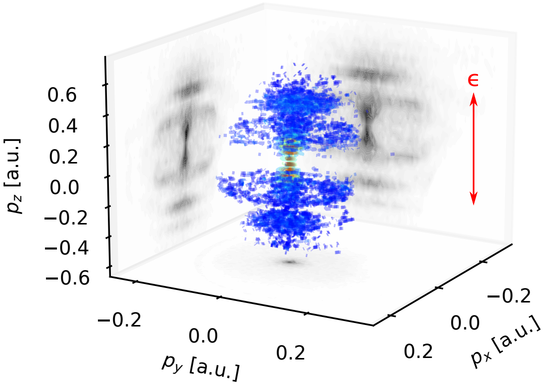

Figure 2: Momentum resolved photoelectrons arising from strong field ionization of Xenon, with projections onto each plane: p_x, p_y and p_z. The laser polarization is in the z-direction (the time of flight axis pointing towards the detector) as depicted by the red arrow in the figure.

extension to four or more particles (which is important for CEI) is complicated by products of two particle correlations which contaminate the "true" four or more particle covariance. We developed a cumulant approach to measuring correlations between four or more particles, which extends covariance to multi-particle measurements. A third less significant project was the development of a simple technique for characterizing the spatial variation in the gain of microchannel plate detectors.

3 Future Plans

Our planned work consists of two main thrusts:

1. We will pursue multimodal studies of excited state dynamics. We will perform systematic studies on a series of molecules with varying rigidity and substitution in order to establish trends and rules of thumb for how the excited state dynamics can be related to basic structural features. We will continue our work on cyclo-octadiene, and contrast these measurements and calculations with new ones on indole and other ring systems. In order to explore longer dynamics present in indole and other molecules, we will also use GPU based electronic structure approaches and machine learning to obtain the potential energy surfaces and forces at lower computational cost.

2. We will use strong field molecular ionization with shaped octave spanning laser pulses as a tool to both prepare and probe entangled electron-nuclear wave packets in molecular cations using shaped 5 fs pulses, as well as covariance velocity map imaging. The measurements and calculations that form the basis of this thrust will be employed to study the coupled electron-nuclear dynamics of wave packets launched in molecular mono- and di-cations via strong field ionization with two cycle laser pulses. We are interested in understanding both the ionization dynamics and the subsequent field free dynamics. The measurements will be compared with theoretical calculations using a hierarchy of methods. We will employ quantum dynamics using the Multi Configuration Time Dependent Hartree (MCTDH) approach for select systems in order to accurately capture the underlying mechanism for the observed entangled motion and coherences. Semiclassical approaches will also be tested and benchmarked against MCTDH in order to explore better their viability in treating the dynamics.

4 Peer-Reviewed Publications Resulting from this Project (2021-2023)

- "Time resolved photoelectron spectroscopy as a test of electronic structure and nonadiabatic dynamics", Pratip Chakraborty, Yusong Liu, Samuel McClung, Thomas Weinacht and Spiridoula Matsika. *J. Phys. Chem. Lett.* 12,21,5099-5104 (2021)

- "Strong-field ionization of water: Nuclear dynamics revealed by varying the pulse duration," A. Howard, C. Cheng, R. Forbes, G. McCracken, W. Mills, V. Makhija, M. Spanner, T. Weinacht, and P. Bucksbaum *Phys. Rev. A*, **103**, 043120, (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)

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Project Scope

The dynamics that take place within just tens to hundreds of femtoseconds following the photoexcitation of a molecular chromophore can play a critical role in how the absorbed energy is directed, allowing it to be used for a specific function (photoinduction) or dissipated harmlessly (photoprotection). Underlying these dynamics is the presence of electronic energy degeneracies in the relaxation pathways of the excited chromophores, known as conical intersections (CIs), which mediate nonradiative electronic transitions known as nonadiabatic transitions. These transitions are known to mediate energy flow in natural biological systems, including the highly effective ultraviolet photoprotection mechanism of DNA, the efficient phototransduction process of the vertebrate vision response [4], and the photoisomerization of the retinal chromophore underlying channelrhodopsin activation [5,6]. 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 [7]. With a $\sim 10^{-14}$-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

During this reporting period we have made further significant steps towards the realization of the ultrafast optical instrumentation needed to demonstrate our proposed spectroscopy method for capturing nonadiabatic transitions.

For this program, a highly ambitious instrument is required, providing synchronized 10-fs light pulses for visible, near-infrared, and mid-infrared spectral ranges, covering the full spectrum from ~450 nm to ~4 μm. Last year, we reported on a major advance, the demonstration of a novel, highly efficient frequency down- or up-conversion process that can not only handle octave-spanning bandwidths, but can also monolithically manage its own large material dispersion to deliver a pulse with a custom spectral phase [8]. As a proof of principle, we reported on the demonstration of an efficient adiabatic down-conversion (ADC) stage that transfers pulses from the near-IR (at Ti:sapphire wavelengths, 680–820 nm) to an octave in the mid-IR (2–4 μm) while preserving its absolute bandwidth via an adiabatic frequency conversion process, and also monolithically managing its own large material dispersion to have near-zero net group delay dispersion (GDD). Our goal was to convert a compressed 10-fs pulse at ω_{NIR} to a compressed, passively CEP-stabilized 10-fs pulse at ω_{MIR} with full photon conversion efficiency in the presence of a strong, narrowband pump at $\omega_p = \omega_{NIR} - \omega_{MIR}$.

First, we now have fine-tuned the experiment, and have achieved a result even closer to this goal. We have demonstrated conversion of an 11.2-fs near-IR pulse input to a 11.6-fs mid-IR pulse output in a single crystal device (Fig. 1) [9]. We used the recently developed FROSt (frequency resolved optical switching) approach [10] to characterize the octave-spanning mid-IR 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.

Second, we have now designed a stage for converting another copy of the near-IR pulse to wavelengths between 1.1-2.2 μm, that operates using a related but alternative mechanism of adiabatic optical parametric amplification (AOPA) and can generate a compressed 7-fs pulse at output (Fig. 2) [9]. This stage (on order) will allow 10-fs resolved transient absorption spectroscopy covering a nearly 3-octave (0.65-4.0 μm) spectral range. Also shown (Fig. 2(c)), the eventual system including two up-conversion stages based on adiabatic sum-frequency generation (ASFG) that will provide additional coverage of the 0.45-0.7 μm range for rhodopsin experiments.

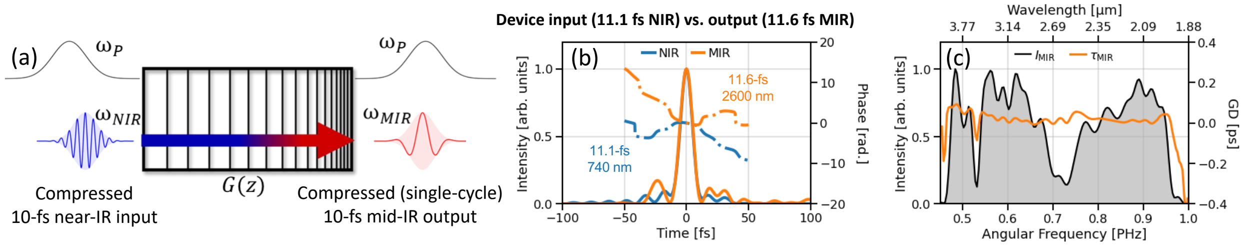

Fig. 1: (a) Concept of demonstrated device: a compressed few-cycle near-IR pulse undergoes bandwidth-conserving down-conversion to a single-cycle mid-IR pulse in a chirped QPM grating with a local poling frequency $G(z)$ designed to impart zero net GDD. Experimental demonstration: (b) an 11.1-fs near-IR input emerges as a 11.6-fs mid-IR output, and (c) output spectrum and flat group delay profile of the device. [11]

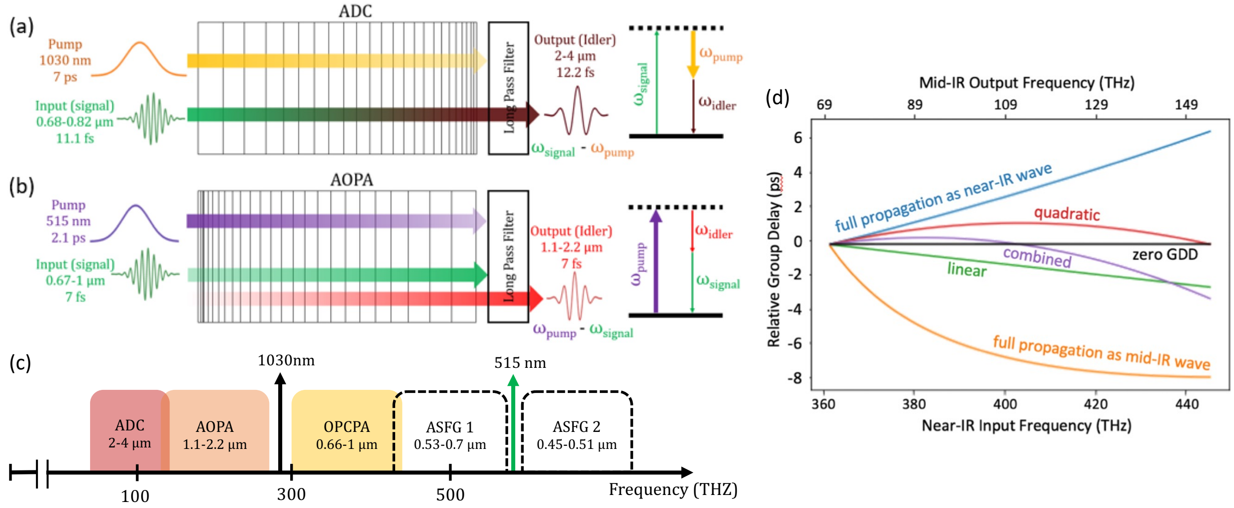

Fig. 2: Combined system that takes a near-IR OPA spanning 0.67-1 micron compressed to 7 fs and uses (a) ADC to generate a compressed mid-IR, 11-fs pulse, and (b) AOPA to generate a compressed 1.1-2.2 micron near-IR, 7-fs pulse [11]. (c) These three pulses will be used to study graphene electron photoheating relaxation dynamics with 10-fs resolution. (c) Together with 2 up-conversion stages to be added, photoexcited rhodopsin can be studies with close to 10-fs IRF over a three-octave-spanning spectral range. (d) Diagram showing possible custom intrinsic dispersion functions [13].

Third, we have shown that nearly any custom dispersion function can be written intrinsically using our method [11]. As dispersion management is among the most challenging aspects of optical systems used for ultrafast spectroscopy when approaching the single-cycle limit, this technique may help to push the boundaries of temporal resolution in ultrafast optical spectroscopy, generally.

Future Plans

We have published three conference papers in 2022-23 on the progress shown above, and are finalizing a manuscript to be submitted to a *Nature* journal. Once we receive the custom AOPA nonlinear crystal, we will implement it into our experimental setup.

Our next step is 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, 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. The expected change in absorption in the mid-IR lasts only 50 fs. We will collaborate with Dr. Giulio Cerullo and Dr. Eva Pogna of Milano Polytechnic to complete these experiments. We will use the synchronized 11-fs near-IR and mid-IR pulses shown in Fig. 1 as the pump and probe, respectively.

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Modeling of Multidimensional X-ray Probes of Chemical Processes and Dynamics in Molecular Systems

DE-SC0022225 previously DE-SC0019484

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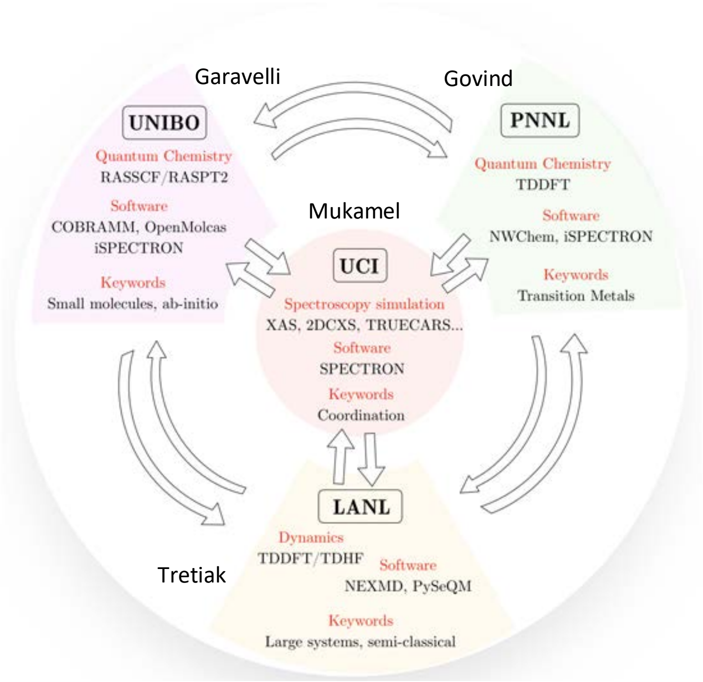
Project Scope

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 the development of robust theoretical and computational tools that can provide predictive modeling capacity of the underlying electronic and structural dynamics. These will be further essential for the design and interpretation of more elaborate multi-pulse experiments.

We are a multi-disciplinary four-institution research team (see overview figure), which combines academia and national laboratories, and spans the broad and necessary expertise in theoretical spectroscopy, nonlinear optics, quantum chemistry, molecular non-adiabatic dynamics, and code development. Our research program is delineated into two interconnected thrusts: methodology development (**THRUST 1**), and application to relevant chemical processes and molecular targets (**THRUST 2**).



Our research effort focuses on developing cutting-edge simulation tools for nonlinear multidimensional X-ray/optical spectroscopies. These techniques combine sequences of ultrafast X-ray and optical pulses to provide a unique experimental toolbox for probing the dynamics of core and valence electronic and vibrational excitations in. molecules as well as material structure. The modeling capabilities developed in this program are made 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 are designed.

Efficient simulation protocols are developed 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) are extended to the X-ray regime and applied to a broad variety of molecular systems, thus laying out XFEL-based multidimensional spectroscopies as a novel diagnostic tool for monitoring electronic and structural dynamics in molecular materials.

Recent Progress

Vibronic Coherences and Molecular Aromaticity in Photoexcited Cyclooctatetraene probed by X-ray Spectroscopy (LANL+UCI): Understanding conical intersection (CI) dynamics is the key for exploring and controlling virtually all photophysical relaxation pathways in molecules. Monitoring their time-resolved dynamics remains a formidable experimental challenge. We have simulated the photoinduced non-adiabatic dynamics of cyclooctatetraene (COT) involving multiple conical intersections (CIs).The computed relaxation times were found in good agreement with experiment. We further investigated the possibility to directly probe the CI passages in COT by off-resonant X-ray Raman spectroscopy (TRUECARS) and time-resolved X-ray diffraction (TRXD). We found that these signals sensitively monitor key chemical features during the ultrafast dynamics involving aromatic and non-aromatic electronic configurations of COT. First, TRUECARS was demonstrated to be capable of distinguishing different CIs along the S3 → S1 relaxation pathway. Second, we found that TRXD, where X-ray photons scatter off electron densities, can resolve ultrafast changes in the aromaticity of COT (Fig. 2). It can further distinguish between planar and non-planar geometries explored during the dynamics, as e.g. the D4h transition state facilitating the S1 → S0 relaxation and two different tetraradical-type CIs. The knowledge gained from these measurements provides unique insights into fundamental chemical properties that dynamically change during non-adiabatic passages. [Yeonsig2023]

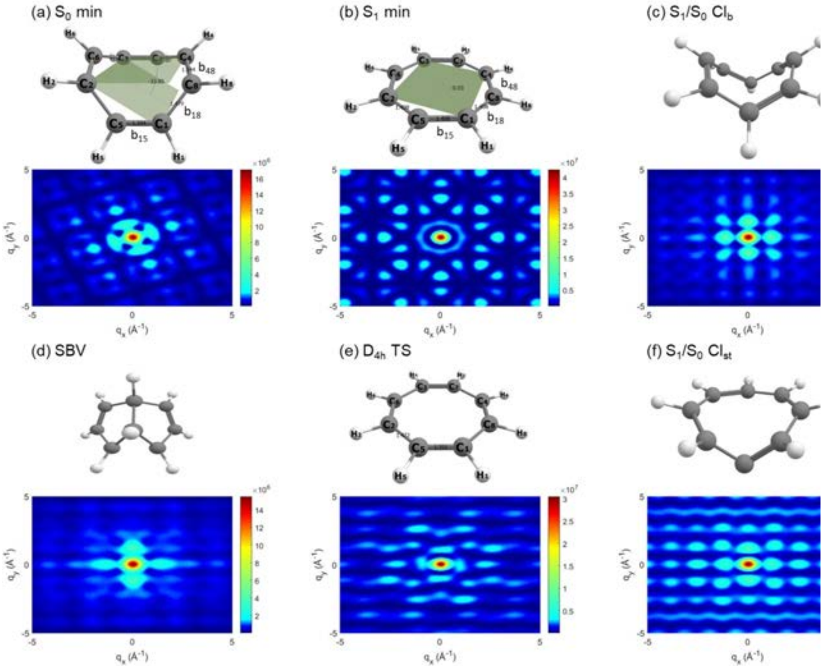


Figure 2. The two-dimensional TRXD elastic scattering pattern for optimized geometries of COT (a) S_0, (b) S_1, (c) CI_b, (d) SBV, (e) D_{4h} TS (TS_{RI}), (f) CI_{st}.

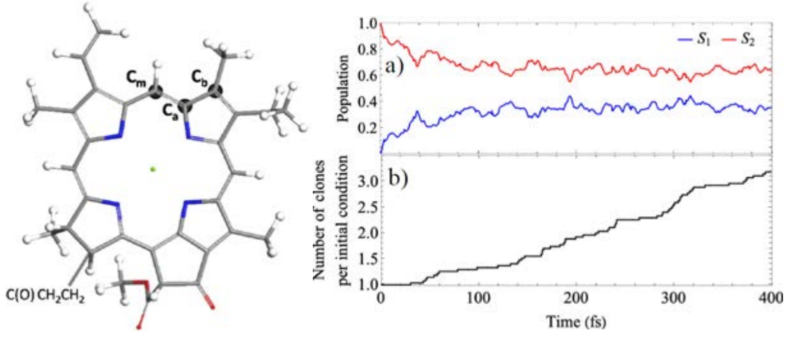


Figure 3. A chlorophyll A molecule (left), calculated nonradiative relaxation timescales and a number of clones per initial condition (right).

Ultrafast Correlation Dynamics between the Qx and Qy Bands in Chlorophyll Molecules (LANL+UCI): The non-radiative relaxation process within the Q-bands of chlorophylls represents a crucial preliminary step during photosynthetic. Despite extensive experimental and theoretical efforts performed in order to clarify the complex dynamics characterizing this stage, a complete understanding of this mechanism is not available. Non-adiabatic excited-state molecular dynamic simulations have been performed to model the non-radiative process within the Q-bands for a model system of chlorophylls. Previous simulation studies based on semi-empirical methods with the fewest switches surface hopping (FSSH) approach showed deviations from experimental measurement due to overestimating the band gap and interband decoherence processes. In this study, we combined TDDFT with our newly implemented Ab initio Multiple Cloning (AIMC) approach to overcome the accuracy limitation. Based on a large set of independent trajectories, the population of the Qx and Qy states have been computed as the average of all the trajectories, estimating the rate constant for the process. Finally, by investigating the Qx–Qy crossing mechanism, we found the most important excited-state dynamics during such relevant photosynthetic process. A manuscript is in preparation.

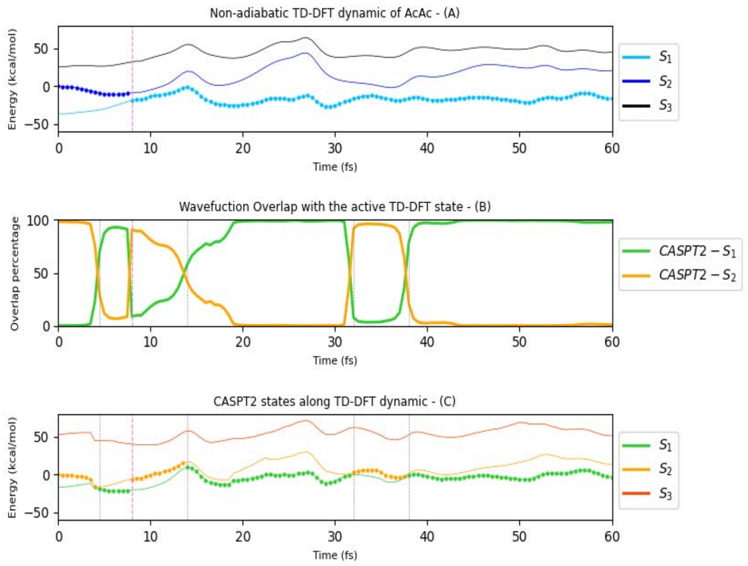


Figure 4. a) Energy of the three lowest excited states over the TDDFT dynamic, highlighting the active one. b) Wavefunction overlap of the two lowest excited states at CASPT2 level with the active TDDFT state. Aside from the change of the active TD-DFT state, the rest of the overlap swaps are caused by the inversion of the two CASPT2 states. c) Energy of the three lowest excited states at CASPT2 level over the TD-DFT dynamic, highlighting the one with the highest wavefunction overlap with the active TD-DFT state, therefore tracking it at CASPT2 level.

Comparison of different levels of theory (LANL+UNIBO+PNNL): To extend our X-ray/optical spectroscopies analysis capacity, matching the signal from different levels of theory (CASSCF/CASPT2, TDDFT and semi-empirical) is required. To that end, it is necessary to have unique characterization of the states. The first task is to align the state between different levels of theory. The LANL and UNIBO groups benchmarked both the valence/excited states, then developed a new algorithm to compute the wavefunction overlap

(WFO) in a series of geometries along a (symmetry preserving) coordinate. This method can track the photo-induced dynamics obtained by different levels of theory. Currently, we are using the Acetylacetone system as the testing ground to demonstrate the possibility to automatize the comparison between CASSCF/CASPT2 and TDDFT valence states along non-adiabatic molecular dynamics (**Figure. 4**). Such delineations and identification of states is critical for indirect validation of the results for excited state molecular dynamics calculated with lower-level theories. The WFO script has been now incorporated in the UNIBO code COBRAMM, eventually allowing to test it on non-adiabatic molecular dynamics performed with different software packages, including NWChem, Gaussian, Molcas, etc. A manuscript is in preparation. [Loreti2023]

X-ray Spectroscopy simulation via MCTDH quantum dynamics (UNIBO): The implementation of an MCTDH (Multi Configuration Time Dependent Hartree) based nonlinear spectroscopy simulation platform has been completed and published. [Segatta2023] The UV/VIS transient absorption spectra of the pyrene molecule (with quantum chemical data recently computed at the CASPT2 level of theory) has been employed as a suitable benchmark. Here, one can explicitly consider the wave-packet overlap term that shapes the spectral features and determines their broadening and decay due to decoherence. The population dynamics is described exactly (i.e. not relying on rate equation models), and the only approximation lies in the modeling of the potential energy surfaces and their coupling (typically captured by a linear vibronic model). The interesting role of the dynamics along the t_3 time (i.e. after the probe has interacted with the system) has been documented at the highest level of theory.

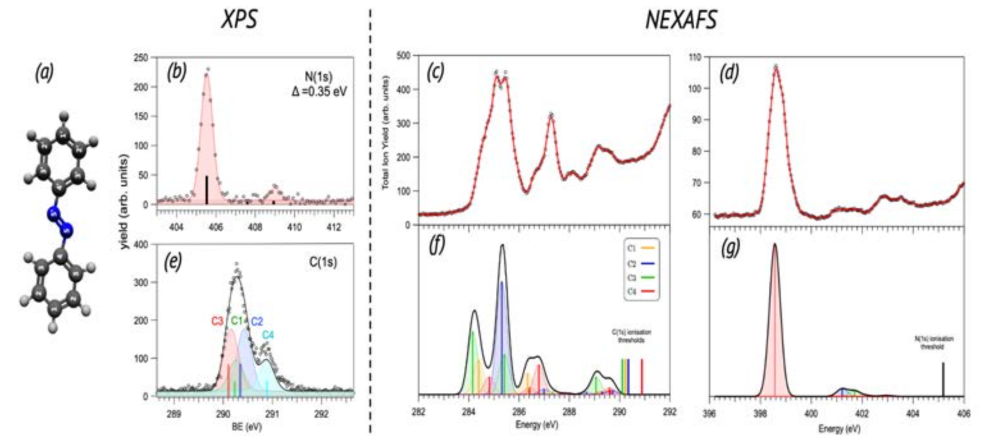


Figure 5. Electronic spectroscopy of *trans*-azobenzene (a) in the core shell: the nitrogen (b) and carbon (e) experimental 1s XPS spectra (reported here with open dots) are compared with the theoretical RASPT2 predictions (vertical bars). The experimental fits (full areas) are also reported in (b) and (e). A shift of 0.35 eV has been applied to the theoretical N(1s) spectra to match the experimental features. Experimental carbon K-edge (c) and nitrogen K-edge (d) NEXAFS spectra are here compared with the corresponding RASPT2 simulations (f and g respectively). Individual contribution from different carbon 1s orbitals in (e) and (f) are depicted with different colors according to the atoms labeling reported in (a).

Extension of the developed MCTDH/spectroscopy platform for X-ray based signals (UNIBO): the platform for nonlinear spectroscopy simulations based on excited state MCTDH quantum dynamics, developed and tested in the UV/VIS window, has been extended for the simulation of UV/VIS pump, X-ray probe experiments (both resonant and non-resonant). Expressions for linear and nonlinear spectroscopy simulation are derived. By leveraging on the peculiar properties of core-excited/ionized states, first- and third-order response functions are recast in the limit of time-scale separation between the extremely short core-state lifetime, and the (comparably longer) electronic state transport and nuclear vibrational motion. The pyrene molecule, whose dynamics has been already parametrized and for which accurate excited state calculations at the C K-edge have been performed, has been used as the first system to be studied. Full quantum dynamics and approximate expressions are compared by simulating X-ray transient absorption spectroscopy at the carbon K-edge in the pyrene molecule. A manuscript has been submitted. [Segatta2023-2]

Extending the CASSCF/CASPT2 XAS approach to larger molecules (UNIBO): the recently developed and published protocol (DOI: 10.1021/acs.jctc.1c00566) for core level CASSCF/CASPT2 spectroscopy simulation has been applied to larger/complex molecular systems. In particular, we computed XPS and XANES signals of azobenzene at both N and C K-edge (where the latter is more complex with respect to the N K-edge, due to the large number of inequivalent carbon centers that should be considered) (**Figure 5**). [Carlini2023] Moreover, in the framework of the collaboration with Elettra synchrotron in Trieste (Italy), we simulated the XANES at the O, N, C K-edge and the Cl L-edge of the hydroxychloroquine molecule and compared those with the measurements performed at the BEAR beamline. A manuscript is in preparation. [Segatta2023-3]

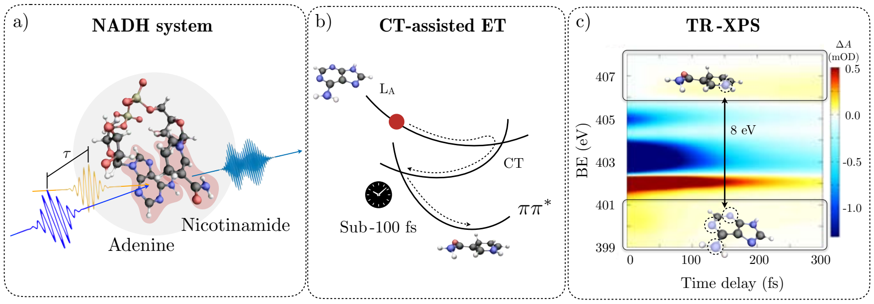


Figure 6. a) Nicodinamide adenine dinucleotide system, together with a sketch of the VIS/UV pump X-ray probe process simulated; b) Schematic of the proposed charge-transfer assisted energy transfer process: the pump-induced populated adeninine L_A state undergoes energy transfer to the nicotinamide $\pi\pi^*$ state, passing trough an intermediate CT state. Such charge redistribution strongly affects the N K-edge signls; c) Simulated TR-XPS spectrum: the transiently populated CT state is tracked by the large shift of the signals from the positively and negatively charged N atoms.

Resonant ultrafast X-ray spectroscopy of biologically active systems (UNIBO): The ultrafast energy transfer (ET) process in photoexcited water solvated nicotinamide-adenine heterodimer (NADH) has been simulated at the CASPT2/MCTDH level of theory in collaboration with Dr. Fabrizio Santoro (CNR, Italy). The polar aqueous solvent environment leads to an active participation of a dark charge transfer state accelerating the vibronically coherent ET process in favorably stacked conformers and solvent cavities. Transient signals have been then modelled at different spectral windows: from the VIS/UV (time-resolved PP, TR-PES) to the X-ray (TR-XANES and TR-XPS, at the N-Kedge) (**Figure. 6**). The different techniques were compared to discern which is more suited to follow the charge-transfer mediated ET dynamics. TR-XPS shows the largest signal shift when the CT state is transiently populated, due to a sudden change of the N partial charges on the two moieties (8 eV shift from the positively charged nicodinamide N to the negatively charged adenine N atoms). A paper on the photophysical process has been submitted to Nature Chemistry [Jaiswal2023]. Another paper on the transient signals is in preparation. [Montorsi2023]

X-ray and Optical circular dichroism as local and global ultrafast chiral probes of [12]helicene racemization (PNNL+UCI+LANL): Chirality is a fundamental property of molecules playing a crucial role in biophysics and drug design. Optical Circular Dichroism (OCD) is a well-established chiral spectroscopic probe in the UV-visible regime. Although, chirality is most associated with a localized chiral center, some compounds such as helicenes are chiral due to their screw-like global structure. In these highly conjugated systems, some electric and magnetic allowed transitions are distributed across the entire molecule and OCD thus probes the global molecular chirality. Recent advances of X-ray sources, in particular the control of their polarization and spatial profiles, are enabling X-ray Circular Dichroism (XCD), which in contrast to OCD, can exploit the localized and element-specific nature of X-ray electronic transitions. XCD therefore is more sensitive to local structures and the chirality probed with it can be referred to as local. During the racemization of helicene, between opposite helical structures, the screw handedness can flip locally, making the molecule globally achiral while retaining a local handedness. We used the racemization mechanism of [12]helicene (**Figure 7a**) as a model to assess the capabilities of OCD and XCD as time-dependent probes for global and local chiralities, respectively. Small chemical shifts between all C atoms in [12]helicene do not allow to resolve them separately to use them as a local windows in XCD. We thus performed double substitutions of F and Cl atoms at opposites sites of [12]helicene in order to link the corresponding XCD to the local chirality in the substitution region. **Figure 7c-d** show the time-dependent OCD signal, the time-dependent XCD signal on the F side and the time-dependent XCD signal on the Cl side along [12]helicene racemization pathway. Only the XCD on the F side is able to pinpoint the final step from the transition state (TS) conformation to the single helix shape (SH) conformation, concomitant with the sudden drop of the potential energy (see **Figure 7b**), with the local change of the molecular handiness and with the change of the local chirality. These simulations demonstrate that XCD provides an excellent spectroscopic probe for the time-dependent local chirality of molecules, providing the basis for using XCD signals as local windows to probe the dynamics of chiral systems at XFEL and synchrotrons facilities. A paper was submitted to Journal of the American Chemical Society and is currently under review [Freixas2023].

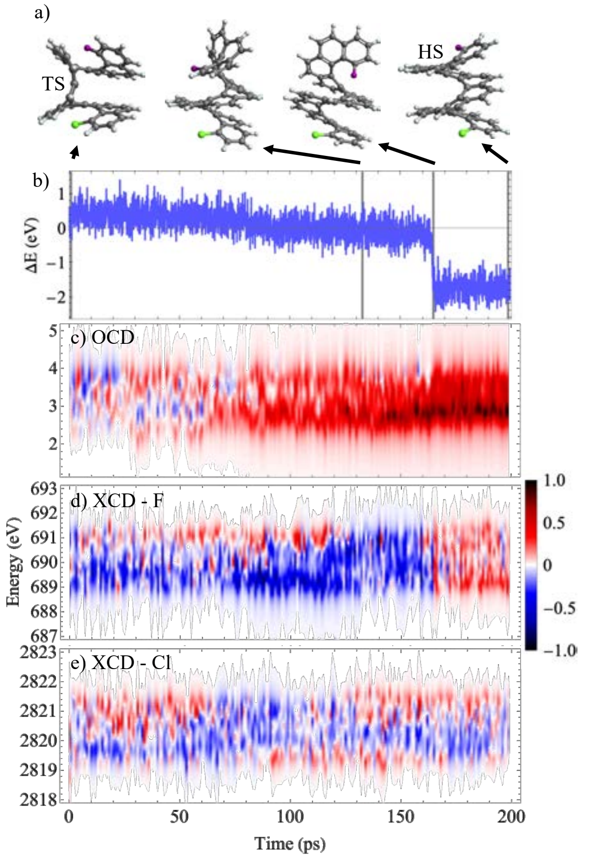


Figure 7. Along [12]helicene racemization pathway: a) selected snapshots, b) potential energy fluctuations, c) OCD signal, d) XCD signal on the F atom side and e) XCD on the Cl atom side.

Combining wave function theory and density functional theory to simulate K-edge X-ray absorption near-edge spectroscopy of aquated transition metal ions (PNNL + UCI): The prediction of X-ray absorption spectra (XAS) of transition metal complexes has important and broad applications in chemistry and biology. We investigated the predictive ability of multiconfiguration pair-density functional theory (MC-PDFT) for X-ray absorption spectra by calculating the metal K pre-edge features of aquated 3d transition metal ions in common oxidation states. MC-PDFT results were compared with experimental spectra and analyzed against results from restricted active space second-order perturbation theory (RASPT2) and time dependent density functional theory (TDDFT). As expected, TDDFT performs well for excited states that can be accurately represented by singly excited configurations but fails for excited states where higher order excitations become important. On the other hand, both RASPT2 and MC-PDFT provide quantitatively accurate results for all excited states irrespective of their character. While core-level spectroscopy with RASPT2 is accurate, it is computationally expensive. Our results show that MC-PDFT performs equally well with significantly lower computational cost and is a viable approach for X-ray spectroscopies. [Ghosh2023-1]

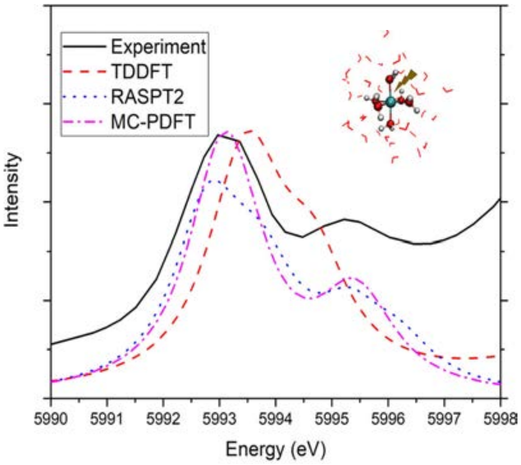


Figure 8: 1s–3d pre-edge spectra for Cr3+ from computation and experiment. The calculated spectra have been aligned with experiment.

Ultrafast X-ray spectroscopies and scattering of the photoinduced charge dynamics in solvated transition metal complexes (PNNL+UCI): The mixed valence trimetallic complex $[(NC)_5Fe^{II}(\mu\text{-}CN)Pt^{IV}(NH_3)_4(\mu\text{-}NC)Fe^{II}(CN)_5]^{4-}$ ($Fe^{II}Pt^{IV}Fe^{II}$ for brevity) in water has been studied extensively due to its ability to undergo a photoinduced, multielectron charge transfer process. The bimetallic analogue, $[(NH_3)_5Pt^{IV}(\mu\text{-}CN)Fe^{II}(CN)_5]$ ($Fe^{II}Pt^{IV}$ for brevity) was synthesized by Bocarsly and co-workers, to better understand the electron transfer process of FePtFe complex. In this study, our focus is to model the ultrafast electron transfer process and compute the ground and excited state X-ray spectroscopy signatures (Fe K-edge XANES, Pt L3-edge XANES, valence-to-core X-ray emission (VtC-XES) as seen by the Fe and Pt centers) and ultrafast fast scattering signals. We have used the QM/MM approach in NWChem to simulate the ground and excited state dynamics of this system. This allows us to treat the water molecules explicitly (**Figure. 2**). For the ground state QM/MM simulations, we have treated the $Fe^{II}Pt^{IV}$ complex with DFT and water molecules are treated using molecular mechanics. The excited-state dynamics on the metal-to-metal charge transfer (MMCT) state was performed at the TDDFT level. We have studied the changes in the hydrogen-bonding interactions between $Fe^{II}Pt^{IV}$ solute and solvent water molecules. Our calculations on the MMCT excited state show that there are three close lying MMCT excited states

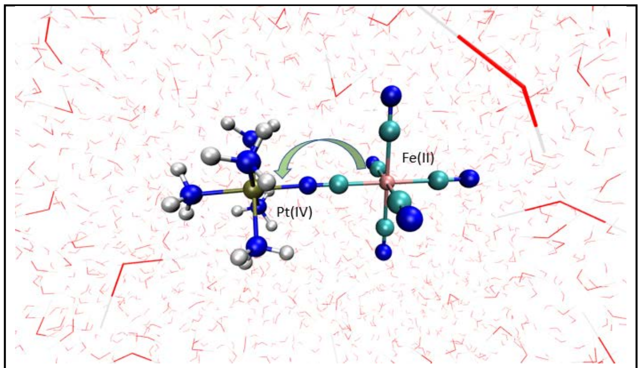


Figure 2. A bimetallic analogue of trimetallic complex $[(NH_3)_5Pt^{IV}(\mu\text{-}CN)Fe^{II}(CN)_5]$ ($Fe^{II}Pt^{IV}$ for brevity)

in the case of $Fe^{II}Pt^{IV}$. Experimental results have shown that the intervalent transition from $Fe^{II} \rightarrow Pt^{IV}$ is at 2.945 eV for the $Fe^{II}Pt^{IV}$ system. TDDFT calculations show three MMCT states at 2.98 eV, 3.03 eV and 3.08 eV, respectively. The initial MMCT excited state relaxation happens very quickly within ~50 fs. The relaxation process involves elongation of the M-CN and M-NH_3 bond distances in the $Fe^{II}Pt^{IV}$ system. We have computed the difference scattering signals of the total, solute-solvent, and solute-solute contributions using the electron density and independent atom models (IAM), respectively. The results using these two approaches are quite different, especially at early times (< 10 fs) and large q ranges (> 2 $Å^{-1}$). IAM is insufficient for describing the change of electron density distributions during the MMCT dynamics. [Ghosh2023-2]

SXRS for dark state targeting (UNIBO): the use of SXRS techniques to target valence excited states has been recently proven experimentally at SLAC. We extended that approach to specifically target dark excited states (such as $n\pi^*$ states in nucleobases, whose role in the photo-deactivation is still debated), and possibly to excited states with different spin multiplicities (**Figure 9**). [Montorsi2023-2]

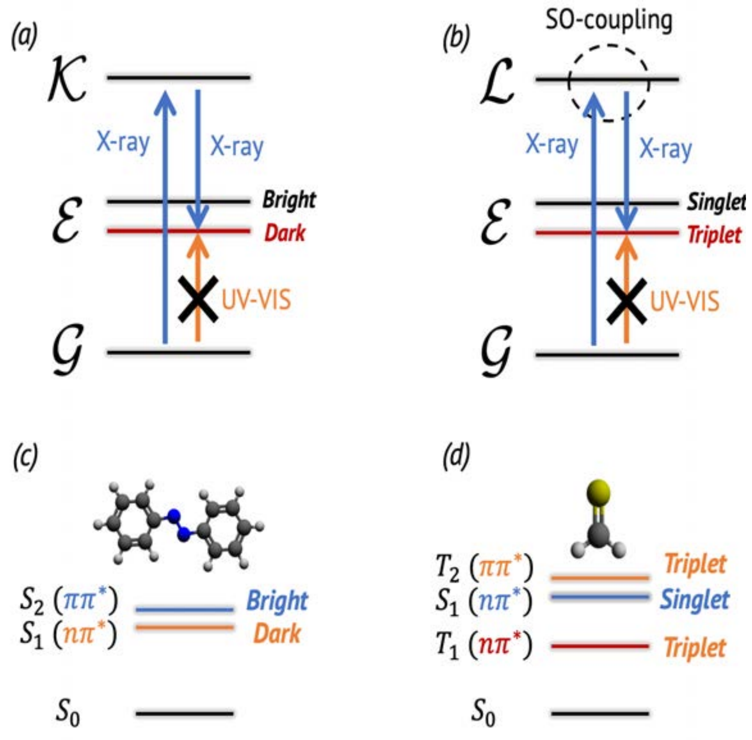


Figure 9. Schematic description of the proposed SXRS mechanism to selectively target optically dark states: (a) SXRS via K-edge states, acting as intermediate states for the population of dark singlet states; (b) SXRS via L-edge states, to selectively populate valence excited triplet states (thanks to the pronounced spin-orbit coupling that characterize such states, giving rise to a strong mixing between core-excited singlets and triplets). These generic schemes have been applied on two different test bed namely: (c) *trans*-azobenzene, for which we demonstrate that the dark $n\pi^*$ state can be populated with a near 100% selectivity via SXRS at the nitrogen K-edge; (d) thio-formaldehyde, for which the selective population of $n\pi^*$ and $\pi\pi^*$ triplet states is demonstrated, leveraging on the pronounced spin-orbit coupling characteristic of the sulfur L-edge.

Software releases (PNNL+LANL+UNIBO): novel implementations in the software developed by our teams (**Figure 10**) are being continuously released to the user community. Only in 2023 we have released major updates in three computational packages. In particular, the NEXMD v2.0 code [NEXMD2023] now implements Ehrenfest and Ab-Initio Multiple Cloning types of non-adiabatic dynamics, along with a number of useful tools for the study of non-radiative relaxation processes, such as the FrozeNM algorithm for performing molecular dynamics constraining generalized directions in the nuclear phase space, like normal modes. Recent developments in NWChem [NWChem2023] including many-body Green's function methods, exact two components relativistic methods, the real-time equation-of-motion coupled cluster cumulant formalism, non-adiabatic molecular dynamics methods, and improvements to existing

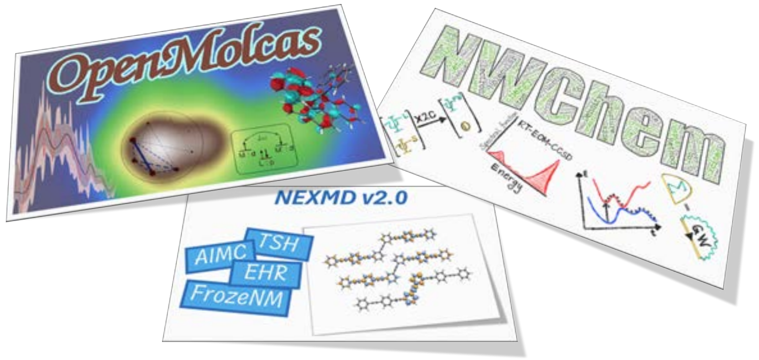


Figure 10. Software developed by our teams showcasing recent capabilities.

methods already present in NWChem. A roadmap review on real-time electronic structure methods [Govind2023] was also published. The OpenMolcas package updates [Molcas2023] now include novel functionalities for RASPT2 (semi)automated simulation of transient VIS/UV/Xray spectroscopy via interfaces to the recently DOE-developed iSpectron code and the COBRAMM package from UNIBO.

Future Plans

Nonlinear Spectroscopy with TDDFT (UNIBO+PNNL): the possibility to compute higher-lying excited states reachable from a given excited state, and the transition dipole moments between these excited states at the TDDFT level was explored in the PBI paper [Segatta2021]. A comparison between these and CASSCF/CASPT2 calculations were performed, and a range of nonlinear spectra of the PBI molecule were simulated and compared with state-of-the-art experiments. This TDDFT approach is being explored with a broader set of molecular systems that have been studied with CASSCF/CASPT2.

Extending TDDFT to tackle conical intersections (PNNL+UNIBO+UCI): TDDFT, as constructed, cannot be used to capture conical intersections between ground- and excited- states due to the lack of doubly excited configurations as singly excited configurations do not couple with the ground state. By diagonalizing the Hamiltonian in a basis of singly excited configurations and a doubly excited configuration, a coupling between the ground state reference and the first excited state can be established. This simplified approach can be utilized to locate conical intersections within the TDDFT framework. We will implement this approach in NWChem. Core-level spectroscopic signals will be computed at the conical intersection geometries. These calculations will be compared with wavefunction-based approaches in collaboration with the UNIBO team.

Ab initio multiple cloning (AIMC) within the QM/MM framework (PNNL+LANL+UCI): The recently developed *ab initio* multiple cloning (AIMC) approach based on the multiconfigurational Ehrenfest (MCE) method provides a powerful and accurate way of describing the excited-state dynamics of molecular systems. The AIMC method is a controlled approximation to nonadiabatic dynamics with a particular strength in the proper description of decoherence effects because of the branching of vibrational wavepackets at a level crossing. We will extend the AIMC algorithm to the QM/MM framework in the open source NWChem computational chemistry program. This extension will provide a high-level nonadiabatic molecular dynamics framework for simulating photoexcited dynamics of complex molecular systems in realistic solvent environments and experimentally relevant ultrafast spectroscopic probes, such as nonlinear coherent optical and X-ray signals.

State-specific solvation and dynamics of charge-transfer states (LANL+PNNL+UCI): Reaching even a qualitatively correct treatment of CT excitations in molecular systems using *ab initio* electronic structure methods is challenging. The state-specific solvation technique, where the dielectric environment responds to the electronic density of a particular excited state, is critical for a quantitative description of electronic structure since solvent stabilization of charge-transfer excitations is very significant. Performing non-adiabatic dynamics with state-specific solvation is currently an open question, which requires the development of novel methodology. We intend to develop non-adiabatic molecular dynamics framework that incorporates state-specific solvation and implement this method to our both codes, ab initio NWChem and semiempirical NEXMD packages. Since state-specific solvation framework is already implemented in both codes, we will augment it with non-equilibrium solvation models allowing to account for solvent dynamics in the non-adiabatic driver. The first implementation will rely on the implicit solvent models with the first application to be done to a small donor-acceptor chromophore using TDDFT technique. Here, calculated dynamics in the electron distribution relevant to the charge transfer transition will be analyzed and linked to time-resolved X-Ray electronic diffraction. Subsequently, we will extend this new capability from implicit solvation to the QM/MM framework (described above) that allows much broader application scope.

Extend the developed MCTDH/spectroscopy platform to other types of the spectroscopy: the platform for nonlinear spectroscopy simulations based on multidimensional MCTDH quantum dynamics, already developed and tested, will be extended to compute other types of the spectroscopy (diffraction, TRUECARS, etc..). This requires the development step of parametrizing such quantities in a clever way (could be the calculation of densities/transition densities / dipoles / polarizabilities in a coarse-grained grid) and to introduce nuclear-coordinates dependent operators in the expressions we have derived so far.

Improving model Hamiltonians for use within the developed MCTDH/spectroscopy platform (UNIBO) for X-ray based signals: the platform for nonlinear spectroscopy simulations based on multidimensional MCTDH quantum dynamics, already developed and tested, will be extended to explicitly handle few non-harmonic reactive modes for modelling photoinduced reactions and bond-breaking/bond-forming processes as well as the underling transient signals following UV/VIS pump, X-ray probe (both resonant and non-resonant). Photoisomerization as well as ring-opening processes in small molecular systems will be employed as test-bed examples to test the methodology and the results will be compared to conventional quantum dynamics studies by handling only the few non-harmonic reactive modes. The photoinduced ring-opening of gas-phase thymine will be used as a benchmark. The current implementation of the MCTDH quantum dynamics will be also extended to the most general harmonic model, including frequency changes and mode mixing (Duschinsky). In the terminology of the field, this means moving from linear vibronic coupling (LVC) model to a quadratic vibronic coupling (QVC) one.

Probing chiral at metal complexes racemization pathways (LANL+PNNL+UCI): Twisting motions in trichelate transition metal complexes are known potential candidates for non-dissociative racemization pathways. These motions are classified as the Bailar twist and the Ray-Dutt twist and involve transitions between conformations having different symmetries. We plan to explore the fingerprints of these motions using X-ray Circular Dichroism signals.

Dependence of X-ray circular dichroism (XCD) on conjugation and distance of the X-ray chromophore (LANL+PNNL+UCI): X-ray Circular Dichroism (XCD) can be tuned to be resonant with core electronic transitions for a given X-ray chromophore and are thus sensitive to the local chirality. The intensity of the XCD signal thus damps with the distance between the X-ray chromophore and the chiral feature giving rise to the signal. The connection, however, between the damping of the XCD signal and the conjugation around the X-ray chromophore substitution site remains unexplored. We plan to study such relation in dendritic model systems, where meta-, ortho- and para-substitutions of the X-ray chromophores might have a different impact on the XCD signal.

X-ray spectroscopy signals of early time photoaquation dynamics in aqueous $[Fe^{II}(CN)_6]^{4-}$ (PNNL + UCI): We have previously studied the long time photoaquation reaction process in aqueous $[Fe^{II}(CN)_6]^{4-}$ and have computationally elucidated the mechanism of the formation of the aquated species along with X-ray spectroscopy simulations. We are currently studying the early time photoexcitation dynamics of this complex. Using extensive DFT-based QM/MM simulations with an explicit treatment of the solvation, we have obtained evidence that the CN ligand dissociates from the main complex in ~200 fs. Transient X-ray absorption near-edge spectroscopy (XANES) and valence-to-core X-ray emission signatures at the Fe and N K-edges are being computed at the TDDFT level to track the early time (~200 fs) dynamics. Additionally, the resonant stimulated X-ray Raman spectroscopy (SXRS) signatures of this early time process should reveal the correlations between valence excitations and Fe core-excitations. All TDDFT calculations and matrix couplings are based on NWChem. We have a collaboration with beamline scientists at SLAC/LCLS who are investigating this system.

Helicene emission profile (UCI + PNNL + LANL): Due to the Helicene molecular geometry, this system is expected to have interesting emission properties, such as circularly polarized luminescence or light with orbital angular momentum. The emission profile can be calculated using the current density vector field, which can be implemented within the NWChem program. The developed methodology could then be applied to different systems exhibiting interesting chiral molecular geometries such as Möbius belts or Trefoil knots.

Peer-Reviewed Publications Resulting from this Project (2022-2023)

Thrust 1

[Segatta2023] "**Nonlinear molecular electronic spectroscopy via MCTDH quantum dynamics: from extract to approximate expressions**," F. Segatta, D. A. Ruiz, F. Aleotti, M. Yaghoubi, S. Mukamel, M. Garavelli, F. Santoro, A. Nenov, JCTC, March 2023. https://doi.org/10.1021/acs.jctc.2c01059

[NEXMD2023] "**NEXMD2 Software Package for Nonadiabatic Excited State Molecular Dynamics Simulations**," V. M. Freixas, et al, J. Chem. Theory Comput. 19, 16, 5356–5368 (2023) https://doi.org/10.1021/acs.jctc.3c00583

[Molcas2023] "**The OpenMolcas Web: A Community-Driven Approach to Advancing Computational Chemistry**", G. Li Manni et al , J. Chem. Theory Comput.
(https://doi.org/10.1021/acs.jctc.3c00182) (2023)

[NWChem2023] "**NWChem: Recent and Ongoing Developments**", D. Mejia-Rodriguez, et al, J. Chem. Theory Comput. https://pubs.acs.org/doi/full/10.1021/acs.jctc.3c00421(2023)

[Govind2023] "**IOP Roadmap: Real-Time Propagation in Electronic Structure Theory**", N. Govind, Y. Kanai, X. Li (Electronic Structure, accepted, 8/2023)

[Segatta2023-2] **"Time-resolved X-ray absorption spectroscopy via MCTDH quantum dynamics"**, F. Segatta, D. Aranda, F. Aleotti, F. Montorsi, S. Mukamel, M. Garavelli, F. Santoro, A. Nenov, (JCTC, submitted, 2023).

[Loreti2023] **"WFOES: Wave-Function Overlap between different Electronic Structure methods for Spectroscopy Simulation"**, A. Loreti, V. M. Freixas, D. Avagliano, S. Mukamel, M. Garavelli, N. Govind, A. Nenov, (in preparation, 2023).

Thrust 2

[Yeonsig2023] "**Monitoring vibronic coherences and molecular aromaticity in photoexcited cylclooctatetraene with a X-ray probe: a simulation study"** Y. Nam, H. Song, V. M. Freixas, D. Keefer, S. Fernandez-Alberti, J. Yong-Lee, M. Gavarelli, S. Tretiak, S. Mukamel. Chem. Sci. 2023, 14, 2971-2982. DOI: 10.1039/d2sc04335a

[Rouxel2022] "**Molecular chirality and its monitoring by ultrafast X-ray pulses**," J. R. Rouxel, S, Mukamel, Chem. Rev. 122, 22, 16802–16838 (2022) https://doi.org/10.1021/acs.chemrev.2c00115

[Carlini2023] "**Electron and ion spectroscopy of Azobenzene in the valence and core shells**," L. Carlini, F. Montorsi, Y. Wu, P. Bolognesi, R. Borrego-Varillas, A. R. Casavola, M. Castrovilli, J. Chiarinelli, D. Mocci, F. Vismarra, M. Lucchini, M. Nisoli, S. Mukamel, M. Garavelli, R. Richter, A. Nenov, L. Avaldi. J. Chem. Phys. 158, 054201 (2023). https://doi.org/10.1063/5.0133824

[Ghosh2023-1] "**A Combined Wave Function and Density Functional Approach for K-Edge X-ray Absorption Near-Edge Spectroscopy: A Case Study of Hydrated First-Row Transition Metal Ions**", S. Ghosh, S. Mukamel, N. Govind, *Journal of Physical Chemistry Letters,* https://doi.org/10.1021/acs.jpclett.3c00611) (2023)

[Freixas2023] "**X-ray and Optical circular dichroism as local and global ultrafast chiral probes of [12]helicene racemization**", V. M. Freixas, J. R. Rouxel, Y. Nam, S. Tretiak, N. Govind, S. Mukamel, JACS (under review 8/5/23).

[Jaiswal2023] "**Sub-100-fs energy transfer in coenzyme NADH is a coherent process assisted by a charge-transfer state",** V. K. Jaiswal et al. (Nature Chemistry, submitted, 2023).

[Ghosh2023-2] **"Quantifying Excited-State Solvation Dynamics in Hydrated Transition Metal Complexes with Femtosecond X-ray Spectroscopy and Scattering**", S. Ghosh, H. Yong, S. Mukamel, N. Govind, (in preparation, 2023)

[Montorsi2023] "Unraveling ultrafast photo-induced charge and energy transfer processes by time-resolved soft x-ray spectroscopy", F. Montorsi, V. K. Jaiswal, D. Aranda, F. Segatta, A. Nenov, F. Santoro, S. Mukamel, M. Garavelli, (in preparation, 2023).

[Segatta-2023-3] "FEL monitored element-selective ground state vibrational dynamics of hydroxychloroquine", R. Mincigrucci et al. (in preparation, 2023).

[Montorsi2023-2] "Stimulated X-ray Raman scattering for selective preparation of dark states beyond optical selection rules", F. Montorsi, M. Garavelli, F. Segatta, A. Nenov (in preparation, 2023).

Theory and Simulation of Nonlinear X-ray Spectroscopy of Molecules

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Progress Report October 2023
DOE DE-FG02-04ER15571

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 excellent probes for electron and energy transfer in molecular complexes. This program is aimed at the design of novel x-ray pulse sequences for probing core and valence electronic excitations in molecules, and at 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 and ultrafast x-ray diffraction. Attosecond electron dynamics in molecules created by resonant x-ray Raman excitation are proposed to be monitored by x-ray diffraction. Combined time-resolved x-ray and electron diffraction is used for the imaging of nuclear wavepacket dynamics.

Recent Progress

Monitoring of Conical Intersection Passage via Electronic Coherences in Twisted X-Ray Diffraction.

A novel time-resolved twisted x-ray diffraction technique was proposed, which allows a direct measurement of transient electronic coherences created at conical intersection (CI) [1]. This was achieved by using x-ray beams carrying orbital angular momentum (OAM). We demonstrated that the population contributions cancel out when the opposite twisted X-rays with ±*l* index are subtracted, while the coherence components survive and provide a direct signatures of electronic coherences. This was demonstrated for the photodissociation of thiophenol (Figure 1), where the temporal profile of the time-resolved difference signal matches with the coherence contribution.

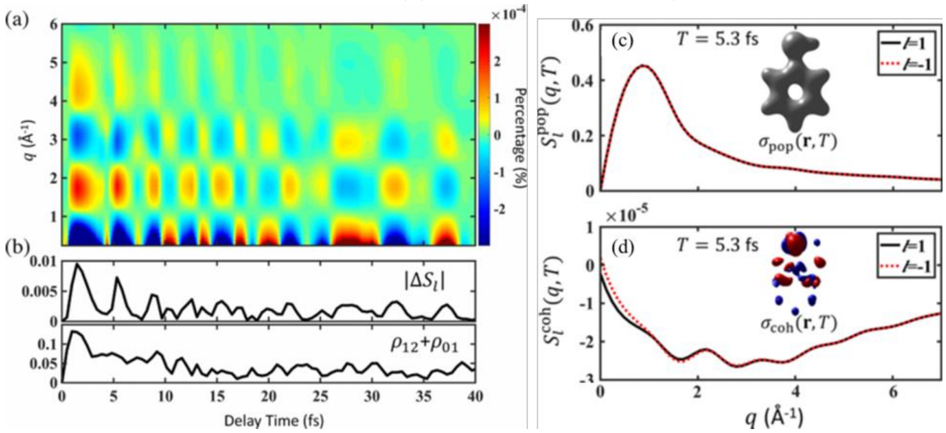

Figure 1. (a) Rotationally averaged diffraction signals, $\Delta S_{l=1}(q,T)$. (b) Absolute value of the difference signal in (a) integrated over q (top) and the total coherence magnitude (bottom) of the S_2/S_1 and S_1/S_0 electronic coherences. Rotationally averaged diffraction signals and charge densities at T = 5.3 fs after excitation, (c) Population and (d) coherence contribution. [1]

The spatial (q). profile reflects the real-space distribution of the coherence charge density. These results cannot be achieved with circular polarized light which does not engage with the molecular charge density during the scattering process, making it identical to x-ray diffraction of plane waves. This new OAM probe paves the way for monitoring photophysical and photochemical processes, and offers additional opportunities for electronic coherent control over conical intersection dynamics.

Imaging Charge Migration and Nuclear Charge Density by Combined X-Ray and Electron Diffraction.

We had shown that time dependent electron and nuclear densities can be directly extracted from the diffraction patterns by combing time-resolved X-ray and electron diffraction techniques [2]. This is achieved by subtracting their signals in the homodyne- and heterodyne-detection regime, respectively. The former scheme was applied to the direct real-space imaging of charge migration in gas-phase 4-fluoro-4'-hydroxybiphenyl [3]. We found that a mixed electronic−nuclear interference in electron diffraction can be clearly singled out by subtracting two standard homodyne diffraction signals. Using the ground-state nuclear structure as a reference, the phase information of this signal allows its inversion to real space and the capture of electronic charge density movies scale (Figure 2). This technique can be used to monitor any attosecond electron dynamics where the nuclei are frozen.

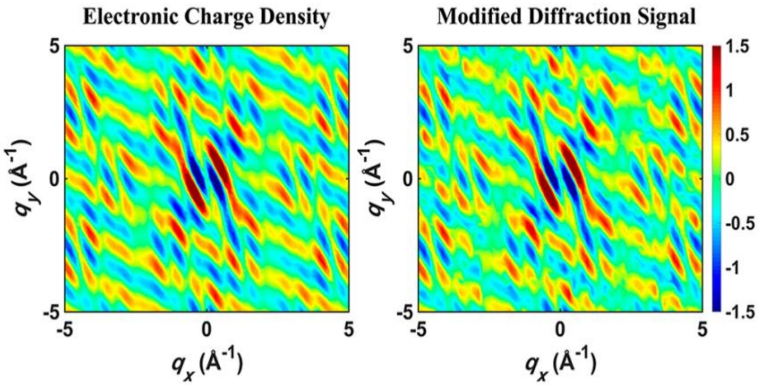

Figure 2. Real part of difference electronic charge density in q-space (left) and modified diffraction signal constructed by mixed electronic−nuclear interference in electron diffraction (right). Both electronic charge density and signal are shown in the q_x–q_y plane (q_z = 0). The results from the oxygen excitation at 2.2 fs are used. [3]

Creation and Detection of Coherent Ring-current Dynamics.

Electronic coherences between ring currents can be induced by broadband circularly polarized optical pulse, and probed by time-resolved X-ray circular dichroism (tr-XCD) [4]. The currents change direction and magnitude. This results in ring current migration among different regions in the molecule, with a period inversely proportional to the energy gap of the coherent states. This

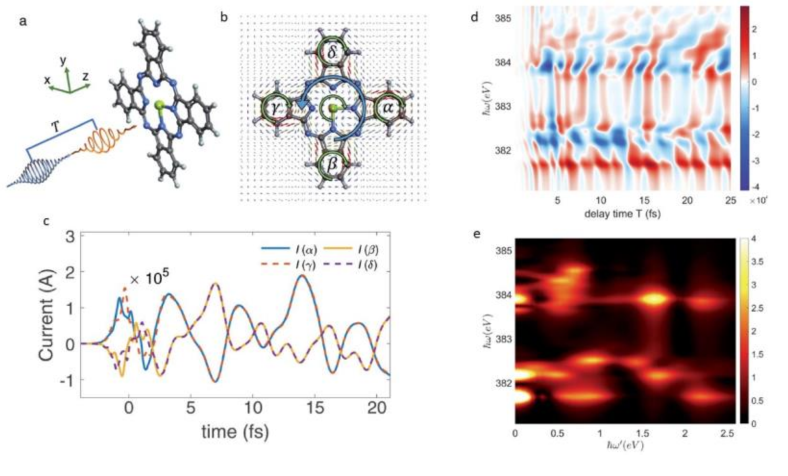

Figure 3. (a) tr-XCD scheme and (b) coherent ring currents formed within the MgPc molecule. (c) local currents at different region of MgPc as a function of time, showing ring current migration. (d) tr-XCD spectrum of nitrogen K-edge and (e) its Fourier transform as a function of oscillation frequency and excitation energy. [4]

dynamics was demonstrated in cyclic conjugated Mg-phthalocyanine (MgPc) by probing nitrogen K-edge with tr-XCD (Figure 3) [4]. By performing Fourier transform of the pump-probe delay time, we obtain the CD spectrum as a function of excitation energy and oscillation frequency. Bright peaks in the spectra can be assigned to pairs of electronic coherences accor by. using the oscillation frequency and excitation energy. This work suggests a way to probe the evolution of ring currents in time domain and separate individual excited state coherence contributing to the coherent ring current in the frequency domain.

Future Plans

Self-heterodyned Diffractive Imaging using Single-electron Pulses

Ultrafast electron diffraction (UED) has been broadly applied to probe molecular structural dynamics in space and time. Using an optical pump-electron probe scheme, whereby a pump laser pulse initiates a photochemical reaction followed by a probe electron pulse whose diffraction pattern reveals the time -evolving molecular structure. However, standard UED uses homodyne detection which gives the expectation values of products of charge density operators $\langle \hat{\sigma}^\dagger \hat{\sigma} \rangle$ instead of the expectation value of charge density $\langle \hat{\sigma} \rangle$. Heterodyne-detected UED, which requires an additional reference wave that interferes with the scattered wave, can directly measure the time-evolving molecular charge density. We will explore how to use single electron pulses to realize self-heterodyned UED. In this method, a single electron pulse goes through electron biprism and splits into two paths. One path interacts with the light-excited molecular sample, while the other serves as a reference local oscillator. The interference of the two paths generates. a diffraction patterns. This single electron scheme can. reconstruct the phase information of the two paths through their interference, thus directly providing the image. This technique provides a novel method for the imaging of charge densities.

Time- and Angle-Resolved Photoelectron Spectroscopy of Conical Intersection Dynamics

Time-resolved photoelectron spectroscopy (tr-PES) measures the kinetic energy distribution of emitted photoelectrons at different pump-probe delay, offering unique insights into photo-induced molecular dynamics. This has been demonstrated in our recent paper, where we had directly probed the conical intersections responsible for the internal conversion of photo-excited uracil. The angular resolution of tr-PES has often been overlooked due to challenges in achieving a molecular frame, and the complexities associated with signal analysis. The photoelectron angular distribution provides a sensitive probe of the electronic character of the molecular orbital being ionized with high spatial resolution even in the XUV regime. The full potential of tr-PES thus remains to be explored. We plan to make use of the angle-resolution of tr-PES to probe two competitive relaxation pathways in photo-excited gas-phase thymine, for which the internal conversion mechanism has been under debate. We expect to use the isoenergetic $\pi\pi^*$ and $n\pi^*$ relaxation channels through their (an)isotropic angular distribution as a novel and highly sensitive probe of conical intersection dynamics. This holds the potential to elevate the spectroscopic sensitivity with respect to the electronic character and potentially reveal new signatures of conical intersections in molecules.

Time-Resolved Helical Dichroism (trHD) of Molecular Chirality Probed by Orbital Angular Momentum X-ray light.

Molecular chirality plays a crucial role in many chemical and biological processes. Circular dichroism, defined as the difference in absorption between left and right circularly polarized light, is widely used to investigate molecular chirality. However, the. CD signals are much weaker than their achiral counterparts due to the mismatch between molecular size and light wavelength. We have previously demonstrated that the helical dichroism (HD) utilizing OAM of the x-ray beam can enhance the molecular dichroic response, which can be further. Enhanced by the spin angular momentum of light. We plan to extend HD into the time domain (tr-HD), as a promising technique for. probing chiral dynamics. We aim to investigate the potential advantages of tr-HD compared to the established tr-XCD, and explore its capabilities and potentials. To that end, we will derive expressions for the tr-HD signal, and simulate typical chiral dynamics . This method is expected to be a more powerful tool for exploring and controlling ultrafast chiral processes.

Peer-Reviewed Publications Resulting from the Project (2022-2023)

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2. *“Novel Ultrafast Molecular Imaging Based on the Combination of X-ray and Electron Diffraction,” Haiwang Yong, Daniel Keefer, and Shaul Mukamel. J. Phys. Chem. A, 127, 3, 835-841 (2023)*
3. *“Attosecond Charge Migration in Molecules Imaged by Combined X-Ray and Electron Diffraction,” Haiwang Yong, Shichao Sun, Bing Gu, and Shaul Mukamel. J. Am. Chem. Soc., 144, 45, 20710–20716 (2022)*
4. *“Coherent Ring-Current Migration of Mg-Phthalocyanine Probed by Time-resolved X-ray Circular Dichroism,” Shichao Sun, Haiwang Yong, Feng Chen, and Shaul Mukamel. Chem. Sci., 13, 10327-10335 (2022)*
5. *“Optical-Cavity Manipulation and Nonlinear UV Molecular Spectroscopy of Conical Intersections in Pyrazine”, Daeheum Cho, Bing Gu, and Shaul Mukamel. J. Am. Chem. Soc. 144, 17, 7758-7767 (2022)*
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7. *“Time-Evolving Chirality Loss in Molecular Photodissociation Monitored by X-ray Circular Dichroism Spectroscopy,” Yeonsig Nam, Daeheum Cho, Jeremy R. Rouxel, Daniel Keefer, Bing Gu, Niranjan Govind and Shaul Mukamel. J. Am. Chem. Soc. 144, 44, 20400–20410 (2022).*
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10. *“Manipulating Attosecond Charge Migration in Molecules by Optical Cavities” Yonghao Gu, Bing Gu, Shichao Sun, Haiwang Yong, Vladimir Y. Chernyak, and Shaul Mukamel. J. Am. Chem. Soc. 145,14856-14864 (2023)*
11. *“Element- and enantiomer-selective visualization of molecular motion in real-time” R. Mincigrucci, J. R. Rouxel, B. Rossi, E. Principi, C. Bottari, S. Catalini, J. S. Pelli-Cresi, D. Fainozzi, L. Foglia, A. Simoncig, A. Matruglio, G. Kurdi, F. Capotondi, E. Pedersoli, A. Perucchi, Nat. Commun., 14, 386 (2023)*
12. *“Molecular Chirality and Its Monitoring by Ultrafast X-ray Pulses” Jérémy R.Rouxel, and Shaul Mukamel Chem. Rev. 122, 16802-16838 (2022)*

Structured VUV, EUV and Soft X-ray Light for Probing Quantum Systems

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Project Scope

The goal of this research is to develop novel short wavelength quantum light sources, and use them to to understand quantum systems. First, we are extending the exquisite control we achieved over structured light (spectral, temporal, polarization, shape, phase and flux) from the extreme UV (EUV) into the soft X-ray (SXR) region. Structured EUV light is now uncovering a wealth of fundamental new science that is directly relevant to the DOE BES mission. Second, we are enhancing the tunability, intensity, and characterization methods, for high-flux, structured, vacuum and extreme UV beams to address challenging applications in molecular dynamics and energy systems. Third, we are using bright VUV-to-SRX beams to probe strongly-coupled charge and phonon dynamics and transport in molecular and energy materials, and also investigate the interaction of OAM beams with quantum systems. We made exciting advances in recent years, with 11 peer-reviewed papers published, accepted or in review in top journals since 2021. Recent graduates from our group went to DOE Laboratories (Sandia (2), Los Alamos (2), Argonne (1), SLAC (1)). Finally, in separate 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.

Recent Progress

Tailoring the Spectrum and Structure of Extreme-Ultraviolet and Soft X-Ray Beams via SAM and OAM [2-6,8]: The extreme nonlinear optical process of high-harmonic generation (HHG) makes it possible to map the properties of a laser beam onto a radiating electron wavefunction, and in turn, onto the emitted x-ray light. 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 imaging fidelity, and to implement unique excitations and probes of chiral structures in molecules, magnetic materials and nanostructures. In past work funded by DOE AMOS, 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.

Very recently we overcame a long-standing challenge by developing a scheme that can generate circularly polarized high harmonics well into the soft x-ray regime. To date, efficiently generating circularly polarized high-order harmonics has been challenging: two-color collinear counter-rotating driving lasers result in a lower phase matched cutoff photon energy, while single-color non-collinear counter-rotating schemes suffer from very low efficiency. We generated circularly polarized attosecond pulse trains by using a structured laser driver which has a rotating polarization and phase grating. Our experimental and numerical results demonstrate the production of left and right circularly polarized harmonics, which naturally separate upon propagation. In contrast to previous schemes relying on multiple colors or noncollinear crossing of multiple beams, our approach uses a single laser color in a high efficiency, collinear geometry. This scheme can also extend into the soft x-ray region to the L-edges of ferromagnets when driven by mid-infrared driving lasers, while most importantly, preserving the same high phase matching cutoff photon energy as for linear-polarized high harmonics.

Tailoring the spectrum of high harmonics via pulse shaping: Controlling the spectral linewidth and brightness of high-harmonic generation in the VUV, EUV and soft X-ray region is important for many spectroscopic applications e.g. photoelectron spectroscopies such as PIMS and ARPES, or high resolution imaging. Such spectro-microscopies benefit, for example, from selective interaction with a single isotope, or narrow linewidth for enhanced energy resolution. In past work we showed that by manipulating the phase of the driving laser to a precision of ~12 attoseconds using a pulse shaper, we could control the HHG linewidth and selectively enhance the brightness of a single harmonic order in the EUV region of the spectrum around ~42 eV. By adjusting the laser waveform, it is possible to better phase the attosecond bursts from each half-cycle of the driving laser, so that they interfere constructively. In recent work, we extended this capability from 42eV to ~100eV, by using more precise, robust and stable pulse shapers and lasers.

Enhancing VUV and soft X-ray harmonics using structured waveguides: We have made further progress on the use of photonic crystal waveguides for HHG, specifically by developing methods to robustly cleave and mount them for both low and high pressure operation, and their use over extended time periods. Structured waveguides dramatically decrease waveguide losses for tightly-focused beams of UV, near-IR and mid-IR light compared with the simple capillary waveguides, confining the high-pressure gas, and allowing HHG with lower-pulse-energy and higher repetition rate driving lasers. By confining the HHG driving laser light to a smaller mode area, the pulse energy requirement for bright SXR HHG can be brought down to the sub-mJ level (from ~2-10mJ in past work).

We also investigated the optimal pathways for generating bright highly-cascaded harmonic VUV combs with high efficiency, beam mode quality, and stability using photonic crystal waveguides. In 2020, we demonstrated DUV/VUV generation at MHz repetition rate using a two-color, highly-cascaded FWM process in a negative-curvature hollow-core fiber. The advantage of this approach is that both even and odd order harmonics are generated that extend well into the VUV, with a combination of narrow intrinsic bandwidth (~40meV) and excellent time resolution (~100fs) ideal for many photoelectron spectroscopy studies. This highly cascaded harmonic generation (HCHG) process requires 100x lower peak intensity compared with HHG ($\sim 10^{12}$ W/cm^2 vs $>10^{14}$ W/cm^2), and pulse energies ~1000x lower (~μJ vs ~mJ). More recently, we found that we can maintain very high VUV flux while reducing the average power and pulse energy compared with our 2020 research. Under optimal phase matching conditions, the generated DUV/VUV beam modes are very high quality, while the RMS flux stability can be < 1%. We also find that the conditions for optimizing different DUV/VUV orders can be very different in terms of the relative intensity of the two-color drive laser and the gas pressure used. Finally, we observed that the VUV output flux saturates at incident laser intensities below that required for ionization, demonstrating that this highly-cascaded harmonic generation process is distinct from high-order harmonic generation.

Probing strong electron-phonon coupling and phase transitions in quantum systems [1,7,9-11]: In past research, we photoelectron spectroscopies to probe excited state charge transfer to ligands, as well as VUV-excited electronic states of molecules relevant to atmospheric chemistry and combustion. Very recently, we completed a very unique experimental investigation of nanoparticles – where at excitation laser intensities higher than those used to drive charge transfer to ligands, we discovered that we could create a unique form of warm dense matter (WDM). This state of matter is usually very challenging to directly probe because of its transient nature, where dynamics can span from femtosecond timescales on up. Previous studies used high-power lasers, pulsed power, and ion beams at mid and large-scale facilities to excite and probe WDM. These experiments are limited to relatively low repetition rates (<120 Hz), that influence what diagnostic measurements are possible. Using intense ultrafast laser pulses, we uniformly heated a sample of isolated ~8 nm metallic nanoparticles to just below the ablation threshold. We then probed the resulting WDM dynamics using velocity-map-imaging photoelectron spectroscopy, which enables uniquely accurate measurements of this exotic state (see Fig. 2). We can directly measure the instantaneous electron temperature, and use this to accurately extract the electron-ion coupling dynamics and hot electron cooling in WD-nanomatter for the first time. We vary the excitation laser fluence to probe the dynamics below and above the melting threshold of the particles to characterize their properties in both solid and WDM phases. By comparing with theories of highly-excited strongly-interacting matter, we found that the state of matter we produce lies at the boundary between hot solids and plasmas. This is evidenced by the fast energy loss of electrons to ions, strong modulation of the electron temperature by variation in volume of the nanoparticle, and the existence of a threshold fluence associated with a change in electron-ion couplings. We extracted higher values of the electron-phonon coupling than had been observed to date, and observed a strong modulation of the electron temperature on ~ 1ps timescales during cooling. These results open a new avenue for experimental WDM research to inform advanced theory. This research benefitted from a theory collaboration with LBNL and LANL. IIt was recently published in Physical Review Letters and featured on the cover in August 2023.

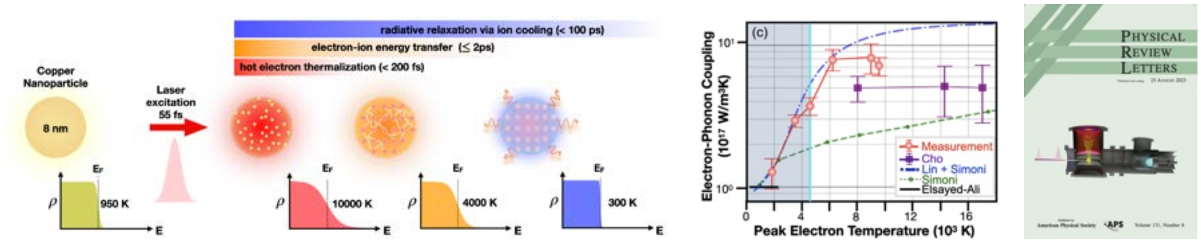

Fig. 1. Exciting and probing dynamics of warm dense Cu Nanoparticles (left) After excitation by a 790-nm pulse, hot electrons thermalize on timescales <50fs. This is followed by energy transfer from the electron bath to the lattice on timescales up to 2 ps. The electron Fermi distribution (electron density (ρ) versus energy (E)) is shown, where E_F is the Fermi energy. (center) Comparison of experimental and theoretical electron-phonon coupling values. (right) Photoelectron spectroscopy research to extract electron-phonon coupling that was featured on the cover of Physical Review Letters, August 25, 2023.

Future work

We are extending bright structured high harmonic beams from the EUV into the soft x-ray regions of the spectrum. We are also exploring how to use structured light to more sensitively excite and probe strongly-coupled dynamics in quantum, 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 are also extending laser pulse shaping into the soft xx-ray region for enhanced brightness and spectral control. Finally, we are developing VUV sources with ~1 µJ energy per pulse, for applications in transient grating spectroscopies and quantum sensing of molecules and materials (e.g. that can be used to extract the electronic, transport and mechanical properties of high-bandgap molecular/layered/energy materials). Methods to make these VUV sources continuously tunable are also being explored.

Peer-Reviewed Publications Resulting from this Project (2021 to Sept 2023)

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2. *Ultrashort vortex pulses and their nonlinear frequency conversion,* C.T. Liao, C. Hernández-García, M. Murnane, Journal of Optics **25** 093001, (2023). DOI 10.1088/2040-8986/ace4dc
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DYNAMICS OF TWO-ELECTRON ATOMIC AND MOLECULAR PROCESSES

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PROGRAM SCOPE: The general goals of this project are to develop or modify existing 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 electromagnetic radiations with full control of its polarization state to chiral and achiral matter. Broadly, we aim to investigate the time-dependent correlated dynamics of interacting few-body quantum systems. Investigations of current interest fall in the areas of strong-field (intense laser) physics, linear and nonlinear attosecond physics, and ultrafast X-ray science. All investigations require large-scale numerical computations, involving, e.g., the direct solution of the full-dimensional time-dependent Schrödinger equation (TDSE) for two-electron atomic or molecular systems interacting with electromagnetic radiation, the time-dependent density functional theory (TD-DFT), the R-matrix time-dependent (RMT), the J-matrix method, the time-dependent perturbation theory, etc. In some cases, our studies are supportive of and/or have been stimulated by experimental work carried out by other investigators funded by the DOE AMOS physics program. Principal benefits and outcomes of this research are improved understanding of how to control atomic and molecular processes with chirped electromagnetic radiation, how to transfer energy and spin angular momentum from chirped electromagnetic radiation to chiral and achiral matter, how to image electron correlation processes while they occur, how to characterize the ionizing laser pulses, how to manipulate the photoemission time delay using chirp, and how to pave the way for quantitatively control of charge migration in matter.

RECENT PROGRESS

A. ***Pulse shaping in strong-field ionization: theory and experiments**:* In collaboration with the research group of Marcos Dantus from Michigan State University, 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. In addition, we changed the amount of chirp in the pulses. Semiclassical as well as fully quantum mechanical TDSE calculations are found to be in excellent agreement with experimental results. However, precise knowledge of the field parameters in the time and frequency domains is essential to afford reproducible results and quantitative theory and experiment comparisons. *(See publication [P1] in the list of project publications below.)*

B. ***Reversible electron spiral by chirped counter-rotating circularly polarized attosecond pulses at zero time delay:*** A novel class of linear, spiral phenomena is discovered in the photoelectron momentum distribution (PMD) when studying photoionization of S-state atoms by a pair of linearly chirped, oppositely circularly polarized attosecond pulses. This controllable effect, dubbed *reversible* electron spirals because of its energy-dependent sense of rotation, is identified, and can be isolated in the absence of time delay for the case of opposite chirp rates. The astrophysical concept of spiral arm pitch angle is borrowed to gain a better insight into the energy-dependence of the reversible spiral rotation, to determine the attochirp and binding energy characteristic of an atomic target. Our results indicate potential applications in attochirpmetry and polarimetry. *(See publication [P2] in the list of project publications below.)*

C. Time-delay control of reversible electron spirals using arbitrarily chirped attopulses: We revisit the study [P2] on electron reversible spirals by demonstrating how varying the pulse chirp rates and time delay between the two pulses provide an exquisite way of manipulating the linear and quadratic spectral phases of the photoelectron responsible for this phenomenon. Potential applications include masking the timing information in photoionization such as Ramsey or Wigner delay. Our reversible spiral prediction has just been confirmed experimentally in 2023 by the Wollenhaupt group in Germany in the femtosecond regime. *This work will be submitted shortly.*

D. ***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 [3-9]). *(See publication [P3] in the list of project publications below.)*

E. Ouroboros-like electron spirals by synchronous crossed laser pulses: We consider the linear process [P3] for crossed linearly and circularly polarized pulses but in the case of zero-time delay, where no spiral cannot occur when the ionizing pulses are transform-limited. Our analytical calculations for the case of photoionization of the H atom forecast the existence of single-armed spiral patterns, dubbed Ouroboros-like spirals, as they resemble the pattern of a snake biting its own tail. This effect can find applications in laser polarimetry. *This work will be submitted shortly.*

F. ***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 [P4] in the list of project publications below.)*

G. Electron photoionization for characterization of a train of attosecond pulses or isolated attosecond pulses with time-dependent polarization state: We study Ramsey interferences [1] of 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. *(Author: J.M. Ngoko Djiokap; This work will be submitted shortly.)*

H. Temporal coherent control of resonant two-photon double ionization of H_2 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 either along or perpendicular to the molecular axis. 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 [P5] in the list of project publications below.)*

I. Molecular orbital tomography of the CO molecule via photoelectron momentum distribution: We study the linear process of photoionization of CO initially in the HOMO and HOMO-1 for a variety of orientations of the laser polarization vector with respect to the molecular axis. It is found that the well-known asymmetry in the HOMO of CO is strongly reflected in the PMD observable. *This work will be submitted shortly.*

J. ***On the topological charge of the transition amplitude in atomic ionization by short pulses:*** The concept of electron vortex lines (EVL) [2] is useful in various problems of quantum mechanics. A connection between vortices associated with singularities in the velocity fields and electron matter-wave spiral vortices [3-6] is established. *(Authors: J.M. Ngoko Djiokap, A.V. Meremianin, and N.L. Manakov; Work in preparation and will be submitted in 2023.)*

K. Time delay effects in resonant harmonic generation of He or Be: Control the multiphoton regime plateau structure (e.g., [11]) is investigated by considering overlapping and nonoverlapping driving laser pulses at resonant frequencies. *This work will be submitted shortly.*

FUTURE PLANS: In addition to preparing research described above for publication, we are currently studying a plethora of research problems that should be completed in the next three years:

(a) **Nuclear motion effects on attosecond processes**: Can vibrational broadening due to quantum uncertainty relation (zero-point energy) [P5] destroy the production of the following in-plane chiral attosecond phenomena of molecular symmetry-mixed dichroism (MSMD) [7] and the dynamical electron vortices [4] from photoionization of the hydrogen molecule?

(b) **Attochirp effects in uncorrelated or correlated multiphoton processes**: Can attochirp be used as a control knob for the uncorrelated, multiphoton, resonant or non-resonant, processes of single-ionization of an S-state atom by a pair of arbitrarily polarized laser pulses eventually separated in time? Can the forward-backward asymmetry in angular distribution from single ionization of helium with or without excitation involving doubly excited states be manipulated using the attochirp? Can attochirp be used to switch from sequential to direct regime in the correlated process of two-photon double ionization of He? In previous work (e.g., [8]) for resonant harmonic generation 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. Can the concept of chirp be useful to avoid any carrier frequency scan?

(c) **Applications of electron vortices by soft x-ray attopulses seeded by FEL:** In collaboration with Kling and Marinelli group from SLAC, we plan to conduct a joint experimental and theoretical effort to study whether spiral signal emerges in the PMD from single ionization of NO. Using both attopulses with a time-delayed infrared laser field could provide novel timing information in photoionization when manipulating the amount of chirp. The theoretical challenge for NO is that it's an open-shell molecule, while CO is a closed-shell one. A natural question is whether spiral signal occurs from photoionization of CO but in the XUV regime?

(d) **Interaction of arbitrarily polarized attopulses with achiral and chiral heteronuclear molecules:** Our interest in chiral molecules is curiosity driven as we want to know whether the actual picture of in-plane chiral patterns [3-7] in the PMD from achiral targets can change when chiral targets are used. We shall first consider H_2O_2 (the simplest chiral target), and then the 1-Chloro-1-fluoroethane. On the other note, we also plan to explore the ionization processes of benzene and its derivatives, and possibly H_3^+ (the simplest two-electron molecular system that can support conical intersection and Jahn Teller coupling), which are both achiral.

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[P2] N.J. Strandquist Jr, and J. M. Ngoko Djiokap, "*Reversible electron spiral by chirped attopulses at zero-time delay,*" Phys. Rev. A **106**, 043110 (2022).

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[P4] J. M. Ngoko Djiokap, "Atomic photoionization by multip*le temporal pairs of slits,*" Phys. Rev. A **104**, 013115 (2021).

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"Low-Energy Electron Interactions with Complex Interfaces and Biological Targets"

Award Number: DE-FG02-02ER15337

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Project Scope: The primary objectives of this program are to investigate the fundamental atomic and molecular physics involved in low-energy (5-250 eV) electron as well as soft x-ray (20-650 eV) interactions with polyatomic molecules that have biological relevance and significance. The energy deposition and relaxation pathways involve deep and shallow core ionization, followed by Auger processes and localized energy exchange events such as intra-atomic and inter-molecular Coulomb decay (ICD) and electron transfer mediated decay (ETMD). These ionization and energy exchange channels lead primarily to formation of holes, ejection of low-energy secondary electrons and production of atomic and molecular fragments. The hole transfer probabilities are enhanced by energy resonances and the inelastic scattering cross sections for low-energy electrons are dominated by direct excitation and formation of transient negative ions (TNIs) via shape and core-excited dissociative electron attachment (DEA) resonances. Since these hole transfer and inelastic electron scattering resonances (SRs) lead to bond breaking, they can contribute significantly to ionization induced "radiation damage". Though hole transfer and low-energy electrons are clearly involved in radiation damage of complex molecules, the relative importance of the rates and dynamics of hole transfer, ICD, and the absolute cross sections for forming TNIs, DEA, and SRs are not well known.

Task 1: Time resolved intermolecular Coulomb decay and electron-transfer mediated decay.

The time-resolved electron dynamics involved in intermolecular Coulomb decay (ICD) in complex molecules was investigated theoretically using real-time time-dependent density functional theory (RT-TDDFT) as implemented in the NWChem simulation package [1]. Specifically, RT-TDDFT was used in conjunction with a complex absorbing potential (CAP) to account for the ionized electrons to simulate ICD in a variety of dimer systems including $(H_2O)_2$, $(HF)_2$, H_2O-HF, Ar-H_2O, Ne-H_2O, and Ne-Ar. The simulation protocol for all of the dimer systems followed the same work flow. The starting dimer geometry was obtained from the minimum energy structure of a CCSD(T) / aug-cc-pVQZ calculation. The initial condition for the RT-TDDFT calculation was generated from a ground-state DFT calculation using LC-PBE/d-aug-cc-pVDZ using a tuned range-separation

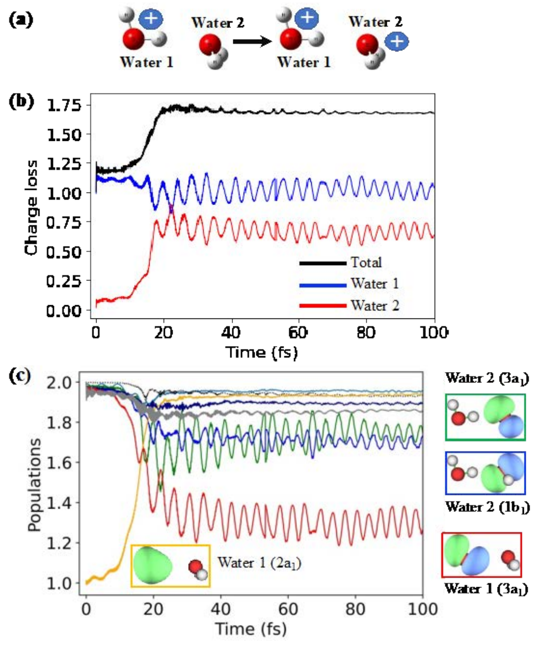

Figure 1. (a) Geometry of the water dimer. (b) The time-dependent charge loss on each water monomer. (b) The population of the localized molecular orbitals on each water monomer.

parameter. The initial hole was generated by manually removing an electron from the desired orbital in the electronic density matrix. Real-time propagation of this non-equilibrium density matrix was then performed for 100 fs using a time-step of ~24 as and a 2nd order Magnus integrator.

Figure 1 presents representative results for the water dimer in which the initial hole was generated in the $2a_1$ (oxygen 2s-like) molecular orbital of water 1; water 1 corresponds to the H-bonding donor in the dimer (Fig. 1a). Figure 1b plots the charge loss on water 1 (blue) versus water 2 (red) and the total charge loss (black) of the dimer. The figure clearly illustrates an increase in charge of the entire system associated with the ionization of water 2, while water 1 remains as a cation. Figure 1c provides more detail indicating that the initial hole in the $2a_1$ orbital on water 1 (orange) is filled from the $3a_1$ state on water 1 (red), while the $3a_1$ (green) and $1b_1$ (blue) states of water 2 are simultaneously ionized. The final state of the dimer system following the electron relaxation dynamics corresponds to two singly ionized water molecules indicative of an ICD process.

We observe similar behavior in all of the hydrogen-bonded systems as well as the Ar-H_2O system indicating that the developed simulation methodology is capable of simulating ICD dynamics in these systems. However, we do find a break-down of the accuracy of RT-TDDFT for Ne-H_2O and Ne-Ar systems, which we attribute to the weaker intermolecular interactions within these systems. Overall, the developed simulation protocol is able to provide accurate and unprecedented detail into the real-time dynamics following inner-valence and core excitations in hydrogen-bonded systems [2]. Current work involves investigating competing pathways associated with electron transfer mediated decay (ETMD) and proton transfer.

The theory work is done in collaboration with Josh Kretchemr (GT). A related experimental collaboration with Thorsten Weber and Dan Slaughter at LBNL has begun that focuses on ICD and ETMD in water dimers, formic acid dimers and water:tetrahydrofuran complexes. Mr. James Zhong, a Georgia Tech. graduate student, was selected this year as a recipient of a DOE SCGSR fellowship to carry out studies on ultrafast energy exchange and charge transfer in hydrogen-bonded dimers and solvated biomolecules at LCLS-II.

Task 2: Spin polarized electron interactions with chiral molecules: Preferential interactions between spin-polarized electrons and chiral molecules is a rapidly growing area of research that could revolutionize nanoscale charge transport and enantioselective molecular synthesis [3]. This phenomenon, typically referred to as chiral induced spin selectivity (CISS), results from coupling between the electron spin state and the quantum spin-polarization field of the chiral molecules [4]. While many experiments have focused on the transmission of un-polarized electrons through a thin molecular film of homo-chiral molecules to produce a high degree of electron spin polarization [5], it is also interesting to determine the damage cross-sections resulting from spin-polarized electron interactions with the chiral molecules. This can be

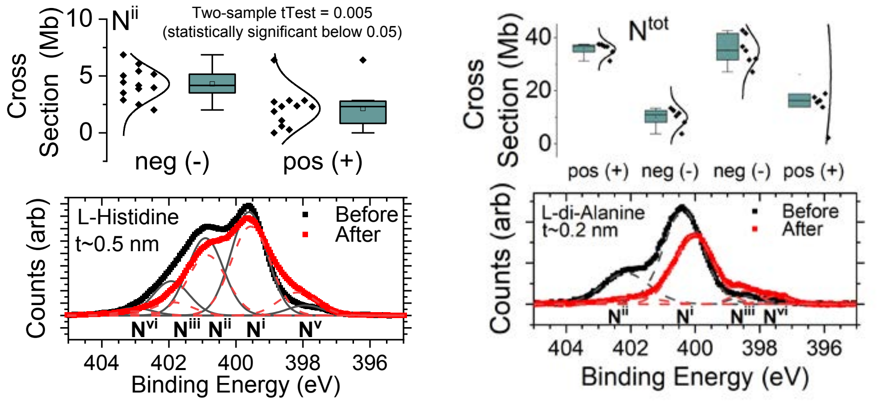

Figure 2. Electron spin dependent damage cross sections and XPS before and after irradiation profiles for L-Histidine and L-di-Alanine

accomplished by exposing a magnetized surface to ionizing radiation to eject secondary electrons from the surface. In a magnetized substrate, where the majority and minority electron spin valence levels are filled unequally, differential scattering cross sections can lead to a net spin polarization of ejected secondary electrons, i.e. spin-polarized electrons (SPE) [6]. The spin-polarization direction of the electron then determines the helicity as it leaves the surface, either positive or negative.

This work was carried out at the Advanced Photon Source at Argonne National Lab and probed the damage of chiral amino acids (L-histidine and L-di-alanine) by SPE ejected from a magnetized cobalt surface. Approximately monolayer thick enantiopure films were vapor deposited and then the surface exposed to 695 eV x-rays to eject SPE. Subsequent interactions with the adsorbed amino acids caused bond breaking and desorption as determined by taking X-ray photoelectron spectroscopy (XPS) spectra as a function of the incident X-ray fluence to monitor the chemical binding states of the N-atoms in the adsorbed molecules. By changing the magnetization direction of the substrate, and thus the preferred spin-polarization direction of the emitted secondary electrons, the differential damage cross-sections for positive vs negative helicity electrons with the enantiopure molecules was determined. Multiple measurements of the damage cross section were made for each electron helicity, and the averages were compared using a two-sample tTest to determine if there was a statistically significant difference. The results for the two amino acids are shown in the images in Figure 2, where the before and after XPS spectra for a single point are given below the box plots showing the statistical distribution of the cross sections determined. The electron helicity was seen to have a large effect on the damage cross section for the L-Histidine molecule where the negative helicity cross section is larger than the positive helicity cross section [7]. Two preliminary N^{tot} damage measurements yield opposite effects which obscure any potential CISS effects. This may be due to thermal desorption of the L-di-Alanine during the experiments. It was noted that the damage cross sections were ~3-4 times larger in L-di-Alanine than L-Histidine. Additionally, the core-levels associated with the molecular zwitterions were more susceptible to secondary electron damage for both molecules, and in Histidine they showed a stronger electron helicity preference than molecules that were directly in contact with the metal surface [7, 8].

Task 3. Time resolved ICD and ETMD in ionic solutions

A collaboration with the AMOP group at Argonne National Lab. on strong-field ionization/time-resolved x-ray transient hole absorption and x-ray emission experiments to examine the dynamics of energy exchange and dissipation in complex solutions containing solvated ions has begun. Initial efforts have focused on LCLS-II beam-time proposals with the Argonne AMOP group.

Future Plans

The future program efforts involve three main tasks that will focus on: 1.) Investigating electron correlated interactions and Coulomb decay channels in condensed molecules and clusters. This includes ICD, ETMD and virtual photon mediated dissociation (VPD). 2.) Probing inelastic electron interactions with hydrated molecules of biological relevance and 3.) Examining correlated interactions, Coulomb decay and electron transfer mediated decay in time-resolved x-ray pump: probe of liquid samples containing solvated ions using LCLS-II.

In addition, the collaboration with LBNL will combine reaction microscopy and ultrafast pump/probe spectroscopy on the Dynamic REAction Microscope (DREAM) at a free electron laser (LCLS-II) to directly observe ICD in a momentum- and time-resolved fashion. This could be representative of radiation damage in bio-systems. To best capture the ultrafast dynamics, two projects are proposed in sequence. First, commission and prepare the DREAM end-station for dimer and pump/probe experiments by collaborating with TMO scientists. Second, establish the interrogation scheme and investigate a smaller dimer system, such as $(N_2)_2$, $(CO)_2$, H_2O-CO, H_2O-rare gas, as a preliminary study in accordance with the current instrumental limitation of low repetition rate (33 kHz) during the startup phase of LCLS-II.

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Presentations acknowledging support from this program

1. "Ultrafast surface science related to radiolysis of oxides - as studied in the IDREAM EFRC", T. M. Orlando, LCLS-II Workshop and User's meeting. Sept. 26, 2023.

SISGR: Structure from Fleeting Illumination of Faint Spinning Objects in Flight

Award Number: DE-SC0002164

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Project Scope

Revolutionary new tools, such as the X-ray Free Electron Laser (XFEL) and the cryogenic electron microsope, represent powerful probes of matter with wide-ranging applications in physics, chemistry, and the life sciences. These unprecedented capabilities offer a powerful means to understand and ultimately control molecular machines and their work cycles at the atomic level and on femtosecond timescales.

To realize their full potential, revolutionary experimental tools must be accompanied by appropriate theoretical platforms. We have developed a powerful data-driven algorithmic platform combining techniques from scattering physics, Riemannian geometry, graph theory, and AI/ML. However, it has proved difficult to quantify the veracity with which information is extracted. We have quantitatively benchmarked the performance of our data-analytical approach against the performance of other leading approaches. The results demonstrate best-in-class performance by our approach (Manifold-EM).

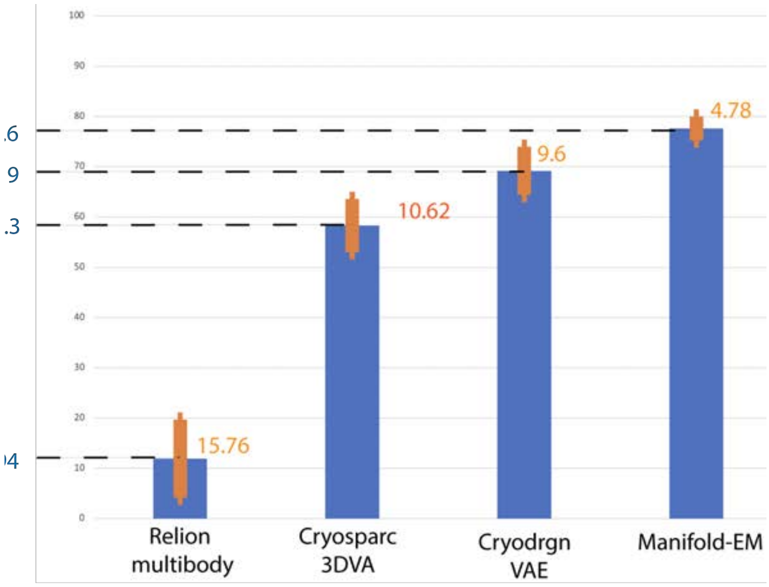

Figure 1: Bar-chart showing on the vertical axis the accuracy values achieved by each of four data-analytical methods, including our approach (Manifold-EM). The red vertical markers represent the error-bars for each data-analytical approach.

Molecular machines undergo continuous conformational motions, a subset of which are functionally relevant. Understanding and ultimately controlling molecular function is predicated on the ability to map and quantify the type and extent of continuous conformational motions and identify the functionally relevant conformational trajectories. For equilibrium and near-equilibrium processes, function proceeds along minimum-energy pathways on one or more energy landscapes, because higher-energy conformations are only weakly occupied. With the growing interest in identifying structure-dynamical trajectories of function, the need for reliable mapping of energy landscapes has become paramount. In response, new data-analytical tools for determining structural variability are emerging. A key question concerns the quantified veracity with which each data-analytical tool can extract functionally relevant structure-dynamical trajectories from a collection of randomy sighted, single-particle snapshots.

Recent Progress

Using synthetic data as independently known ground-truth, we have quantitatively benchmarked the ability of four leading algorithms to determine molecular energy landscapes and identify the functionally relevant conformational paths on these landscapes [1,2]. Such benchmarking is essential for systematic progress toward atomic-level movies of molecular function.

1. Extracting more information from the data

Our algorithms have demonstrated the capability to extract from noisy and highly incomplete experimental data recorded with substantial timing uncertainty, the three-dimensional structure [1,3], conformations [3], energy landscapes [4,5], work cycles [4], and structural dynamics [6] of molecular machines in function [7]. Our latest algorithms have extracted few-femtosecond, atomic-resolution structure-dynamical information from noisy, 99% incomplete snapshots recorded with 100fs timing uncertainty [8]. At the same time, they have extended the complexity of accessible systems from those consisting of ~10 atoms [9] to systems containing more than 2,000 atoms [8]. As the complexity increases exponentially with the number of atoms, our algorithms open new vistas in the study of the ultrafast dynamics of molecular systems.

2. New insights

Our results on the ultrafast atomic-level changes associated with the femtosecond de-excitation dynamics of the Photoactive Yellow Protein (PYP) via a conical intersection [8] reveal previously inaccessible vistas, including oscillatory charge dynamics involving often ignored regions surrounding the chromophore. These results are corroborated by independent spectroscopic measurements of PYP [8, 10]. In addition, our results reveal the structure-dynamical trajectories leading to the vicinity of, and "through", the PYP conical intersection, elucidating the properties of the potential energy surfaces involved in PYP de-excitation [8].

Our machine-learning analysis of experimental data enables simple but 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.

Future Plans

1. **Develop, validate & disseminate a suite of easy-to-use algorithms for extracting ultrafast structure-dynamical information from XFEL data.**

Our current algorithms are designed for use by experts. As such, they offer little non-expert guidance on how the algorithms are to be used. We are developing and disseminating a user-friendly suite of algorithms for extracting structure-dynamical information from noisy, incomplete data recorded with substantial timing uncertainty. The final software platform will include online tutorials for non-expert users. This objective will substantially advance the ability of the broad scientific community to extract information from structure-dynamical data, and understand the structural dynamics of molecular systems. Experience with developing cryo-EM algorithms for non-expert use (see e.g., https://github.com/GMashayekhi/ManifoldEM_Matlab) has shown that successful dissemination entails a substantial effort.

Nonetheless, broad access to a powerful, easy-to-use suite of data-analytical algorithms is expected to transform the nature, extent, and quality of information extracted from hard-won experimental data by the broader Atomic, Molecular, and Optical Sciences (AMOS) community.

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7. Machine-learning Routes to Dynamics, Thermodynamics and Work Cycles of Biological Nanomachines, A. Ourmazd, in **X-Ray Free Electron Lasers: Applications in Materials, Chemistry and Biology**, U. Bergmann, V. Yachandra, and J. Yano, Editors. Royal Society of Chemistry, 418-433 (2017).
8. Few-fs resolution of a photoactive protein traversing a conical intersection, A. Hosseinizadeh, N. Breckwoldt, R. Fung, R. Sepehr, M. Schmidt, P. Schwander, R. Santra, and A. Ourmazd, **Nature** 599, 7886, 697-701 (2021).
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2. Energy landscapes from cryo-EM snapshots: a benchmarking study, R. Dsouza, G. Mashayekhi, R. Etemadpour, P. Schwander, and A. Ourmazd, **Scientific Reports** 13, 1372 (2023).
3. Dynamics retrieval from stochastically weighted incomplete data by low-pass spectral analysis, C. M. Casadei, A. Hosseinizadeh, G. F. X. Schertler, A. Ourmazd, and R. Santra, **Structural Dynamics** 9, 044101 (2022).
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8. A glycan gate controls opening of the SARS-CoV-2 spike protein, T. Sztain et al., **Nature Chemistry** 13 963-968 (2021).
9. Selecting XFEL single-particle snapshots by geometric machine learning, E. Cruz-Chu et. al., **Structural Dynamics** 8, 014701 (2021).
10. 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, Vol. 6 (2021).

Control of Molecular Dynamics: Algorithms for Design and Implementation

Award Number: DE-FG02-02ER15344

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A. Program 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 has 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 addresses several key topics in this regard. For example, progress in this area has been hindered by the prohibitive cost of large-scale many-body quantum dynamics simulations needed to explore the principles and possibilities of molecular control. However, the emergence of nascent quantum-computing devices suggests that efficient simulations of many-body quantum dynamics, especially, based on the variational principle in conjunction with artificial neural networks in machine learning, may be on the horizon. The chemical dynamics opportunities that such nascent devices offer will continue to be a focus of our research. Notwithstanding, we have always been interested in taking a control perspective in the wider chemical-physical sciences and the ensuing practical implications. This line of research has been fruitful and will continue. Importantly, 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. During the current DOE grant period, from November 2022 to August 2023, a broad variety of research topics were pursued in the general area of understanding and controlling quantum dynamics phenomena as well as additional topics of fundamental importance in chemical system modelling and high value application of control concepts in chemistry outside of the quantum regime. A summary of these accomplishments is provided below.

B. Recent Progress:

During the current DOE grant period, from October 2022 to September 2023, 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] <u>Quantum tracking control of the orientation of symmetric top molecules:</u> In this study, we have generalized our earlier work on singularity-free quantum tracking control of a linear rigid rotor orientation in 2D to the task of tracking the orientation of symmetric top molecules in 3D. The goal of quantum tracking control is to identify shaped fields to steer observable expectation values along designated time-dependent tracks. In principle, these fields can be determined via an iteration-free procedure, by directly inverting the underlying dynamical equations governing the controlled observables. To this end, we have derived equations for the control fields capable of directly tracking the expected value of the 3D dipole orientation vector along a desired path in time. We showed this framework can be utilized for tracking the orientation of linear molecules as well, and present numerical illustrations of these principles for symmetric top tracking control problems. **[2] <u>Machine learning of quantum control utilizing artificial neural networks:</u>** In this work, we have formulated an efficient supervised learning method to train artificial neural-network (ANN) many-body quantum states in real time, aiming to mitigate two prevalent errors that often hinder the efficacy of time-dependent variational Monte Carlo method. Specifically, we performed minimization of the distance between the parameterized ANN quantum state and the evolved many-body quantum states, which is calculated *a priori* using an accurate short-time propagator at each time step, in a sequence of small occupied submanifolds within the full many-body Hilbert space. The corresponding short-time unitary propagator for evolving the quantum state in small time steps is approximated by an accurate 2nd-order Taylor series. We demonstrated the high accuracy and stability of this new method in learning the controlled dynamics of 2D Heisenberg lattices. Our simulations of 4x4, 6x6, and 8x8 2D lattice systems showed that the necessary number of ANN parameters for accurate learning of evolving states increases cubically with the number of spins in the system. **[3] <u>Deprotonation of phenol linked to a silicon dioxide surface using adaptive feedback laser control with a heterodyne detected sum frequency generation signal</u>**: In this work, we demonstrated successful laser control of a surface reaction by combining the adaptive feedback control (AFC) technique with surface sensitive spectroscopy to determine the optimally shaped laser pulse. Specifically, we demonstrated laser induced deprotonation of the hydroxyl group of phenol bound to a silicon dioxide substrate. The experiment utilized AFC with heterodyne detected vibrational sum frequency generation (HD-VSFG) as the surface sensitive feedback signal. The versatile combination of AFC with HD-VSFG provides a route to potentially control a wide range of surface reactions. **[4] <u>Chemically Sensitive Fluorescence Imaging of Colliding Microdroplets:</u>** We showed a simple optical capability for generating spatially resolved chemical concentration maps of mixing fluids using a chemically sensitive dye, 1-hydroxy-3,6,8-pyrenetrisulfonic acid, detected by planar laser induced fluorescence. To demonstrate an application of this capability, we have investigated the collision and mixing of a pair of microdroplets in air. The two microdroplets were composed of different fluids, methanol and water, with the dye initially in the methanol droplet. When the droplets collide and mixing process develops, the fluorescence of the dye shifts from blue to green as the solvent environment changes. A series of spectral-temporal images of the collision and subsequent mixing were recorded, from which we extracted the distribution of the two intermixing droplet species reflected in the spatially resolved dye spectra. These images revealed material transfer between droplets in both coalescing and non-coalescing droplet collisions. **[5] <u>The Surprising Ease of Finding Optimal Solutions for Controlling Nonlinear Phenomena in Quantum and Classical Complex Systems:</u>** In this work, we addressed the often-observed surprising ease of achieving optimal control of nonlinear phenomena in quantum and classical complex systems. The circumstances involved are wide-ranging, with scenarios including manipulation of atomic scale processes, maximization of chemical and material properties or synthesis yields, Nature's optimization of species' populations by natural selection, and directed evolution. Specifically, we presented a conjecture, based on present findings, that the systematics of readily finding good outcomes from controlled phenomena may be unified through consideration of control landscapes with the same common set of three underlying assumptions: the existence of an optimal solution, the ability for local movement on the landscape, and the availability of sufficient control resources whose validity needs assessment in each scenario. The overarching observation is that only relatively short searches are required despite the common high dimensionality of the available controls in typical scenarios. **[6] <u>The Early Era of Laser-Selective Chemistry 1960~1985: Roots of Modern Quantum Control:</u>** This study showed that the roots of quantum control may be linked to endeavors to manipulate chemical reactions with lasers and thus reaches as far back as the invention of the laser in 1960. Physicists revolutionized the scientific world when they invented the laser in 1960. During the next two decades, fruitful interplay occurred between theoreticians and experimentalists seeking progress in laser-selective chemistry. In the Early Era, defined as

1960~1985, scientists gradually realized the immense complexity of the problem of performing tailored manipulations at the molecular scale. These efforts opened the doors to a new, broader scientific field of research called quantum control which developed in the Modern Era, defined as ~1985 to the present time. **[7] <u>Efficient Hamiltonian encoding algorithms for extracting interfering pathway amplitudes in the Dyson series:</u>** In this work, we have developed two new Hamiltonian encoding algorithms for revealing the mechanism behind the dynamics governing controlled quantum systems. These new algorithms calculate the amplitudes of pathway classes by using techniques from graph theory and algebraic topology to exploit patterns in the set of allowed transitions, greatly reducing the number of transitions to be modulated. Moreover, they were shown to provide an exponential decrease in both computation time and memory utilization with respect to the dimension of the system. To demonstrate the use of these techniques, they were successfully applied to two illustrative state-to-state transition problems. **[8] <u>The Top-Manifold Connectedness of Quantum Control Landscapes:</u>** In this work, we explored the topology of the top manifold of quantum control landscapes, via large-scale optimal control simulations. The control of quantum systems has been proven to possess inherently trap-free optimization landscapes under proper assumptions. Specifically, we randomly sample a plurality of optimal controls in the top manifold and employed special algorithms to assess if a continuous path can link two arbitrary solutions. It was shown that, within all tested examples, such a continuous path can always be found, implying that the top manifold is path-connected. The importance of this finding opens up the possibility to simultaneously optimize ancillary multiple objectives using the top manifold as control resources while maintaining full fidelity of the original goal that defined the landscape.

C. Future Plans:

In the coming year, **(1)** we plan to study the dispersion and "volume" of saddles in control space to reveal their nature and significance for quantum control performance. This will allow us to examine the previously observed serendipitous ability to locate special initial fields that permit climbing quantum control landscapes along a straight path to the highest fidelity. We also plan to further examine, both theoretically and numerically, the top of quantum control landscapes corresponding to where a primary physical objective achieves its optimal value. **(2)** We plan to accelerate simulations for many-body quantum dynamics under control by building on our initial research in this area to use special artificial neural network (ANN) tools, not for their traditional use with “big data”, but rather to deal with the “big quantum equations” involved. Our preliminary research indicates that a suitable synergism of dual use of ANN and Schrödinger equation can compress quantum systems for efficient construction of an effective "working space" for a particular many-body system. The goal here is to convert the traditional forbidding exponential scaling of the dynamics with respect to the number of particles to now have comfortable polynomic scaling by exploiting the compressed quantum dynamics working space. **(3)** We plan to perform mechanism analysis utilizing algorithms customized to quantum control applications. Our preliminary research has shown the feasibility of reaching this goal through expressing the mechanism in terms of a hierarchy of quantum interfering pathways. A like procedure will be considered for control experiments taking into account the prior determined optimal control and ideally interpreting the encoded→decoded experiments physically without the need for dynamical modelling. The laboratory form of the algorithm will encode the field and decode the observables. The new research will expand the algorithmic tools to increase their efficiency and enable them to treat a variety of physical scenarios for assessing the mechanism of controlled quantum dynamics.

D. Peer-Reviewed Publications Resulting from this Project (2021-2023):

[1] 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).

[2] 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).

[3] Multilevel 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).

[4] Optimization landscape of quantum control systems, X. Ge, R.-B. Wu, and H. Rabitz, Complex System Modeling and Simulation, 1, 77 (2021).

[5] 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).

[6] Progress toward favorable landscapes in quantum combinatorial optimization, J. Lee, A. B. Magann, H. Rabitz, and C. Arenz, Phys. Rev. A. 104, 032401 (2021).

[10] The Promise of Mutation Resistant Drugs for SARS-CoV-2 that Interdict in the Folding of the Spike Protein Receptor Binding Domain, F. Bergasa-Caceres and H. Rabitz, COVID (MDPI), 1, 288-302 (2021).

[11] Optimization Landscape of Quantum Control Systems, X.-Z. Ge, R.-B. Wu, and H. Rabitz, IEEE-CSMS, 1, 77-90 (2021) (June 2021).

[7] Selective photo-excitation of molecules enabled by stimulated Raman pre-excitation, Y. Wang, F. Laforge, A. Goun, and H. Rabitz, Phys. Chem. Chem. Phys., **24**, 10062, DOI: 10.1039/d2c00868h, (2022).

[8] Sequential optical response suppression for chemical mixture characterization, A. Magann, G. McCaul, H. Rabitz, and D. Bondar, Quantum, **6**, 626 (2022).

[9] A Generalized Kernel Method for Global Sensitivity Analysis, J. Barr and H. Rabitz, J. Uncertainty Quantification, 10, 27-54 (2022).

[12] The optimization landscape of hybrid quantum–classical algorithms: From quantum control to NISQ applications, X. Ge, R.-B. Wu, and H. Rabitz, Annual Reviews in Control, in press (2022).

[13] Deprotonation of phenol linked to a silicon dioxide surface using adaptive feedback laser control with a heterodyne detected sum frequency generation signal, A. Goun, E. Frederick, A. Er, S. Bernasek, and H. Rabitz, Phys. Chem. Chem. Phys., 24, 19443 (2022).

[14] Chemically Sensitive Fluorescence Imaging of Colliding Microdroplets, Z. Quine, A. Goun, F. Laforge, H. Rabitz, and C. K. Law, Phys. Fluids, 35, 052002 (2023).

[15] Kernel-Based Global Sensitivity Analysis obtained from a Single Data Set, J. Barr and H. Rabitz, Reliability Engineering & System Safety, 235, 109173 (2023).

[16] The Early Era of Laser-Selective Chemistry 1960~1985: Roots of Modern Quantum Control F. O. Laforge, J. Lee, and H. Rabitz, J. Phys. Chem. Lett., 14, 5283-5296 (2023).

[17] The Surprising Ease of Finding Optimal Solutions for Controlling Nonlinear Phenomena in Quantum and Classical Complex Systems, H. Rabitz, B. Russell, and T.-S. Ho, J. Phys. Chem. A (2023).

[18] Quantum tracking control of the orientation of symmetric top molecules, A. B. Magann, T.-S. Ho, C. Arenz, and H. Rabitz Phys. Rev. A in press (2023).

"Atoms and Ions Interacting with Particles and Fields"
Award No. DE-SC0012193

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Program Scope

This theory project focuses on the time evolution of systems subjected to either coherent or incoherent interactions represented by fields and particles, respectively. This study is divided into three categories: (1) correlations between two electrons in highly excited states or in double continua, (2) processes for one electron in time dependent or non-separable potentials, and (3) the interaction of atomic electrons with strong electromagnetic fields. Some of the techniques we developed have been used to study collision processes in ions, atoms, and molecules. In particular, we have used these techniques to study the correlation between two (or more) continuum electrons and electron impact ionization of small molecules.

Recent Progress (Publications 10/2022-9/2023)

X-ray physics: The graduate student Akilesh Venkatesh led a project, Ref. [3], to understand the possibility for imaging electron wave packet dynamics using pulsed x-ray scattering. In previous work, we demonstrated a method for modeling non-linear Compton scattering. We then extended these programs to simultaneously include photons of frequency ω and 2ω to investigate the phase difference that appears in the interference term between these indistinguishable processes. In the new work, Akilesh led a project to investigate the possibility for detecting properties of electron wave packets using pulsed X-rays. To study the properties of a wave packet, the probe must have a duration smaller than the timescale of the electronic superposition. If the X rays themselves are pulsed, then the scattering can depend on the phases of the different components of the electron wave packet. Akilesh used the numerical programs developed in the previous work to calculate the scattering probabilities for different electron wave packets. The goal was to understand what properties of the electron wave packet can be probed with a pulsed X-ray beam. We showed that the x-ray scattering pattern reflects the weighted Fourier transform of the instantaneous electronic wave function if the electronic state of the atom/molecule can be measured after scattering. We explored several cases for the initial electronic wave packet and detected final electronic states to gain an idea of what properties can be detected.

Thermalization in lineland: When two identical particles collide in 1D, they simply exchange their velocities. This means that the usual mechanism for thermalization in gases (collisions between pairs of particles) does not work in 1D. The main thermalization at low density must be through the collision between three particles. A graduate student, Mohamed Eltohfa, and two undergraduates, Colton Griffin and Xinghan Wang, investigated this process for short range interaction potentials and classical particles. We developed a classical scattering matrix that controls the rate that a particle scatters from the range between v and v+dv to the range between v' and v'+dv. We derived scaling rules for the scattering where the rates are governed by three dimensionless quantities. We also carried out molecular dynamics simulations for many particles to demonstrate the effectiveness of the scattering theory. We have completed the computational part of this project and Tohfa is writing the manuscript which will be submitted to Phys. Rev. E.

There were two graduate students supported by this grant during the past year. Akilesh Venkatesh started research in January 2019 and very quickly come up to speed. He finished three 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 graduated December 2022 and is currently a postdoc at Argonne National Laboratory working with Phay Ho. Mohamed Eltohfa started research in January 2023 working on the thermalization in lineland project. He has finished most of the computational part of the project and is in the process of writing a manuscript for submission to Phys. Rev. E.

Future Plans

Electron collisions in a laser field: The collision of an electron with a neutral atom or charged ion can lead to purely elastic scattering as well as absorption or emission of photons during the scattering process. In certain geometries, the photon absorption/emission is suppressed. The calculated and measured cross sections for the suppressed geometries can differ by more than an order of magnitude. We will perform calculations using variational quantum scattering methods to understand the source of this discrepancy.

Thermalization in lineland: We will attempt to extend the calculation of thermalization in 1D to include quantum mechanical effects. The three particle collisions which are the basis of the calculation of the scattering matrix reduces to a 2D quantum system in center of mass coordinates. The main difficulty will be in formulating the equations to extract the appropriate scattering parameters.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

[1] Akilesh Venkatesh and F. Robicheaux, “Interference in nonlinear Compton scattering using a Schrodinger-equation approach,” Phys. Rev. A **103**, 013111 (2021).

[2] 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).

[3] Akilesh Venkatesh and F. Robicheaux, “Simulations for x-ray imaging of wave packet dynamics,” Phys. Rev. A **106**, 033125 (2022).

Light-induced couplings to study and control electronic interactions and electron-nuclear dynamics

Award Number: DE-SC0018251
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Project Scope

This project investigates the light-induced couplings to study and control the correlated and coupled electron and nuclear dynamics in atoms and molecules. Tunable wavelength, multi-pulse, pump-probe techniques, using XUV, NIR, and MIR fields, are employed to study the electronic processes. Attosecond transient absorption spectroscopy, four-wave-mixing, and velocity map imaging, are the main experimental techniques utilized on this project. Specific research topics include 1) optical control of electronic excitation and relaxation, 2) light induced control of coupled electron-nuclear dynamics, 3) study of coherent charge migration. The wide range of tunable laser fields available for this project enable a systematic study of resonant and non-resonant couplings, leading to new strategies for controlling few-body dynamics. The use of multi-pulse schemes provides new control possibilities while also providing means to disentangle the role strong fields in traditional XUV-IR experiments. Attosecond soft-x-ray pulses will provide elemental sensitivity in the study of correlated charge dynamics.

Recent Progress

We employed multi-wave-mixing and transient absorption to probe electron dynamics and electron-nuclear couplings. In contrast to the traditional approach, our tunable attosecond transient absorption employs an independently adjustable IR probe frequency to resonantly drive or detune the light-induced couplings between excited states. We used these capabilities to control the formation and decay of autoionizing polaritonic states. We conducted photoelectron interferometry to understand the impact of short-range electron-core interactions on the phases of quantum beats in two-color ionization. We extended the four-wave-mixing to high-order non-linear mixing processes to probe the excited state dynamics. Furthermore, we observed the possibility of using the Rydberg electron interaction to probe conical intersection dynamics in polyatomics. Collaborations with UCF, Berkeley, and Purdue groups have been vital in this project.

Optical control of autoionization dynamics:

Previously we demonstrated controlled stabilization of an atom against ionization through the destructive interference in the ionization pathways of the polaritons (PRL **127**, 023202 (2021)). Continuing our work, we explored the parameter space of intensity, polarization, frequency, and time-delay to study entangled, autoionizing, light-matter states. Specifically, the tunability of the dressing-IR field allows us to manipulate the interactions between the $3s^{-1}4p$ bright autoionizing states and the light-induced one-photon and two-photon counterparts of the dark autoionizing states ($3s^{-1}3d$, $3s^{-1}5s$, and $3s^{-1}4f$) in argon, thus leading to the formation of up to four polaritonic branches at high intensities. We varied the photon energy and intensity of the control IR pulse to systematically explore the parameter space and observed excellent agreement with *ab initio* simulations by Argenti group at the University of Central Florida. Both experiment and theory show that polaritonic splitting increases with the laser intensity. By changing the IR frequency, we controlled the resonant couplings and thus the number of polaritonic branches observed in both experiment and theory. These results were published in PRA 105, 063107 (2022). By selectively including states in simulations, we identified each polaritonic interactions and observed the avoided crossings between branches. We aim to extend these studies to molecular systems, where autoionization is governed by multielectron interactions, and is also accompanied by nuclear dynamics, leading to correlated interplay between electronic and nuclear degrees of freedom.

<u>High-order non-linear mixing to probe excited states</u>:

Non-linear interactions such as four-wave-mixing have become instrumental in attosecond XUV spectroscopy. Using XUV high harmonics in conjunction with collinear NIR and MIR fields, we extended this approach to high-order-mixing between various colors. Specifically, we find that atomic resonances in neon exhibit a significant cross section for six-wave mixing. The MIR probe frequency tunability in our multicolor scheme is employed to access several optically dark resonances and probe the quantum beat of a coherent electronic wavepacket using background-free XUV emission as a diagnostic (Figure 1). These results were published in Optics Express 30, 46520 (2022). This technique can be easily extended to other atomic and molecular systems, and opens the door to multi-dimensional non-linear spectroscopy, which can probe coherences and non-adiabatic couplings between the excited states.

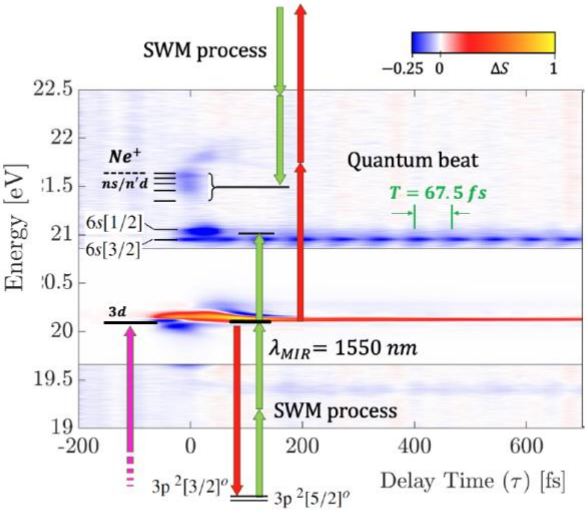

Fig. 1 A differential spectrogram for three-color mixing, where simultaneous XUV and NIR pulses pump neon while a delayed MIR probe leads to six-wave-mixing emissions from the 6s doublet and ns/nd' Rydbergs. Former shows quantum beat stemming from the intermediate 3p doublet separation.

We have also conducted XUV-IR wave mixing study for the doubly excited states of Krypton. Specifically, we found that there exist several doubly excited states around 24 eV, however their electronic configurations are yet to be identified. Using four-wave-mixing, we observed XUV emission that shows beating with a time-period matching the energy difference between a singly and a doubly excited state. The interference between these two pathways is mediated by other resonant states and involves multi-electron transitions. The identification of doubly excited states requires a full R-matrix treatment, and we are working with our collaborators to study these states.

<u>Electron-core interactions and the phase of quantum beats in ionization</u>:

Time-resolved photoelectron interferometry has been proven to be an effective tool to measure the quantum beats of electronic wave packets in atoms and molecules. The energy dependence of beat signals in the continuum has been used to characterize the amplitudes and phases of ionization pathways in a variety of systems, involving multicolor ionization pathways, strong-field modification of the electronic structure, and correlated electron dynamics. Our study was motivated by the desire to understand how short-range interactions between the outgoing electron and the ion core manifest in the phase of the quantum beats.

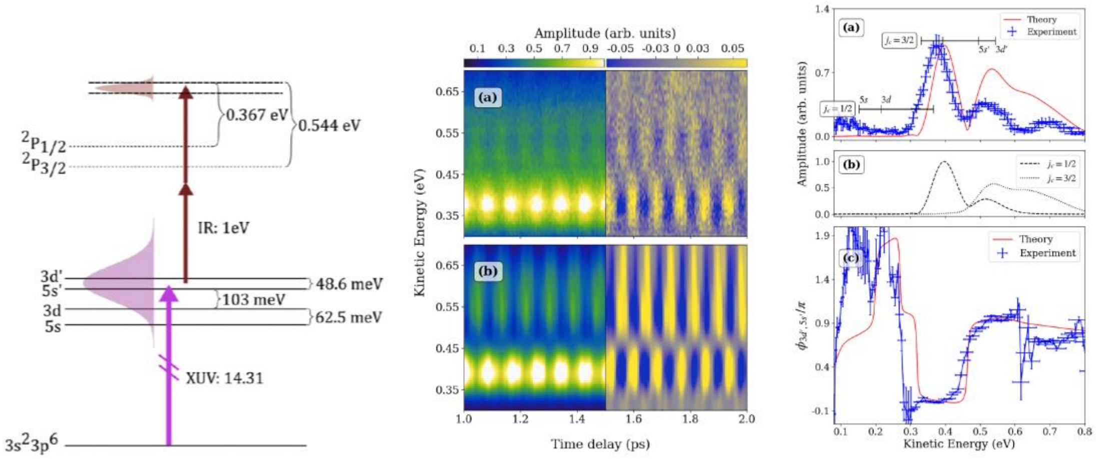

Fig. 2. Tunable two-photon ionization of XUV excited 3d-5s wavepacket in Argon. The experiment (top) and theory (bottom) show quantum beating in two spin-orbit split ionization channels. Two beat signals show a phase difference, which is attributed to the short range electron-core interactions.

We apply two-color photoelectron interferometry to investigate a wave packet composed of the excited states of argon, as illustrated in Figure 2. We created a 3d-5s electronic wavepacket in Argon with XUV attosecond pulse train and ionized it through two-photon interaction with a tunable IR. Outgoing electron wavepacket interferes in the continuum, leading to a quantum beat at the energy difference between 3d and 5s states. However, the argon ion features a double continua due to spin-orbit splitting of 180 meV, with the ion's $j_c = 3/2$ ground state and the $j_c = 1/2$ excited state lying 15.76 eV and 15.94 above the neutral ground state, respectively. We observed that the quantum beat occurs in both continua, but the two beats are not in 'in-phase'.

To understand the origin for this phase difference we collaborated with Chris Greene group at Purdue to perform MQDT analysis and calculate time-dependent beat signals. Comparison of theoretical simulations with the experimental measurements allowed us to interpret the amplitudes and phases of ionization signals. We expressed the observed phase differences in terms of the off-diagonal elements of the short-range scattering matrix and the dipole matrix elements to the continuum eigenchannels. Thus, we were able to understand the origin of the phase difference in the quantum beats, and this can serve as an important tool to investigate electron-core interaction during the ionization process. These results were published in PRA 108, 033107 (2023). As a next step, we will analyze the angular anisotropy parameters in the ionization channels to obtain additional insights into the electron-core interaction dynamics.

<u>Probing conical intersection dynamics through Rydberg electron probing:</u>

To pursue the study of coupled electron-nuclear dynamics and the light induced modification of conical intersections, we employed transient absorption to study the Rydberg series near the conical intersection formed by the $A^2\Pi_u$ and $B^2\Sigma_u^+$ electronic states of CO_2 molecular ion. We used the 11th harmonic to excite these states and observed the signature of several members of the Henning sharp and diffuse series converging to the B ionic limit (Figure 3). This system constitutes a Rydberg electron attached to an ion core that has an electron hole driven between the σ and π orbitals by the bending and asymmetric stretch vibrations of the molecule. The loosely bound Rydberg electron undergoes autoionization, and as expected, the experimental results show that higher Rydberg states exhibit longer lifetimes. Interestingly, when the autoionization lifetime is substantially long, we find that the transient absorption exhibits an oscillatory signal on the timescales of 110 fs. This timescale is similar to the conical intersection dynamics timescale that we had observed in our previous studies utilizing dissociation as a probe channel. These results indicate that Rydberg electron can be a sensitive probe of the non-adiabatic dynamics in the molecular core. By differentiating the signal from different Rydberg states, we also hope to understand how the interaction with outer electron modifies the conical intersections dynamics in the ion core.

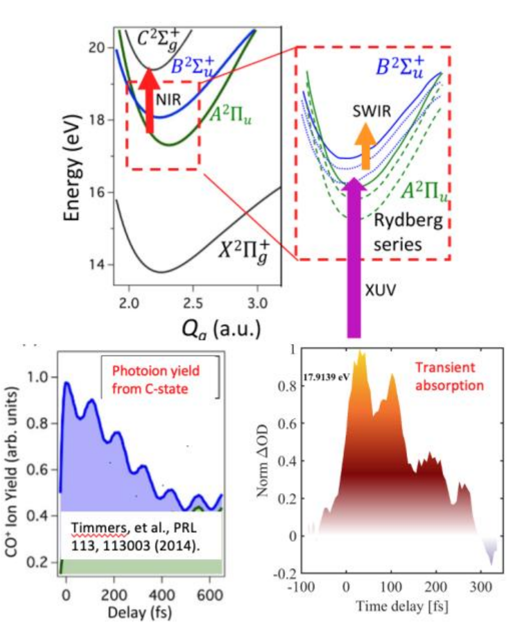

Fig. 3. Attosecond transient absorption study in CO_2 to probe the Henning sharp and diffuse Rydberg series members converging to the B ionic state that forms a conical intersection with the A ionic state. The transient absorption signal shows oscillations like the previously observed ion-yield signals for the conical intersection dynamics.

Future Plans:

We will continue our efforts towards light-induced control multielectron interactions and electron-nuclear couplings. Apart from working with neutral and metastable systems, we will also explore electron dynamics associated with the ionic states of atoms and molecules. With the new laser system, we can reach higher XUV photon energies, allowing us to conduct elementally specific probing of charge dynamics in complex molecular systems.

Peer-Reviewed Publications Resulting from this Project (2021-2023)

1) Nathan Harkema, Coleman Cariker, Eva Lindroth, Luca Argenti, Arvinder Sandhu, “Autoionizing Polaritons in Attosecond Atomic Ionization”, Phys. Rev. Lett. **127**, 023202 (2021).
2) 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).
3) Sergio Yanez-Pagans, Coleman Cariker, Moniruzzaman Shaikh, Luca Argenti, Arvinder Sandhu, “Multipolariton Control in Attosecond Transient Absorption of Autoionizing States”, Physical Review A 105, 063107 (2022).
4) Islam Shalaby, Nisnat Chakraborty, Sergio Yanez-Pagans, James Wood, Dipayan Biswas, Arvinder Sandhu, “Probing ultrafast excited-state dynamics using EUV-IR six-wave-mixing emission spectroscopy”, Optics Express 30, 46520 (2022).
5) Alexander Plunkett, James K. Wood, Miguel A. Alarcon, Dipayan Biswas, Chris H. Greene, Arvinder Sandhu, High resolution metrology of autoionizing states through Raman interferences, Journal of Physics: Conference Series, 2494, 012003 (2023).
6) Miguel A. Alarcón, Alexander Plunkett, James K. Wood, Dipayan Biswas, Chris H. Greene, and Arvinder Sandhu, “Quantum beats in two-color photoionization to the spin-orbit split continuum of Ar”, Phys. Rev. A 108, 033107 (2023).

Coherent Probes of Molecular Charge Migration

Science Using Ultrafast Probes: DE-SC0012462

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Project Scope

In the field of ultrafast science, the initiation and detection of charge migration (CM) stands out as an important milestone. This correlation driven, multi-electron response may result when a molecule is forced out of equilibrium by rapid ionization or excitation. The electrons react first, over timescales approaching the attosecond, with the nuclei following on the femtosecond scale, potentially leading to a host of downstream physical or chemical processes such as dissociation, charge transfer and photoelectric energy conversion. Given its ubiquitous and fundamental role, the ability to accurately predict, observe, and potentially control CM stands out as a key goal for ultrafast science. With continued advances in experimental and theoretical tools and techniques, significant progress is being made toward computing and measuring the full evolution of CM-based dynamics, from the primarily electronic response reflected by attosecond changes in the local charge density, to femtosecond coupled electronic-nuclear dynamics. Indeed, reaching this important milestone has become a significant driver of cutting-edge experiment and theory in AMO science.

Since 2015, the ATTO-CM network has worked to establish itself as a resource on fundamental questions related to both the nature of CM in specific families of functionalized molecules, and on the development of experimental techniques needed for its observation. This has been enabled by our emphasis on taking an integrated approach, blending theory and experiment in all phases of the research, as illustrated in Figure 1. The objective of the ATTO-CM team is to advance ultrafast science in the US both at the university laboratory scale and at large facilities, using a concerted effort of theorists and experimentalists. Our emphasis is on the implementation of time-resolved probes of CM, and its interplay with nuclear dynamics, in gas and liquid phases using a versatile toolbox of experimental techniques to initiate and measure CM dynamics. Our ultimate goal is to develop experimental probes that can provide direct access to specific time-resolved information in chemical systems. 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.

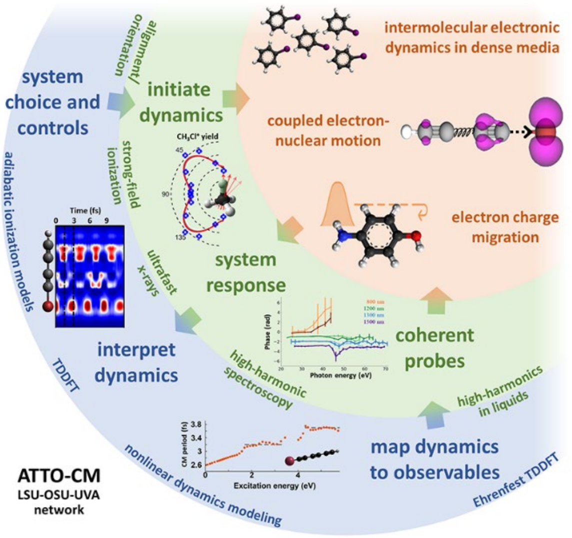

Figure 1: How theory and experiment interact in the ATTO-CM network to address fundamental aspects of charge migration (center). Blue band: theoretical tools; Green band: coherent probes and measurements.

Recent Progress

In our effort to understand and observe CM with ultrafast light fields we have focused on three main thrusts: “Mechanisms of charge migration”, “Time resolving charge migration dynamics”, and “Expanding the charge migration toolbox”. 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: Mechanisms of charge migration* – We have completed our work on the chemical functionalization of bromobezene deriviates as it relates to CM [Folorunso 2023]. Our findings demonstrate that this type of para-functionalization has only a minor effect on the CM period but has a major effect on hole contrast, *i.e.*, how much charge migrates through the molecule. Building on our previous work on elucidating an “attochemistry” picture of CM, we investigated the role of lone pair electrons in CM. Our results show that the lone pair picture can also be used to qualitatively predict CM, furthering the concept that a set of fundamental chemistry principles underlie CM. Finally, we have shown that the tools of nonlinear dynamics can be employed in the TDDFT framework to study CM. This may result in efficient high order time propagation schemes [Mauger 2023] to investigate the effects of nuclear motion on CM.
2. *Thrust 2: Time resolving charge migration dynamics* – We have expanded our investigation of CM using HHG to coherently probe the types of periodic CM modes identified in Thrust 1. Taking the example of aligned bromobutadiyne (BrC_4H) undergoing CM, we have demonstrated numerically that we can track the location of the hole along the molecular backbone at a given time using frequency matched sideband spectroscopy [Hamer 2023]. To further the study of CM in molecular systems, we have begun to use attosecond pulses produced via HHG using a 400-nm driving wavelength, allowing us to separate multiple ionization channels within the RABBITT sidebands. The OSU node has continued their collaboration on experiments aimed at measuring CM in aminophenol using isolated attosecond pulse pairs produced at LCLS. Results in the para-aminophenol isomer have revealed a time-dependent resonant absorption, and CM is the most likely explanation of this time dependence. Moving beyond the gas phase, we have broadened our experimental investigations to include attosecond spectroscopy using liquid-phase HHG and have begun a theoretical effort that includes molecular dynamics simulations in addition to TDDFT.
3. *Thrust 3: Expanding the charge migration toolbox* – The ATTO-CM team continues to explore strong-field ionization (SFI) as a pump and probe of CM. One barrier to using this experimental protocol is the cost of obtaining highly accurate angle-dependent rates. We have developed approximate techniques that can provide angle-dependent SFI rates with reasonable accuracy at a fraction of the traditional cost [Wahyutama 2022], which has resulted in new quantum chemistry tools that will be available to the community at large. On the experimental side, have been making critical equipment upgrades at UVA to enable tests of new approaches for detecting CM through frequency-matched ionization and dissociative ionization. The new experiments will seek to initiate and probe CM using SFI for the pump and probe steps in a single-ionizing pulse.

Thrust 1: Mechanisms of charge migration

Thrust 1 of the ATTO-CM network uses first-principles simulations to discover how CM occurs in molecules and what properties regulate it. Through these, the LSU node aims to determine the relationship between structure and CM in organic molecules. Some of the key questions we are investigating include: Which types of experimentally practical molecules support CM? How does chemical functionalization affect CM? How can these dynamics be understood using (atto)chemistry principles? Progress in Thrust 1 continues to be instrumental in shaping recent and future research directions in the other two Thrusts of the network.

Attochemistry regulation of charge migration: In the last year of this project, we completed and published our work on how chemical functionalization of bromobezene deriviates modulates CM [Folorunso 2023]. Building on our previous work on the effects of bonding, length, and halogen functionalization on CM in quasilinear molecules [Folorunso 2021], we use real-time time-dependent density-functional theory (TDDFT) with basis sets and hybrid exchange-correlation functionals to simulate CM. We start the migration using constrained DFT [Eshuis 2009], which emulates a sudden-ionization approximate initial state. Our findings demonstrate that this type of para-functionalization has only a minor effect on CM time but has a major effect on hole contrast, *i.e.*, how much charge migrates through the molecule. This modulation of the contrast correlates with the Hammett parameter for the functional group which, broadly speaking, suggests that the electron donating strength of a group dictates the mobility of the CM mode. Thus, strong electron donors such as amines (-NH_2) make excellent candidates for future CM study.

Recently, we have also performed simulations to determine the role of the orientation of lone pair electrons on CM. This builds on our previous studies where CM was observed to occur via hopping in a molecule's π system [Folorunso 2021]. Specifically, we investigated the effect of lone-pair electrons in the bromoacetylene (Br-C≡C-R, R=acceptor group) family of functionalized molecules as a simple representative example. In all the cases we considered, we find that the CM occurs via hopping from (i) a p-shaped hole on the halogen, to (ii) above and below the C≡C triple bond (*i.e.*, the π bond), and finally into (iii) the region of space on the acceptor that corresponds to the location of the lone pair electrons. Figure 2 illustrates this hopping from the halogen to the lone-pair electrons for the Br-C≡C-NO_2 molecule, with the hole ultimately ending localized on the -NO_2 group on the four equivalent lone pair sites. This has significant interpretive and predictive utility. Lone pair electrons can loosely be thought of as a localized density representation, which is useful for predicting bonding and geometry. Somewhat surprisingly, our results show that the lone pair picture can also be used to qualitatively predict CM, furthering the concept that a set of fundamental “attochemistry” principles likely underlie CM.

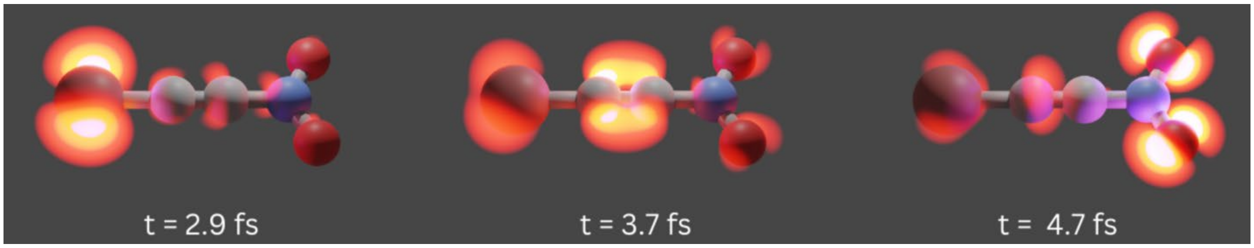

Figure 2: Snapshots of the hole density during CM in 1-bromo-2-nitroethyne (Br-C≡C-NO2). The CM occurs via hopping from (left) the halogen, into (middle) the C≡C triple bond, then finally on to (right) the oxygen atoms in the nitro group. At 4.7 fs the hole occupies regions of space corresponding to the locations of the lone pair electrons. This suggests that lone pairs act as hole acceptor sites in CM.

Efficient numerical schemes for TDDFT simulations: Following our initial success with using nonlinear dynamics tools to study CM [Mauger 2022], the LSU node has detailed the canonical Hamiltonian structure of the Kohn-Sham TDDFT equation and leveraged it to derive efficient, high-order, symplectic schemes for grid-based simulations using local DFT functionals (that only depend on the density and potentially its spatial derivatives) [Mauger 2023]. Symplectic schemes are specifically designed to preserve the Hamiltonian structure and generally provide superior results, *e.g.*, when long simulation times are considered. We are currently working on extending these symplectic schemes to arbitrary functionals and basis-set discretization, similar to what is used in the NWChem package [Valiev 2010]. In [Mauger 2023] we also showed that semi-classical coupling to the nuclear degrees of freedom, in the Ehrenfest framework [Castro 2014], possesses a canonical Hamiltonian structure. This opens the door to further extending these efficient high-order schemes to investigate the effects of nuclear motion on CM. More generally, the Hamiltonian structure provides a framework in which various nonlinear-science techniques can be applied, notably to analyze and understand the intricate dynamics of systems involving many coupled degrees of freedom, like CM.

Thrust 2: Time resolving charge migration dynamics

Thrust 2 of the ATTO-CM network focuses on using XUV and x-ray light to coherently probe CM in a wide range of molecules. From our initial focus on molecular HHS in the gas phase [Hamer 2021, Hamer 2022, Tuthill 2022] we have broadened our experimental investigations to attosecond spectroscopy using XUV photoionization and liquid-phase HHG. Progress in Thrust 2 is driven by the continued close collaboration between theory and experiments. Theoretically, we have demonstrated that by matching the frequency of the HHS driving light to that of the CM mode identified in Thrust 1 we can track where the hole is along the molecular backbone at a given time [Hamer 2023]. We are also working to improve our capability to quantitatively simulate and compare harmonic yields in liquid and gas-phase molecules. At the facility scale, we have continued our close involvement in a series of experiments within the Attosecond Science campaign using the XLEAP mode of the LCLS to measure CM in different isomers of aminophenol.

XUV attosecond spectroscopy of molecular electronic dynamics: The OSU node uses attosecond pulses produced via HHG to study CM on attosecond timescales. However, molecular ionization via a harmonic comb can easily result in spectral congestion. To reduce the spectral congestion, we use a 400-nm driving wavelength leading to 6 eV separation between odd harmonic orders. With these, we can separate multiple ionization channels within the RABBITT sidebands. We have completed a proof-of-principle experiment to characterize a shape resonance in the C ionization channel of CO_2. The shape resonance, which occurs at 42 eV, was theoretically predicted and subsequently experimentally confirmed via photoelectron angular asymmetry measurements [Carlson 1991, Lucchese 1991]. Interestingly, no enhancement in the total ionization yield was observed, with inter-channel coupling considered as the leading proposed mechanism [Siggel 1993]. We have confirmed this inter-channel coupling by simultaneously measuring the ionization delay of the first four ionization channels of CO_2.

We retrieve the ionization delays using the RABBITT technique, averaging the results over five separate measurements to improve accuracy. To isolate the delays specific to each CO_2 ionization channel, we subtract the RABBITT measurement from an inert gas with a similar ionization potential to the cationic state, adjusting the reference gas used for each channel. Figure 3 shows the channel-specific ionization delays across the resonance (symbols) and compare them to the simulated resonant signature in the B channel cross section (curve), including inter-channel coupling [Siggel 1993]. We see a significant delay excursion in the A and B channels with little excursion in the X and C channels. This agrees with theoretical calculations of the photoionization cross section, which predicts a strong coupling of the C channel to the A and B channels but not the X channel [Lucchese 1990]. The lack of excursion in the C channel also implies that we are measuring primarily direct photoelectrons from the C continuum channel while the resonantly excited electrons transition to the B channel within hundreds of attoseconds, within the resonance lifetime [Kamalov 2020]. This measurement establishes the capability of the OSU node to measure attosecond-scale

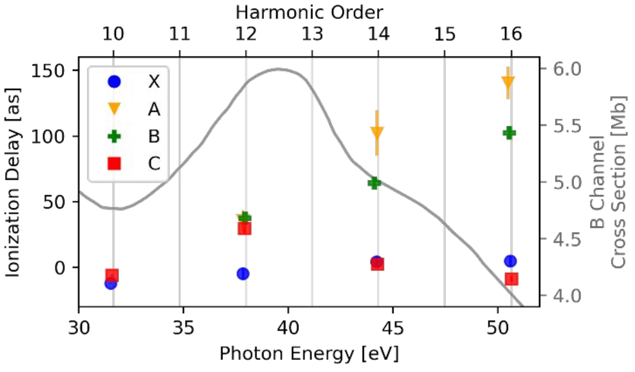

Figure 3: (markers, left axis) ionization delays of the first four cationic states of CO_2. For comparison, we also show the calculated B-channel cross section including inner-channel couplings (curve, right axis).

electron dynamics with the spectral resolution needed for complex molecules.

Soft X-ray attosecond spectroscopy at the LCLS: The OSU node continues to participate in the Attosecond campaign at the LCLS ("Real-time Observation of Ultrafast Electron Motion using Attosecond XFEL Pulses" – PIs: J. Cryan, A. Marinelli, and P. Walter) within which three beam times have been completed. These experiments aimed to measure CM in aminophenol using isolated attosecond pulse pairs. The first pulse is tuned to ~250 eV, a photon energy lower than all the atomic K edges, and initiates the CM via valence ionization, which coherently populates a superposition of cationic states [Grell 2023]. The second pulse is scanned over an oxygen K edge to measure the x-ray absorption spectrum as a function of the delay between the pulses. The time-dependent electronic density is probed via the below-threshold core-to-valence hole-filling transition (XAS) or core state direct ionization (XPS).

Results from the XAS experiments in the para-aminophenol isomer have revealed a time-dependent resonant absorption, as shown in Figure 4. The signal has two unique features: a quick decay within 2 fs followed by a revival around 5 fs. These features agree well with simulations, which confirm CM as the source of time dependence. The quick decay results from delocalization of the hole at the oxygen site, followed by a revival of the hole density at 5 fs owing to the coherent nature of the superposition. The revival is weaker than the initial signal and can be encapsulated via an exponential decay factor representing a change in the magnitude or position of the resonance or population decay through non-adiabatic couplings, both due to nuclear motion. A manuscript on these results is in preparation.

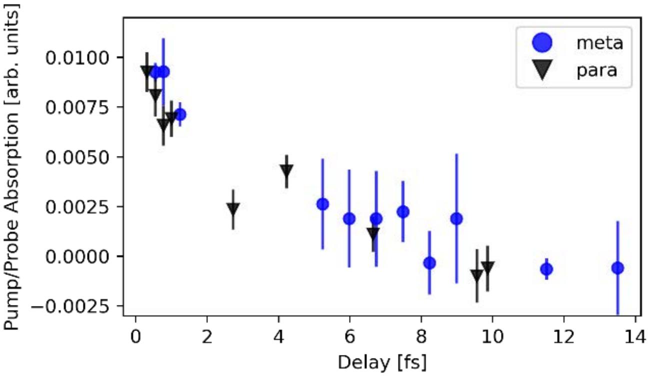

Figure 4: Pump-probe delay-dependent x-ray absorption of aminophenol for the para and meta isomers. Absorption is measured over the below-threshold pump-induced resonance.

We repeated the XAS experiment with meta-aminophenol to study the effect of isomerization on CM. The resonant signal shown in Figure 4 reveals a similar but distinct trend as compared to the para isomer. Again, we see a quick decay within 2 fs followed by a revival. However, the revival in the meta isomer occurs at a longer delay. Hence the isomerization, which is known to affect the valence state distribution, results in a shift in the coherent revival time. Removal of experimental systematics is ongoing to finalize the signal. The OSU node has also continued analyses on the para-aminophenol XPS experiments to investigate time-dependent changes in K-shell binding energies due to CM. We have measured oxygen K-shell binding energies as a function of delay and are refining our results via improved background-signal subtraction.

Frequency-matched strobo-spectroscopy (FMSS) of charge migration: The LSU node continues its investigations of using HHG to coherently probe the types of periodic CM modes identified in Thrust 1. In [Hamer 2022] we showed that we can identify periodic CM, and read out the CM frequency, by tracking the energies of sidebands in HHG spectra, a technique we called HHSS. These sidebands originate from the time-dependent beat in the CM+HHG signal whenever the driving laser frequency is incommensurate with the CM frequency. Over the past year, taking the example of aligned bromobutadiyne (BrC_4H) undergoing CM, we have further demonstrated numerically that we can track the location of the hole along the molecular backbone at a given time using FMSS. FMSS uses a few-cycle, frequency-matched laser pulse to induce HHG in the molecular cation undergoing periodic CM. The frequency matching condition is chosen such that the electron hole is at the same place along the molecular backbone at each half-cycle of the laser field.

FMSS then uses the modulation of the harmonic signal depending on the location of the electron hole within the molecule. By scanning the delay between the initiation of the CM and the arrival of the HHG-driving pulse we can follow the motion of the CM along the molecular backbone.

Figure 5 (a) shows the particle-like CM in BrC_4H, over half a period of the CM, which we probe using FMSS. All simulations are done using TDDFT, as implemented in the open-access software Octopus [Tancogne-Dejean 2020], To avoid disrupting the CM dynamics, we set the laser polarization direction (arrows) perpendicular to the molecular backbone. In panel (b), we show the relative harmonic intensity when varying the delay between the CM and driving pulse. Because different harmonics are emitted at different times within one half-laser cycle, we obtain the delay- and harmonic-frequency-dependent modulation of the HHG signal. In our case, we find that the harmonic yield is highest when the hole is away from the Br at the time of emission, as illustrated in panel (a). A manuscript detailing our results is currently under review [Hamer 2023].

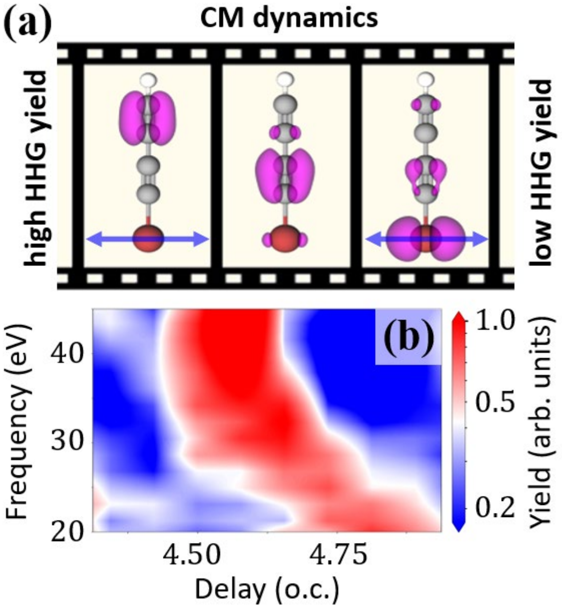

Figure 5 (a) Snapshots of hole density in particle-like CM dynamics in BrC_4H. (b) Resulting delay- and harmonic-frequency-dependent modulation of the HHG yield induced by the CM dynamics.

Liquid high-harmonic generation (LHHG) spectroscopy: The OSU node continues to investigate the effect of the solute for LHHG in a solution. We have identified minima in the emitted spectra that appear to correlate with the size of the first solvation shell in the solute-solvent mixture, according to preliminary calculations. This suggests that the solute may manifest itself through solvation shell characteristics imparted on the net LHHG spectrum.

The LSU node has initiated molecular-dynamics calculations to simulate the location of the first solvation shell in pure solvents as well as in solvent-solute mixtures [Thompson 2022]. We are in particular focusing on how the first solvation shell around the solute molecule changes depending on the type and concentration of the solute. We have also initiated model-HHG calculations to incorporate a simplified description of a solvation shell and its potential impact on the harmonic yield.

Quantitative calculation of HHG yields: The LSU node continues to compare HHG yields in different six-membered ring molecules (benzene, cyclohexene, and cyclohexane, respectively colored black, blue, and red in Figure 6) by performing grid-based TDDFT calculations [Tancogne-Dejean 2020], with the goal of comparing to the experimental yields in [Alharbi 2015]. This involves averaging over a distribution of randomly oriented molecules in the gas phase, using a Lebedev grid

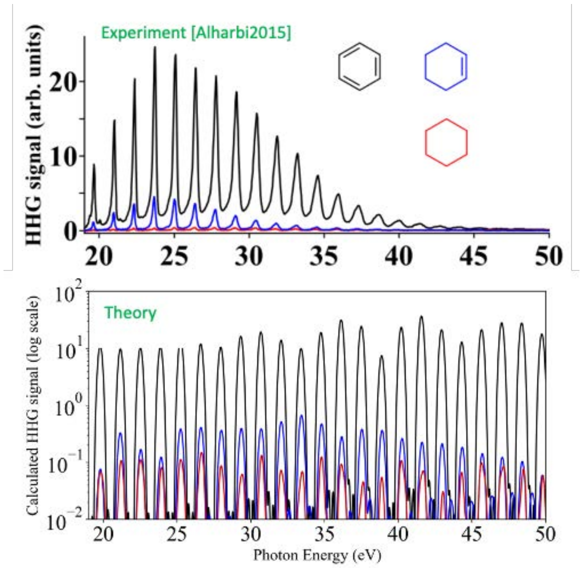

Figure 6: (top) Experimental [Alharbi 2015] and (bottom) calculated HHG yields in six-membered ring molecules, for 1825-nm driving fields (few tens of TW/cm² intensities).

[Lebedev 1975]. We find that, in some cases, low-lying orbitals contribute disproportionately to the harmonic yield and that this can be understood in terms of their ionization potentials within the TDDFT calculation. We also find that a simple scaling of the individual-orbital yields by a tunnel-ionization correction factor can significantly improve the comparison to experimental results, in which benzene yields were found to dominate over cyclohexene (-ane) yields by a factor of approximately 10 (20). This work has been presented at multiple undergraduate research symposia, and a manuscript is in preparation.

Thrust 3: Expanding the charge migration toolbox

Our efforts in Thrust 3 focus on the manifold of laser-induced phenomena, including ionization, excitation, and dissociation, that can both initiate CM motion (serving as a "pump") and can be subsequently influenced by CM dynamics (the "probe"). These processes, and what we can learn from them, can be strongly dependent on the relative alignment or orientation of a target molecule relative to the laser polarization. The ATTO-CM team continues to explore strong-field ionization (SFI) as a pump and probe of CM. While it is a convenient experimental tool, highly accurate angle-dependent rates can be difficult and time-consuming to obtain. Accordingly, much of our recent theoretical work in this area has centered on developing approximate techniques that can provide angle-dependent strong-field ionization rates with reasonable accuracy at a fraction of the traditional computational cost and then benchmarking those calculations using more accurate numerical methods and experiments. Experimentally, we are upgrading our apparatus to enable tests of new approaches for detecting CM through frequency-matched ionization and dissociative ionization.

Frequency-matched strong-field ionization (FMI) spectroscopy of CM: The principal idea behind FMI spectroscopy is to use strong-field ionization, within a single laser pulse, to both create a localized hole and probe the time-dependent modulations in electron density via a second ionization event. The technique exploits both the temporal localization of the first and second ionization events near the peak of an optical field cycle as well as the spatial localization of the ionization events at specific sites in a molecule afforded by molecular functionalization [Sándor 2019]. If the frequency of the ionizing laser is tuned so that the periodicity of the field maxima matches that of the CM, then the hole created at a designated molecular site during one field maximum will have returned to its point of origin upon successive field maxima, potentially leading to a detectable enhancement (or suppression) of the double ionization yield and the identification of the CM period. Previous experiments performed jointly by the UVA and OSU nodes explored the use of near and mid-infrared pulses with durations approaching 100 fs in an attempt to utilize FMI Spectroscopy to detect CM in singly-ionized halogenated hydrocarbon rings, as predicted by TDDFT calculations performed at LSU (see Thrust 1). We have been upgrading the laser apparatus and experimental chambers at UVA in preparation for next generation experiments that will involve a number of key improvements.

First, we will employ significantly shorter, few-cycle pulses. Shorter pulses should reduce the substantial molecular fragmentation that we observed with longer pulses and limit the second ionization event to substantially narrower time windows, potentially avoiding substantial dephasing of the CM due to nuclear motion. Shorter pulses will also lessen the impact of transient resonances that enhance the probability for non-adiabatic ionization that is not temporally confined to the field maxima. We are installing a stretched hollow-core fiber compressor that will enable the creation of few-cycle visible and near infrared pulses with adjustable central wavelengths through spectral filtering. To access the few-fs CM periods predicted for typical target molecules (*e.g.*, halogenated benzene derivatives) we intend on superimposing a few-cycle visible/infrared pulse with its second harmonic, to create asymmetric optical fields with maxima occurring once, rather than twice, during the optical period of the fundamental.

Second, we will utilize fragment momentum imaging detection to identify molecular fragments, that are produced via double ionization, and that are aligned perpendicular to the ionizing field. As with the HHSS [Hamer 2022] and FMSS [Hamer 2023] methods explored by the LSU node in Thrust 2, this will allow us to focus on molecules for which the CM motion along the primary molecular axis is not significantly influenced by the strong, perpendicular ionizing field. The magnitude of the ion momenta will allow us to distinguish fragments resulting from dissociative single-ionization vs dissociative double ionization. Although the use of short pulses will limit the time available for molecular expansion after the first ionization event, we can use the fact that the fragments with the greatest momenta are produced from double ionization prior to any molecular expansion to further filter for double ionization from the parent ion. This will avoid contamination of our signal from molecules that were in the process of dissociating and, therefore had no well-defined CM. We can further use the known directionality of the field and ion fragments to search for indications of non-adiabatic effects resulting in enhanced or suppressed ionization depending on the relative directions of the ionizing field and the directions of travel of the CM hole.

Guided by recent and planned two-color experiments at UVA, in the last year the LSU node has performed simulations to determine whether SFI can be used to measure CM. Specifically, in a molecule undergoing CM, we have focused our efforts on using a frequency-matched second-ionization pulse to track the CM. In this scheme a first pulse starts the CM (for us in the sudden approximation and emulated with constrained DFT [Eshuis 2009], like in Thrust 1) and the delayed, frequency-matched, second pulse probes it via SFI. The CM is “measured” through the variation of the double ionization yield with respect to the delay between the two pulses. For simulations, we use a similar TDDFT approach to the attochemistry work in Thrust 1, with the addition of large diffuse basis functions and a complex absorbing potential to absorb the outgoing flux of ionized electron densities. Like in the FMSS of Thrust 2, we set the polarization of the time-delayed second-ionization pulse perpendicular to the molecular backbone so as to not perturb the CM with the field.

Figure 7 shows the frequency-matched, delay-dependent, double-ionization yield for bromoacetylene during CM for the case of a single color field. The ionization yield is enhanced when the field maximum occurs at times when the hole is on the C≡C triple bond. Conversely, the yield is minimum when the hole is on the Br, with approximately 30% increase in the maximum vs minimum yields. We observe similar features with a quasi-static field (not shown), where the instantaneous ionization rate is maximum when the hole is on the C≡C triple bond, ~25% faster than when the hole is on the Br. A similar effect has been observed in simulations of iodoacetylene probed with an 800 nm few-cycle pulse, where the instantaneous SFI rate is enhanced when the hole is on the C≡C [Schlegel 2023]. Taken together, these results confirm that the instantaneous ionization is fastest when there is extra electron density, *i.e.*, less hole, on the Br atom. Overall, these simulations show that CM causes appreciable modulation in SFI, and these modulations correlate with the "location" of the hole in the molecule.

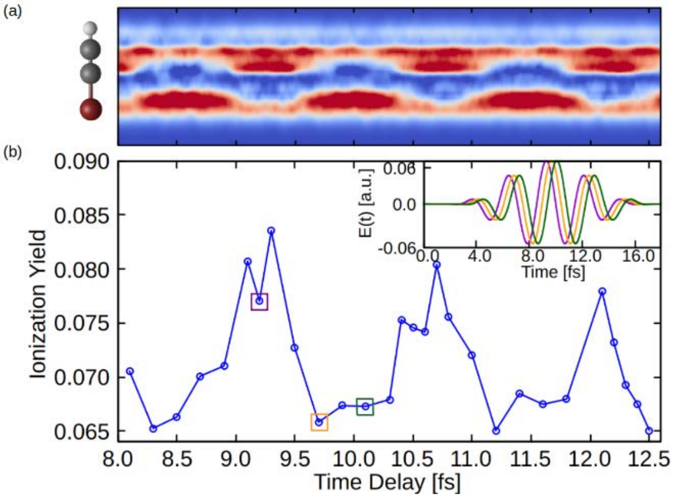

Figure 7: (a) CM in bromoacetylene. (b) Double ionization yield as a function of time-delay between a first and second ionizing laser pulse. The yield is enhanced by 30% when the field has a maximum at the same time as when the hole is on the C≡C bond, i.e.*, there is relatively more density around the Br.*

Fast ionization yield simulations using weak-field asymptotic theory (WFAT): As discussed above, fast yet accurate calculation of ionization rates of molecules exposed to visible to mid-infrared laser fields is an essential component to multiple experimental and theoretical aspect of the ATTO-CM network work. To that design, we have extended the integral-representation of many-electron WFAT (IR-ME-WFAT) [Tolstikhin 2014] to using DFT orbitals [Wahyutama 2022]. This approach combines the efficacy of static rate simulations, thus bypassing computationally expensive time propagation of wave functions, with treating multi-electron effects at the DFT level of theory. In benchmark simulations of SFI of NO and OCS with multi-cycle near-IR pulses, we have observed excellent agreement between our DFT-based IR ME-WFAT and direct TDDFT simulations, but with two orders of magnitude speedup in computational time [Wahyutama 2022]. We will leverage the efficacy of DFT-WFAT to screen for CM-friendly targets over a large range of parameters and families of molecular compounds. We have implemented IR ME-WFAT as a module for the open-source quantum-chemistry package NWChem [Valiev 2010] and are currently working towards its integration into the main branch of the software repository.

Cross-training and interactions between the network partners

We have maintained continuous communication between all the nodes of the network, including:

- 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.

These active exchanges have allowed us to maintain a strong collaborative community among the PIs, students, and postdocs.

Future Plans

The continued interaction between the three nodes of the ATTO-CM network is a cornerstone of our collaboration. We fully intend to continue our current interactions, *i.e.*, with regular communication (zoom, emails, shared website, etc.) and exchange visits between the nodes. In what follows, we briefly explain the main avenues we intend to pursue to advance our efforts to coherently probe CM in molecules.

Simulating the initiation of CM: The LSU node has started investigating direct numerical simulation of the ionization step that initiates CM, using TDDFT in Octopus [Tancogne-Dejean 2020]. Our platform for CM dynamics will be bromobutadiyne (BrC_4H), since it has been shown to support facile CM modes. We will investigate a variety of approaches to creating the initial hole using an ultrashort laser pulse, spanning from one-photon, to few-photon, to tunnel ionization. Preliminary results are encouraging: we find that both attosecond XUV and few-femtosecond intense infrared pulses initiate some modes of CM.

Attochemistry regulation of charge migration: In the coming year, the LSU node will continue to use TDDFT simulations to determine the role of bonding and lone pair electrons on CM. This will include a wider range of systems, the use of pseudohalogens as hole creation sites, and the effect of molecular-bond rotations. Since rotations of bonds affect the overlap between the p/pi/lone pair electrons, we expect them to influence the CM. Indeed, our preliminary results suggest that rotation around the -OH bond in alcohols can essentially shut off the CM.

XUV attosecond spectroscopy: The OSU node is working to introduce wavelength tunability to the visible HHG driver in their RABBITT apparatus via sum-frequency generation of the laser's fundamental wavelength and the output of a tunable OPA. With this, we aim to produce wavelengths in the range of 490-600 nm, thus enabling to map out the entire energy space in the XUV attosecond spectroscopy of Thrust 2 [Gorman 2019]. We have demonstrated HHG using this visible tunable source and are working to increase the harmonic cutoff. While still limiting spectral congestion, with this setup we will increase our spectral resolution and thus the temporal resolution. We are also designing an oven for vapor delivery of condensed phase samples. Our initial plan is to study the effect of shape resonance decay due to CM using halogenated benzene series as the first targets [Despré 2015, Bruner 2017].

LCLS attosecond spectroscopy: The OSU node will continue its participation in the LCLS Attosecond Campaign with continued analyses on meta-aminophenol XAS and para-aminophenol XPS. The campaign has also submitted a proposal for a fourth beamtime in Run 22 in 2024. If accepted, we will use two isolated attosecond x-ray pulses to induce two instances of impulsive stimulated X-ray Raman scattering (ISXRS) in para-aminophenol. Each pulse will create a different valence excited state wave packet which will interfere coherently and be probed via UV laser ionization [O'Neal 2020]. By varying the attosecond pulses' delay we can measure the strength of the valence excited state coherences. This will also give access to the damping of the coherences due to the coupling of electronic-nuclear motion, which we have been measured previously and has extensively been shown to be important for CM in the literature.

Liquid high-harmonic generation (LHHG) spectroscopy: The OSU node will continue measurements of LHHG in different solutions, varying the driving wavelength and intensity to fully characterize both the mechanism of LHHG and the influence of the driving-medium characteristics on the output spectrum. LSU will continue MD simulations [Thompson 2022] and will continue to develop HHG model-calculations in the liquid phase. LSU will also initiate CM dynamics in the liquid phase, using the results of MD simulations as a starting point.

Frequency-matched strong-field ionization (FMI) spectroscopy of CM: Going forward, in conjunction with UVA, the LSU node will perform SFI simulations that have both explicit pump and probe fields, in a two-color (1ω, 2ω) configuration, for different pump-probe polarization combinations. In addition to the systems discussed in Thrust 1, we will also study iodine-functionalized rings ($I\text{-}C_6H_4\text{-}R$, R=H, NH_2, etc) and related polyaromatics (*e.g.*, iodonaphthalene derivatives), where the larger system size is predicted to increase the time it takes for the hole to move across the molecule [Folorunso 2021]. For this, we will use spin-orbit coupled TDDFT with pseudopotentials for the I. Additionally, to more closely relate to UVA fragmentation measurements, we will quantify the instantaneous bond softening (time-dependent bond strength) during CM via electron localization. This will allow us to correlate modulations in fragmentation with modulations in SFI, albeit qualitatively.

At the UVA node, the new stretched hollow-core fiber compressor should be operational by the end of the calendar year. We will then develop/test approaches for producing phase-locked, two color asymmetric few-cycle fields with selectable central wavelengths. Those pulses will then be employed in FMI experiments using molecules for which the LSU group has predicted (i) the creation of robust CM through strong field ionization and (ii) a significant dependence of further ionization on the location of the hole during subsequent field maxima.

THz driven molecular alignment/orientation in dense room temperature targets: The creation of well-aligned/oriented, dense molecular targets is required for implementing FMSS and other high-harmonic spectroscopies designed to probe CM. THz-driven field-free molecular alignment/orientation can be a preferred approach for manipulating the molecular rotational distribution, as it avoids electronic excitation and/or dissociation that can accompany alignment/orientation resulting from Raman redistribution driven by intense optical alignment pulses. Several years ago, the UVA group demonstrated that the degree of THz-induced orientation could be enhanced by first preparing the molecules using a weak optical Raman excitation pulse. However, the degree of achievable orientation was still quite low at higher rotational temperatures, making it extremely difficult to perform experiments involving larger molecules in a cell or in a dense jet where rotational cooling is limited. However, a recent theoretical paper [Tutunnikov 2022] has predicted that substantial THz orientation/alignment can be achieved in room temperature samples using a slightly modified approach to the one previously demonstrated at UVA. We are currently preparing experiments to test the effectiveness of the predicted "orientation echo" technique as a function of rotational temperature. If successful, the method could enable an important class of experiments involving HHS from oriented molecules and will be tested on a HHG beamline at OSU.

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[Folorunso 2021] A.S. Folorunso, A. Bruner, F. Mauger, K.A. Hamer, S. Hernandez, R.R. Jones, L.F. DiMauro, M.B. Gaarde, K.J. Schafer, and K. Lopata, "Molecular Modes of Attosecond Charge Migration," Phys. Rev. Lett. 126, 133002 (2021)

[Folorunso 2023] A.S. Folorunso, F. Mauger, K.A. Hamer, D.D. Jayasinghe, I. Wahyutama, J.R. Ragains, R.R. Jones, L.F. DiMauro, M.B. Gaarde, K.J. Schafer, and K. Lopata, Attochemistry Regulation of Charge Migration, J Phys Chem A 127, 1894 (2023)

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Ultrafast Non-adiabatic Dynamics in VUV Excited Molecules with Electric-Field-Resolved Nonlinear Spectroscopy

Award number: DE-SC0024234
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1 PROJECT SCOPE

Coherence is a fundamental concept in quantum mechanics which plays an important role in many quantum phenomena. A detailed understanding of coherence, including various decoherence/dephasing mechanisms in electronically excited molecules is essential for the development of quantum coherent control protocols for laser driven control of chemical reactions. This is particularly important near conical intersections (CIs) which are ubiquitous in excited states of polyatomic molecules and play a key role in energy redistribution of excited states into multiple degrees of freedom. While coherent excitations and ultrafast non-adiabatic dynamics near CIs have been well studied in the past, detailed exploration of decoherence/dephasing processes near CIs, on few-femtosecond time scales, are largely lacking. To address this gap, Electric-Field-Resolved nonlinear optical measurements of vacuum- ultraviolet (VUV) excited molecules will be used in this project to obtain direct and detailed information about decoherence during non-adiabatic dynamics near CIs. The primary goal is to obtain insight into the coherent evolution of coupled electron-nuclear non-adiabatic dynamics in *valence excited* molecular systems, on few-femtosecond time scales. This will be achieved through a unique application of Electric-Field-Resolved nonlinear optical spectroscopy to study excited molecules. Experimental measurements combined with theoretical modeling of the dynamical excited state nonlinear response, performed in collaboration with theory experts, will offer detailed insight into non-adiabatic dynamics on ultrafast time scales.

2 RECENT PROGRESS

We have recently completed setup of the high-harmonic generation (HHG) beamline to generate VUV pulses (5th harmonic of 800 nm femtosecond pulses). Since the beginning of the project in 08/2023, we have started benchmarking measurements with different Four-Wave Mixing (FWM) schemes involving VUV and near infrared (NIR) pulses in which an NIR or ultraviolet (UV) signal pulse is emitted.

In previous work, we have demonstrated capabilities to measure the electric field of very weak (picojoule to femtojoule) nonlinear signal pulses from gas phase molecules in their electronic ground state [1]. In this study, we found that measuring the temporal phase and hence the temporal chirp of the weak nonlinear optical signal provides direct access to the electronic contribution of the nonlinear response. **Figure 1** shows the temporal electric field amplitude and phase measured for a third-order nonlinear optical signal in the Degenerate Four-Wave Mixing (DFWM) scheme. **Figure 2** shows the measured chirp of the nonlinear signal for cases where electronic-only and electronic + rotational contributions to the nonlinear response exist. The chirp was found to be sensitive to the electronic-only nonlinear response, whereas no chirp was measured at time delays

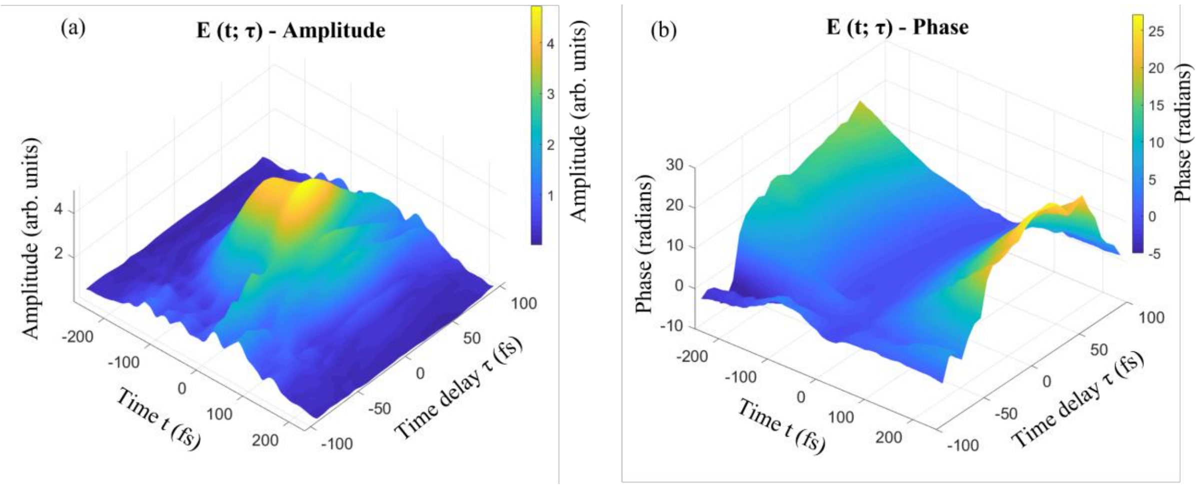

Figure 1: Data from the electric field measurement of a nonlinear optical signal using DFWM in CO_2 molecules [1]. (a) The third-order nonlinear signal E-field amplitude and (b) E-field phase as a function of real time (t) and time delay between Gate and Probe pulses (τ). This demonstrates the rich data available from the electric field-resolved nonlinear spectroscopy approach.

where the rotational contribution was significant (for example near 200 fs delay, red triangles in **figure 2**). For a detailed discussion, see ref [1]. We have subsequently also applied this approach to impulsively aligned molecules where we measure the nonlinear signal chirp in the molecular frame (manuscript in preparation). Based on progress made in these previous works, Electric-Field-Resolved nonlinear spectroscopy will be used on VUV excited molecules to study ultrafast non-adiabatic dynamics.

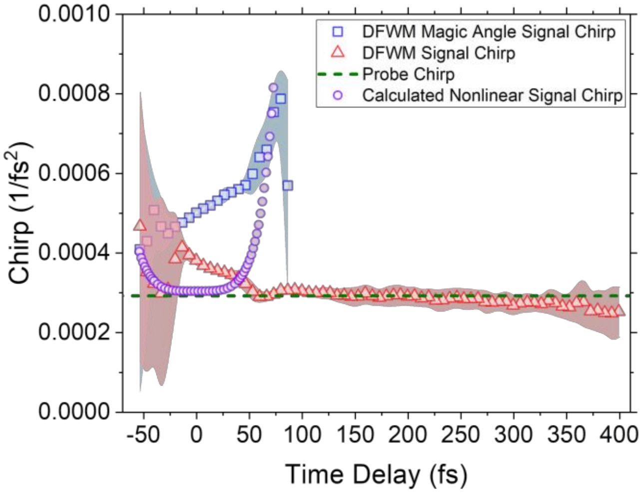

Figure 2: Measured chirp of the nonlinear signal electric field for the magic-angle (electronic contribution only) and non-magic angle (rotational and electronic contribution) DFWM signal. Calculated signal chirp for electronic contribution only also shown. More details in [1].

3 FUTURE PLANS

We will first use solid targets such UV fused silica and magnesium oxide crystals to detect strong nonlinear signals for optimization, and we will then move to gas-phase targets such as ethylene and carbon dioxide. UV pulses (3rd harmonic of 800 nm) obtained from HHG in argon gas will be used in the benchmarking experiments after which we will use 5th harmonic (7.75 eV) and 7th harmonic (10.85 eV) pulses with gas targets. To obtain nonlinear signal in the UV and NIR wavelength range (for electric field measurement) after VUV excitation, we will use multiple Four-Wave Mixing (FWM) schemes such as using two non-collinear VUV beams (generated using a mask) in combination with NIR pulses. Upon detection of nonlinear signals from gas-phase targets, we will proceed with spectral interferometry for electric field measurement of the nonlinear signal. This will be followed by electric field measurements of nonlinear signals from pre-aligned and VUV excited molecules. In parallel to these efforts, we will collaborate with theory experts such as Prof. Loren Greenman (Kansas State University), who is a PI in the AMOS program, to connect the nonlinear signal electric field observable to ultrafast non-adiabatic dynamics.

4 REFERENCES

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5 PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (PROJECT START DATE: 08/2023)

No publications to report.

Heterodyne time resolved spectroscopy in the extreme ultraviolet

Grant DE-SC0024508

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Project Scope

The overall project scope is a full quantum tomographic dynamical picture of molecular systems with an initial focus on two molecules that are responsible for the greenhouse effect, CO_2 and C_2H_4. The proposed effort has two main thrusts.

Under the first thrust we will further develop an interferometric extreme ultraviolet (XUV) transient absorption spectroscopy technique (iTAS) to study the phase evolution of field free or field driven atoms and molecules. From a spectroscopic point of view, our technique can provide information about the phase of the wavefunction in a molecule and its dynamical evolution with sub-mrad resolution in the XUV.

The second thrust will make use of a new high resolution 3D velocity map imaging device that can measure photoelectron distributions in full momentum space at a high repetition rate in coincidence with photoions. The detector will be coupled to a high power, high repetition rate laser system capable of producing high flux XUV photons at 200kHz.

Once both techniques have been established, we will continue towards the quantum tomographic reconstruction of molecular systems. This involves the measurement of the full density matrix of a molecule in an excited state.

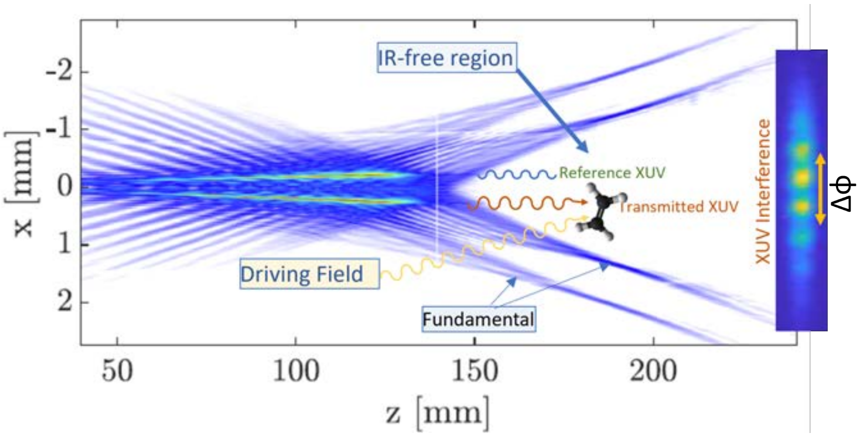

Figure 1: Schematics of our proposed heterodyne XUV spectroscopy or interferometric XUV TAS. Two non-colinear attosecond XUV pulse trains are generated from two Bessel-foci. XUV pulses generated on the top focus are transmitted directly to the detector screen creating the ”reference”. The bottom XUV beam or ”arm” is transmitted through a sample that is excited by a driving or pump pulse. After interaction with the medium, this second XUV also reaches the detector and interferes with the reference arm of the interferometer. Changes in the maxima and minima interference pattern correspond to changes in phase or relative delays between both XUV arms.

Electronic and ro-vibrational wavepacket interferometry

The overall idea of heterodyne XUV spectroscopy is explained in Fig. 1. Two non-collinear XUV pulses are generated through HHG driven by two tilted Bessel-like beams to create a self-referencing XUV interferometer. To date we have data demonstrating phase noise between two non-local XUV beams (89nm) of ≈ 0.1mrad, corresponding to a temporal jitter of ≈ 6zs. Such phase precision will allow us to make very precise dynamical phase measurements.

To show the relationship between the experimental observable and molecular structure, we theoretically describe the process of the interaction of two non-local XUV beams with a medium. This part of the proposal is done in collaboration with Prof. An-Thu Le.

Briefly, as XUV photons travel through a medium there is secondary light emission due to the induced dipole acceleration, with the dipole

$$\mathbf{d}(t) = Q_e \langle \Psi(t) | \hat{\mathbf{r}} | \Psi(t) \rangle. \tag{1}$$

In our case there will be two spatially-separated sources of emission which we assume as two XUV plane waves that propagate with no IR fields, as is the case with Bessel-like HHG. The two beams will interact with two media having index of refraction n_α and optical thickness L_S^α where $\alpha = 1, 2$ for source 1 or 2. We will assume source 1 to be the reference.

Spectral measurements of electric fields are determined by the Fourier transform of the time-average of the pointing vector at the detector $\mathbf{r}_d$, $\mathbf{S}_D$,

$$\langle \mathbf{S}_D \rangle (\mathbf{r}_d, \omega) = \Big| \sum_\alpha E_\vartheta^{(\alpha)}(\mathbf{r}_d, \omega) \Big|^2 \mathbf{e}_r, \tag{2}$$

yielding the well known equation of the intensities,

$$\langle \mathbf{S}_D \rangle (\mathbf{r}_d, \omega) = I^{(1)}(\mathbf{r}_d, \omega) + I^{(2)}(\mathbf{r}_d, \omega) + I_{\text{int}}(\mathbf{r}_d, \omega), \tag{3}$$

where $I_{\text{int}}(\mathbf{r}_d, \omega)$ is the interference term given by,

$$I_{\text{int}}^{(1,2)}(\mathbf{r}_d, \omega) \propto \left| d_z^{(1)}(\omega) \right| \left| d_z^{(2)}(\omega) \right| \cos \left[\phi_{dip}^{(1)}(\omega) - \phi_{dip}^{(2)}(\omega) + \Delta\theta_{\text{opt}}(\mathbf{r}_d, \omega) \right], \tag{4}$$

with $\phi_{dip}^{(\alpha)}(\omega) \equiv \arg \left[\tilde{\ddot{d}}_z^{(\alpha)}(t) \right]$ is the spectral phase of the dipole and $\Delta\theta_{\text{opt}}$ a difference in optical phase. Thus, the argument of the cos in Eq. 4 is the difference in complex phase between the two fields $E^{(\alpha)}$. An experimental measurement of $I_{\text{int}}^{(1,2)}(\mathbf{r}_d, \omega)$ will provide a direct observation of the argument of the dipole $\phi_{dip}^{(\alpha)}(\omega)$.

Heterodyning and homodyning in the XUV

In homodyne detection a signal is mixed with a local oscillator (LO) before it is been detected. The interference of the two provides a phase-sensitive measurements of light and radio waves. Heterodyne measurements are equivalent but the frequency of the LO is shifted from the signal. Both methods and their variants allow for complete reconstruction of the state of light. Homo and heterodyne techniques have been used for many decades thanks to their great signal to noise ratio (SNR). Our interferometric technique described here could be represented as a heterodyne measurement in the sense that the XUV signal far from the fundamental and, its phase shifted from the reference, due to target excitation after interaction with the fundamental (see Eq. 4). On the other hand, our measurements are spectrally resolved and interference occurs only at each harmonic frequency as in the case for homodyning techniques. Further, we will show that our interferometric technique can be balanced or unbalanced opening the door for quantum optics measurements in the XUV.

UV probe of ultrafast-induced molecular dynamics

The main progress in this thrust is the development of a 3D velocity map imaging (3D VMI), capable of measuring time of flight ions in coincidence. High resolution electron 3D momentum distributions are relevant for our proposed studies since, when extracting information about the molecular frame, we do not want to make any assumptions about the symmetry of the orbital. We are now able to see features, such as ring interlocking (see Fig. 2), that have not been observed before, thanks to the resolution of our detector.

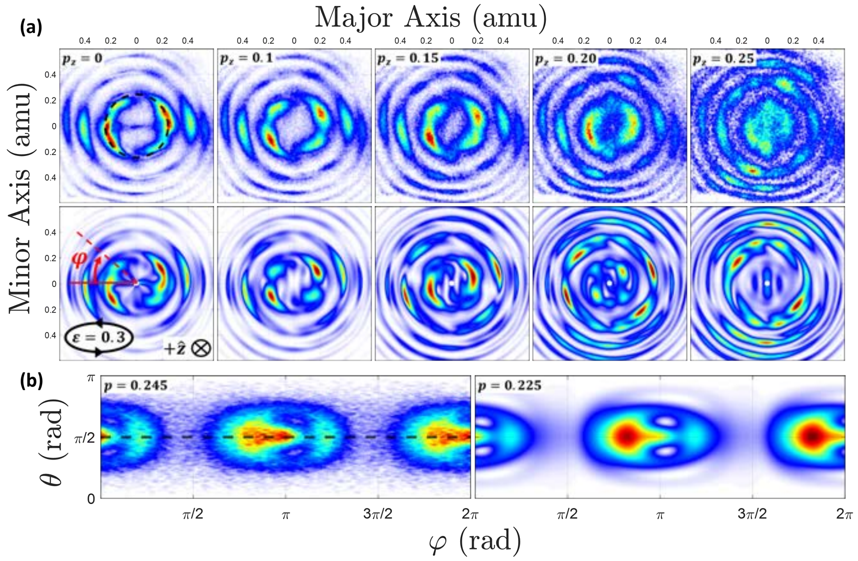

Figure 2: Experimental and simulated results for Xe$^+$ ionized by elliptically polarized laser pulses. (a) Slices of the 3D photoelectron momentum distribution in the plane of polarization for various p_z; experiment and simulation are represented in the top and bottom rows respectively. Experimental distributions are integrated over a range ±0.05 amu from the quoted p_z. (b) Spherical PADs of the first ATI ring for experiment (left) and simulation (right). Both are generated at the maximum of their first ATI peak, the experimental peak at $p = 0.245$ amu (integrated over ±0.007 amu) and simulation at $p = 0.225$. Dashed black lines in (a) and (b) represent same line, placed at the peak of the first ATI shell for $\theta = \pi/2$. All distributions are self normalized for easy visualization of structure.

Calculations were done by Prof. A.-T. Le, numerically solving the time dependent Schrödinger equation. The agreement between theory and experiment, for all three momenta is extremely good. Both theory and experiment recover the circular dichroism of the photoelectron distribution.

We are in the process of coupling an XUV source to this 3D VMI to perform 3D interferometric XUV + IR photoelectron measurements.

Laser development

From a practical point of view, acquiring interferometric 3D VMI data will require large amounts of data. Therefore, for these set of experiments we will use a repetition rate of 200kHz-500kHz. At this rate we have 1.5mJ-750μJ of energy per pulse, respectively, and pulse duration of $\sim$ 120fs . At either repetition rate we will have enough peak power for both XUV generation and excitation of the sample.

Peer-Reviewed Publications Resulting from this Project (Project start date August 16th 2023)

No publications to report.

Structural Molecular Dynamics Using Ultrafast Gas X-Ray Scattering

Award # DE-SC0017995

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I. Project Scope

Understanding the structures and chemical dynamics of molecules in states far from equilibrium is of great importance for basic energy science and myriad applications. Scientists have measured molecular structures for over 100 years, laying a foundation for a vast range of disciplines from engineering to drug design. Yet all those structures were for molecules in their ground state and, for the most part, frozen in a crystal lattice. But Chemistry is about the transformation of molecules, i.e. the transition from one stable structure to another. Therefore, to advance chemistry there is an urgent need to measure molecular structures during chemical reactions, in short lived states on time scales of femtoseconds, and in geometries that are dramatically different from those of the ground state equilibrium structures.

This project develops complementary 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 methods are ultrafast time-resolved gas phase x-ray scattering, which is performed at the LCLS light source at SLAC National Accelerator Laboratory, MeV electron scattering, also performed at SLAC, and time-resolved Rydberg fingerprint spectroscopy, which is conducted at Brown University. 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 methods routinely measure the structures of molecules in excited states with a time resolution of <100 fs. The x-ray scattering experiments are performed in close collaboration with researchers at SLAC National Accelerator Laboratory. By advancing the state-of-the-art of the experiment the project contributes to the continued development of research infrastructure at SLAC. The tremendously enhanced capabilities of LCLS-II are fully taken advantage of. This includes in particular the high photon energy of the hard x-rays now available and, in future years, hard x-rays at high repetition rates.

To explore the coupled nuclear and electron dynamics of important molecular systems during prototypical chemical reactions, complementary spectroscopic and scattering techniques are advanced and applied to representative model systems that illustrate a wide range of ultrafast chemical dynamics phenomena. Of special interest are the motions through conical intersections, charge delocalization and charge migration. Model systems currently under investigation include 1,3-cyclopentadiene and its methylated derivatives, N,N-dimethylpiperazine and related cyclic triamines, and a variety of small molecules. 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 delivers important benchmarks that are valuable to the continued development of computational codes.

II. Recent Progress

Successful beam times at LCLS have resulted in important advances in femtosecond time-resolved x-ray scattering as reported previously:

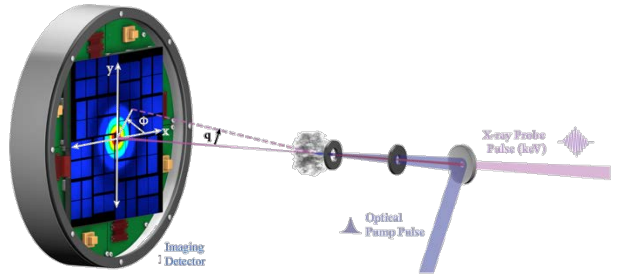

Figure 1: Experimental scheme: The molecules in the interaction region are intercepted by a linearly polarized UV laser (blue) and, at some time delay, by the X-ray pulse (red). Absorption of the UV pump pulse launches the structural molecular response. The X-ray probe is variably delayed with respect to the UV pump pulse to image the time-dependent dynamics. Scattering signals are captured by the detector.

- We have expanded our list of molecules for which we studied the ultrafast molecular dynamics by adding cyclopentadiene and quadricyclane to the previous roster that included 1,3-cyclohexadiene, trimethyl amine, N-methyl morpholine and dimethyl piperazine.
- We have measured complete, time-dependent excited state structures of these polyatomic molecules. The structures so obtained are largely experimental, with only the electronic correction terms derived from theory. Those electronic correction terms are typically small in comparison to the signals from the time-evolving structures.
- We learned how to determine the spatial orientation of transition dipole moments within the molecular frame from the anisotropy of the pump-probe scattering patterns.
- We worked with our collaborators to develop codes to calculate the total scattering signal from molecules in excited states.
- We uncovered how the passage through conical intersections in 1,3-cyclohexadiene is affected by the initial excitation energy. Subsequent experiments on cyclopentadiene further explore the dependence of the reaction paths on the optical excitation wavelength.
- We disentangled the contributions of electronic and nuclear geometry changes to the x-ray scattering patterns.

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.

Quantitative Measurement of X-Ray Scattering Signals

The exceptional brightness of LCLS enables measurements of gas phase scattering patterns of unprecedented quality. As a result, we are now sensitive to small deviations of the measured signals from the almost universally used independent atom model (IAM). To achieve a quantitative measurement, a number of corrections need to be applied to the experimental scattering signals, and given the growing userbase, we have worked out careful procedures to obtain quantitatively accurate scattering patterns. Important corrections include:

- ➢ Bad pixels of the detector need to be masked. A correction factor arising from the detection sensitivity of the detector on the angle of the incoming x-rays needs to be applied, and the detector manufacturer’s calibration matrices need to be implemented.

- Calibration of the detector position, in particular the distance from the scattering cell.
- Correction for the polarization of the x-rays. For linearly polarized radiation, the factor is $sin^2(\phi) + cos^2(\phi)cos^2(2\theta)$.
- Corrections resulting from the scattering and pixel geometry of the detector, which are accounted for by a geometric correction factor of $cos^3(2\theta)$
- A systematic, q-dependent correction to the spatial resolution and the intensity caused by the length and geometry of the sample cell, and the effusive gas expansion through the pinholes through which the x-rays enter and exit the cell.
- Correction factors for the transmission of the Beryllium window of the scattering cell and the Aluminum coating on the detector.

Applying all these corrections results in scattering patterns that are in near quantitative agreement with theoretical patterns for neon. The remaining deviations, of unknown origin, are used as final correction terms. With that, the agreement between theoretical and experimental patterns of many molecular systems becomes very good, although final deviations remain.

Sulfur hexafluoride is widely used to align the scattering apparatus and to calibrate the detector distance. As seen in figure 2, we now obtain excellent agreement between experiment and theory. Yet there remain some residuals, which the figure plots as a percent deviation between theory and experiment. It is not unexpected, that the independent atom model is insufficient to quantitatively describe the scattering patterns. Even with a CASSCF(6, 4)/6-311G *ab initio* calculation, there remain characteristic differences that are attributed to the theoretical treatment. Much higher level calculations are possible in molecular systems with fewer electrons, and for those we are studying the deviations as a function of the size of the basis set. The total scattering signal measures the electron pair correlation functions, which are difficult to capture with even high-level calculations. Continuing efforts are directed toward evaluating those effects and accounting for them.

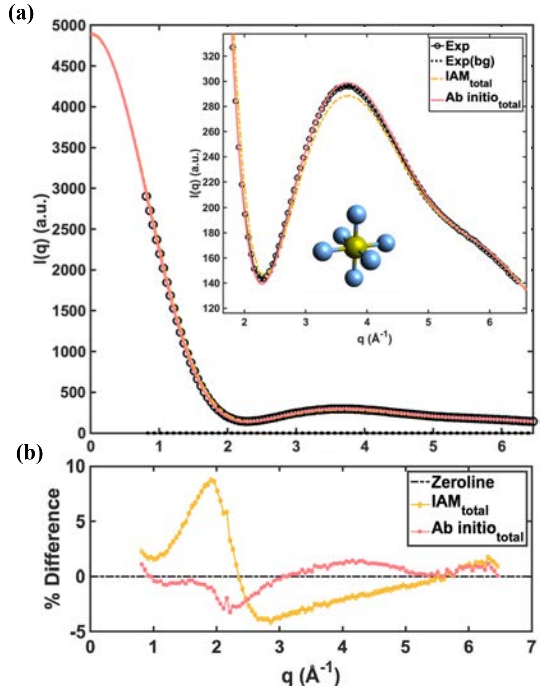

Figure 2: (a) Experimental (circles) and theoretical scattering patterns for SF_6 (inset: enlarged scale). Shown are the experimental scattering signals and the background signal (dots), in comparison to the total signal calculated with the IAM and ab initio. (b) Residuals between experiment and theory.

Fast Dynamics in Quadricyclane

As described elsewhere in this abstract book, we have studied the UV-induced interconversion between quadricyclane (QD) and norbornadiene (NB) in a project led by M. Centurion. At the FERMI beam line, we measured the time-resolved photoelectron spectra and discovered a very fast decay process that involves a complicated passage through a conical intersection.

At Brown University, we have applied multi-photon ionization photoelectron spectroscopy to study this fast decay as a function of excitation wavelengths between 195 and 220 nm. We were able to observe signatures of the fast decay discovered at FERMI, and indeed were able to note a wavelength dependence of it. However, the reaction is too fast to quantitatively analyze with confidence. We are building a new photoelectron spectrometer that will feature a much-improved time resolution and plan to return to this system at a future point in time.

III. Future Plans

In the coming months, we are looking forward to a number of exciting beam times that we either lead, or where we collaborate with others. Already scheduled for the fall of 2023 are:

- ➢ "Gas phase x-ray scattering at higher photon energies", PI X. Cheng, X-10000 October 2023 at LCLS – CXI.
- ➢ "Structural Insight into Norrish Type-I Reactions of Cyclic Ketones" PI A. Green, L-10060, October 2023 at LCLS – CXI.
- ➢ "Ultrafast imaging of the formation of highly strained cyclic molecules" PI M. Centurion, U101, November 2023 at the MeV instrument at SLAC.
- ➢ "Ultrafast Ring Conformer Reactions" PI P. M. Weber, U100, November 2023 at the MeV instrument at SLAC.
- ➢ "Probing electron dynamics with ultrafast x-ray scattering" PI R. Forbes, 2023B8024, December 2023 at SACLA, Japan.

Additional beam times have been approved and will be scheduled for the winter and spring of 2024. In particular, we hope to build on our beam time LX65, where we investigated the ultrafast dynamics of cyclopentadiene. In an upcoming LCLS beam time, we plan to expand the range of wavelengths used to pump the molecules to their excited states, and we will explore how methylation affects the time scales and outcome of the internal conversion reaction.

IV. Peer-Reviewed Publications resulting from this Project (2021-2023)

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2. "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.
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