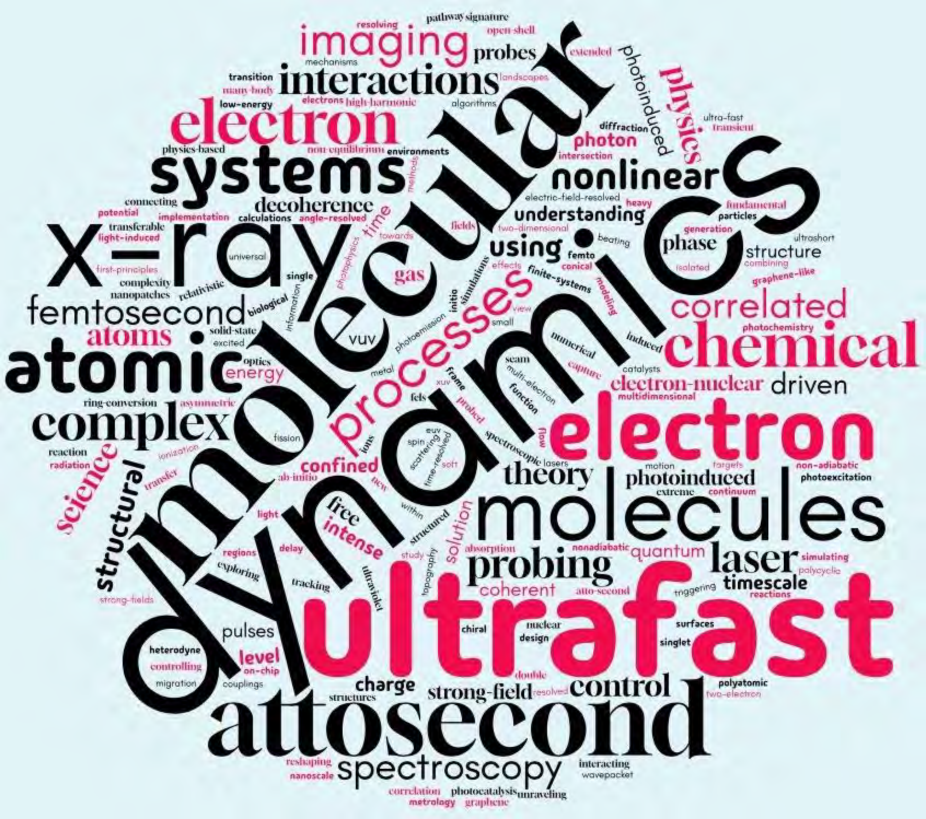
2024
Atomic, Molecular, and Optical Sciences Research PI Meeting



DoubleTree by Hilton Washington DC North/Gaithersburg
Gaithersburg, Maryland

October 28-30, 2024

U.S. DEPARTMENT OF ENERGY | Office of Science

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

Program and Abstracts

2024
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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.

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FOREWORD

This volume summarizes the 44th 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 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 Program continues to evolve its emphasis towards research that elucidates ultrafast dynamics in molecular systems of increasing complexity. The foundational knowledge and techniques produced by this research portfolio constitute crucial contributions in support of the BES mission.

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 two forward-looking panel discussions in the afternoons of Day 1 and Day 2. The discussions highlight the potential for transformative impact of DOE light sources. Specifically, the sessions will present opportunities to significantly advance AMOS that are afforded by the massive datasets with high time resolution that can now be generated and will discuss challenges in achieving them.

The first session, organized by Tom Weinacht and Phay Ho, is entitled, “Do experimentalists have a big data problem?” This session highlights new opportunities to significantly advance understanding of chemical dynamics. Leveraging vast data volumes with unprecedented time resolutions, however, requires innovative theory, modeling, and analysis approaches. The session will address the challenges and opportunities to exploit these complex experimental datasets, with a focus on advanced methods for many-body data. The second session, organized by Ken Schafer and Phay, is entitled, “When will your electrons talk to my nuclei? Tracking coherences from attosecond to femtosecond timescales.” This session is also driven by advances at DOE light sources and the massive datasets that can enable new insights into charge transfer and ultrafast dynamics. However, these advances may outpace the development of theoretical models needed to fully interpret the data. The panel discussion will explore key gaps in current theories and computational codes in areas such as coherences and non-adiabatic dynamics in photochemical processes, and discuss opportunities for improving quantum simulations.

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 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.

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 AMOS Program over the past year. A special thanks again go out to Phay Ho, who in his third year as a detailee to BES from Argonne National Laboratory continues to provide outstanding contributions to the Program, including the organization of this PI meeting and working with our PIs to develop the panel discussion sessions. Finally, we are grateful to the chairs and speakers in the panel discussions for their time in expertise in driving stimulating discussions of these important topics.

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

2024 Atomic, Molecular and Optical Sciences Research PI Meeting

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

October 28–30, 2024 (Times are EDT)

Monday, October 28

7:30 AM	*Breakfast*	
Opening Remarks		
8:30 AM	*Welcome and Introductory Remarks* **B. Gail McLean**	Director, Chemical Sciences, Geosciences, and Biosciences Division U.S. Department of Energy
New Researchers and Projects		*3-minute, 1-slide summary*
9:00 AM	**Barry Dunietz**	Kent State University
9:03 AM	**Steven Manson**	Georgia State University
9:06 AM	**Jeremy Rouxel**	Argonne National Laboratory
9:09 AM	**Ahmad Hosseinizadeh**	University of Wisconsin, Milwaukee
9:12 AM	*Break, 3 minutes*	
Lab Programs	***Amy Cordones-Hahn** (Chair) SLAC National Accelerator Lab*	*10-minute presentation, 5-minute Q&A*
9:15 AM	*Ultrafast Chemical Sciences* **Philip H. Bucksbaum**	SLAC National Accelerator Laboratory
9:30 AM	*Atomic, Molecular, and Optical Sciences* **Oliver Gessner**	Lawrence Berkeley National Laboratory
9:45 AM	*Atomic, Molecular, and Optical Physics* **Linda Young**	Argonne National Laboratory
10:00 AM	*Structure and Dynamics of Atoms, Ions, Molecules and Surfaces* **Artem Rudenko**	J.R. Macdonald Laboratory, Kansas State University
10:15 AM	*Break, 15 minutes*	
Session 3	***Niranjan Shivaram** (Chair) Purdue University*	*20-minute presentation, 10-minute Q&A*
10:30 AM	*X-ray Probes of Condensed Phase Photoinduced Dynamics* **Anne Marie March**	Argonne National Laboratory
11:00 AM	*Investigations of Organic Photochemistry with X-ray Spectroscopy and Imaging* **Thomas Wolf**	SLAC National Accelerator Laboratory
11:30 AM	*Recent Advances in Stimulated X-ray Emission Spectroscopy* **Uwe Bergmann**	University of Wisconsin, Madison
12:00 PM	*Working Lunch*	

SPECIAL SESSION 1	***Do Experimentalists Have a Big Data Problem?***
1:00 PM	Moderator: **Thomas Weinacht** (Stony Brook University) Panelists: **Philip H. Bucksbaum** (SLAC National Accelerator Laboratory), **James P. Cryan** (SLAC National Accelerator Laboratory) and **Todd Martinez** (SLAC National Accelerator Laboratory)
2:30 PM	*BREAK, 30 MINUTES*
SESSION 5	***Alexandra Landsman*** *(Chair) Ohio State University* *20-minute presentation, 10-minute Q&A*
3:00 PM	*Imaging Structural Dynamics in Isolated Molecules with Ultrafast Electron and X ray* **Martin Centurion** University of Nebraska
3:30 PM	*Following Ultrafast Electronic and Nuclear Dynamics in Strong-field Processes* **Anh-Thu Le** University of Connecticut
4:00 PM	*Dissociation Dynamics of Small Molecular Systems Probed by Multidimensional Momentum Imaging* **Thorsten Weber** Lawrence Berkeley National Laboratory
4:30 PM	*Frequency Upconversion into the VUV-EUV and Soft X-ray Spectral Regions Using Photonic Crystal Waveguides* **Henry Kapteyn** University of Colorado, Boulder
5:00 PM	*ADJOURN, DINNER ON YOUR OWN*

Tuesday, October 29

7:30 AM	*Breakfast*
Session 6	***Eitan Geva*** *(Chair) University of Michigan* *30-minute presentation, 10-minute Q&A*
8:30 AM	*Transient Absorption and Reshaping of Ultrafast Radiation* **Metta Gaarde** Louisiana State University
9:00 AM	*Multiphoton Ionization and Interfering Pathways* **Christopher Greene** Purdue University
9:30 AM	*Dynamics of Core-excited States in Atoms and Molecules Studied by Attosecond Four-wave Mixing* **Daniel Neumark** Lawrence Berkeley National Laboratory
10:00 AM	*Dispersion-free Rescattering Photoelectron Wave Packets in Multiphoton Ionization* **Cosmin Blaga** J.R. Macdonald Laboratory, Kansas State University
10:30 AM	*Break, 30 minutes*
Session 7	***Steve Manson*** *(Chair) Georgia State University* *20-minute presentation, 10-minute Q&A*
11:00 AM	*Attosecond Electron Dynamics using X-ray Free Electron Lasers* **James P. Cryan** SLAC National Accelerator Laboratory
11:30 AM	*Ionization Dynamics in Aqueous Systems* **Linda Young** Argonne National Laboratory
12:00 PM	*Working Lunch*
Special Session 2	***When Will Your Electrons Talk to My Nuclei? Tracking Coherences from Attosecond to Femtosecond Timescales***
1:00 PM	Moderator: **Kenneth Schafer** (Louisiana State University) Panelists: **Luca Argenti** (University of Central Florida), **Kenneth Lopata** (Louisiana State University) and **Spiridoula Matsika** (Temple University)
2:30 PM	*Break, 30 minutes*
Session 9	***Jin Qian*** *(Chair) Lawrence Berkeley National Laboratory* *20-minute presentation, 10-minute Q&A*
3:00 PM	*Imaging Photochemistry in Action* **Daniel Rolles** J.R. Macdonald Laboratory, Kansas State University
3:30 PM	*Dynamics and Control of Strong-Field Dissociative Ionization in Polyatomic Molecules* **Marcus Dantus** Michigan State University
4:00 PM	*Ultrafast Dynamics and Diffraction of Excited States* **Todd Martinez** SLAC National Accelerator Laboratory
4:30 PM	*Break, 15 minutes*
Session 10	***Jeremy Rouxel*** *(Chair) Argonne National Laboratory* *20-minute presentation, 10-minute Q&A*
4:45 PM	*Non-linear Resonant X-ray Interactions: Experiments and Imaging Coupled Vibrational, Rotational and Electronic Motion in a Triatomic Molecule* **Vinod Kumarappan** J.R. Macdonald Laboratory, Kansas State University

5:15 PM	*Combining Trajectory Surface Hopping with Pump-probe Spectroscopies to Understand Nonadiabatic Dynamics of Polyatomic Molecules* **Spiridoula Matsika** Temple University
5:45 PM	*ADJOURN, DINNER ON YOUR OWN*

WEDNESDAY, OCTOBER 30

7:30 AM	*BREAKFAST*
SESSION 11	**Barry Dunietz** *(Chair) Kent State University* *20-minute presentation, 10-minute Q&A*
8:30 AM	*Catalysis in Extreme Field Environments* **Matthias Kling** SLAC National Accelerator Laboratory
9:00 AM	*Recent Progress in Quantum Chemical Methods for Simulating Core Spectroscopy* **Martin Head-Gordon** Lawrence Berkeley National Laboratory
9:30 AM	*From Structure to Function* **Abbas Ourmazd** University of Wisconsin, Milwaukee
10:00 AM	*BREAK, 15 MINUTES*
SESSION 12	***Ahmad Hosseinizadeh*** *(Chair) University of Wisconsin, Milwaukee* *20-minute presentation, 10-minute Q&A*
10:15 AM	*Unveiling a New Regime of Electron Spin Coherence for Molecular Quantum Information Science* **Ryan G. Hadt** California Institute of Technology
10:45 AM	*Imaging Electron Dynamics with Time-Resolved Momentum Microscopy* **Thomas Allison** Stony Brook University
11:15 AM	*Attosecond science: Generation, Metrology and Application* **Louis F. DiMauro** Ohio State University
CLOSING	
11:45 AM	*Closing Remarks* **Thomas B. Settersten** Lead for Fundamental Interactions Team and Acting Program Manager for AMOS Program
12:00 PM	*ADJOURN*

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Laboratory Research Summaries (by Institution)

Argonne National Laboratory

J.R. Macdonald Laboratory

Lawrence Berkeley National Laboratory

SLAC National Accelerator Laboratory

University Research Summaries (by PI)

AMO Physics at Argonne National Laboratory

Gilles Doumy, Phay Ho, Anne Marie March, Jérémy Rouxel, Linda Young
Chemical Sciences and Engineering Division
Argonne National Laboratory, Lemont, IL 60439
gdoumy@anl.gov, pho@anl.gov, amarch@anl.gov, jrouxel@anl.gov, young@anl.gov

Overview

The Argonne AMO Physics program explores frontiers of x-ray science as enabled by accelerator-based light sources and, in so doing, lays the foundation for ultrafast x-ray applications in other scientific domains. We leverage the evolving properties of 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 and probe non-equilibrium states with atomic-scale spatial and/or temporal resolution. The experimental work is supported by theoretical developments, often using massively parallel codes on the 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 recently renewed EFRC on Ion Dynamics in Radioactive Environments and Materials, IDREAM.

The program is structured in three complementary subtasks. The first subtask aims at a quantitative understanding of nonlinear x-ray interactions encountered in studies with XFELs in pursuit of two long-held dreams - single-particle imaging and nonlinear x-ray spectroscopies. Intense attosecond x-ray pulses potentially provide a new damage-free single-particle imaging modality by using resonance phenomena such as Rabi cycling to enhance elastic scattering - as we study in a collaborative experimental/theoretical effort. We aim for a quantitative understanding of resonance phenomena both in isolated molecules and during propagation through dense media as foundation for nonlinear x-ray spectroscopies. A new effort studying sum and difference frequency generation in non-centrosymmetric liquids has been initiated.

In the second subtask we strive for a first-principles understanding of ultrafast molecular dynamics induced by x-ray single-photon interactions encountered in natural environments and at synchrotron light sources that result in x-ray damage of molecules and materials. A coordinated theoretical/experimental effort has introduced a quantum molecular model for inner-shell decay cascade dynamics to model ion/photon/electron coincidence studies of isolated molecules. We extend these studies from isolated to solvated molecules. We plan to explore interactions with x-ray beams with orbital angular momentum in a collaborative effort involving the APS and other DOE-supported researchers. We also initiate a new effort using symmetry-based probes of transient molecular dynamics.

The third subtask focuses on understanding photo- and x-ray-initiated chemical dynamics in solutions by observing localized atomic and electronic dynamics. The APS is used for timescales of picoseconds and longer while XFELs focus on attosecond and femtosecond phenomena. New high-repetition rate capabilities at the APS, LCLS and our own laser laboratory enable precision measurements of chemical dynamics in solutions and extensions from transient absorption to more photon-hungry x-ray emission methods. Building upon our demonstration of all x-ray attosecond pump/attosecond probe spectroscopy in pure liquid water, where we showed that the observed transient absorption spectral snapshots truly freeze nuclear motion, we move to more complex electrolyte solutions of fundamental and applied interest. Efforts to use diffraction probes (both x-ray and ultrafast electron) are being initiated. In these endeavors, vital preparatory work is done with laser pump/probe instruments at the Argonne Center for Nanoscale Materials (CNM).

This past year was particularly notable: the APS ended its upgrade and demonstrated the world's best emittance of 46 pm and has already ramped the current to 130 mA of the target 200 mA. The Aurora Exascale Computer installed its last component in June 2023 and demonstrated exascale performance in May 2024. Leveraging the initial successes of porting Monte-Carlo/Molecular Dynamics code to NVIDIA GPUs, we are actively readying the code to utilize the Intel GPUs in Aurora to enable studies of x-ray induced molecular dynamics in complex environments. A new collaborative LDRD has been awarded to establish capabilities at the APS to probe sequentially populated intermediates in optically pumped chemical reaction cycles. An effort to incorporate AI/ML in predicting core-electron binding energies and Auger spectra has been supported through the Eric and Wendy Schmidt AI for Science Program. The IDREAM EFRC was renewed for the second time; we co-lead the thrust on ultrafast radiolysis in solutions where the emphasis, complementary to our main program, is on systems of interest for legacy waste. Our new staff member, Jérémy Rouxel has launched exciting research directions in nonlinear x-ray processes, interactions with structured x-ray light and symmetry-based probes of molecular dynamics. He has also been awarded a DOE Early Career Award entitled "Chiral Dynamics in Asymmetric Catalysts Probed by X-rays".

1 Subtask 1: Nonlinear x-ray interactions

1.1 Imaging and molecular dynamics with intense attosecond x-ray pulses

P. J. Ho, L. Young, G. Doumy, J. R. Rouxel, A. Venkatesh, Y. Nam, C. Knight[a], T. Gorkhover[b], S. Kuschel[c], C. Bostedt[d], A. Marinelli[e] and other collaborators

Project Scope: Single-shot coherent diffractive imaging of structure and dynamics of non-crystalline samples in their native environment remains elusive due to sample damage. However, the advent of attosecond X-ray pulses presents new opportunities to mitigate radiation damage and explore dynamics at a new intensity frontier, where the X-ray Rabi oscillation rate surpasses the inner-shell decay rate. We aim to explore the effects of Rabi oscillation for achieving enhanced x-ray scattering and controlling molecular dynamics with intense x-ray pulses.

Recent Progress: Current XFEL facilities can generate intense attosecond pulses with energies up to hundreds of microjoules in the soft and hard x-ray regimes [29–33], offering a unique opportunity to explore quantum control of inner-shell electrons on ultrafast timescales. These high-intensity, nearly Fourier transform-limited pulses can induce a coherent, oscillatory population transfer (Rabi oscillation) between two energy levels via resonant coupling, which scales with field strength.

In collaboration with Tais Gorkhover and Stephan Kuschel's groups, we have been exploring ways to enhance single-particle imaging (SPI) efficiency [34, 35, 5]. This year, we performed resonant x-ray scattering studies in the hard x-ray regime at SACLA and LCLS, targeting Fe and Au nanoparticles. Analysis and model development are underway. Additionally, we completed our analysis of scattering data from single neon droplets obtained at LCLS using XLEAP and 20-fs pulses across the Ne K-edge. The intense XLEAP pulses allowed us to exploit x-ray-induced Rabi cycling for damage reduction in the single-particle, coherent diffraction approach.

Building on the neon cluster experiment and recent interest in Rabi oscillation dynamics at short wavelengths[36–38], we developed a time-dependent Schrödinger equation (TDSE) approach within a non-relativistic quantum electrodynamics (QED) framework to study resonant x-ray scattering under intense x-ray pulses [39]. This method allows us to investigate how coherent x-ray electron dynamics influences scattering signals from Ne^+. We account for both resonant fluorescence and elastic scattering channels, while also considering competing processes such as photoionization and inner-shell decay. By calculating the angular distribution and energy spectrum of scattered photons, we reveal interference effects between the elastic scattering and resonant fluorescence pathways, which notably produce a small asymmetry in the energy spectrum.

The contrast and appearance of fringes in the angular distribution are highly sensitive to interference between the elastic and resonant fluorescence channels. For small pulse areas, the interference depends on the initial state of the transient resonance, while for large pulse areas, the interference between these channels diminishes. Our study further demonstrates the impact of x-ray-driven Rabi oscillations on the total photon yield. The photon yield from transient resonance exhibits a strong dependence on the pulse area, deviating from the predictions of linear scattering models. Rather than increasing with pulse intensity, the yield reaches an upper limit. Resonant scattering is found to be at least an order of magnitude stronger than non-resonant conditions. Our results show that x-ray Rabi dynamics can be leveraged to control scattering responses, providing new insights into interference mechanisms and enhancing scattering efficiency in high-intensity x-ray regimes [40].

Future Plans: We will develop accurate time-dependent quantum approaches for characterizing the scattering response, interfering quantum pathways, decay and molecular fragmentation dynamics in multi-atom and molecular systems exposed to intense x-ray pulses. The results obtained will complement experimental efforts at the XFEL facilities.

1.2 Nonlinear resonant core-excitations in molecules

G. Doumy, E. Pelimanni, A. E. A. Fouda, P. J. Ho, R. Puettner[f], G. Grell[g], S. Bokarev[h], M. Meyer[i], M. Simon[j], I. Ismail[j], S. Sorensen[k] 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 [41], as well as create induced resonances and multiple resonant excitations. 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, including ultrafast nuclear dynamics in the core-excited states. We aim to study these processes in small molecules as an experimental and theoretical benchmark.

Recent Progress: XFELs can drive multi-core-ionization/excitation processes in the femtosecond timescale of typical core-hole lifetimes in molecules. When a molecule experiences a first core ionization, the binding energy of the remaining core electrons experiences a significant increase. The molecule can also exhibit induced core resonances which promise to improve on the ability to extract the chemically sensitive information encoded in the binding energy of so-called double-core-hole (DCH) states [4], through the higher site selectivity of the resonant step. It was also shown that these DCH states are extremely sensitive to ultrafast nuclear dynamics [8].

On the other hand, we demonstrated that fully resonant sequential multi-core excitations to exotic neutral multi-core excited states ($K^{-1}K^{-1}V^{2}$) are also feasible [42, 10]. Notably, the resonant transition energies are only slightly affected by a preceding resonant excitation at a different atomic site in the molecule ($\sim$ 1-2 eV) [42, 10, 43], in contrast to sequential ionization energies ($\geq$10 eV). Thus, multiple resonances at different atomic sites of the same element can in fact be covered within the spectral content of a single SASE pulse. We have experimentally confirmed the formation of double-core-excited molecule in the Nitrogen molecule at the SQS endstation of the EuXFEL[10], by comparing electronic decay spectra obtained at high and low x-ray intensity (see Fig. 1). The high intensity signal included distinct peaks corresponding to the unique decay channels where one of both of the core-excited electrons take an active role (so-called participator-spectator and participator-participator decays). The observed features are in very good agreement with calculated decay spectra obtained using a more realistic approach for continuum states involved in the processes.

This work in the nitrogen molecule demonstrated a new, nonlinear resonant spectroscopy, and ties into our efforts to explore the site-sensitivity of different x-ray probes in larger molecules. The prototypical ESCA molecule (ethyltrifluoroacetate) is well know for showing four distinct C K-edge photoemission peaks, originating from different chemical shifts. However, selective K-shell ionization at specific C site does not produce significantly different breakup patterns since Auger decay populates the same dicationic states in every case. Conversely, measurements of the resonant Auger spectra as a function of photon energy along the pre-edge resonances yield site-specific behaviors stemming from both the site of the excitation and the final state hole locality[6]. This showcases the ability of resonant Auger spectroscopy to selectively probe structural changes at specific functional group sites in a larger molecule.

Future Plans: This first experiment in N_2 has established this system as a great testbed for developing a better understanding of non-linear x-ray absorption processes occurring using XFEL pulses, and in particular in x-ray pump/x-ray probe techniques [2, 28] which are becoming more and more accessible at several facilities worldwide. We aim to continue using it to push for advanced

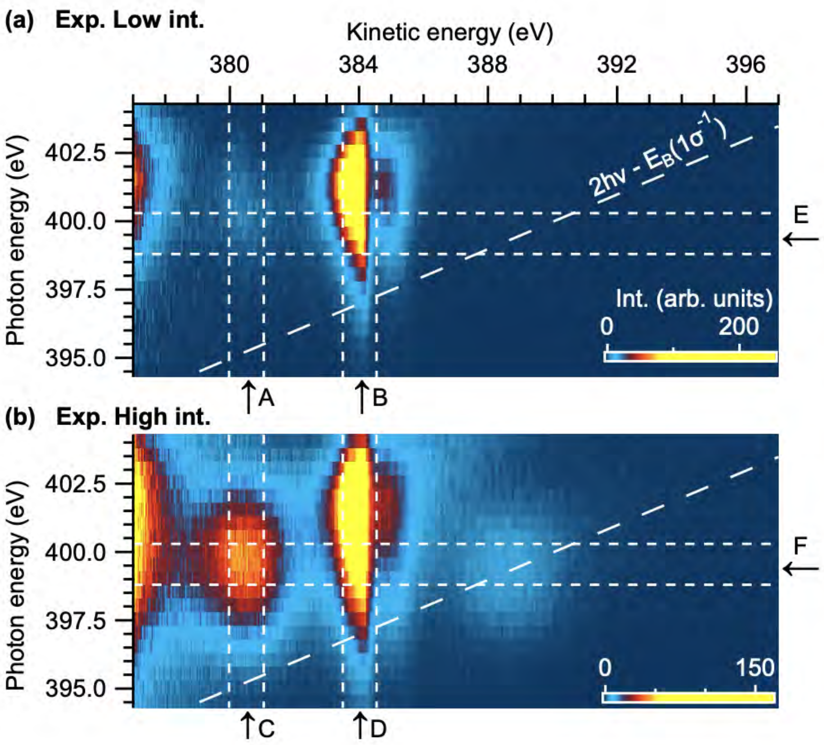

Figure 1: **(a,b)** Auger electron spectra in N_2 as a function of the photon energy at low (a) and high intensity (b). The high intensity map features distinct peaks maximized at photon energies red-shifted from the low-intensity core resonance, in agreement with the calculated prediction of a lower energy for the second resonant excitation.

theoretical and experimental studies, including possibilities for control over the double excitation process through manipulation of the x-ray pulse or use of a pulse sequence, coupled with advanced shot-to-shot spectral diagnostics and correlation techniques.

1.3 Advanced nonlinear x-ray spectroscopies

L. Young, P. J. Ho, G. Doumy, S. H. Southworth, J. R. Rouxel, K. Li[l], M. Gaarde[m], M. Meyer[i], T. Pfeifer[n], Ch. Ott[n], J.-E. Rubensson[o], A. Marinelli[e], J. Cryan[e], S. Li[e], K. Larsen[e], L. Cheng[p], C. Svetina[q], M. Chergui[r] and other collaborators

Project Scope: It has long been a dream to port ultrafast nonlinear spectroscopies from the optical to x-ray regimes, and thereby have a means to trigger and monitor valence-electron motions with high temporal and spatial resolution [44]. Building upon an understanding of intense x-ray–atom/molecule interactions in the isolated particle regime [45–56], we aim to extend observed nonlinear x-ray phenomena, such as amplified simulated x-ray Raman scattering (SXRS) [57] into full-fledged high-resolution, core-level spectroscopies. Other techniques, such as second-order x-ray sum-frequency generation, have only been demonstrated as proof of concept and we aim to demonstrate their applicability to probe liquid phase systems.

Recent Progress:

Stochastic stimulated x-ray Raman spectroscopy: XFELs now deliver nearly transform-limited pulses with sub-femtosecond duration with the potential for MHz repetition rates [31] 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. However, transient absorption measurements at high intensity will be subject to nonlinear propagation effects such as stimulated Raman scattering [57, 58], amplified spontaneous emission, pulse compression [59] which form the basis of proposed nonlinear x-ray spectroscopies [60]. While attosecond x-ray pulses are available, access remains limited, and the use of SASE pulses for stochastic spectroscopies is of interest [61]

This year we have finished analysis of some of our results from the 2022 EuXFEL campaign studying propagation of intense SASE x-ray pulses through dense Ne and CF_4 gases and submitted two papers for review [62, 63]. We have demonstrated stochastic super-resolution stimulated x-ray Raman spectroscopy as a simple, readily achievable method to populate and probe valence-excited states. Through covariance analysis we achieved the spectral resolution determined by SASE spike widths (0.1 eV for a 40-fs pulse) and circumvented instrumental resolution [62] in a dense neon gas target. The 10^8 directional amplification relative to spontaneous Raman scattering, simple experimental configuration and coming combination of high-repetition rate x-ray sources and detectors, makes stochastic super-resolution stimulated x-ray Raman spectroscopy an attractive method to probe femtosecond electron transfer processes in larger systems [64]. The study highlighted the advantages of having a non-invasive monitor of the incident SASE spectrum[1] and implemented our 3D TDSE/MWE propagation codes [65] on the Argonne Leadership Computing Facility to simulate the stochastic stimulated x-ray Raman spectra.

In CF_4 gas we performed a high-intensity transmission spectroscopy study of multiphoton-induced ultrafast molecular fragmentation dynamics. The approach unlocks the direct intra-pulse observation of transient fragments, including neutral atoms, by their characteristic absorption lines in the transmitted broad-band x-ray spectrum. The dynamics with and without initially producing fluorine K-shell holes were studied by tuning the central photon energy. Overall, this study demonstrates the potential of high-intensity x-ray transmission spectroscopy to study ultrafast molecular dynamics with sensitivity to specific intermediate species and their electronic structure.

Even-order nonlinear spectroscopies: Despite being central phenomena in nonlinear interactions, even-order nonlinear spectroscopies have been scarcely explored in the hard X-ray regime. Experimental demonstrations of the existence of the effects have been achieved [66, 67] but have not been applied further. In recent works, we have demonstrated theoretically how even-order nonlinear X-ray signals, in particular Sum- and Difference-Frequency Generation (SFG, DFG), do not vanish in noncentrosymmetric liquids [7]. We have also explored possibilities using optical entangled photons and quantum interferometry to separate interaction pathways contributing to DFG [3]. Finally, we have also shown that the use of cross-polarized linearly polarized X-ray pulses used in a Transient Grating setup can also probe molecular asymmetry [9], even if it is a third-order techniques.

Future Plans: We plan to complete analysis and publication for previous experimental campaigns on x-ray propagation through neon gas with attosecond pulses at the LCLS [68] and with SASE pulses at the EuXFEL which used a multimodal approach that incorporated both imaging x-ray emission at 90° and dispersed transmission [69]. We will continue to explore x-ray induced propagation dynamics using the multimodal approach with two-color pulses studying more complex systems, SF_6 and O_2, at the EuXFEL in October 2024. We will extend our stimulated Raman simulation toolkit to include molecular systems, with the aim to move to the liquid phase in the future.

Further simulations of SFG/DFG processes from liquids for systems that can directly be investigated at XFEL will be conducted, with the aim to estimate signal levels and sensitivity requirements. Beamtimes mixing soft/tender x-rays with optical beams in an SFG/DFG process will be proposed accordingly. Collaborations with C. Svetina on Transient Grating techniques will be pursued as a theoretical support for the long-term project ”Dynamics of nanoscale phenomena in solids and liquids studied with X-ray Transient Gratings at European XFEL”.

2 Subtask 2: Ultrafast molecular photophysics

2.1 Inner-shell decay cascades in molecular environments and solution

P. J. Ho, G. Doumy, A. E. A. Fouda, E. Pelimanni, S. Li, Y. Nam, S. H. Southworth, L. Young, V. Baht[l], D. A. Walko[s], P. R. Stollenwerk[t], L. Cheng[p], A. Verma[j], M. Simon[j], R. Püttner[f], and other collaborators

Project Scope: Understanding the decay processes in molecules following the creation of inner-shell vacancies is important for understanding the x-ray damage of molecules and materials, and for medical applications with Auger-electron-emitting radionuclides. Recent studies demonstrate that these decay cascades involve the environment (e.g. solvent) early in the process. We aim to experimentally characterize and develop theoretical methods to account for the effects of the molecular environment, local and nonlocal decay mechanisms and solvents on the decay and study the resulting molecular dynamics.

Recent Progress: Early motivations for this research program were to take advantage of the intense, tunable, high-resolution x-ray beamlines at the Advanced Photon Source for x-ray photoionization and vacancy cascades in heavy atoms and molecules containing heavy atoms [70, 71, 16]. X-ray and inner-shell interactions and applications have also been explored [11, 18, 15]. Those experiments and theory have set the stage for future investigations of environmental factors such as solvation that are important in chemical dynamics.

X-ray induced electron and ion fragmentation dynamics: 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. The 1s hole states in heavy elements have large x-ray fluorescence yields that transfer the hole to intermediate 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. 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. As a result, we can map the charge states and kinetic energies of the two correlated fragment ions associated with core-excited states produced during the various steps of the cascades. To understand the dynamics leading to the ion data, we developed a computational model that combines Monte-Carlo/Molecular Dynamics simulations with a classical over-the-barrier model to track inner-shell cascades and redistribution of electrons in valence orbitals and nuclear motion of fragments.

Post-collision interactions in heavy atoms: As a follow up experiment on post-collision interaction (PCI) at the K edge of Kr [11], our Scienta electron analyzer was used to characterize PCI at the Xe K edge at 34565 eV [18]. Both experiments investigated PCI between the K shell photoelectrons and Auger decays from L_2 vacancies produced by $K - L_2$ fluorescence. The fluorescence step adds an additional time delay of 0.24 fs in Kr and 0.068 fs in Xe, so that, for each excess energy, the 1s photoelectrons have moved further from the core before Auger decay and PCI are initiated. The fluorescence delays effectively increase K shell lifetimes and result in smaller PCI shifts than are observed upon direct L_2 photoionization. This expectation was confirmed in experiments conducted by our collaborators at the GALAXIES beamline of the SOLEIL synchrotron in France [72]. A simple expression for calculated PCI shifts [73] is in good qualitative agreement with the measured variations of the PCI shifts vs excess energy. Our collaborators have also further demonstrated the effects of Kr K fluorescence delays in comparison with PCI shifts made directly at the L_2 edge [74]. In combination, the Kr and Xe experiments have extended understanding of sub-femtosecond fluorescence delays and post-collision interaction in heavy atoms.

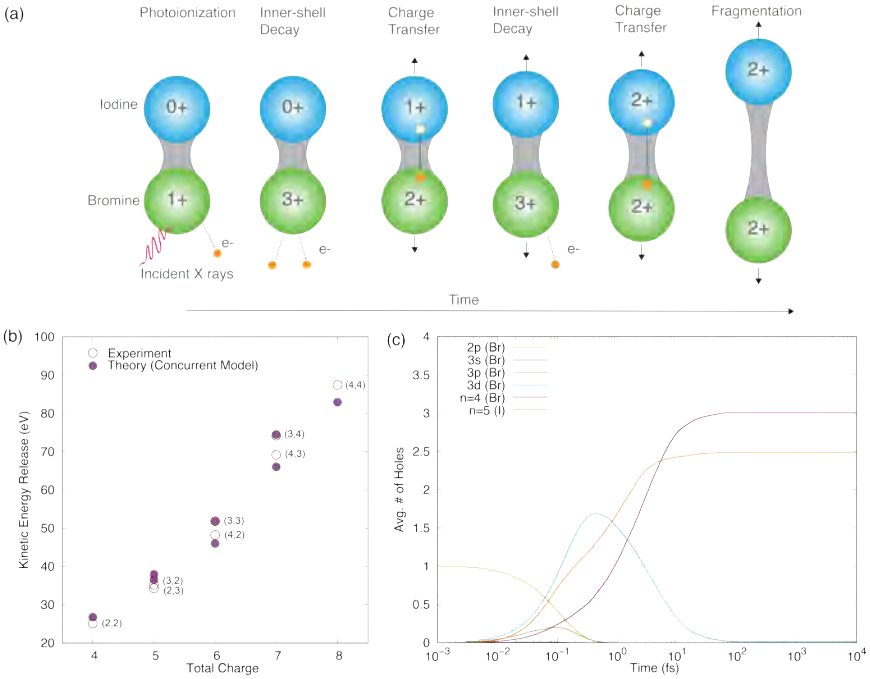

Figure 2: (a) Inner-shell deexcitation and fragmentation dynamics of IBr. (b) Kinetic energy distributions of various ion fragmentation pairs of IBr measured at 13486 eV in coincidence with Br $K\alpha$ emission. The open and filled circles are the experimental data and calculated results, respectively. (c) Average number of vacancies in each subshell of Br and the valence shell of I as a function of time, starting from a vacancy in 2p of Br.

Argonne Auger-Meitner Radioisotope Microscope: Nuclear decays of radioisotopes produce inner-shell electron vacancies that decay by radiative and radiationless transitions. The emitted Auger electrons can destroy the DNA and membranes of nearby tumorous cells[75, 76]. For this application, it is important to know the numbers and energies ("Auger multiplicities") of the emitted electrons in order 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. 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 [77]. In collaboration with the AMO group, the electron/ion coincidence detection chamber was commissioned and calibrated using APS x rays to photoionize Kr at the 14.3 keV K edge. This provided data with which to simulate the electron and ion trajectories and detection efficiences of the new instrument. Additional measurements of electron/ion coincidences using a 1064 nm laser and its harmonics to photoionize small molecules are in progress.

Quantum Molecular Model for Inner-shell Decay Cascade Dynamics: We have previously modeled the decay and the subsequent molecular processes using MC/MD simulations that describe the electronic structure at an atomic level, thus omitting molecular bonding effects [16]. We addressed the gap by introducing a novel approach that couples Auger-Meitner decay to nuclear dynamics across multiple decay steps, by developing a decay spawning dynamics algorithm and applying it to potential energy surfaces characterized with *ab initio* molecular dynamics simulations [78]. We showcased the approach on a model decay cascade following the K-shell ionization of IBr and subsequent K_β fluorescence decay. We examined two competing channels that undergo two decay steps, resulting in ion pairs with a total charge state of 3 +. This approach provides a continuous description of the electron transfer dynamics occurring during the multistep decay cascade and molecular fragmentation, revealing that the combined inner-shell decay and charge transfer timescale are approximately 75 fs. Our computed kinetic energies of ion fragments agree well with the experimental data. The results of this work have been submitted for publication.

Future Plans: We will perform time-dependent x-ray dynamic simulations, as well as electronic structure codes, to simulate the x-ray-induced molecular dynamics in both gas and condensed phases and compute experimental observables on petascale and exascale computers. The theoretical effort will complement the experimental efforts of liquid phase electron spectroscopy using hard x-rays at synchrotrons (APS-U, SOLEIL) and XFEL facilities.

2.2 X-ray induced dynamics with OAM beams

J. R. Rouxel, P. J. Ho, L. Young, A. Venkatesh, Y. Nam, H. Yong[u], C. Schwartz[v], D. Haskel[s], M. Wojcik[s], L. Assoufid[s], C. David[d], B. Rösner[d].

Project Scope: It is now possible to generate x-ray beams carrying an Orbital Angular Momentum (OAM), also called twisted or vortex beams. Their exotic topological nature engages with molecular chirality in a more tunable fashion than circularly polarized light, thanks to the larger space of controllable parameters at play, and have thus generated an increased interest recently. An important effort by the optics and x-ray communities have thus been dedicated at improving the generation [79] and characterization [80–82] of OAM beams. While their use for spectroscopy and scattering was limited, recent publications [83–86] have demonstrated that their interactions with matter can lead to novel spectroscopic and diffraction techniques [87, 88].

We aim to explore how OAM beams interact with molecules in spectroscopic and diffraction techniques, in collaboration with scientists at UCSD, UNLV, APS and PSI, by probing static asymmetric systems or by triggering dynamics with them. We plan to design a robust OAM beam generation setup that could be deployed at various APS beamlines. This will be supported by a theoretical effort showing how the OAM beam asymmetry leads to modified interactions and molecular dynamics.

Recent Progress: We have previously shown than Helical Dichroism (HD), the differential absorption of beams with carrying opposite OAM, can distinguish opposite enantiomers [85]. HD is expected to provide information complementary to Circular Dichroism measurements, while profiting of different experimental advantages. HD is expected to scale favorably from a tighter focus and is not bounded to a single ±1 value like techniques relying on circular polarization. We have also shown how time-resolved X-ray diffraction using OAM probe beams can be sensitive to molecular electronic coherences [87], making them an potential tool to monitor conical intersections in molecular dynamics.

An important limitation of previous experimental efforts was that the OAM generation and characterization constituted a significant effort and specialized beamlines, and thus prevented beamtimes to focus solely on the light-matter interactions aspects. To survey possibilities for this novel effort, we have started collaborative discussion with APS beamline scientists, the APS x-ray optics group and other scientists outside of Argonne interested to use this capability once available. We have identified that a movable setup consisting of spiral Fresnel zoneplates [89] and the needed optics and stages could be designed and pre-aligned using a beamline providing full beam characterization via ptychographic measurement [85]. At other beamlines dedicated to spectroscopy or diffraction techniques, the setup would be installed without additional alignement and the beam OAM quality can be checked using an OAM sorter. The latter is another device that can spatially separate the different OAM components of an incident beam [80, 82].

Future Plans: We plan to start the design of the OAM beam generation setup in collaboration with the UNLV scientists and the Argonne x-ray optics group. The fabrication of spiral Fresnel zoneplates themselves will be led by the UNLV team who recently received an EPSCoR funding in that direction while the AMO physics group will design the movable OAM setup in collaboration with beamline scientists. Theoretical efforts to predict diffraction and absorption observable by x-ray OAM beams at various photon energies will be conducted. Once available, we plan to use the OAM setup to carry systematic investigations of Helical Dichroism and of x-ray diffraction from chiral liquids with OAM beams at the APS.

2.3 Symmetry-based probes of transient molecular dynamics

J. R. Rouxel, G. Doumy, P. J. Ho, L. Young, M. Asplund, Y. Nam, C. Callegari[r], R. Mincigrucci[r], C. Svetina[i,q].

Project Scope: One of the challenges of ultrafast molecular dynamics is to identify which pathways are undertaken by a photoexcited molecule along potential energy surfaces. In some cases, the various pathways have a different symmetry and can thus be distinguished by symmetry-sensitive probes. The most striking example is a molecular pathway that can branch into paths containing mirror symmetries or not.

Recent Progress: For this novel activity, we have identified an adequate system, 1,3-cyclohexadiene (CHD), that undergoes a ring opening upon photoexcitation [90]. In this type of reaction, the well-known Woodward-Hoffmann rules dictate whether a ring opening reaction is dis or conrotatory. In the latter, the molecule reaches a helical transient state while this is not the case for distoratory dynamics. Experiments at FEL facilities have given new insights on photoinduced ring openings: Weber et al. [91] have measured ultrafast x-ray scattering of the CHD ring opening reaction and could confirm that the measured scattering patterns matched the ones simulated by ab initio quantum chemistry methods.

We have identified that the use of time-resolved photoelectron circular dichroism (PECD) would provide a direct measurement of this asymmetric transient state and have proposed an experiment at the FERMI FEL. Other typical reactions involving asymmetric states, e.g. the cis-trans isomerization of azobenzene [92], are also being considered. As part of this effort, we numerically studied the nuclear dynamics of helicene molecule [17] using time-resolved x-ray circular dichroism (XCD) as a probe. Efforts on XCD and on chiral compounds in their ground state will now be part of the Early Career Award project.

Future Plans: EUV and soft x-ray FELs have developed PECD beamlines with adequate temporal resolutions to carry out these experiments in the gas phase. Experiments will be proposed at these facilities and will be supplemented by nuclear dynamics simulations, which must include the effect of conical intersections along the propagation.

3 Subtask 3: Chemical dynamics in solution phase

3.1 Role of the environment on the reactivity of metal complexes

A. M. March, G. Doumy, J. R. Rouxel, R. Wallick, S. H. Southworth, L. Young, W. Gawelda[g], G. Vanko[w], Z. Nemeth[w], A. Andersen[x], N. Govind[x], D. Hayes[y], M. Chini[z], Y. Nagata[aa]

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. Our focus is on iron complexes solvated in water as both iron and water are earth abundant and therefore important for a fair, worldwide sustainable energy future. We aim to utilize newly available experimental tools along with QM/MM simulations to gain new insights into the reactivity of these complexes, and also of the influence of the environment on the reactivity of metal complexes in solution, specifically the behavior of counterions along with solvation shell dynamics.

Recent Progress: Our recent studies have focused on two complexes in water solutions: hexacyanoferrate, $[\mathrm{Fe^{II}(CN)_6}]^{4-}$, and the ferrate(VI) ion, the latter in collaboration with the group of Dugan Hayes at the University of Rhode Island. $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ and its redox couple $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ (often referred to as ferrocyanide and ferricyanide), are of interest across a wide range of disciplines, either as the ions themselves or as precursors to prussian blue. Notably, they are of interest for battery research and environmental remediation. The two primary reaction channels for ferrocyanide, which can be photoinduced, are oxidation and aquation. The ferrate(VI) ion becomes highly reactive in the presence of UV light, suggesting potential uses in water remediation. Precise control of the reactivity of these complexes could be impactful and is why we believe they warrant detailed mechanistic explorations.

We have previously investigated these complexes using using x-ray absorption spectroscopy with the MHz repetition-rate laser-pump/x-ray-probe capabilities our group has built at the Advanced Photon Source[93, 20]. This past year additional XAS results on the ferrate(VI) ion were published[24] that, along with optical spectroscopy, showed that in deuterated water there was a suprising 10-fold increase in the decay of one of the intermediates compared to that in water. This was found to be due to a difference in the vibrational coupling to a single solvent molecule. We also have carried out MHz pump-probe nonresonant Fe 1s XES measurements on both these complexes using the MHz pink-beam setup we built at the APS[94]. Our ferrocyanide measurements included the Kα, Kβ, and valence-to-core spectral regions and focused on the aquation reaction. The measured Kβ line support the assignment of triplet spin state for 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 mostly confirmed the experimental results, but small discrepancies between the datasets for the two beamtimes indicated that systematic errors were on par with our small ($< 0.1\%$) transient signals and needed careful treatment. We anticipate that this analysis will allow us to extract meaningful, subtle spectral signatures in the Kα, Kβ, or vtc XES regions that yield new insight, beyond simple confirmation of our expectations. Once complete, this analysis will enable us to also interpret the aqueous ferrate(VI) ion XES transient signals. We have also carried out optical transient absorption measurements with our newly built optical transient absorption setup; a study of the temperature dependence of the reaction rate supports our QM/MM MD simulation's prediction[93] that fluxionality plays a role in the reaction; spectral analysis allowed us to understand that a small amount of pentacoordinated species survives in equilibrium with the aquated species at long time; and the identity of the counterions ($\mathrm{Na^+}$ vs. $\mathrm{K^+}$) affects the reaction dynamics. These findings call for incorporation of the counterions in the QM/MM MD simulations. Our simulations so far were achieved within a collaboration with A. Andersen and N. Govind at PNNL. In a synergistic effort with subtask 1.3, we have collaborated wtih Y. Nagata to simulate the ultrafast solvent response to a resonant stimulated X-ray Raman process in a Zn-Ni metalloporphyrin dimer solvated in water[27], to investigate a potential new spectroscopy tool.

Future Plans: For our experimental efforts we plan to make use of time-resolved soft x-ray spectroscopy at BESSY-II, tender x-ray spectroscopy at SwissFEL, and hard x-ray spectroscopy at APS to probe various counterions of the aqueous ferroycanide complex. These x-ray methods will be complemented by measurements using our in-house MHz OTA, which we will continue to develop. Additionally, we plan to develop in-house QM/MM capabilities to predict and analyze structural observables from diffraction data, including time-resolved pair-distribution functions (PDF). These will support X-ray scattering experiments conducted at the APS to monitor the relative positions of counterions.

3.2 Probing complex reaction pathways across multiple timescales

A.M. March, G. Doumy, C. Elles[ab], J. Blakemore[ab], R. Sension[ac], J. Penner-Hahn[ac], X. Zhang[s], C. Liu[s]

Project Scope: For light-induced reactions in liquids, chemistry often occurs across a wide range of timescales, from the femtosecond regime of the initial electronic excitation out to the microsecond regime (or longer) where one finds diffusion controlled bimolecular reactions. The traditional pump-probe technique synchronizes the initial photophysical and photochemical reactivity of many molecules within an ensemble so that their mechanistic pathways can be observed with experimental techniques. A challenge emerges when the pathways are complex, for example those involving branching or competing pathways or very reactive species that are formed at a later stage of the reaction. Signatures of different species may be present in a measured transient signal in these cases, but without detailed knowledge of the relative contribution and precise signatures it becomes extremely difficult if not impossible to extract meaningful mechanistic insight. We are trying to tackle these challenges with a three-pronged approach. First, we will utilize newly available tools such as the high rep rate capabilities at LCLS that promise observation of subtle transient signals on the femtosecond timescale and the APS Upgrade that provides a factor of two more x-ray flux in fine-spaced fill patterns that are optimal for tracking processes concurrently over picoseconds, nanoseconds, and microsecond timescales. Second, we will incorporate a multimodal approach, using various optical and x-ray spectroscopy/scattering techniques to gain a variety of complementary information. Third, we will incorporate multiple laser pulses, as double pumps and/or probes, in combination with x-ray probes to observe, and perhaps influence, subsequent chemical reactivity of aqueous metal complexes after their initial photoexcitation through photoexcitation of photoproducts and/or solvent.

Recent Progress: We are collaborating with Xiaoyi Zhang, beamline scientist in charge of the Time-Resolved X-ray Research group at APS, to implement our MHz repetition rate x-ray spectroscopy capabilities at Sector 25. We have previously demonstrated the ability to measure in the finely spaced 324 bunch mode at APS[95] and showed that an asynchronous pumping strategy enables efficient collection of picosecond, nanosecond, and microsecond data in single scans.[21] These technical capabilities are being readied for use with the commissioning of the Sector 25 APS-U beamline as the APS is building back up its capabilities. In addition, together with the beamline scientists at Sector 25, we have secured a new 3-year LDRD funding to implement double-laser pump capabilities using in part our Duetto laser, as well as our HERFD-XAS expertise and capabilities. Our scientific investigations will build upon these technical advances.

A prime target for these investigations is a series of Mn-based CO_2 reduction catalysts with the form $Mn(CO)_3(bpy)Br$, bpy = 2,2-bipyridyl that we have been studying in collaboration with groups at the University of Kansas and the University of Michigan. These complexes act as CO_2 reduction catalysts, but degrade rapidly upon light exposure. Our aim is to understand in detail this degradation. Initial transient optical measurements suggested a fast CO removal followed by solvent attachment and subsequent dimerization, but open questions remain. Our collaboration has performed extensive x-ray absorption spectroscopy measurements on multiple timescales at the APS and LCLS at both Mn and Br K-edges, providing local probes on the metal center and on the Br ligand whose role is uncertain.

Analysis is focusing on the early timescale measurements, and is complemented by calculations of both the pre-edge region using the ORCA package and the XANES region using FDMNES. The initial photoabsorption step is captured immediately at both Mn and Br edges, and exhibits the characteristics of a multi-center charge transfer. The rapid decay of this state is captured at both edges, but following this step no change is observed at the Br edge, while the Mn edge signature continues to evolve. Possible Br detachment or migration from axial to equatorial position is being explored, as well as the timing of solvent attachment following the known loss of a CO ligand. We suspect that more than one pathway may be evident in our measurements.

In addition, anisotropic measurements were also performed. Comparison of a complex with the bpy ligand to one with a more rigid ligand, both with nearly identical optical absorption properties, yielded surprising results; the bpy complex exhibited almost no anisotropy while the rigid-ligand complex yielded a transient x-ray absorption signal exclusively in the direction perpendicular to the dipole excitation. This surprising finding has motivated a request for more data to confirm and complete it.

Future Plans: The immediate goal regarding the Mn complexes is to finalize our understanding on the short time scale, before extending this knowledge to the longer time scales (nanoseconds to microseconds). We believe that these systems are prime candidates for the multiple optical pump setup that will be developed at Sector 25, since there is already literature suggesting that the full behavior upon light illumination involves several optical excitation steps.

3.3 Ionization-induced dynamics in solution phase

L. Young, S. Li, K. Li, G. Doumy, S.H. Southworth, C. Otolski, A. M. March, P.J. Ho, J. Rouxel, M. Asplund, Z.-H. Loh[ad], J. E. Rubensson[o], Y. Kumagai[ae], R. Santra[b,af], L. Inhester[af], A. Sopena Moros[af], S. Bhattacharyya[af], K. Kunnus[e], G. Dakovski[e], D. DePonte[e], M.-F. Lin[e], S. Moeller[e], C. Pearce[x], E. Nienhuis[x], J. LaVerne[ag], T. Orlando[ah], L. Lu[ai], X. Li[ai], O. Bjorneholm[o], B. Schwartz[aj] and other collaborators

Project Scope: Understanding the elementary processes that initiate radiation damage in condensed phases [96, 97] remains a elusive problem where limited mechanistic information exists. Here novel time-resolved x-ray spectroscopy and scattering methods offer a probe of chemical reaction mechanisms following ionization in aqueous systems within a radiolysis "spur". Newly developed XFEL x-ray pump/probe techniques enable one to monitor the initial events following inner-valence and core-ionization, and, in combination with laser-ionization of valence orbitals, a means to dissect the full range of ionization phenomena on the ultrafast timescale.

Recent Progress: *Dynamics and spectroscopy in valence-ionized liquid water:* Earlier we established the prominent x-ray spectroscopic absorption resonance of the hydroxyl radical (OH·) in liquid water and measured its formation via ultrafast ($\sim 50-$fs) proton transfer [98] and its resonant inelastic x-ray scattering spectrum [99]. The hydroxyl radical, an extremely strong oxidizing agent, is one of two primary products in the radiolysis of liquid water, the other being the hydrated electron $e^-(aq)$, a very strong reducing agent. This year we completed a combined theoretical/experimental study [25] where we identified x-ray absorption signatures for all products of the proton-transfer reaction, OH·, H_3O^+ and $e^-(aq)$. Our experimental results, supported by *ab initio* calculations, confirmed the formation of a cavity in which the solvated electron is trapped. We showed that the solvation dynamics are governed by the magnitude of the random structural fluctuations present in water. As a consequence, the solvation time is highly sensitive to temperature and to the specific way the electron is injected into water.

Attosecond pump/attosecound probe x-ray spectroscopy of liquid water:

This year we published the first attosecond-pump/attosecond-probe x-ray spectroscopic study in a condensed phase target, liquid water [26]. We used a synchronized attosecond x-ray pulse pair from the LCLS x-ray free-electron laser [28] to study the electronic response to valence ionization in liquid water through all x-ray attosecond transient absorption spectroscopy (AX-ATAS). Our analysis showed that the AX-ATAS response is confined to the subfemtosecond timescale, eliminating any hydrogen atom motion and demonstrating experimentally that the 1b1 splitting in the x-ray emission spectrum is related to dynamics and is not evidence of two structural motifs in ambient liquid water. The methodogy freezes all nuclear motion and allows to model spectrocopic snapshots with time-independent *ab initio* electronic structure methods.

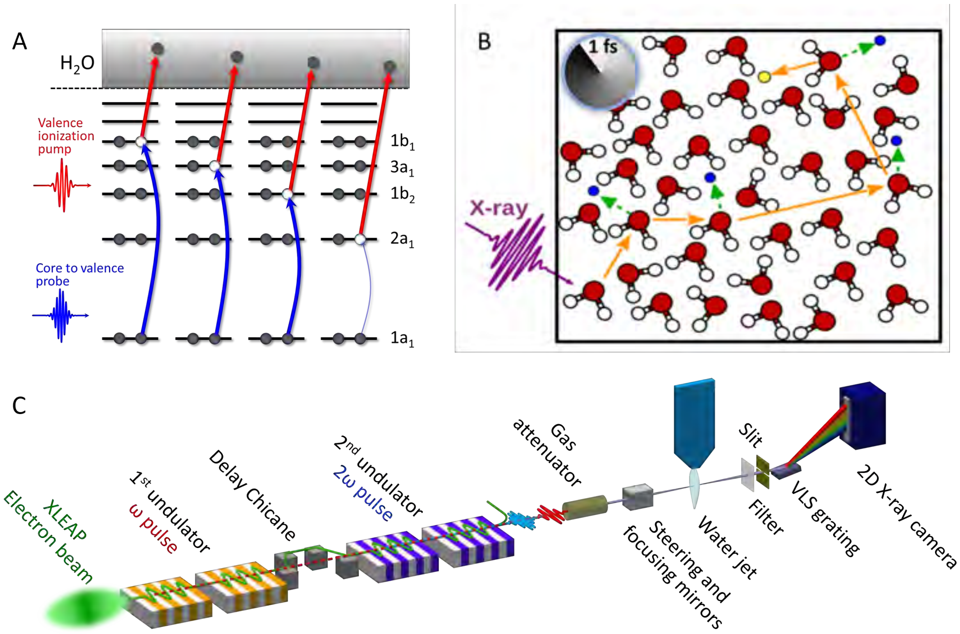

Figure 3: All x-ray attosecond transient absorption spectroscopy (AX-ATAS) in liquid water. Two synchronized attosecond pulses with photon energies related by $\omega/2\omega$ are incident on a water sheet jet and the transmitted 2ω probe beam is energy dispersed onto a 2D camera. **(A)** The ω pulse has sufficient energy to ionize an electron from anywhere in the valence band while the 2ω pulse probes the core-to-valence transition region near 530 eV. **(B)** Electrons resulting from the initial x ray-induced valence ionization go on to collisionally ionize nearby water molecules in the liquid phase sample on the sub-femtosecond timescale. **(C)** The first undulator array, tuned to ω, imprints a microbunching that is reused in the second undulator array, tuned to 2ω, to produce an attosecond x-ray pulse pair with small interpulse jitter [28].

Dynamics and spectroscopy in valence-ionized NaCl solutions:

This year we have taken the first step toward understanding valence ionization dynamics in systems more complex that pure water, by studying aqueous solutions of NaCl. We led an experiment at the EuXFEL aiming at monitoring electron solvation in the presence of Na^+ cation traps. The experiment built upon our earlier studies that provided clear x-ray absorption signatures of relevant species H_2O^+, OH·, e^-(aq), H_3O^+ near the oxygen K-edge. These enable the simultaneous tracking of both the electron and hole localization dynamics. In addition, access to the Na K-edge allowed us to monitor the electron solvation process locally at the Na^+ cation trap. Control of the electron ejection radius and the introduction of Na^+ cation traps within the ejection sphere will provide more insight into solvation dynamics. The experiment leveraged the SASE-3 beamline at the SCS-CHEM endstation equipped with beamsplitting off-axis zoneplate (BOZ) optics and the single-shot-capable DSSC detector. This configuration which been shown to provide shot-noise-limited x-ray absorption spectra with time resolution in pump/probe mode of $\sim$ 50 fs without jitter correction [100].

Future Plans: We plan to continue studies of solution phase ionization dynamics on more complex systems using a variety of novel experimental methods including attosecond x-ray pump/probe spectroscopies. Studies of non-local decay mechanisms (ICD, ETMD) around metal ions in the time domain is planned to complement theoretical studies [101] and traditional energy domain studies of these processes using electron spectroscopy [102], where overlapping spectra complicate the experimental analysis. Following participation in an early science experiment with liquid jets at the MeV UED facility at SLAC in September 2024, a new effort using electron diffraction, which unlike x-ray diffraction is sensitive to the hydrogen atoms, to probe solvent structure around the excess electron in both pure water and NaCl solutions is being evaluated *in silico*.

Affiliations of collaborators

[a] Argonne Leadership Computing Facility, Argonne National Laboratory, Lemont, IL.
[b] Universität Hamburg, Hamburg, Germany.
[c] Technischen Universität Darmstadt, Darmstadt, Germany.
[d] Paul Scherrer Institute, Villigen, Switzerland.
[e] SLAC National Accelerator Laboratory, Menlo Park, CA.
[f] Freie Universität, Berlin, Germany.
[g] University of Madrid, Spain.
[h] University of Rostock, Germany.
[i] European XFEL, Hamburg, Germany.
[j] Université Sorbonne, Paris, France.
[k] Lund University, Lund, Sweden.
[l] University of Chicago, Chicago, IL.
[m] Louisiana State University, Baton Rouge, LA.
[n] Max Planck Institute for Nuclear Physics, Heidelberg, Germany.
[o] Uppsala University, Sweden.
[p] Johns Hopkins University, Baltimore, MD.
[q] Madrid Institute for Advanced Studies, IMDEA Nanociencia, Madrid, Spain.
[r] Elettra Sincrotrone Trieste, Basovizza, Italy.
[s] Advanced Photon Source, Argonne National Laboratory, Lemont, IL.
[t] Physics Division, Argonne National Laboratory, Lemont, IL.
[u] University of California, San Diego, La Jolla, USA.
[v] University of Nevada - Las Vegas, Las Vegas, NV.
[w] Wigner Research Centre for Physics, Hungarian Academy Sciences, Budapest, Hungary.
[x] Pacific Northwest National Laboratory, Richland, WA.
[y] University of Rhode Island, Kingston, RI.
[z] The Ohio State University, Columbus, OH.
[aa] Max Planck Institute for Polymer Research, Mainz, Germany.
[ab] University of Kansas, Lawrence, KS.
[ac] University of Michigan, Ann Arbor, MI.
[ad] Nanyang Technological University, Singapore.
[ae] Nara Women's University, Japan.
[af] Center for Free-Electron Laser Science, DESY, Hamburg, Germany.
[ag] University of Notre Dame, South Bend, IN.
[ah] Georgia Tech University, Atlanta, GA.
[ai] University of Washington, Seattle, WA.
[aj] University of California, Los Angeles, CA.

Peer-Reviewed Publications Resulting from Subtask 1 (2022-2024)

[1] K. Li, J. Laksman, T. Mazza, G. Doumy, D. Koulentianos, A. Picchiotti, S. Serkez, N. Rohringer, M. Ilchen, M. Meyer, et al., "Ghost-imaging-enhanced noninvasive spectral characterization of stochastic x-ray free-electron-laser pulses", Communications Physics **5**, 1–8 (2022).

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[3] H. K. Yadalam, M. Kizmann, J. R. Rouxel, Y. Nam, V. Y. Chernyak, and S. Mukamel, "Quantum Interferometric Pathway Selectivity in Difference-Frequency-Generation Spectroscopy", The Journal of Physical Chemistry Letters **14**, 10803–10809 (2023).

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Peer-Reviewed Publications Resulting from Subtask 2 (2022-2024)

[11] S. Li, D. Koulentianos, S. H. Southworth, G. Doumy, L. Young, D. A. Walko, R. Püttner, J. D. Bozek, D. Céolin, A. Verma, et al., "Manifestation of postcollision interaction in krypton LMN Auger spectra following K-shell photoionization", Physical Review A **106**, 023110 (2022).

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Early Career: Chiral Dynamics in Asymmetric Catalysts Probed by X-rays
DE-FOA-0003176

Jérémy R. Rouxel
Argonne National Laboratory
9700 S Cass Ave, Lemont, IL 60439
jrouxel@anl.gov

Project Scope: Chiral molecules are molecules devoid of any plane of mirror symmetry, i.e. centrosymmety is broken. They often come in pairs, called enantiomers, and are ubiquitous in several fields of chemistry including catalysis [1], synthesis and stereochemistry.

This Early Career Research Program aims at gaining fundamental insights into molecular chirality by developing chirality-sensitive x-ray spectroscopies that can provide previously inaccessible local structure information. Our goal is to demonstrate that x-ray chiral techniques can reveal qualitatively new structural information encrypted in the distance between the resonantly probed atom and the chiral center [2]. The mechanistic knowledge obtained will help in understanding how chirality is transferred from a chiral molecule to an achiral one.

We aim to exploit several converging advances to address that challenge. Recent progress in polarization control at large-scale facilities, novel theoretical considerations regarding the interaction of light with chiral matter, and a renewed interest in developing different probes of molecular chirality, have set the stage for development of the new field of x-ray spectroscopy of molecular chirality [3, 4].

To establish the methodology for static experiments, we will first focus on small and widely available chiral molecules. Then, transition metal catalysts relevant to asymmetric catalysis and photocatalysis will be the primary targets for both static and time-resolved experiments.

Recent Progress: We started the project by conducting predictive simulations of X-ray Circular Dichroism (XCD) in small organic molecules (fenchone, limonene, proline) that we will use as test cases to develop XCD in the soft x-ray regime. These simulations are also supportive of beamtimes proposed at synchrotron facilities. Collaborative efforts to add liquid-phase delivery at the APS POLAR beamline and polarization control for the time-resolved APS beamlines were also kickstarted.

Future Plans: We will develop experimentally the methodology of XCD to probe chirality in liquids with resonant x-rays at synchrotrons, taking advantage of their upgraded stability and brilliance. We will target both tender/hard and soft x-ray beamlines (e.g. at the APS and SOLEIL synchrotron respectively). We will tackle the synthesis of relevant photocatalytic compounds, such as enantiopure $Ru(bpy)_3$, to obtain quantities manageable for beamtime conditions.

The theoretical efforts will continue to focus on accurate electronic structure calculations, typically using multi-configurational self-consistent field methods, of systems of increasing complexity, including chiral transition metal catalysts. We will also focus on developing QMMM capabilities to study solvent effects on the observed spectra.

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Peer-Reviewed Publications Resulting from this Project (2022-2024)

No Publications to report.

Structure and Dynamics of Atoms, Ions, and Molecules

Artem Rudenko, Daniel Rolles, Itzik Ben-Itzhak, Cosmin Blaga, Brett Esry, Loren Greenman,
Meng Han, Vinod Kumarappan, Chii-Dong Lin, Uwe Thumm
J. R. Macdonald Laboratory, Department of Physics, Kansas State University,
Manhattan, KS 66506

Award Number: DE-FG02-86ER13491 rudenko@phys.ksu.edu

1. Overview

The J.R. Macdonald Laboratory (JRML) explores the interaction of short and intense laser pulses with atoms and molecules, focusing on visualizing, understanding and ultimately controlling the resulting ultrafast dynamics. The main goal of this work is to advance our understanding of a variety of problems in ultrafast gas-phase chemical science. 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 study light-matter interactions in a very broad wavelength range, from the midinfrared to the hard X-ray domain, advancing experimental techniques as well as the corresponding theoretical and computational approaches. 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, including many groups within the DOE-AMOS program. Several JRML members conduct experiments at large-scale national and international accelerator-based light sources, such as X-ray free-electron lasers (LCLS, European XFEL, SwissFEL, FLASH, FERMI, SACLA) and synchrotron radiation facilities. At the JRML site, we currently run experiments with four femtosecond laser systems, including recently added 100-kHz KONZA laser customized for ultrafast photochemistry experiments, which will strongly benefit projects relying on multi-coincident measurements, and the ATTO-PHAROS laser, which has already generated near-single-cycle pulses with stabilized carrier envelope phase and will become the basis for a revived in-house attosecond experimental program at JRML In addition, JRML operates several high-harmonic generation sources, a variety of molecular, nanoparticle and ion beams, and a large number of complementary charged-particle imaging and spectroscopy instruments.

On the personnel side, Meng Han joined the JRML group at the end of 2023. In close collaboration with other JRML experimentalists and local theory groups, he has started to develop a research program focused on attosecond science. Among other scientific goals, Meng's research group aims to bridge the gap between the femtosecond chemistry and attosecond physics, elucidating the role of the electron phase in the earliest stages of chemical reactions.

Current JRML research projects are organized in three major scientific thrusts: "Correlated dynamics and ultrafast photochemistry", "Strong-field physics", and "Attosecond and ultrafast X-ray science". These themes serve as broad categories since the boundary between them is not always well defined. Almost all of our projects are collaborative, taking advantage of the expertise of several groups in the JRML and beyond. The following progress summaries provide brief updates on a select subset of our ongoing projects in each of these thrusts.

2. Correlated dynamics and ultrafast photochemistry

Photochemical molecular reactions 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 structural dynamics and energy flow in complex systems, we must first build the ability to observe and describe correlations in isolated molecules and simple reactions. At JRML, we use complementary tools to explore the dynamics of chemical processes, including coincidence detection of neutral and ionic molecular fragments, impulsive alignment of molecules, and ab initio theoretical methods. By combining theoretical modeling and computational approaches with the results from our experiments, we seek to gain a more complete picture of the correlated dynamics in molecular processes.

2.1. Investigating ring conversion reactions with Coulomb explosion imaging and other ultrafast structural imaging techniques – Rolles, Rudenko

Project scope: UV-induced ring-opening and ring-conversion reactions have attracted considerable interest in the ultrafast physics and chemistry community because they generally combine 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. Such reactions have been recently studied using time-resolved XUV photoelectron spectroscopy (TRPES) in combination with ab initio molecular dynamics calculations [1,2, P57], using ultrafast electron diffraction (UED) at the MeV-UED facility [3, P59] or ultrafast X-ray scattering [4-6] at LCLS/SLAC. While many of these studies demonstrated an overall excellent agreement between theory and experiment, several key elements of the theoretical predictions, including the actual ring-transformation motion, which is typically predicted to occur on sub-100 fs time scale, were not experimentally accessible. In this project, we apply a complementary Coulomb explosion imaging (CEI) approach, which is capable of providing a detailed atom-by-atom picture of the initial ring-conversion step.

Recent progress: We have recently shown that the CEI technique can visualize the geometry of planar [P2] and non-planar [P61] molecules with about a dozen atoms by revealing a clear signature of the position of each molecular constituent in the 3D momentum space. Here we show how this version of CEI can be applied for imaging transient structures in photoexcited molecules. We specifically focus on the example of UV excitation of furan at 200 nm, where the main reaction pathway is much debated [7,8], with some studies concluding that ring puckering (rather than ring opening), followed by a return to the electronic ground state of the ring-closed molecule, is dominant [8]. We probed the dynamics by time-resolved CEI employing intense 25-fs NIR pulse as a probe [9]. By directly imaging the motion of the individual atoms of the carbon backbone of the molecule and comparing the experimental momentum images (shown in Fig. 1a-c) with CE simulations for ring-opening (Fig. 1d-f) and ring-puckering trajectories, we reveal the presence of a strong ring-opening pathway that is completed in less than 70 fs. For the intact molecule, both experimental and simulated Newton plots show four distinct maxima corresponding to the four carbon ions in the ring. However, as the pump-probe delay increases, the maxima start bleeding into each other, and the maximum corresponding to the carbon atom C3 extends towards the center of the plot. The occurrence of such low-momentum C^+ fragments only shows up in the simulations

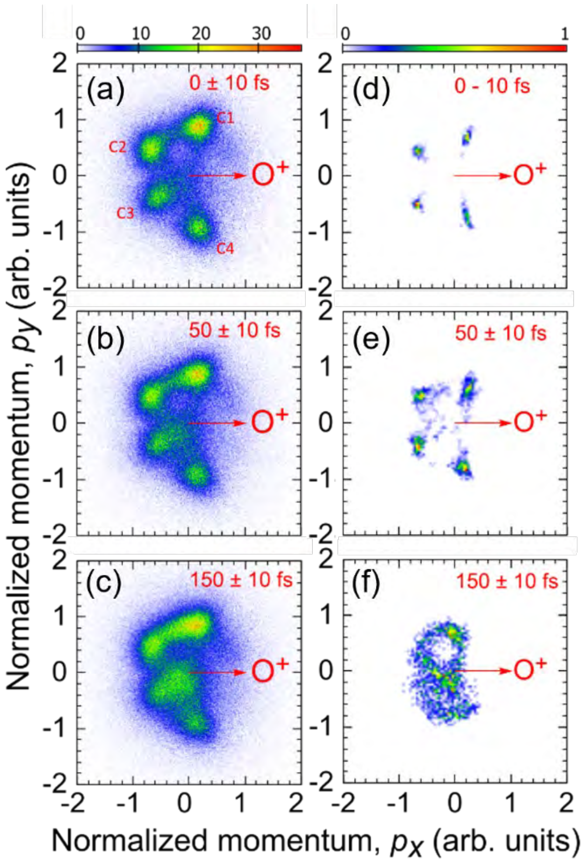


Fig. 1: Time-resolved CEI of furan. **(a-c)** Time-resolved Newton plots for carbon ions from the pump-probe experiment in the delay ranges indicated at the top right of each panel. **(d-f)** Simulated Newton plots of the ring-opening reaction, generated from the geometries obtained from the calculated trajectories. The molecular plane is defined by carbon C1 or C2, which were identified by their fragment ion KE (adapted from [9]).

of the ring-open isomer with a nearly linear C2-C3-C4 carbon chain, while no C^+ fragments with near zero momentum are observed in the simulations of ring-puckering or for "hot" ring-closed geometries, thus providing a clear signature of the formation of an open-ring product. By plotting the mean value of the momentum of the carbon ion reflecting C3 as a function of a pump-probe delay, we can deduce the 65±1 fs time constant for the ring opening step [9].

Future plans: We are currently extending the approach illustrated above for several other ring-opening and ring-conversion reactions. Particular systems that we plan to study include UV-excited thiophenone at 266 nm and isoxazole / oxazole molecules pumped by 200 nm radiation. For the former case, where we recently published TRPES [1] and UED [P59] results for the same reaction, we focus on determining the exact time scale of the initial ring opening step, which was not accessible with the temporal resolution of our previous experiments, and on the identification of several open-ring photoproducts that differ primarily by the position of the hydrogen atoms that are hard to resolve by the TRPES and UED experiments. Here, we will also compare the CEI results for the NIR and X-ray probes of comparable duration. For the latter case, by comparing the UV-induced dynamics of isoxazole and isooxazole isomers, we hope to gain a systematic understanding of the competition between ring opening and ring puckering, the signatures of these processes in ultrafast experiments, and the ensuing molecular fragmentation or interconversion into other photoproducts. To achieve this goal, we will compare the results of ongoing CEI experiments with the MeV-UED data that we acquired in January 2024.

2.2. Advances in theoretical treatment of Coulomb explosion imaging – Greenman, Rolles, Rudenko, Esry

Project scope: At JRML and elsewhere, Coulomb explosion imaging (CEI) is nowadays commonly used as a structural probe for excited-state dynamics. Theoretical descriptions of such systems are used to interpret the observables and shed light on molecular dynamics. Furthermore, the observables are in momentum space, and theory has been advanced to invert momentum-space images directly to geometries. Such inversion techniques will allow a more complete interpretation of CEI experiments.

Recent progress: We report on the interpretation of CEI experiments in the halomethanes CH_2I_2 and CH_3I, whose dynamics upon excitation at various UV wavelengths have been extensively investigated experimentally at JRML. The theoretical interpretation of such experiments is complicated by the presence of spin-orbit interactions in the iodine atom, and by correlation effects greatly affecting parts of the potential energy surfaces (PESs).

Our model was built for the CH_2I_2 molecule, where we concentrated on the C-I bond lengths and the I-C-I angle. We performed high-level electronic structure theory for a grid of about 400,000 points on this PES slice. The electronic structure we determined to be adequate was multireference configuration interaction (MRCI) as implemented in MOLPRO with a (12,8) active space, triple- ζ basis set, and 24 calculated states. We determined that, consistent with experiments and previous theoretical predictions, a transient geometry with a shortened I-I distance was formed during the excited-state dynamics. Contrary to the previous prediction, and unclear from the experiment, however, we predict this transient formation to be a very small effect compared to direct dissociation of the I-I bond.

In Fig. 2, the general trend to dissociation and the formation of the transient can be seen. For the 3A’ state and the 4A” state especially, contracted I-I distances can be seen at times near 100 fs, which is again consistent with the experimental evidence for transient formation. Conical intersections were not approached in our calculations, so non-Born-Oppenheimer effects were not considered in the trajectory analysis

The approach developed for CH_2I_2 was used to also build a model for CH_3I and compared to another CEI experiment performed at JRML [P40,P76]. In this model, the C-I bond length was considered along with the umbrella angle of the CH_3 fragment and one H-C-I angle. A similar level of electronic structure theory was performed as for CH_2I_2. Minor improvements were made to the surface fitting procedure, and Landau-Zener surface hopping was added to the trajectories to account for non-adiabatic effects. For CH_3I, CEI experimental features were reproduced well by the theory. Additionally, sub-100-fs dynamics was predicted that was not observed in the experiment due to the experimental resolution.

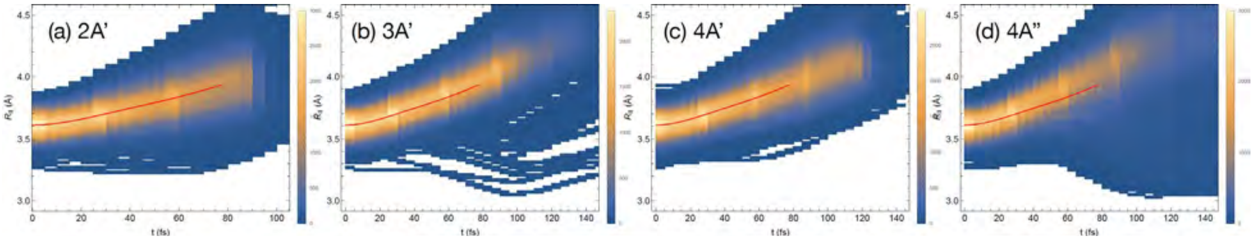


Fig 2: The I-I distance for trajectories started on different excited states as a function of time. Signals are shown for 50,000 trajectories on each state. Most trajectories directly dissociate while a few show a contracted I-I distance.

In addition to these direct simulations of CEI experiments, we continue to improve a model we are building for inversion of CEI momentum-space images. While scattering experiments and electron or X-ray diffraction experiments can frequently be related directly to geometries or related pair distribution functions, CEI experiments provide a momentum-space image. Usually, these images are compared to forward simulations of Newtons equations for a given charge state for a distribution of initial positions and momenta based on the geometries of interest. It would be greatly beneficial to have the ability to invert momentum images to geometries directly. Such inversions are difficult due to non-uniqueness of the result, but we feel that we have developed a method that mitigates such effects. Our inversion procedure discretizes the set of initial conditions consistent with a given momentum image, and forward propagates all of them. In this manner, all geometries consistent with a given momentum image may be reproduced and accepted based on some closeness criterion on the final momenta. Furthermore, clustering of the resulting geometries allows the reduction of non-unique answers to classes of nearby geometries. We have used this technique to invert experimental CEI images of the OCS molecule that were recorded at JRML.

Future plans: Our model for CH_2I_2 is readily extensible, and we plan to use it to describe a number of additional molecules. JRML experiments are planned or ongoing for the CH_3I molecule (photoionization and excited-state dynamics), CD_4 molecule and its ion. We plan to extend the model to all of these molecules (or to additional circumstances as for CH_3I). Additionally, it seems that rotation of the outgoing fragment is extremely important in CEI experiments and all experiments with excited-state fragmentation, and we plan to better incorporate these effects into the model by allowing for more relative rotational degrees of freedom. We also plan to perform further validation of all of these models against full-dimensional simulations including surface-hopping dynamics and wave packet dynamics calculations.

2.3. Understanding multi-body molecular fragmentation – Ben-Itzhak, Esry, Rudenko, Rolles

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. Quantitative understanding of such breakup processes is important for many applications, including the CEI experiments discussed above. 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 We are advancing our theoretical ability to describe these complicated processes from first principles.

Recent progress: Previously, we studied the formation of hydrogen-rich fragments of ethanol following double ionization by a strong laser field, in which we determined the probability associated with the site of origin of each hydrogen atom (see [P55]). This was accomplished, using deuterium tagging, also for "incomplete-breakup channels", i.e., the cases of H_3^+ formation accompanied by the loss of neutral fragment(s) in addition to the detected ion pair. This year, we explored three- and four-body breakup, employing the native frames analysis method [10, P82], in several polyatomic molecules, like ethanol, formic acid, and more recently formaldehyde.

Three-body breakup of the HCOOD formic acid isotopologue to $D^+ + O^+ + HCO^+$ reveals two sequential pathways involving D^+ or O^+ elimination in the first step, followed by unimolecular dissociation of the HCO_2^{2+} or $HDCO^{2+}$ intermediate dications, respectively. These sequential fragmentation channels are identified and separated from each other and from the direct breakup to $D^+ + O^+ + HCO^+$ using native frames analysis. In Fig. 3, we show the two sequential breakup channels as Newton diagrams before (left) and after (right) their separation by the native frames analysis. Furthermore, this separation allows us to determine that the pathway involving O^+ elimination first is about half of each of the other two comparable pathways. In the direct breakup to $D^+ + O^+ + HCO^+$, the hydroxyl hydrogen is eliminated while the hydrogen-carbon bond survives, as determined by deuterium tagging. Answering the question which of the two oxygen atoms is ejected, in other words which oxygen-carbon bond is broken, is a challenge. Hopefully, a comparison of the measured momenta of the D^+, O^+, and HCO^+ fragments to Coulomb explosion modeling (underway) of this breakup channel may reveal which oxygen is ejected.

More recently, we explored the strong-field fragmentation of formaldehyde focusing on the 4-body breakup channels of the D_2CO^{4+} and D_2CO^{5+}. Our measurements of the $D^+ + D^+ + C^+ + O^+$ – the (1,1,1,1) channel – are consistent with recent results revealing a sequential breakup via a $D^+ + D^+ + CO^{2+}$ intermediate step [11, P42]. The 4-body native frame analysis of our data indicates that cleavage of both C–D bonds occur simultaneously, as a symmetric stretch along the bonds, i.e., supporting the validity of the axial recoil approximation of the first breakup step. The metastable CO^{2+} survives longer than its rotational period, thus providing the uniform angular distribution in the fragmentation plane used to separate this sequential breakup from the direct fragmentation to the same final products. Analysis of other 4-body breakup channels, specifically (1,0,2,1), (1,1,2,0), and (1,1,2,1), is underway.

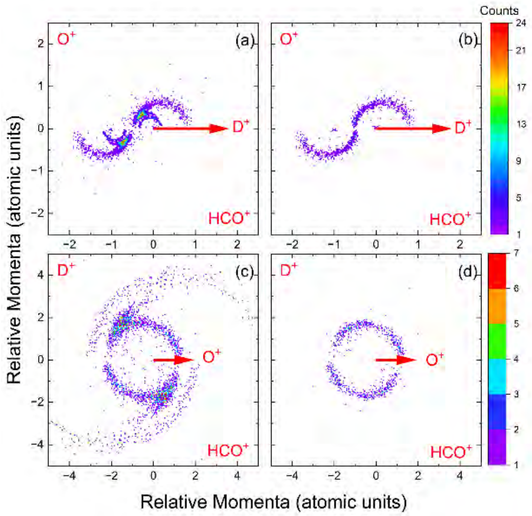


Fig. 3: Newton diagram of $D^+ + O^+ + HCO^+$ coincidence events. All events are relative to the momentum of the first ejected fragment, which defines the x-axis: (a) D^+ and (c) O^+. (b) and (d) the same as (a) and (c), but only for the respective sequential breakup channels separated by native frame analysis [1-2].

Future plans: We plan to continue examining multi-body fragmentation dynamics in neutral molecules and molecular ions. In the latter, we will focus on atomic and molecular elimination processes, using our ability to measure neutral fragments to distinguish between the elimination of two atoms from a single molecule, for example, $CH_2ICl^+ \div CH_2^+ + ICl$ or $CH_2^+ + I + Cl$. We note that the detection of the two atoms is an experimental challenge.

2.4 Imaging coupled vibrational, rotational, and electronic wave packet dynamics in triatomic molecules - Kumarappan, Thumm, Rudenko, Rolles

Project scope: Light-driven triatomic molecules exhibit rich ultrafast dynamics including couplings between electronic, vibrational and rotational motion, yet are small enough to allow for detailed theoretical modelling. The goal of this project is to develop a quantitative understanding of correlated electron-nuclear wave packet dynamics in triatomic systems induced by interactions with NIR or XUV light. We employ time-resolved Coulomb explosion imaging or dissociative ionization by intense NIR pulses to probe the dynamics, and perform quantum mechanical simulations to characterize and image the molecular wave packets that exhibit coupled rotational, vibrational and electronic dynamics.

Recent progress:

Coulomb explosion imaging of coupled rotational, vibrational and electronic motion in SO_2^+

We used strong-field-ionized sulfur dioxide molecules as a model system to map large- amplitude bending vibrations. When neutral SO_2 is ionized from its ground state (with an O-S-O bond angle of 119°) to the $\tilde{X}\ ^2A_1$ ground state of the ion, Frank-Condon factors place the wave packet away from the equilibrium bond angle (134°) of the cation. As sketched in Fig. 4a, this launches a large-amplitude bending-mode vibrational wave packet that we have successfully imaged using strong-field-induced Coulomb explosion as a probe. Our accompanying calculations suggest that several vibrational states are populated. The nearest-neighbor energy differences are ~400 cm^{-1} for up to $v = 8$, and the data clearly shows this quantum beat (Fig. 4b), which corresponds to a period of about 85 fs. In particular, the $O^+ + S^+ + O^+$ coincidence channel shows a clear signature of this wave packet in the O^+–O^+ angle of the asymptotic fragment momenta, in the kinetic energy (KE) released, and the KE spectrum of the S^+ ion. In addition, we observe weaker but noticeable signatures of the bending vibrations in the electronic ground state of neutral SO_2 around 520 cm^{-1}.

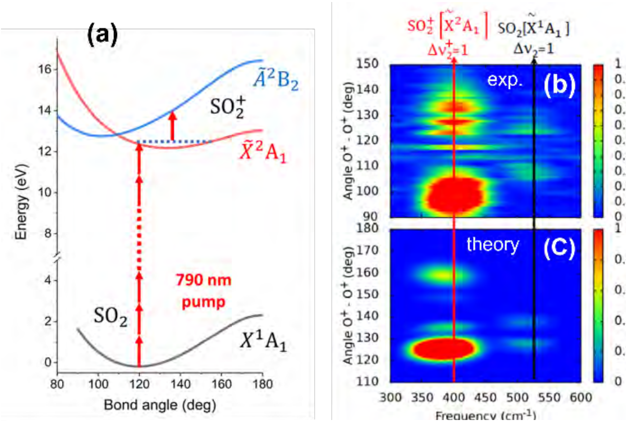


Fig. 4: **(a)** Potential energy curves for the ground state of neutral SO_2 and for the ground and first excited states of SO_2^+. **(b, c)** FFTs of the $O^+ + S^+ + O^+$ coincidence channel yield as a function of the (O^+,O^+) momentum angle obtained from the experimental data (b) and from the simulation (c).

To understand these results, we numerically simulated the nuclear vibronic wave packet evolution for 30-fs, 800-nm pump and probe pulses in full dimensionality, describing the pump step by solving the nuclear TDSE on the coupled *ab initio* PESs for the ground states of the neutral molecule and monocation. We first calculated the ionization yield as a function of the bond angle. Then, matching classical trajectories to the grid-based numerical nuclear wave packet, we modeled CE into the $O^+ + S^+ + O^+$ channel by vertically projecting the nuclear motion onto the potential energy surface of the triply-charged molecule, approximated as purely Coulombic, and propagated the nuclear wave packet to sufficiently large internuclear distances on the (O^+, O^+, S^+) asymptote to achieve numerical convergence. While the calculations, shown in Fig. 4(c), clearly show the structures reflecting bending vibrations in both cationic and neutral SO_2 molecule, there are some noticeable discrepancies with the experiment. In particular, the measured spectra suggest that the molecule bends to smaller angles than can be accounted for

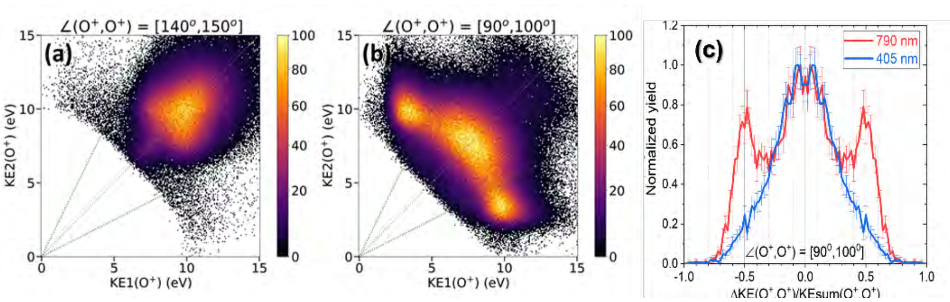


Fig. 5: KE sharing between the O^+ ions in the O^++S^++O^+ coincidence channel. Panel **(a)**, filtered for large O^+–O^+ angles, shows mostly symmetric KE sharing, whereas the data for small angles **(b)** clearly show a large asymmetric component due to the excitation of the asymmetric symmetric mode. Both (a) and (b) are integrated over all pump-probe delays greater than 200 fs in a scan to 2 ps delay. **(c)** Distribution of events with small O^+-O^+ angles as a function of KE difference between the O^+ ions following ionization by a single laser pulse at 790 nm (red) or 405 nm (blue). The latter data clearly show the absence of asymmetric KE sharing component at 405 nm. Adapted from [12].

by bending vibration in the $\tilde{X}\ ^2A_1$ state, although the observed period is consistent with this bending vibration (see [12] for details).

These discrepancies between model calculations and experimental data appear to be consistent with the excitation of the cation to the $\tilde{A}\ ^2B_2$ state. These two states are resonantly coupled by 800 nm light at a bending angle of about 130°. Thus, either the pump or the probe pulse can excite cations to the $\tilde{A}\ ^2B_2$ state when the ground state wave packet is near 130° bond angle. Once excited to the $\tilde{A}\ ^2B_2$ state, the wave packet will be able to reach 80°, although it is likely to be non-adiabatically coupled back to $\tilde{X}\ ^2A_1$ near a conical intersection at 108° (see Fig 4(a)). The branching space of the CI consists of bending and asymmetric stretch coordinates. Fig. 5(a,b) show that kinetic energy is shared asymmetrically between the O^+ ions when the OSO angle is small but not when it is large. This is a clear signature of non-adiabatic coupling near the CI, which changes the electronic and vibrational symmetries of the cation. According to calculations by Leveque *et* al. [13], the transfer to the lower adiabatic surface occurs within ~20 fs — a shorter time scale than the duration of both the pump and probe pulses in the experiment. The disappearance of asymmetric energy sharing component for CE with 405 nm pulses (Fig. 5(c)) confirms the role of the resonant excitation to $\tilde{A}\ ^2B_2$ state at 790 nm.

Apart from vibronic dynamics on two electronic surfaces, rotations also play an essential role in such experiments. According to MO-ADK theory, the molecule is most likely to be ionized when the laser polarization is along the C_2 axis because the HOMO has a large lobe on the S atom. However, the coupling from the $\tilde{X}\ ^2A_1$ to the A˜ $2B_2$ state is maximized when the O–O axis is along the laser polarization. That is, the molecule must rotate a quarter turn between the two steps for both of them to be efficient. The O–O axis is also the most polarizable one in both the neutral and cationic ground states of the molecule. Thus, the required rotational motion can be driven through impulsive alignment by rotational Raman transitions in either state. Direct evidence of alignment is seen the laboratory frame angular distribution of the S^+ ion, for instance, which peaks perpendicular to the laser polarization about 200 fs after the pump pulse.

XUV-pump - NIR/VIS-probe dissociative ionization of CO_2*:*

Over the last year, we implemented a versatile numerical model for the dissociative ionization of CO_2 molecules, including all vibronic degrees of freedom [P60]. We applied this model to simulate charge oscillations in CO_2 molecular cations produced by XUV ionization and calculated fragment KER and PE spectra resulting from their dissociation in intense NIR probe fields [12,14]. For single ionization of CO_2 by femtosecond 18-eV XUV pump pulses, we modeled the coherent nuclear dissociation dynamics of the pump-pulse-excited molecular cation on its five lowest potential energy surfaces in full (3D) dimensionality, subject to its exposure to delayed 400 or 780 nm probe pulses [P60]. We provided pump-probe delay-dependent fragment KER spectra and characterized the nuclear wave-packet dynamics and intramolecular charge transport in terms of quantum beats between specific stationary vibronic

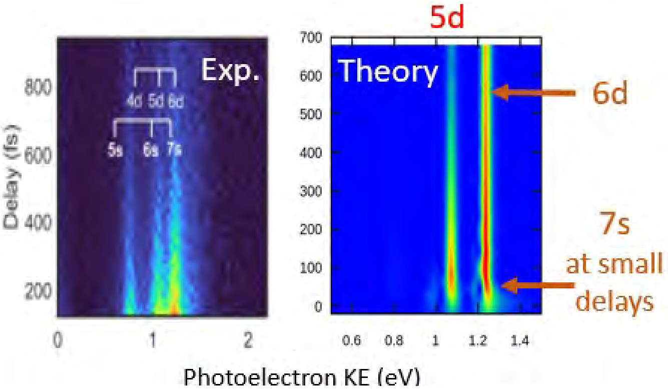


Fig. 6. Measured (left) and simulated (right) PE spectra for XUV-pump – IR-probe dissociative ionization of CO_2 The experimental plot is adapted from [16].

levels in CO_2^+. We identified main contributions to the nuclear motion from the vibronic levels in the cationic $A^2\Pi_u$ and $B^2\Sigma^+_u$ adiabatic states, confirming measured valence-hole oscillation periods of 115 fs and 3 ps [14,15, P60]. In addition, we implemented PE continuum channels, extending our new close-coupling computer code for dissociative ionization of triatomic molecules. As illustrated in Fig. 6, our first photoelectron (PE) spectra for XUV-pump - NIR-probe dissociative ionization of CO_2 identify two of three prominent peaks in the preliminary experimental data from Prof. Sandhu's group [16] as due to XUV excitation of the 5d and 6d states in the Henning sharp sequence of molecular Rydberg states that converge to the second electronically excited CO_2^+ state.

Future plans: The model of cationic dynamics in coupled $\tilde{X}\ ^2A_1$ and $\tilde{A}\ ^2B_2$ states and our ability to visualize the wave packet using CEI enables us to investigate details of the dynamics near the CI. In particular, since this coupling is initiated by a single photon from a large-amplitude vibrational wave packet in the $\tilde{X}\ ^2A_1$ state that remains coherent over several vibrational periods, we have the ability to launch a wave packet on the $\tilde{A}\ ^2B_2$ state at different bending angles and energies by using a weak, tunable control pulse. We plan to exploit this to carry out a detailed study of the coupled rovibronic dynamics in the vicinity of the CI. From the theory side, we plan to extend our model [12, P60] by removing its restriction to initially linear 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. It thus alters the population transfer between relevant adiabatic states in the molecular cation. Following up on our recent findings for SO_2 and CO_2 [12,14], we plan to scrutinize the dependence of KER spectra on the relative linear polarization directions of pump and probe pulses and extend our modelling of dissociative ionization to H_2O and other triatomics. We further aspire to examine the effects of non-adiabatic couplings between specific vibronic normal modes of the triatomic cations as quantum beats in KER and in coincident photoemission spectra.

2.5. Light control of intramolecular nuclear dynamics by vortex electron localization – Han, Rudenko, Thumm

Project scope: Control of molecular bond breaking with light fields is a long-term goal in modern molecular science. Although laser pulses with tailored waveforms can be used to control the photoelectron emission direction from molecules, the direct interaction between light fields and molecular nuclei is rather limited for femtosecond pulses, mainly due to the heavy nuclear mass and the limited force imposed by the light fields. In this project, we explore an optical mechanism for controlling correlated electronic and nuclear dynamics employing bi-circularly polarized two-color laser fields.

Recent progress: Strong-field-induced dissociative ionization of hydrogen molecules is a prototypical laser-driven process that has attracted much attention over the last three decades. There, the dominant photoelectron emission approximately follows the laser vector-potential direction at the instant when the electric field reaches its maximum, while the protons are primarily emitted along the molecular axis. In this study, we overturn the stereotype that proton emission in strong-field dissociative ionization of H_2 molecules has to occur along the molecular axis. As illustrated in Fig. 7. using bi-circularly polarized two-color laser fields, we observe a spiral distribution of the proton emission asymmetry in the polarization plane and a counter-intuitive electron-proton angular correlation. These surprising observations can be explained by the two-dimensional localization and interference of coupled electron-nuclear wave packets with non-zero

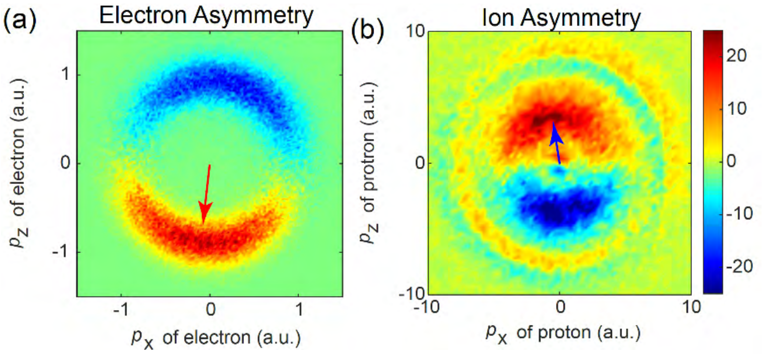


Fig. 7: Measured coincident electron **(a)** and proton **(b)** asymmetry plots for strong-field ionization of H_2 by phase-stabilized two-color field. The asymmetry is defined as a difference map between the measured 2D momentum distributions for relative phases of 0 and π between the 800 nm and 400 nm circularly polarized fields (from [17])..

magnetic quantum numbers that form so-called vortex states or vortices. The interference of these vortices can map the relative time delay of the nuclear motion between different pathways to the slope of the spiral fringes with respect to energy. Most of our experimental findings are reproduced by a quantum simulation including both electronic and nuclear degrees of freedom, and by a semi-classical-trajectory model for the electron-nuclear wave packet propagation. Our study suggests an approach for shaping and enhancing the interaction between laser fields and molecular nuclei and triggers open questions for follow-up investigations. More details are provided in Ref. [17].

Future plans: As a next step, we plan to repeat this experiment employing CEP-stabilized near-single-cycle light pulses now available at JRML, when the CEP can serve as a knob to control correlated electronic and nuclear dynamics. Furthermore, we will extend this approach to larger, heteronuclear molecules such as HCl.

3. Strong-field physics

Strong laser pulses allow 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 wave packets and enabling studies of molecular dynamics on the level of a few femtoseconds or less. On the other end of the range, they can excite extensive rotational coherences and provide us access to the molecular frame. Investigations of the interaction of strong laser fields with atoms and molecules have led to a wealth of new tools including impulsive alignment, high-harmonic generation (HHG) spectroscopy, laser-induced electron diffraction (LIED), and time-resolved CEI. Our main goal in this thrust area is to exploit the versatility of strong-field physics to both image and control electronic and nuclear motion.

3.1. Laser-Induced Electron Diffraction as isomer and conformer tool – Blaga, Lin

Project scope: LIED is a tabletop ultrafast molecular imaging method based upon the photoelectron rescattering mechanism in intense, femtosecond fields [18,19]. Proposed theoretically as an ultrafast alternative to conventional gas-phase electron diffraction (CED) by Zuo et al [20] after the 1994 discovery of the rescattering plateau by Paulus [21], accurate and reliable molecular structure retrieval using LIED became a reality only after the development of molecular tunneling [22] and the quantitative rescattering theories [23] at JRML and the deployment of mid-IR drivers. Ever since, JRML remained at the forefront of LIED development and deployment, demonstrating the imaging of first molecular bond relaxation in O_2 (with Ohio State) [24], first molecular bond breaking in acetylene (with IFCO, Spain) [25], and the oblateprolate breathing mode of C_{60} [26]. These experiments demonstrated LIED's resolving power, typically reaching few picometers and few fs (see [P54] for a recent review).

Recent progress: During the last year, we continued our LIED efforts exploring isomers and conformers, classes of compounds that are difficult to image with methods that use randomly orientated samples such as CED and UED. In randomly orientated samples, the molecular interference term in the elastic, electron-molecule differential cross section acquires a $\sin(qR_{ij})/qR_{ij}$ term, where q is the momentum transfer and R_{ij} is the distance between atomic sites i and j. As R_{ij} increases, this term becomes smaller. This makes distinguishing isomers and conformers difficult, as they have the same bond lengths among immediate neighbors and only differ at large interatomic distances. In the case of LIED, the $\sin(x)/x$ term does not exist as the removal of the imaging electron favors certain molecular orientations even in randomly orientated samples. Thus, in general, LIED has less "spatial randomness" compared to CED and UED.

The chosen target isomers were n-butane and isobutane, the simplest conformers. Using 3.0 and 3.5 um drivers, we recorded photoelectron angular distributions from which cross sections were extracted. The experiments showed clear and consistent isomer differences regardless of laser parameters. In the case of isobutane, the isomer lacking conformers, the extracted DCS resembles the CED results, since the tunnel ionization rate doesn't depend significantly on orientation. For n-butane, however, the DCS showed clear deviations from the CED result (which as stated above, closely resembles that of isobutane). Modeling the DCS with the independent atom model, we demonstrated that the measured DCS can only be fitted by incorporating the conformer ratio with their corresponding tunnel ionization rate. Therefore, our study reveals that LIED can distinguish between isomers with ease and that it possesses conformer sensitivity as well. These results are shown in Fig. 8. A manuscript for this project is in the resubmission phase [27].

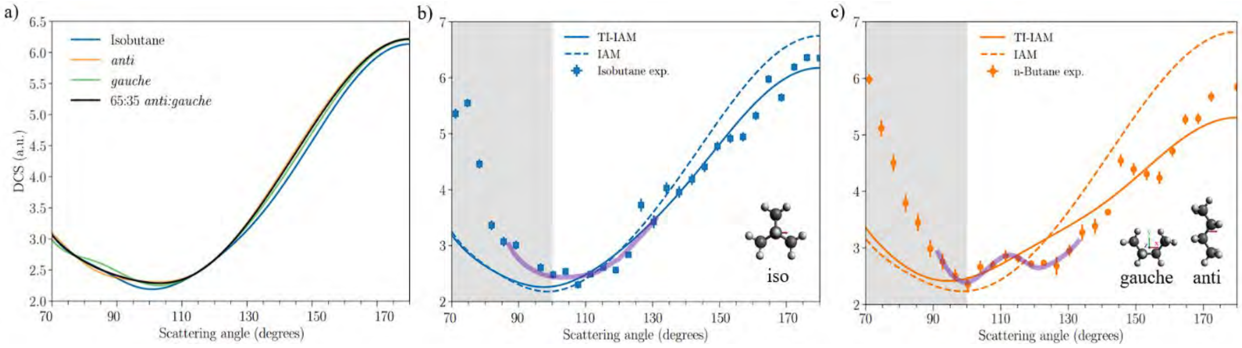


Fig. 8: Laser induced electron diffraction on butane isomers for 50 eV electron scattering energy.
(a) Theoretical differential cross sections calculated under the independent atom model for *random* molecular orientations, as it would be the case for conventional electron diffraction or ultrafast electron diffraction. DCS differences are very small – especially for conformers – and become smaller still at higher momentum transfers. **(b)** LIED experiment with 3 um pulses generating ~40 TW/cm^2 in isobutane (symbols) compared to random IAM (dashed) and tunnel-ionization corrected IAM (solid line). The grey area denotes direct electrons. The purple line highlights the U-shaped DCS near 100 degrees scattering angles, similar with the IAM result. **(c)** Same as (b), but for n-butane. The purple line highlights the W-shaped DCS around 110 degrees, a reproducible result that does not depend on laser wavelength or intensity. At 110 degrees, the DCS of n-butane is approximately 30% higher than the DCS for isobutane, proving LIED's isotopic sensitivity. The isomer and conformer geometries are illustrated in the insets (from [27])..

In addition to our LIED-based scientific efforts, we recently finalized the development of the first LIED target chamber aimed at pump-probe studies and mid-IR capabilities at 100 kHz repetition rates. Previously, recording an angular distribution was time consuming, often requiring

5-8 hrs data runs for a single LIED "image", rendering pump-probe experiments prohibitive. To address this issue, our new time-of-flight chamber can now record data at 8 angles at a time, from previous 1, accomplished using segmented, impedance matched homebuilt multichannel plate detectors. The electronics were updated and can now accommodate the 100 kHz repetition rate of our newly acquired laser. All these gains allow us to collect data 800 times faster than before. Finally, during the Summer 2024, we started construction of a new tunable mid-IR LIED driver based on optical parametric amplification that will operate at 100 kHz. The white light continuum generation module and a single pass amplification stage have been completed successfully. Using only 8W of the available 320W of the 1030 nm pump, the system produces 1.6W at mid-IR wavelengths. We are now in the process of adding two more amplification stages. Upon completion, we expect >50W of average power at mid-IR wavelengths.

Future plans: Employing the new experimental capabilities outlined above in combination with the analysis schemes and theoretical tools to model LIED for a broad range of molecules. We plan to perform dissociative UV-pump, LIED-probe studies on butane isomers. A preliminary mass spectroscopy study on these compounds that we have recently performed at JRML revealed that tunnel photoionization leads to C-C bond cleavage, primarily with the production of propyl ions and methyl radicals. Therefore, the aim of these studies will be to determine and time the fragmentation dynamics in iso- and nbutanes, with a particular emphasis on conformer and isomer structure.

3.2. Dispersion-free rescattering photoelectron wave packets in strong-field ionization - Blaga

Project scope: The spatio-temporal structure of rescattering electron wave packets in multiphoton or strong-field ionization is a central theme in strong- field and attosecond science, playing a key role for the LIED technique described in the previous section. Despite more than three decades of studies, the details of this structure, which, among others, are responsible for the complex features observed in high-energy above-threshold ionization (ATI) [21], remain elusive. In this project, we study the formation of a dispersion-free attosecond photoelectron pulse, which can largely explain the intriguing behavior of observed high-energy ATI enhancements.

Recent progress: In collaboration with the Agostini-DiMauro group at OSU and Schafer group at LSU, we investigated ATI enhancements within the "rescattering plateau" in noble gases and small hydrocarbons (methane, ethylene, acetylene) as a function of laser intensity and wavelength, both experimentally and theoretically. Systematic data analysis along with the numerical integration of the TDSE revealed that these enhancements originate at predictable laser intensities present in the focal volume, for which parts of the photoionized electron wave packet are trapped near the parent ion core and begin circulating without dispersion cycle after cycle. The lack of dispersion allows the wavepacket to grow throughout the laser pulse until losses (diffraction and/or ground-state depletion) balance the gain. This forms a mirrorless matter-wave analogue to a mode-locked laser oscillator. The cavity round-trip time is locked to the period of the laser field and can be controlled by wavelength tuning. The return phases of the formed quasi-solitonic pulse are universal and do not depend on target or laser parameters. Dispersion of this wave packet is controlled by balancing the ponderomotive forces of the laser with the ionization potential of the target and can be engineered by adjusting laser pulse chirp, intensity, or relative phase of bichromatic laser fields, a Q-switching mechanism that allow controlled turn on/off of the quasi-soliton during the laser pulse. A manuscript on this work will be submitted shortly [28].

Future plans: The formation of such well-controlled, ultrashort electron bunches might impact various ultrafast molecular technologies. Among other directions, we plan to explore its implications for previous and planned LIED studies and to revisit several open questions in non-sequential double ionization. For the latter process, the newly developed picture of a dispersion-free attosecond rescattering electron wave packet will allow us to understand and potentially control the subtleties of correlated two-electron dynamics driving this reaction.

3.3. Strong-field-driven dynamics in diatomic molecules – Thumm, Han

Project scope: Ionization of molecules by short, intense light pulses typically excites nuclear wave packets that continue to propagate coherently in several electronic states of the residual molecular cations. Within this project, we develop conceptual, analytical, and numerical tools to image and control the dynamics of such wave packets in photoionized molecules in intense NIR laser fields. Motivated by emerging experiments at JRML and FEL facilities, we are extending our investigations of dissociative ionization to include (i) pump-pulse excitation to intermediate Rydberg and autoionizing states of small molecules, (ii) the calculation of coincident PE and fragment KER spectra, and (iii) laser-induced fluorescence.

Recent progress:

Imaging autoionizing states of diatomic molecules

We are developing a close-coupling formulation for the evolution of the molecular state during DI, including the ground, excited, and electronic continuum states of the neutral molecule and several states of the singly-charged molecular cation. In support of ongoing coherent-control experiments at FERMI lead by Prof. Sansone in Freiburg, we carried out first calculations for fixed nuclei, negligible ground-state depletion, and heuristically Fano-parameterized [29] intermediate autoionizing states. The experiments employ three harmonics, HH_{5-7}, of the FERMI FEL seed laser with controllable relative phases to ionize N_2 via two-photon absorption to final states of identical energy along two paths, $N_2 + HH_5 + HH_7$ and $N_2 + HH_6 + HH_6$. The paths involve either a neutral autoionizing state, belonging to the Hopfield absorption series, N_2 (ndσ_g $^1\Sigma^+_g$), or intermediate continuum states.

XUV-pump - NIR-probe photoemission spectra

A second addition to our numerical tool set is the inclusion of discretized photoelectron continuum channels [13,30,31] in close-coupling dissociative ionization calculations. Our first applications, including the N_2 electronic ground and autoionizing B $^2\Sigma^+_u$ 3σ π_g state, the three lowest adiabatic states of N_2^+, and 1000 electronic continuum states, approximately reproduce the main signatures in measured delay-dependent PE spectra [32] (see Fig. 9).

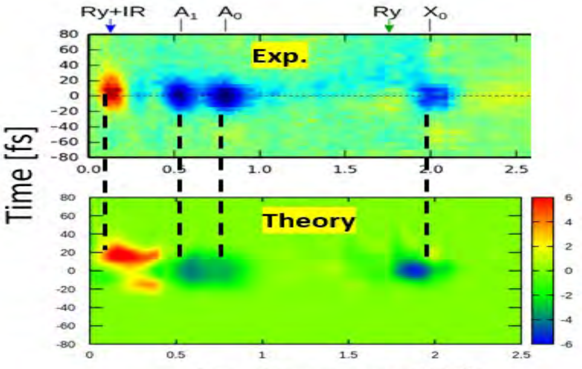


Fig. 9: Measured [32] (top) and simulated (bottom) N_2 (XUV+IR) minus XUV-only PE spectra for 17.5 eV XUV pump and 1.6 eV IR probe pulses.

Strong-field-induced fluorescence and lasing in air

How air fluorescence during filamentation is best exploited for air lasing is unclear and requires detailed knowledge of the conditions that may (or may not) lead to vibronic and electronic population inversion. Supporting the ongoing air-fluorescence and air-lasing experiments with CEP-stable laser pulses at JRML, we started *ab initio* calculations for the electronic and vibronic excitation dynamics in neutral and cationic N_2 molecules. Our initial results for the NIR-pulse-driven vibronic-state evolution reproduce the CEP dependence of the intense 391 nm fluorescence in N_2^+ observed in first experiments of Han's group at JRML.

Future plans: Our exploratory results for autoionization approximately describe the HH-phase-dependent modulation of the PE yield and its phase shift imposed by the autoionizing resonance. We plan to further investigate this two-path scheme for (a) detecting FEL HH CEP and (b) diagnosing the imprint of competing autoionization and photoemission on fragment KER and PE spectra. We intend to extend the continuum discretization calculations to full 3D, providing angle-resolved PE spectra and including vibronic excitations, which will allow us to examine the correlated nuclear and electron motion. Finally, we plan to provide a detailed assessment of expected fluorescence yields and best conditions (laser-pulse parameters and air pressure) for enhancing selected fluorescence lines and enabling lasing in N_2^+ and N_2. We will also explore the potential of these experiments for robust CEP characterization.

3.4. Probing vibronic coherence using strong field double ionization - Lin

Project scope: Excitation and ionization of a molecule by ultrashort light pulses can create a superposition of electronic states, or an electronic wave packet (EWP) that determines the intramolecular charge motion in the first few femtoseconds. Subsequently, the EWP will be coupled to nuclear motion, introducing vibronic decoherence that can potentially lead to charge transfer. Probing the vibronic coherence is thus vital to understanding and controlling chemical reactivity. Due to the complexity, theoretical calculations are often made with many assumptions such that the calculated results cannot be directly compared to experiments. Based on a recently developed density matrix approach, we applied the method to simulate pump-probe experiments and predict results that can be directly compared to experimental observables.

Recent Progress: During the last year, we focused on applying our recently developed density matrix theory for dissociative sequential double ionization of molecules to studies of decoherence of EWPs by vibronic coupling to nuclear motion [P56,P75]. In this work (led by the JRML postdoc Dr. Isaac Yuen, who is now a faculty at Kennesaw State University), we consider N_2 as an example and use a 6,fs, 800-nm laser pulse to tunnel ionize the X, A, and B states of N_2^+, thus launching an EWP on several cationic states. We use two different types of probe pulses to image this wave packet. One is another NIR pulse, which further ionizes N_2^+ to N_2^{2+} and dissociates it into $N^+ + N^+$ fragments. Their KER and emission angles can be measured, providing information about the EWP evolution. Another scheme, which will be discussed in Sec. 4.1, employs an attosecond soft X-ray probe.

We then apply our theoretical method to model the pump-probe experiments on N_2 (as well as O_2), simulating the experimental observables for sequential double ionization at different pump-probe delays [P56]. As shown in Fig. 10, we observe that the KER spectra for N^++N^+ (a) and O^+ +O^+ (d) beat with varying intensities versus the time delay and the pattern revives at later times. The fast beatings are due to the electronic coherence among the X, A, and B states, while the intensity decrease at a longer time is a consequence of the coupling between electronic and vibronic motion. The vibronic coupling enters in the off-diagonal terms of the density matrix elements and can affect the branching ratios of dissociative double ionization vs total double ionization, see Fig. 10 (c) and (e). The imaginary part of the off-diagonal elements (e and f) obtained from the calculations can be extracted from the experimental data directly, as explained in the cited paper above.

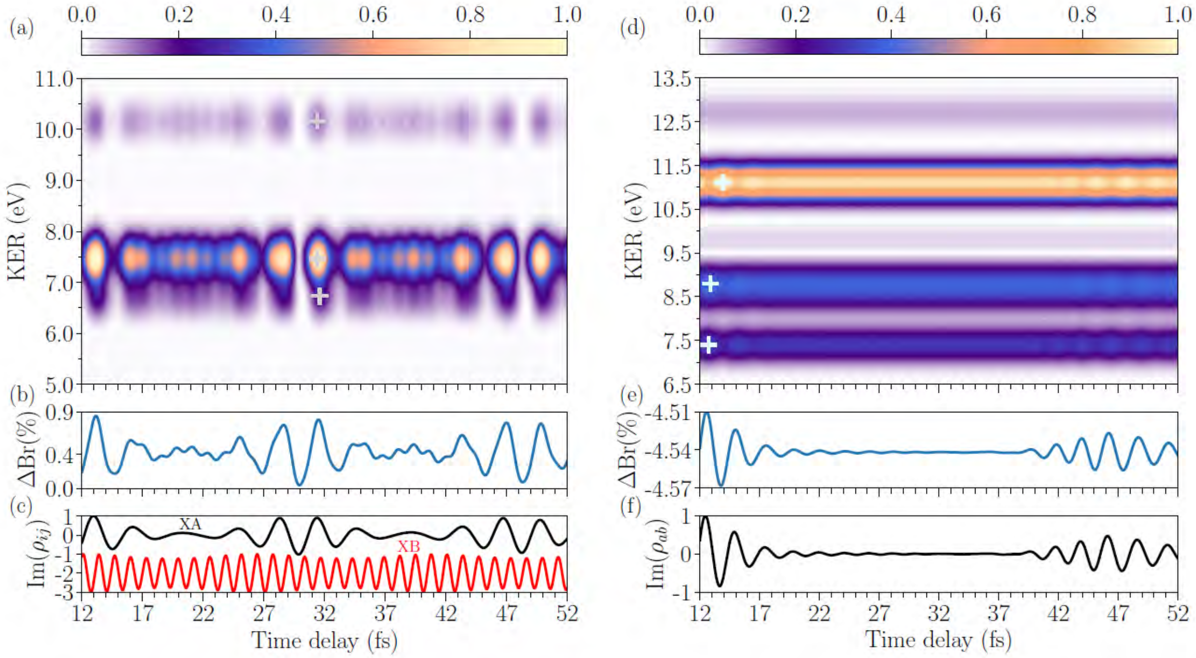


Fig. 10: (a), (d) Simulated KER spectra for (a) $N^+ + N^+$ and (d) $O^+ + O^+$ as a function of pump-probe delay. The markers show the phase differences of the beating between different KER peaks. Note that in (d), the spectra are more negative with higher values. **(b),(e)** Branching ratio of $N^+ + N^+$ and $O^+ + O^+$ over their respective total dication yield as a function of pump-probe delay, subtracted by the probe-only ratio. (c) Imaginary part of the off-diagonal density matrix elements between the $X^2\Sigma_g^+$ and $A^2\Pi_u$ states (black) and the $X^2\Sigma_g^+$ and $B^2\Sigma_u^{++}$ states (red) of N_2^+ at θ= 45°. (f) Same as (c), but for the $a^4\Pi_u$ and $B^4\Sigma_g^-$ states of O_2^+(from [P56]).

Future plans: Our theory was formulated for short pump/probe pulses where we require nuclear motions to be frozen whenever the pump or probe pulses are present. In general, few-cycle pulses available today are not suitable since they tend to have long pedestals away from the central peak. With the emergence of new laser technology, however, carrier-envelope-phase stabilized few-cycle lasers of 3 or 4 femtoseconds are emerging. Once such pulses are used in pump-probe experiments, we will carry out concurrent theoretical calculations to compare with experiments. Before such experimental results become available, in the coming year, we will investigate pump-control-probe simulations. Our goal is to identify efficient control pulses to reach optimal probe signals. We believe that efficient control of chemical reactivity can be achieved by controlling the electron wave packet generated by the pump pulse.

3.5. Vibrational Cooper minima used to verify strong-field induced dissociation pathways – Ben-Itzhak, Kumarappan, Esry

Project Scope: Vibrational Cooper minima due to weak dipole coupling, i.e., dips in the molecular dissociation probability of certain vibrational levels, were observed in strong-field dissociation of the fundamental hydrogen molecular ion as minima in the kinetic energy release spectrum [33]. We demonstrate in two independent experiments, that these vibrational Cooper minima occur more generally and can be used as "fingerprints" to pick out the final electronic state and dissociation pathway.

Recent Progress: In the first experiment, employing a few-keV ion beam target, we show the wavelength dependence of the vibrational Cooper minima observed in the KER spectrum of O_2^+ dissociation induced by 396-nm and 264-nm photons. These results are presented in Fig. 11 for two different wavelength. The ticks mark the expected KER for specific vibrational levels in the a $^4\Pi_u$ state, indicating a definite minimum at $v = 2$ for 264-nm while the $v = 2$ state dominates the 396-nm spectrum. These minima appear at the locations predicted by our first-order perturbation-theory calculations.

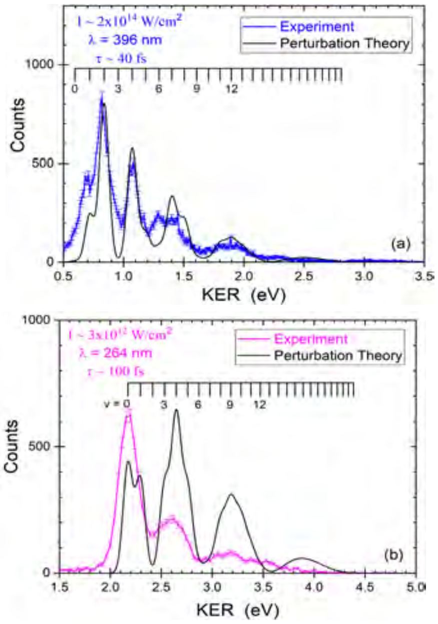


Fig. 11: The KER spectra upon dissociation of O_2^+ to $O^+ + O$ by 396-nm **(a)** and 264-nm **(b)** photons**.** The symbols represent the measured data, with 1σ errors, while the solid lines present the probability density calculated for a $^4\Pi_u$ to f $^4\Pi_g$ transitions using first-order perturbation theory. Adapted from [34].

In the second experiment, which relies on rotational wave packet spectroscopy, the expected vibrational Cooper minima are seen in a different observable (see Fig. 12), specifically at multiple spin-rotation quantum beat frequencies measured by a pump-probe technique on O_2 to measure dissociation of O_2^+ with rovibrational resolution in the frequency domain. In this case, these minima are used to identify the dissociation pathway. The same pattern of five vertical lines (associated with $v = 0$–4) repeats for different values of Ω and J, four of which are highlighted by stick spectra, calculated locations of $v = 0$–4, $\Delta J = 2$, $\Delta\Omega = 0$ Raman lines in the $\Omega = 1/2$ and $\Omega = 3/2$ fine-structure levels (denoted in Fig. 12(a) by cyan and magenta, respectively, see [34] for details). The absence of $v = 2$ is immediately evident.

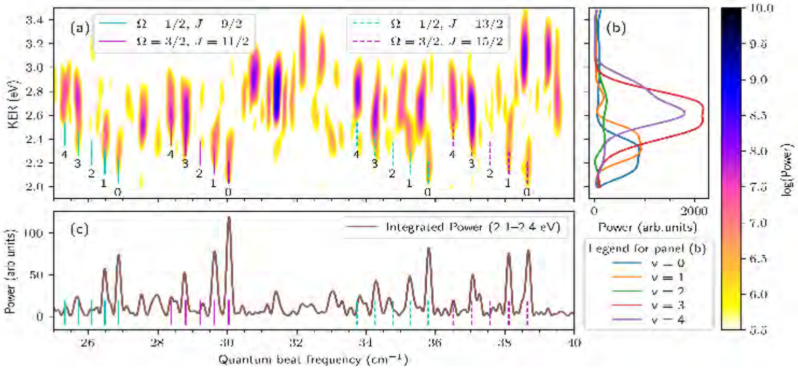


Fig. 12: (a) A portion of the FFT-KER data selected to highlight the single-photon dissociation of the a $^4\Pi_u$ state of O_2^+ by 264-nm pulses. **(b)** KER spectra integrated over quantum beat frequency for v = 0–4 for the lines identified by the $J = 11/2$, $\Omega = 3/2$ (solid magenta) stick spectrum. In each case, the QB frequency is integrated over a range of 0.2 cm^{-1} centered on the calculated frequency of the QB. In each case, the QB frequency is integrated over a range of 0.2 cm^{-1} centered on the calculated frequency of the QB. **(c)** QB spectrum integrated from 2.1 to 2.4 eV. Adapted from [34].

Future plans: As we established that vibrational Cooper minima do occur in a system more complex than H^+ and are imprinted in observables besides KER spectra, we expect them to appear as “fingerprints” of the dissociation pathways and the states involved in dissociation in other molecules. Correspondingly, we plan to employ both experimental schemes used here to explore vibrational Cooper minima in more complex polyatomic systems.

3.6 Ab initio theory for extracting the carrier-envelope phase from stereo ATI measurements - Esry, Kumarappan

Project Scope: We use our parametric formalism for carrier-envelope phase (CEP) effects to derive an ab initio analytic expression for the parametric asymmetry plot (PAP) produced by stereo ATI measurements. This result suggests a nonlinear least squares fit to the PAP that makes it possible to retrieve the CEP of each shot with higher accuracy and fewer assumptions than the methods currently used.

Recent Progress: The carrier-envelope phase (CEP) ϕ of a pulsed laser is defined from its electric field, $E(t) = E_0(t) \cos(\omega t + \phi)$. Its effects are negligible for many-cycle pulses, but can play an important role in the few-cycle limit [35–40]. It is thus important to be able to correctly measure it, and the most commonly used method for momentum-imaging experiments was proposed and developed by Wittmann et al. [41]. The resulting CEP meter (CEPM) enables shot-by-shot measurement and has been built in several labs, including ours [39].

In the CEPM, right and left photoelectron spectra are measured that are then integrated over a high energy range, ΔE_H , and a low energy range, ΔE_L, within the plateau region [35,41]. The corresponding normalized spatial asymmetries, A_H and A_L, are constructed from these as the ratio of their difference over their sum. The insight from Ref. [41] was to produce a parametric asymmetry plot (PAP) of A_L versus A_H and thus define a geometric angle θ for each shot. Retrieving the CEP then amounts to obtaining the mapping $\phi(\theta)$.

The most common CEP retrieval method [35, 41,42] uses the fact that the pulse generation process produces a CEP with a uniform random distribution. This implies the relation

$$d\varphi = \frac{2\pi\rho(\theta)}{N} d\theta, \tag{1}$$

where $\rho(\theta)$ is the shot density and N is the number of shots. The data is binned in θ and Eq. (1) integrated to obtain $\phi(\theta)$. It can be applied to any shape of PAP, but the retrieval error is minimized with a circular PAP [35, 42].

With our parametric formalism for CEP effects [43], however, we can generate ab initio analytic expressions for A_H and A_L. Details are given in [44,45], and the result is

$$\mathcal{A}_{H/L} = \sum_{k=1,3,5,\ldots} b_k^{H/L} \cos(k\varphi) + c_k^{H/L} \sin(k\varphi). \tag{2}$$

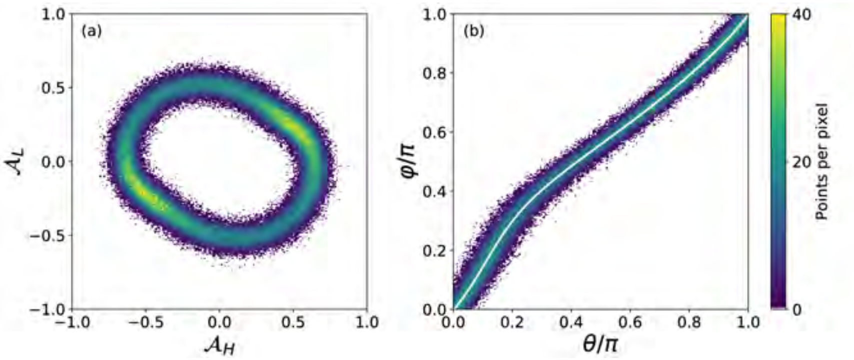
Our formalism provides a physical interpretation for all the terms in Eq. (2), but the key outcome is that the asymmetries can simply be written as a discrete Fourier series in the CEP with only odd frequencies. We can also show that the PAP should have inversion symmetry, providing a clear signature for the symmetry of the CEPM itself. Should the CEPM's symmetry be broken — as is frequently seen in the PAPs in literature — Eq. (2) still holds but includes all frequencies. With this ab initio result, we ought to be able to do better than the experimental method. While it is quite good, we are indeed able to retrieve the CEP with higher accuracy and fewer assumptions by directly fitting $A_{H/L}$ in Eq. (2) to the measured PAP, combined with

$$\varphi(\theta) = \theta + \sum_p \alpha_p \sin(p\theta). \tag{3}$$

This choice conforms with the required symmetry and gives a manageable number of fit parameters. A nonlinear least-squares fit to the experimental PAP gives $\{b^{H/L}_k, c^{H/L}_k, \alpha_p\}$, which enables calculation of ϕ from θ via Eq. (3) for each shot.

To demonstrate the efficacy of our method, we simulated an experimental PAP by choosing the CEP for each shot randomly from a uniform distribution in $[0, 2\pi)$; calculating $A_{H/L}$ from Eq. (2) for a given choice of b_k and c_k with k=1,3,5; and then adding errors to each $A_{H/L}$ by sampling a normal distribution with standard deviation $\delta A_{H/L}$. Figure 13 shows a typical example.

We compare our method for CEP retrieval (TM) with the experimental method (EM) on the simulated data, using the absolute RMS errors $\delta\phi$ as the key figure of merit. We additionally compare these to the deviation $\delta\theta$ of the simulated θ from the actual θ since $\delta\theta$ is a nominal lower bound for $\delta\phi$. To apply Eq. (1), we use 180 bins in θ with a uniform width of ∼35 mrad — as in Ref. [42]. In our nonlinear fit, no knowledge of the fit parameters was assumed and values of p from 1 to 15 and k=1,3,5,7 were included. Figure 13(c) summarizes the results. Our method gives about a 10% reduction in the retrieval error over the experimental method. It is also clear that our method yields nearly optimal $\delta\phi$, lying only about 1% higher than $\delta\theta$. One example of the resulting mapping $\phi(\theta)$ is shown in Fig. 13(b).



(c)

$\delta\mathcal{A}_{H/L}$	$\delta\varphi^{\mathrm{EM}}$	$\delta\varphi^{\mathrm{TM}}$	$\delta\theta$
0.05	101.4	91.2	90.3
0.07	141.2	128.1	126.8
0.1	201.3	184.7	182.5

Fig. **13:** **(a)** Simulated PAP with 200 000 shots and $\delta A_{H/L}$=0.05. **(b)** Mapping from the geometric angle θ to the CEP ϕ. The white line shows $\phi^{TM}(\theta)$ from our method. **(c)** RMS errors $\delta\phi^{TM/EM}$ (reported in mrad) in the extracted CEP. Also shown is the nominal smallest possible error $\delta\theta$ (adapted from [45]).

Future plans: Additional tests examined how the CEP-extraction accuracy is affected by the average PAP radius, by the loss of symmetry, by the number of shots, and by the shape of the PAP. Across all tests, the conclusions from Fig. 13(c) hold: our method outperforms the experimental method and lies within a few percent of the $\delta\theta$ limit. While our exploration of the parameter space is not exhaustive, we expect our method to perform similarly for an arbitrary PAP.

Moreover, it achieves its near-optimal accuracy already for a few thousand shots, in part because it does not require binning the data. And, it does not rely on the assumption that the CEPs are uniformly distributed, making it possible to use for locked-CEP pulses sent to the CEPM. Given its simplicity, robustness, and accuracy, it appears to be an near-optimal choice for retrieving CEPs from PAPs. The greatly reduced requirements on the shape of the PAP and the number of shots should prove useful to CEP-dependent experiments.

4. Attosecond and ultrafast X-ray science

The development of strong-field physics resulted, among many exciting discoveries, in the generation of attosecond light pulses via HHG process. Over the last two decades, these HHG-based attosecond pulses enabled studies of electron dynamics in atoms and molecules on sub-fs time scale [46]. In parallel, the development of XFELs provided numerous experimental opportunities to perform imaging experiments with nearly atomic resolution and combined site-specificity of X-ray spectroscopies with femtosecond time resolution [47]. Very recently, XFELs also developed attosecond capabilities, delivering timed pairs of synchronized sub-fs X-ray pulses [P70]. These developments bring attosecond and XFEL science closer together and open up a variety of novel experimental avenues. In this thrust, we combine several projects aimed at exploiting facility-based and table-top capabilities on the crossroad between these two sub-fields to map coupled electronic and nuclear dynamics in gas-phase molecules in real time. While some of the projects here utilize the advantages offered by short, intense X-ray pulses for CEI, strategically, this thrust is particularly focused on studying ultrafast charge dynamics (charge transfer and charge migration). Intramolecular motion of electronic charge is one of the most important primary events in numerous photo-induced processes in physics, chemistry and biology. Understanding charge dynamics at the microscopic level is essential for achieving fundamental insights into these phenomena and, from a longer-term perspective, for improving technological applications related to energy conversion and storage. Here we exploit the fact that X-rays can target core-level electrons, which are localized at specific atomic sites in a molecule.

4.1. Attosecond physics with HHG sources – Lin, Han

Project scope: Electron dynamics that occur at the tens to hundreds attosecond timescale determine the initial steps of chemical reactions. Elaborate experimental high-order harmonics spectra combined with machine learning algorithms for data analysis enable mapping electron dynamics in simple molecules in tens of attoseconds time steps. HHG spectroscopy can also be used to extract subtle changes of nuclear geometry of molecules on a few-femtosecond to sub-femtosecond time scales. Alternatively, such attosecond or few-femtosecond dynamics can be probed by attosecond transient absorption spectroscopy (ATAS), which uses HHG as a light source. In this project, we continue advancing schemes for extracting information on ultrafast spatio-temporal evolution of electronic and nuclear wave packets from HHG and ATAS data.

Recent progress: In our earlier work, we extracted information on charge migration in strong-field-ionized N_2, CO_2 [P8] and C_4H_2 [P33] molecules from the experimental HHG spectra (obtained by the group of Profs. P. Lan and P. Lu in Wuhan). In the C_4H_2 example, we reconstructed the resulting electron-hole motion along the linear carbon chain with the speed of the center-of-charge ranging from 4.5 Å /fs to 2.8 Å/fs, depending on the alignment of molecules with respect to laser polarization. During the last year, we showed that similar HHG spectra from NH_3 and ND_3 can be used to trace the picometer-scale change of the bond length and tenth of a degree change in bond angle from the atto-chirp of the harmonics within one to two femtoseconds after tunnel ionization [P66]. In addition, we showed that Fano resonances can undergo dramatic shape change within a few hundred attoseconds if driven by a shaped XUV pulse with a sharp spectral minimum [P67] and developed a scheme to characterize such shaped attosecond pulses [P69].

In parallel, we developed a comprehensive theory for ATAS of charge migration in molecules encompassing the entire pump-probe process [P63]. Here, an intense NIR pump induces the dynamics (as discussed in Sec. 3.4), which are then probed by a soft X-ray or XUV attosecond pulse. ATAS experiments represent one of the most direct ways of probing charge migration if the needed ultrashort pulses are available. However, ATAS theory is rather complex since accurate photoabsorption cross-sections are sensitive to details of molecular structures, especially in the excited states populated by the pump pulse. Existing models for calculating molecular ATAS do not account for molecular orientation. As a result, the selection rules for some states are not observed and the orientation averaging is not carried out. Applying the theory to N_2, we demonstrate that the emergence of coherent signals critically depends on the consideration of molecular rotation. This work narrows the gap between ATAS experiments and theory, paving the way for monitoring electronic motion and controlling chemical reactivity in molecular systems.

Future plans: While in the last few years, the JRML work on studying attosecond dynamics with ATAS and HHG spectroscopy was mainly theoretical, we plan to add a new in-house experimental direction centered around the generation of isolated attosecond pulses, providing the basis for the development of an XUV ATAS setup. Guided by the newly developed theory, we will apply this new experimental capability to study charge migration in several simple model systems. In parallel, we will continue theoretical work on retrieving the details of correlated electronic and nuclear wave packet motion from the HHG and ATAS data obtained by our external collaborators.

4.2. Attosecond capabilities and first experiments at LCLS – Rolles, Rudenko, Greenman

Project scope: The main goal of this project is to exploit the recently demonstrated LCLS-2 capability to deliver pairs of attosecond soft X-ray pulses with tunable time delay in order to induce and image charge migration processes a sub-fs to few-fs time scale. Here, we exploit the site-specificity of X-ray – molecule interaction to obtain spatially and temporally resolved snapshots of the evolving electron-hole density. These experimental studies aim to provide benchmark data for state-of-the-art computational models of ultrafast charge motion.

Recent progress: Our main experimental effort on this topic during the last cycle was active participation in the LCLS "attosecond campaign" — a broad community effort aimed at real-time observation of ultrafast electron motion, led by J. Cryan and A. Marinelli. Utilizing a recently developed capability to generate pairs of few-hundred attosecond X-ray pulses [P70], several campaign beamtimes took place at the TMO instrument at LCLS over the last couple of years. Our involvement at LCLS was facilitated by the presence of one of our KSU graduate students, Kurtis Borne, enabled by a DOE-SCGSR graduate student fellowship. Kurtis played a major role in the re-design and testing of a new magnetic bottle electron spectrometer that is being used for the attosecond campaign experiments, as described in [48].

The focus of the attosecond campaign experiments was to investigate attosecond charge migration in aminophenol triggered by inner-valence ionization. The photon energy of the pump pulse was set well below the carbon K-shell absorption edge such that only valence and inner-valence ionization was possible as long as no more than one photon from the pump pulse was absorbed. The ensuing electronic wave packet dynamics were then probed by a second sub-femtosecond X-ray pulse at twice or three times the photon energy of the pump pulse ("2ω" and "3ω", respectively), which arrived at a tunable delay between 0 and 10 fs after the pump pulse. In the 2ω case, the probe-pulse photon energy spanned a range of predicted resonant transitions from the oxygen 1s level to the inner-valence hole states created by the pump, leading to emission of resonant Auger electrons. Alternatively, the induced dynamics were probed by detecting carbon and nitrogen 1s photoelectrons. The 3ω probe pulse (well above oxygen K-edge) also enabled measurements of oxygen 1s photoelectrons.

Analysis of the data from the campaign beamtimes, which investigated different aminophenol isomers, shows that the delay-dependent resonant Auger spectra exhibit a transient signal evolving on a timescale of hundreds of attoseconds, consistent with theoretical calculations that include both electronic and nuclear dynamics of the molecule. A first publication from this campaign demonstrating the novel two-color attosecond X-ray pump-probe capabilities has appeared in early 2024 [P70]. A second manuscript with the results of the experiment on aminophenol is currently being finalized and will be submitted soon.

Future plans: While the attosecond campaign experiments mainly focus on charge migration processes triggered by *inner-valence* ionization or by non-linear stimulated X-ray Raman scattering, we also plan to explore the charge dynamics in the outer-valence shell initiated by core-shell ionization [49,50]. This scheme will allow us to ensure very high degree of initial charge localization, potentially delivering a clear picture of the spatio-temporal evolution of local electron-hole) density propagating across a prototypical polyatomic molecule. In collaboration with the group of K. Lopata at LSU, we developed a successful LCLS proposal to study this type of charge migration in 4-chlorocinnamaldehyde (C_9H_7ClO) using time-resolved X-ray transient absorption spectroscopy (trXTAS) as a probe. The corresponding experiment is scheduled for March 2025 and will be carried out in close interaction with Lopata's group, which simulated both the expected attosecond dynamics and the trXTAS observables.

4.3. Coulomb explosion imaging with intense XFEL pulses –Rudenko, Rolles

Project scope: As can be seen from the examples discussed in Secs. 2.1 - 2.4, CEI with table-top NIR lasers offers a versatile and attractive structural imaging tool. Nevertheless, there are several obvious or potential advantages of using short and intense X-ray pulses to drive CEI. First, the highly charged ionic states that are required for CEI typically constitute a much larger fraction of the total ionization yield when intense X-ray pulses are used to ionize the molecule. Second, a signal to background ratio can be significantly improved if a molecule contains one or more heavy atoms with large X-ray absorption cross section. Third, a strong element-specificity of X-ray absorption in combination with subsequent ultrafast charge rearrangement can enhance the CEI sensitivity to some particular molecular configurations or photoinduced reaction channels. This part of the JRML program focuses on CEI applications that can be most efficiently realized employing XFEL pulses.

Recent progress: Following up on the success of the first CEI experiments at the European XFEL, which focused on the molecules containing a heavy iodine atom with very large X-ray absorption cross section [P1,P2], we have shown that this technique can be also efficiently used for molecules consisting of only light elements (like toluene and other C_7H_8 isomers) [51]. For such molecules, we can also obtain the CEI patterns with comparable contrast using intense NIR pulses from table-top lasers. However, comparing the NIR CEI data for thiophenone molecules containing a sulphur atom with the XFEL results obtained above S 1s edge, we obtain much sharper CEI patterns for the latter case. This is particularly obvious when considering 3D proton emission patterns: the measured proton momenta in the XFEL experiment clearly reflect the positions of the corresponding hydrogen atoms, either within or out of the molecular plane [52]. In a follow-up experiment, we found that such momentum-space images of the peripheral hydrogen atoms can be used to measure the temporal evolution of a molecular structure during internal conversion upon UV-excitation [53].

As another example, we have shown that XFEL-driven coincident CEI can be used to map molecular iodine elimination from laser-irradiated CH2I2, a reaction that involves the breaking of two molecular bonds and the formation of a new one. Here, we exploit the site specificity of X-ray inner-shell ionization and subsequent charge rearrangement processes to isolate a specific reaction channel that accounts for no more than 10% of the total reaction yield. We pump the molecule with 15 fs, 800 nm NIR laser pulse and probe the resulting dynamics by CEI with ~20 fs EuXFEL pulses at 2 keV [54]. The results of this experiment are illustrated in Fig. 14. We isolate the events with low KE of the C^+ fragment and high sum KE of both iodine ions (see panels a, b) reflecting the formation of molecular iodine, trace the initial reduction of the I-I distance (panels a, c) and subsequent vibrations of the I_2^+ product (panel c). For comparison, in panel (d), we show the measured delay-dependent angle between the two iodine momenta deduced from the molecules that remain bound. This angle exhibits a clear oscillation resulting from the bending vibrations of $CH_2I_2^+$ cation.

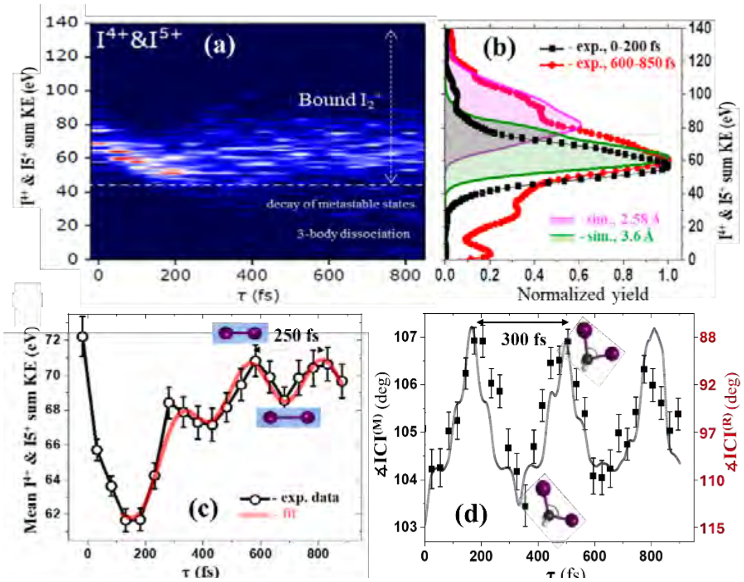


Fig. 14: Imaging of I_2^+ formation with the $C^+/I^{4+}/I^{5+}$ coincidence channel. (a) Time-dependent sum KE of I^{4+} and I^{5+} for the events with low C^+ KE. **(b)** Normalized projections of the data in **(a)** for 0 < τ < 200 fs (black) and 600 fs < τ < 850 fs (red). The shaded areas depict the simulated sum KED for an I-I separation of 2.58 Å (magenta) and 3.60 Å (green). The simulation was performed by Phay Ho (Argonne). **(c)** Delay-dependent mean value of the I^{4+} and I^{5+} sum KE, derived from the data above the white line in (a). **(d)** Mean value of the momentum-space I-C-I angle ∡ICI$^{(M)}$ (left) and the corresponding the real-space angle ∡ICI$^{(R)}$ as a function of NIR/x-ray delay for the $C^{2+}/I^{3+}/I^{3+}$ channel. Adapted from [54]

Future plans: Recent progress in XFEL-driven CEI has been enabled by the availability of the European XFEL, which operated at the effective repetition rates of ~0.5 - 1 kHz. Recent developments at LCLS-II, which currently operates at 8 kHz and is expected to reach 300 to 100 kHz repetition rates, in conjunction with the newly constructed DREAM instrument at TMO pave the way to another breakthrough in time-resolved CEI. With these capabilities, we expect to be able to create quantitative movies of ultrafast nuclear motion in photochemical reactions, particularly focusing on proton or hydrogen motion. Several LCLS proposals along these lines have been submitted for the first round of DREAM operation.

4.4. Imaging intramolecular charge transfer in 4-aminobenzonitrile derivatives – Rolles, Rudenko

Project scope: We exploit the element specificity and sensitivity of X-ray absorption and ionization to the local charge density in order to image intramolecular charge transfer (ICT) in 4-aminobenzonitrile derivatives in the gas phase, including the prototypical 4-(dimethylamino)benzonitrile (DMABN) system, which has been intensively studied in the context of ICT, predominantly in the liquid phase. In contrast to purely electronic charge migration with typical time scales of one femtosecond or less, charge-transfer dynamics are driven by nuclear motion and typically occur within a few tens of femtoseconds.

Recent progress: We have employed time-resolved X-ray photoelectron spectroscopy (trXPS) and transient absorption spectroscopy (trXTAS) in order to investigate the role of different electronic states in UV-induced excited-state dynamics of 4-(dimethylamino)benzonitrile (DMABN) and 4-(diisopropylamino) benzonitrile (DIABN) and to search for signatures of a "twisted intramolecular charge transfer (TICT) state" (see Fig. 15a), which is predicted to play a crucial role in the ICT process in these molecules. Our preliminary trXPES data (taken at SwissFEL in May 2024), shown in Fig. 15, manifest rich fs- and ps-scale dynamics suggesting the involvement of several excited states. We have also acquired trXTAS spectra for DMABN as well as trXPR and trXTAS spectra for DIABN, all of which show robust time-dependent signals that can be compared to simulated XPS and XAS spectra in order to identify the electronic states that are involved.

Future plans: We are currently analyzing the data from the SwissFEL beamtime and plan to compare the experimental findings to detailed predictions of the XPS and XAS spectra and molecular dynamics by M. Schuurman's theory group at NRC Ottawa as well as to valence-shell TRPES data from the Stolow group at NRC. Combining both experimental data sets and comparing them with simulations, we expect to resolve the long-standing controversy regarding the DMABN excited-state dynamics in the gas phase and to characterize the ICT process in both DMABN and DIABN. Since the key question for both systems relates to the geometry of the TICT state driving the CT process, we also plan to image the nuclear dynamics and, in particular, the dimethylamino twist upon the same UV-photoexcitation by Coulomb explosion imaging.

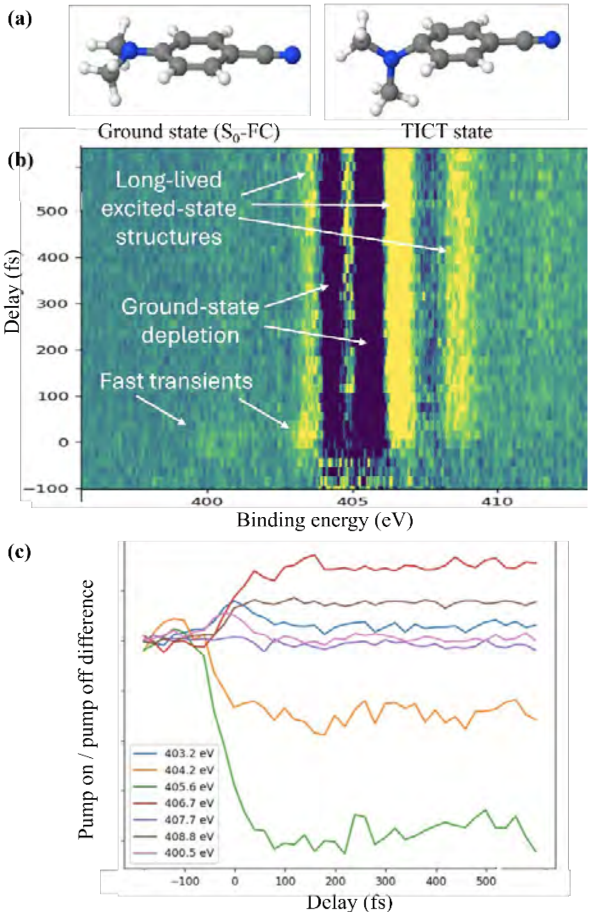


Fig. 15: Preliminary time-resolved XPS spectra of DMABN. (a) Sketch of the molecular geometries of DMABN in its ground state and in the predicted twisted charge transfer (TICT) state. (b) Preliminary experimental delay-dependent XPES spectra upon 267-nm excitation, shown as a difference map of the data taken with and without the pump laser. (c) Delay dependence of individual PE peaks.

Peer-Reviewed Publications Resulting from this Project (2022-2024):

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

Oliver Gessner, Martin Head-Gordon, Stephen R. Leone, Robert R. Lucchese, C. William McCurdy,
Daniel M. Neumark, Jin Qian, Thomas N. Rescigno, Daniel S. Slaughter, Thorsten Weber

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

*OGessner@lbl.gov, MHead-Gordon@lbl.gov, SRLeone@lbl.gov, RLucchese@lbl.gov,
CWMcCurdy@lbl.gov, DMNeumark@lbl.gov, JQian2@lbl.gov, TNRescigno@lbl.gov,
DSSlaughter@lbl.gov, TWeber@lbl.gov*

Project Scope: The AMOS Program at LBNL seeks to answer fundamental questions in atomic, molecular, and chemical sciences that are central to the mission of the Department of Energy's Office of Science. The Program consists of a variety of closely coupled experimental-theory efforts, united by the overarching goal to provide deep insight into the 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 spectroscopy methods 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 generate spatially isolated four-wave mixing (FWM) emission signals, as dictated by phase-matching. The transient emission signals encode the evolution of excited states and therefore represent background-free measurements of XUV-induced chemical dynamics. Attosecond XUV FWM spectroscopy disentangles the complex spectral effects in traditional transient absorption and has so far proved 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]. This technique has also allowed for ultrafast decaying dynamics measurements directly in the time-domain in atoms such as Kr [Fidler et al. **2019**, *J. Chem. Phys. 151*, 114305] and Ne [Puskar et al. **2023**, *Phys. Rev. A 107*, 033117], molecules such as O_2 [Lin et al. **2021**, *Faraday Discuss. 228*, 537] and CO_2 [Fidler et al. **2022**, *Phys. Rev. A 106*, 1], and solids such as NaCl [Gaynor et al. **2021**, *Phys. Rev. A 103*, 1]. A refined understanding of attosecond FWM signal generation, achieved in collaboration with theorists M. Gaarde and K. Schafer at Louisiana State University, shows a time-dependent accumulation of an AC Stark phase grating [Fidler et al. **2019**, *Nat. Comm. 10*, 1384]. These developments have also inspired the implementation of a variant of XUV multidimensional spectroscopy [Marroux et al. **2018**, *Sci. Adv. 4*, eaau3783].

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 probed the Auger-Meitner (AM) decay of dipole-allowed (bright) and -forbidden (dark) core-excited states in xenon [Puskar et al. **2024**, *in preparation*]. An XUV pulse at ~65 eV excites an electron from the spin-orbit split $\{4d_{5/2,\,3/2}\}$ core-level states into the $6p_{5/2}$ and $6p_{3/2}$ XUV-bright states. Each 6p state has two neighboring XUV-dark states, the 6s and 6d states, resonantly accessible by NIR pulses. For the 6p states, the measured lifetimes match the spectral-linewidth-derived values from synchrotron experiments (~5.5 fs). However, the 6s and 6d states show surprisingly different lifetimes: all the measured lifetimes of these other core-excited many-body quantum states are in the ~20 fs regime. These results suggest that the orbital symmetries and, hence, the purely quantum mechanical exchange term in the autoionization matrix element play a dominating role in the coherent sum of the direct and exchange terms in the inter-electronic interactions, thereby leading to destructive interference in the overall coherent sum and extending the lifetimes for all 6p/6s dark states in xenon. This hypothesis is currently being explored, and input from theory is solicited.

In addition, recent FWM experiments have successfully extracted the natural lifetimes of the doubly-excited $^1P^o$ 2s*n*p Rydberg series and the $^1S^e$ $2p^2$ dark state in helium in the 60 – 65 eV region [Rupprecht, Puskar et al. **2024**, submitted to *Phys. Rev. Res.*]. The extracted lifetimes (17.6 fs, 72.6 fs, 180 fs, 324 fs, and 603 fs for the 2s2p, 2s3p, 2s4p, 2s5p, and 2s6p bright states, respectively, and 119 fs for the $2p^2$ dark state) are in excellent agreement with theoretical predictions and showcase the ability of noncollinear FWM spectroscopy to accurately measure lifetimes from tens to hundreds of femtoseconds in a quantum-state specific manner [Fig. 1-1(a) and 1-1(b)]. Furthermore, the spectral line shapes of the measured FWM signals were observed to be Lorentzian in nature, independent of the more complex Fano absorption line shape of these autoionizing states [Fig. 1-1(c)]. This is a direct consequence of the phase-matching condition of noncollinear FWM, which separates the decay of highly excited states from different potentially interfering mechanisms like photoionization. As the NIR intensity in the FWM scheme is an important parameter with its trade-off between FWM signal intensity versus influence on the quantum states themselves, an upper threshold of 0.3 Rabi cycles for an accurate lifetime determination is identified.

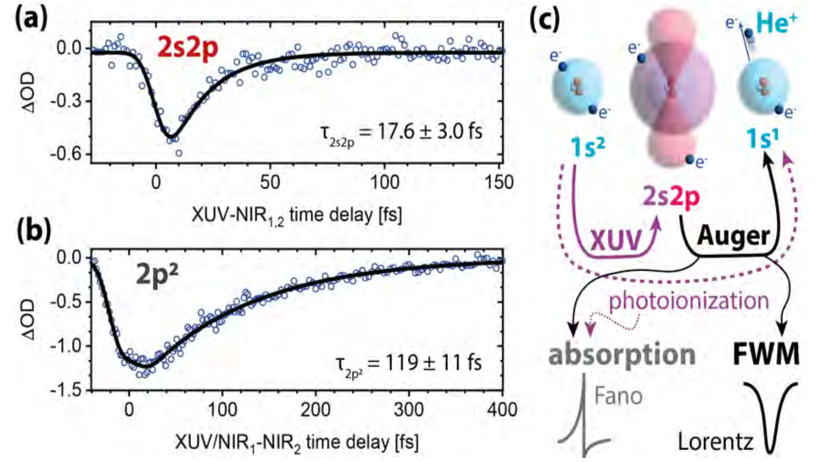

Fig. 1-1: FWM in He doubly-excited states. Experimental lineouts (blue dots) and fits (black lines) depict **(a)** a 17.6 fs decay lifetime for the 2s2p bright state and **(b)** a 119 fs decay lifetime for the $2p^2$ dark state. **(c)** Excitation and relaxation pathways contributing to the absorption and FWM spectral line shapes of the 2s2p state signatures.

With this threshold identified, recent FWM experiments have also probed these same doubly-excited states in the strong-field regime ($\geq 10^{14}$ W/cm^2 NIR intensity) [Rupprecht et al. **2024**, *in preparation*]. Oscillations, bifurcations, and splittings of the FWM signatures are present in the collected signal, and we expect to extract the Rabi cycling between the 2s2p bright state and the $2p^2$ dark state in real time. 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 small quantum systems and exquisitely complement our theoretical understanding of the Rabi frequency.

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 for the HHG process. These pulses are provided by an existing optical parametric amplifier. Recently, the design of the required HHG-cell has been finalized and a prototype built. Furthermore, the generation of ≤ 20 fs ultraviolet pulses at 400 nm and 266 nm via second- and third-harmonic-generation of 800 nm laser light is in preparation. These pulses will be used as noncollinear pulses in the FWM scheme and potentially as actinic pulses to initiate photochemical dynamics (in a UV-SXR-VIS-VIS pulse sequence).

Future Plans: Future FWM experiments will directly probe excited states in the soft X-ray (SXR) spectral region. On the way towards reaching the chemically-relevant carbon K-edge (~300 eV), the higher anticipated photon flux at the sulfur $L_{2,3}$ edge (~180 eV) will allow for characterizing the effect of electron correlation on bright- and dark-state lifetimes of the $L_{2,3}$ 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 frequency-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 electronic-correlation effects such as AM 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 us to 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

Energy- and angle-resolved molecular photoionization measurements are sensitive to the coupled motion of electrons and nuclei in molecules. 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, electron transfer, atom and ion migration, energy exchange between electrons and nuclei as well as vibrational dynamics such as bending and stretching of molecular structures, which are at the core of many photochemical reactions and the focus of our studies. We investigate these phenomena via differential cross sections that we extract from electron-ion coincidence measurements in 3D-momentum space, which we pursue in small quantum systems applying reaction microscopy, a.k.a. COLd Target Recoil Ion Momentum Spectroscopy (COLTRIMS). The investigations are realized using XUV synchrotron radiation, 2-photon absorption-ionization schemes with our tabletop intense XUV laser system, and two soft X-rays from single free electron laser pulses. Our studies focus on fundamentally important systems ranging from small and midsize polyatomic molecules (e.g., H_2, D_2O, CCl_4, CH_4, C_2H_4, CH_3OH, HCOOH) to more complex systems (such as H_2O-H_2O, HCOOH-HCOOH, and Pyrrole-d-H_2O dimers in Subtask 2) that are within reach of both complete experimental characterization and accurate theoretical treatment and interpretation. This enables tight coupling of the experiment and the theory thrusts, which directly inform and inspire each other.

Tracking Ultrafast Non-Adiabatic Dissociation Dynamics of Water and its Isotopologues

(Lucchese, McCurdy, Rescigno, Slaughter, Weber)

Recent Progress: We completed our series of studies on the complex dissociation dynamics of water ions. Combined synchrotron XUV electron-ion coincidence experiments and first-principles calculations elucidated the photoionization and dissociation dynamics of isolated heavy water molecules that generated the rare $D^+ + O^+ + D$ reaction channel upon direct double ionization with a single 61 eV photon. The study, which was performed at the Advanced Light Source (ALS), provided new insights into reaction coordinates, transition rates of intermediate species, and the crucial role of spin-orbit coupling (SOC) mediated charge transfer in the OD^+ intermediate of this sequential breakup pathway. We revealed how the dissociation process enables favorable conditions for SOC, which then steers the transient OD^+ ion towards either the dominant $D^+ + D^+ + O$ breakup channel or the rare $D^+ + O^+ + D$ outcome. In the latter case, we found that the OD^+ intermediate undergoes a complex $OD^+(a^1\Delta, b^1\Sigma^+) \rightarrow OD^+(A^3\Pi) \rightarrow OD^+(X^3\Sigma^-) \rightarrow OD^+(B^3\Sigma^-)$ transition sequence employing SOC, atomic-SOC, and charge-exchange, respectively, in order to produce the measured $O^+ + D$ reaction products. We revealed that the relative yield of this competing OD^+ dissociation channel is highly sensitive to the vibronic state populations of the

OD^+ transient, which in turn determines the low kinetic energy release (KER) in this relatively slow sequential dissociation process [Iskandar et al. **2023**, *J. Chem. Phys. 159*, 044311].

We complemented this study by investigating the high-KER contribution of the OD^+ dissociation dynamics of this rare $D^+ + O^+ + D$ fragmentation channel [Iskandar et al. **2024**, *J. Chem. Phys. 161*, 094301]. Here, we identified three competing ultrafast dissociation scenarios that are initiated by differing degrees of both symmetric and asymmetric stretching of the deuterated water dication. The measured particle momenta, angular, and energy distributions of electrons and ions, detected in coincidence, reveal the distinct geometries and electronic states of the dication. We see that small or large symmetric and asymmetric stretching of the bonds determine the specific reaction pathways. Using multi-reference configuration-interaction calculations, we further tracked their dissociation routes via SOC and charge transfer at crossings and seams on the potential energy surfaces that ultimately lead to the observed $D^+ + O^+ + D$ fragmentation channel. Notably, we can distinguish between two direct dissociation reactions and a fast sequential dissociation pathway. For the latter, our native frame analysis revealed the geometry of the molecule and its orientation with respect to the polarization vector that triggers this rare 3-body breakup channel. The unique combination of experiment and theory also unraveled the characteristic time of ~65 fs between the first and second step of this sequential breakup reaction.

The three-body dissociation dynamics was further investigated in the quadruple ionization of water isotopologues, H_2O, D_2O, and HDO, via two X-ray absorption at the EuXFEL [Guillemin et al. **2023**, *Struct. Dyn. 10*, 054302]. Similar structural changes such as asymmetric bond elongation and bond-angle-opening mechanisms occur for all three systems, but with distinct isotope effects along the series. In particular, dynamical patterns are slower in D_2O, and structural asymmetry arises in the fragmentation of HDO, due to the mass asymmetry. The native frame analysis indicated that a clear two-step dissociation cannot be identified, possibly because a full sequential fragmentation takes more time than the pulse duration of the ionizing X-ray beam of < 25 fs, which quenches this breakup process by further ionizing and Coulomb-exploding the ionic intermediate.

Future Plans: Building on our progress towards the detailed understanding of the dissociative multiple ionization of water and its isotopologues, we are now systematically increasing the complexity of our target molecule by replacing one hydrogen atom with a methyl-group. The fragmentation dynamics of select reaction channels of deuterated methanol is investigated for CH_3OD and CD_3OH via valence photo double ionization (vPDI) with 54 eV photons at the ALS. We are particularly interested in proton and molecular hydrogen migration and roaming, as well as bond fission and formation that are initiated by vibrational excitation (mostly in the proton rich methyl group) during the dissociation process. The analysis and interpretation of our experiment is challenging, because there are many reaction channels (~17) that compete and partly or fully overlap in our crucial PhotoIon-PhotoIon Coincidence (PIPICO) time-of-flight spectra. After a thorough survey, we have identified and isolated the $CHD^+ + OH^+ + H$ fragmentation channel in the photodissociation of CH_3OD^{2+} with sufficient statistics. Through Newton diagrams and by applying the native frame analysis, we aim to find clues in which sequence the hydrogen and deuteron traded places during the photo reaction. In this regard, other fragmentation pathways of interest that we isolate in our experiments are the two-body breakup channels $CH_2O^+ + HD^+$, $CHO^+ + H_2D^+$, and the three-body reaction channel $CHO^+ + HD^+ + H$. Each of these PIPICO features are direct evidence of roaming or hydrogen/deuteron migration, or a combination of both, which compels us to investigate these channels in the momentum domain.

Electron Correlation in Polyatomics (*Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: Electron-electron correlation is studied in the vPDI of C_2H_4 by 40 eV synchrotron (ALS) single-photon ionization. We put the emphasis of our investigations on the symmetric breakup channel $CH_2^+ + CH_2^+$ as well as the deprotonation channel $C_2H_3^+ + H^+$ and analyzed them state-selectively. Besides direct double ionization of the $C_2H_4^{2+}$ dication, we found contributions from the dissociation of super-excited cation states $C_2H_4^{+*}$ in both reactions. We recently studied the role of a super-excited cation state in the dissociation of water upon vPDI, which produced a decaying long-lived (few ps) O* fragment that autoionized at long internuclear distances [Iskandar et al. **2023**, *Phys. Chem. Chem. Phys. 25*, 21562]. The super-excited states in $C_2H_4^{+*}$ can also feed such slow fragment autoionization channels to produce highly unequal energy sharing of the correlated photo- and autoionization-electrons, yielding sharp energetic features (see Fig. 1-2: $E_p \in [0.95; 1]$ and $E_a \in [0; 0.05]$). Yet, they appear to also act as resonances in the double ionization continuum that exhibit broad peaks with, in this case, intermediate electron energy sharing ($E_{p1} \in [0.1; 0.45]$ and $E_{p2} \in [0.55; 0.9]$), pointing to very short lifetimes (< 1 fs). The excitation process takes place during the electron-electron knock-out of the resonant double ionization in the Franck-Condon region. The resonances are broadened due to post collision interaction of the correlated electron pairs. Our previous experiments on the vPDI of C_2H_4 already showed such broad peaks in the electron energy sharing when a stabile $C_2H_4^{2+}$ dication was created [Gaire et al. **2014**, *Phys. Rev. A 89*, 013403]. Yet, at that time, we did not correlate this finding with the excitation of super-excited states, although the population of such short-lived super-excited states in the direct PDI had been predicted by the LBNL theory group for (*e,2e*) double ionization of He atoms almost two decades ago [Horner et al. **2005**, *Phys. Rev. A 71*, 010701(R)]. The analysis of this intriguing ionization process in the photo double ionization of molecules is ongoing in collaboration with the LBNL theory team (see the described efforts in Subtask 3).

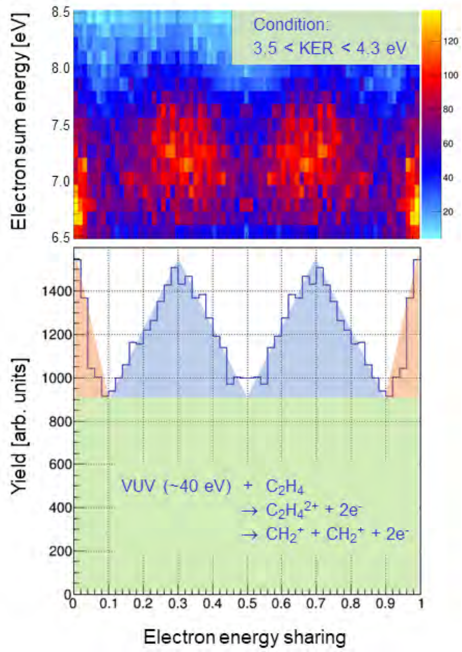

Fig. 1-2: Electron energy sharing of the two emitted electrons upon vPDI of C_2H_4 with ~40 eV single photons for selected KER of the ($CH_2^+ + CH_2^+$) symmetric breakup channel (3.5 < KER < 4.3 eV). Top: electron sum energy as a function of electron energy sharing, indicating that the super-excited states differ from the cation states, which are responsible for fragment AI, by about 0.5 eV. Bottom: yield distribution of the electron energy sharing showing contributions from direct double ionization (green), fragment AI (orange), and super-excited $C_2H_4^{+*}$ cation states (blue).

Future Plans: In the ongoing collaborative analysis of the experiment on the vPDI of C_2H_4, the single differential electron energy sharing cross sections will be complemented by electron-ion energy maps and RFPADs that are exquisitely sensitive to electron-electron correlation. In particular, we intend to compare the recently extracted RFPADs for the symmetric breakup channel producing $CH_2^+ + CH_2^+$ with RFPADs of the $C_2H_3^+ + H^+$ deprotonation channel. The investigation of the deprotonation channel will then be complemented by a double ionization study on CH_4. Our recent state selective experiments of the vPDI and core ionization of CH_4 at the ALS, which are initiating dissociation into $CH_3^+ + H^+$, suggest that the lowest triplet state $^3T_1$ of the methane dication is only populated in the valence ionization, and not in the core ionization that is followed by AM decay. The absence of any contribution from the lowest electronic state associated with the $^3T_1$ term seems to indicate spin-selectivity in the AM emission process. We aim to understand this preliminary finding by analyzing the internal energy of the CH_3^+ fragment ion to better understand the possible role of conical intersections in the dissociation dynamics of this deprotonation channel. This work is a collaborative effort with J. Rajput (University of Delhi) and J.B. Williams (University of Nevada Reno).

Electron Localization in the 2-Body Dissociation of Small Molecules Upon Core and Valence Ionization *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: In this project, which leverages the unique experiment and theory capabilities at LBNL, electron localization is studied in the Cl(2p) core ionization of CCl_4 followed by AM decay using the ALS. We currently investigate the RFPADs for the most prominent two-body breakup channel $Cl^+ + CCl_3^+$ for three different photoelectron energies and four orientations of the polarization direction of the incoming light with respect to the recoil axis of the fragmentation. With *ab initio* calculations from the LBNL theory team, the RFPADs reveal that the AM decay and dissociation dynamics of the system allow for a partial determination of the RFPAD related to the localized core-hole (see Fig. 1-3). As in our previous work on the F(1s) core ionization of CF_4 [McCurdy et al. **2017**, *Phys. Rev. A 95*, 011401(R)], the RFPADs show a clear dependence on the KER. For low KER, the axial recoil approximation appears to partly fail, and any "memory" of where the core-hole was created is lost. For the highest KER, the RFPADs exhibit the most pronounced structure, which suggests that with higher KER, ultrafast dissociation occurs on shorter timescales, preserving the fingerprint of core-hole localization at the bond that breaks. It appears that slower dissociation produces the low-KER feature, where any signature of the localized core-hole is evidently lost during dissociation. The analysis in collaboration with the LBNL theory team is ongoing (see also Subtask 3).

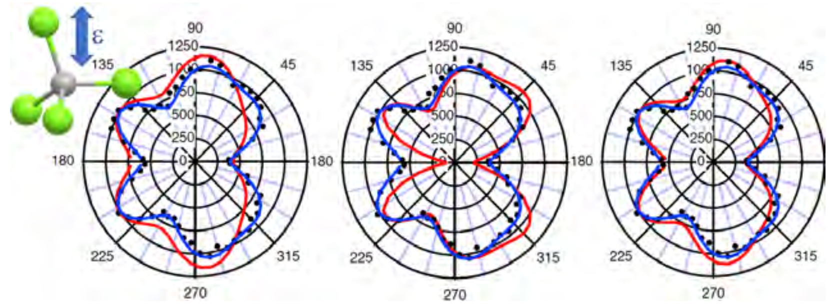

Fig. 1-3: RFPADs of the photoelectrons with 3.5 eV in the dissociation of the CCl_4^{2+} dication into $CCl_3^+ + Cl^+$ upon Cl(2p) ionization for 3.5 eV < KER < 6.25 eV. The detected Cl^+ is going to the right, and the linear polarization vector of the incoming light is at right angles to this ion emission direction (see inset). Black points and error bars: experiment. Blue curve: fit to the experimental data based on associated Legendre polynomials. Red line: *ab initio* calculations assuming a completely delocalized hole (left), a fully localized hole (middle), and a 70:30 mix (right).

Electron localization was also studied via synchrotron VUV ionization and rovibrational excitation of H_2^+, followed by the dissociation with a weak subsequent NIR pulse at the ALS with 80 ps and 10 ps pulses, respectively. After unraveling why not all of the prepared vibrational states can be dissociated with the NIR pulse, small time-dependent and time-independent asymmetries were detected in the MFPADs that represent a mixing of the $1s\sigma_g$ and $2p\sigma_u$ states of H_2^+. This state mixing is likely due to combinations of electron retroaction [Heck et al. **2019**, *Phys. Rev. Res. 1*, 033140] and the interference of two or more laser photodissociation pathways. The puzzling asymmetry in the MFPADs, when the dissociating NIR pulse arrives 10's to 100's ps after VUV photoionization, will require further investigation. In collaboration with the LBNL theory team, we will inspect the gerade/ungerade two-electron wave-function of $e^- + H_2^+$ for possible entanglement that could perhaps explain this dissociation dynamics.

Two-photon XUV photoionization experiments will also be performed in our ultrafast laser lab to study the molecular dynamics in resonant and nonresonant two-photon dissociative ionization. To enable the extension of our energy-domain studies of dynamics in dissociative photoionization to the ultrafast time-domain, we completed the commissioning of the new 55 kHz Yb-slab amplified laser system and XUV beamline. The compressed and down-collimated 85 W, 45 fs, 1030 nm infrared laser generates ~350 µJ pulses of 515 nm in a BBO crystal by second harmonic generation (SHG). The 515 nm SHG laser light is then transported in helium, using dichroic mirrors to transmit and discard the residual 1030 nm infrared light, expanded and focused via a lens (f = 50 cm) into a gas cell containing either krypton or argon for high harmonic generation (HHG). To avoid damage to the XUV components by the 515 nm pulse at such high repetition rates, the XUV beam is transmitted through a series of apertures to block most of the fundamental. It is then transported by a grazing-incidence dichroic multilayer mirror, which efficiently reflects the XUV and transmits the remaining fundamental, into the filter chamber of the beamline. The XUV pulses are currently measured with calibrated photodiodes after an aluminum filter that transmits all orders above the 5th harmonic of 515 nm or with a bandpass filter that is sensitive only to the 3rd harmonic of the 515 nm SHG light. Efforts are ongoing to precisely align and collimate the XUV beam to the COLTRIMS endstation, in order to fully characterize the XUV spectrum by atomic photoelectron spectroscopy and to perform femtosecond time-resolved electron-ion coincidence experiments. First ion and electron test spectra, which were recorded with the 3D-momentum spectrometer (dimensions: electron-side = 10 + 20 cm, ion-side = 20 cm; electric extraction field = 12.5 V/cm; magnetic guiding field = 3.66 G) in the endstation, are shown in Fig. 1-4.

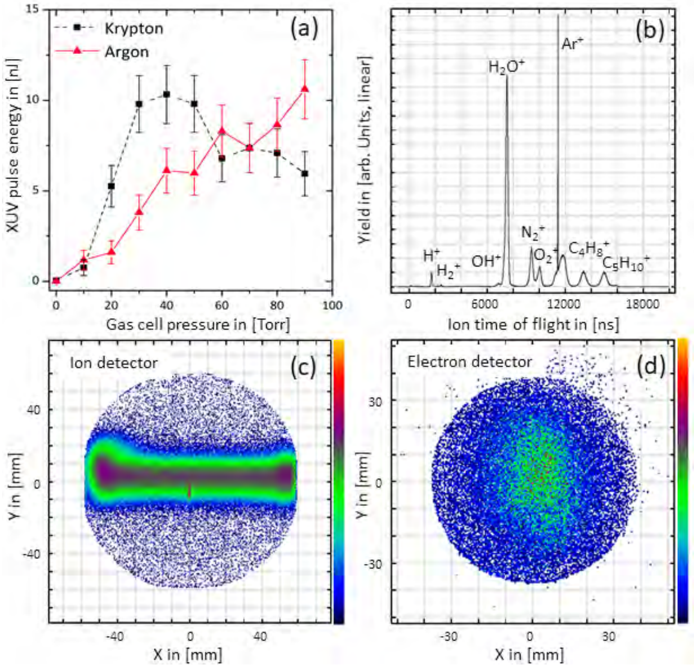

Fig. 1-4: (a) 3rd-harmonic XUV signal at 7.2 eV as a function of gas cell pressure for HHG in krypton and argon, measured with a bandpass filter to reject the residual 515 nm fundamental 4 m after the HHG gas cell. The driving 515 nm laser has a pulse duration of ~70 fs and energy of ~350 µJ. It is focused by a lens (f = 50 cm) to a ~40 µm focus (FWHM) a few mm downstream of the 5 mm long HHG cell. The estimated XUV pulse energy is corrected for the fundamental rejection mirror reflectivity (~10%) and the bandpass filter transmission (~10%).

Recoil-ion and electrons measured after photo ionization of a thin Ar gas jet target with ≥7th harmonics of the 515 nm fundamental: (b) ion time-of-flight spectrum, showing the ionic fragments of the vacuum background and the gas jet. (c) ion detector picture (log. yield scale, arb. units), showing the ionization of the incoming and back-reflected VUV beam in the residual background (stripe) and the gas jet (sharp red spot). (d) electron detector (lin. yield scale, arb. units) for kinetic energies up to 7 eV.

Future Plans: With our new laser system, HHG source, and beamline now configured for high repetition rates as described above, we aim to measure angle- and energy-resolved ion and photoelectron spectra by photoionization using femtosecond XUV pulses at 55 kHz. With sufficient XUV intensity, a brief series of commissioning experiments will follow up on our recent investigation of strongly coupled intermediate electronic states in two-photon single valence ionization of O_2 [Larsen et al. **2023**, *J. Chem. Phys. 158*, 024303], for which the LBNL theory team recently reproduced the kinetic energy distribution of the photoelectrons by including autoionizing and doubly-excited Rydberg states (see Subtask 3). These results can be further challenged with different XUV photon energies and the ability to track the ratio of stable O_2^+ cations with respect to the dissociation of the O_2* intermediate during the photo-absorption process. This will give insight on the role and pathway of the excited O_2* states that form an avoided crossing and how the wavepacket in it can be coupled to the continuum. Together with the LBNL theory team, we will then target polyatomic molecules like CO_2 and N_2O to study electronic and vibrational state-selective dissociation processes using electron-ion coincidence 3d-momentum imaging.

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: Following our recent investigations of the dynamics of dissociative attachment of electrons to organic acids and amides, we investigated the influence of methyl substitutions on the anion dissociation dynamics. Unlike methanol, an electronic Feshbach resonance in ethanol dissociates by electron attachment to produce hydroxyl anions. The characteristics of this anion resonance were previously poorly understood, and we have identified its symmetry and Rydberg character by measuring the laboratory-frame anion fragment angular distributions in an experimental collaboration with S. Ptasinska (U. Notre Dame) [Chakraborty et al. **2023**, *Phys. Rev. A 108*, 2469].

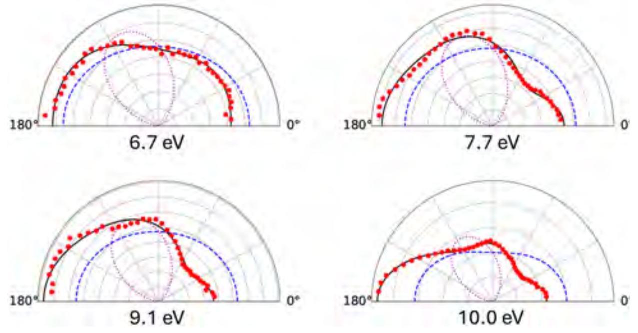

Fig. 1-5: Angular distributions for O-D break following electron attachment to deuterated acetic acid CH_3OOD, at the four distinct resonances indicated by their attachment energies. In each panel the incident electron direction is 0° (left to right). Assuming the axial recoil approximation holds, the experimental data (red circles) are fitted with models having A' (dashed blue curve: s + p symmetry, and solid black curve: s + p + d symmetry) and A'' (dotted purple: p + d) symmetry, indicating that each of the four resonances shown here have A' symmetry.

The symmetries of transient anion resonances that dissociate acetic acid to produce acetyloxyl and hydride were also investigated by anion fragment momentum imaging. From the laboratory-frame dissociation angular distributions (see Fig. 1-5), we found two Feshbach resonances that dissociate by O-H break have A' symmetry, and a third higher-energy resonance, which dissociates by both C-H break and O-H break, also has A' symmetry. The latter fragmentation channel has not been reported previously. The experiments also revealed, for the first time, a fourth A' resonance for 10 eV electron attachment, which is dissociating by O-H break [Hasan et al. **2024**, *J. Chem. Phys.* manuscript under review]. This work is performed in collaboration with M. Centurion (U. Nebraska Lincoln).

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

O. Gessner, S. Leone, D. Neumark, J. Qian, D. Slaughter, Th. Weber

Excited-State Dynamics Probed by Ultrafast Core-to Valence Transient Absorption Spectroscopy *(Gessner, Leone, Neumark)*

The study of the UV photochemistry of small heteroaromatic molecules provides a crucial framework for understanding fundamental excited state molecular dynamics, particularly the interplay between electronic and nuclear motion in moderately complex systems. In this activity, femtosecond inner-shell transient absorption spectroscopy is combined with high-level *ab initio* calculations to gain insight into fundamental photochemical processes, including isomerization, dissociation, and ring-opening reactions, on their fundamental time- and length-scales.

Recent Progress: In our recent work, Toulson et al. **2023**, *J. Chem. Phys. 159*, 034304, we monitored UV (268 nm) induced dynamics in 2-iodothiophene, using femtosecond XUV probe pulses in the range of the core-to-valence transitions at the iodine N-edge (~50 eV). The atomic site-specificity of the transient inner-shell absorption signals was instrumental for gaining a detailed view of a two-step dissociation mechanism, coupling an initially accessed, bound ππ* excited state to a dissociative πσ* state via a conical intersection (CI).

Interestingly, we did not observe evidence for ring-opening of 2-iodothiophene, a key relaxation pathway anticipated based on previous fragment imaging studies. Yet, this pathway involves the cleavage of a carbon-sulfur (C-S) bond in the molecule, to which the iodine N-edge measurements were not particularly sensitive. To address this issue, we have modified our experimental setup to enable probing at the sulfur $L_{2,3}$-edge (~170 eV) using a differentially pumped high-order harmonic generation (HHG) setup paired with a high-power optical parametric amplifier (OPA). Fig. 2-1 shows a HHG spectrum from the reconfigured transient X-ray absorption (TXA) setup, extending beyond 200 eV. We are currently working on optimizing the flux and stability of the HHG source for use in sulfur $L_{2,3}$-edge TXA studies. This capability will provide much more direct and sensitive

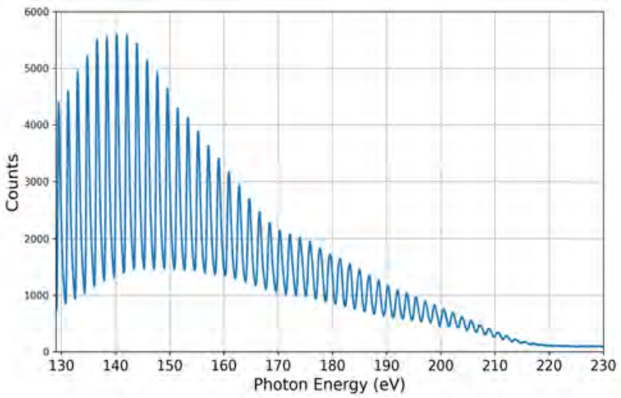

Fig. 2-1: High-order harmonics spectrum generated in helium using a 1200 nm driving laser.

access to electronic and structural changes in the vicinity of the sulfur atom including possible ring-opening reactions.

Future Plans: With these new capabilities, our next goal is to perform detailed, comparative measurements on UV-excited 2-iodothiophene from the perspectives of the iodine and sulfur atomic sites to explore various relaxation pathways. Next, we aim to explore fundamental photo-induced processes in analogous sulfur-containing molecules.

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

(Gessner, Leone, Neumark)

Ultrafast electron diffraction (UED) has emerged as a powerful tool to probe structural dynamics in molecules on femtosecond timescales. Our recent work focused on utilizing MeV-UED to investigate the UV photochemistry of bromoform ($CHBr_3$) following 267 nm excitation. UED provides direct insight into the molecular geometries of reaction intermediates that are otherwise challenging to observe. Our experiment at the LCLS MeV-UED facility revealed significant new details about the bifurcation of reaction channels following UV excitation, highlighting the roles of both direct dissociation and isomerization processes.

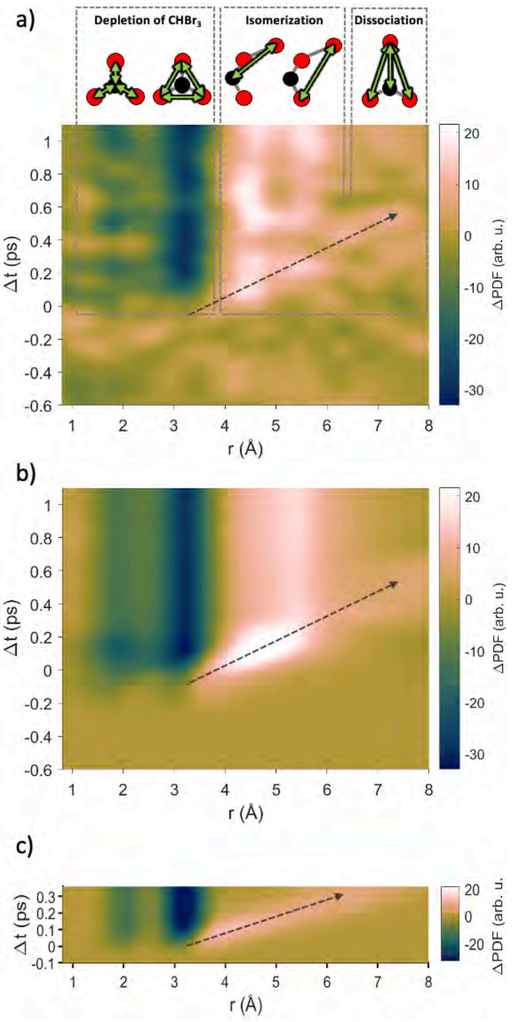

Fig. 2.2: Time-dependent difference pair-distribution functions (ΔPDF) of bromoform after 267 nm excitation. a) experiment and b) global fit. c) shows the average ΔPDF of a direct dissociation trajectory manifold in an *ab initio* molecular dynamics simulation. Sketches in a) show the dominant molecular structures and atom pairs corresponding to the ΔPDF features [Hoffmann et al. **2024**, *J. Am. Chem. Soc.*, accepted].

Recent Progress: Significant strides have been made in characterizing various reaction pathways following 267 nm excitation of bromoform. Structures of transient intermediates have been determined and their relative reaction yields quantified, offering unprecedented insight into the early stages of the molecule's UV photochemistry.

The advances were enabled by the development of a global fit analysis in momentum space, which is unaffected by potential conversion artifacts that may appear in real-space UED data after transformation. The method has proven to be particularly effective in distinguishing and quantifying the yields of two competing reaction channels described in the literature, i.e., direct dissociation and isomerization.

One of the key findings is the successful identification of isomerization as a dominant relaxation pathway. The MeV-UED experiments provide clear evidence for the formation of an iso-$CHBr_3$ (Br-CH-Br-Br) isomer within 200 fs after UV excitation. The isomerization pathway accounts for 60% of the initial reaction yield and significantly influences the subsequent dynamics, with the isomer exhibiting lifetimes exceeding 1.1 picoseconds.

The combination of real-space and momentum-space analyses also sheds light on the structural evolution of bromoform during the ultrafast dissociation process. Fig. 2.2 shows the time-dependent difference pair-distribution functions (ΔPDF), i.e., changes in the relative abundance of specific atom-pair distances, induced by the UV pump pulse. Dark features indicate signal depletion, lighter features signal enhancement.

Pump-induced depletion of C-Br and Br-Br distances $r<4$ Å, associated with the parent molecule, are complemented by newly emerging signals, corresponding to a theoretically predicted isomer geometry (4 Å$<r<$6.3 Å, Fig. 2.2a,b) and a diagonal feature (dashed arrow) that closely follows an average dissociation trajectory signal derived from an *ab initio* molecular dynamics simulation ($r>3$ Å, Fig. 2.2c).

The direct dissociation pathway, leading to the formation of $CHBr_2$• and Br• radicals, proceeds on a timescale comparable to that of isomerization, with both channels sharing very similar molecular geometries before diverging after ~200 fs.

The findings clarify the role of isomerization in the earliest stages of the bromoform UV photochemistry, which has been a focus of theoretical and experimental work for several decades. They are also compatible with the involvement of roaming-like relaxation mechanisms suggested in previous work, where partial dissociation and reorientation of fragments occur in the long-range (3–8 Å) region of the molecular potential, including the van der Waals region. The relatively high yield and unexpectedly long lifetime of the isomer challenge existing theoretical predictions and underscore the need for further computational studies to fully elucidate the underlying reaction mechanisms. A manuscript describing the work has just been accepted for publication in JACS.

Future Plans: Building on the successful gas phase UED campaign described above, we will extend our investigations of the UV-photochemistry of bromoform to the solution phase, where the dynamics are expected to be significantly more complex due to interactions of the bromoform solute with the surrounding solvent. We will participate in a beamtime during the liquid-phase UED (LUED) Early Science program at the LCLS MeV UED facility, which will focus on ultrafast isomerization and competing photochemical processes of solvated bromoform. The experiments are designed to distinguish between the rapid, direct isomerization and a previously reported slower, solvent cage-induced isomerization mechanism. The latter involves transient trapping of a fragment bromine atom by the solvent cage, followed by recapture by the parent fragment, a process that could reveal new insights into the formation of iso-bromoform in solution. Additionally, we will investigate potential competing relaxation pathways that are unique to the liquid phase, including the formation of solvolysis products.

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

In this effort, ultrafast time-resolved X-ray photoelectron spectroscopy (TRXPS) and time-correlation X-ray photoelectron spectroscopy (TCXPS) are employed at synchrotrons and X-ray free-electron lasers (XFELs) to capture photo-induced, short-lived intermediates underlying charge migration and chemical transformations at surfaces, interfaces, and in heterogeneous photocatalytic systems.

Elucidating Charge Carrier Dynamics in a Nanoplasmonic Water Splitting Photocatalyst

(Gessner, Neumark, Qian)

Recent Progress: Photoelectrochemical water splitting is of significant interest as a potential contributor to a greener, renewable, and net carbon-free energy infrastructure. We previously used picosecond TRXPS to quantify photoinduced charge transfer in 20 nm gold nanoparticle (AuNP) sensitized nanoporous TiO_2, a model water splitting photocatalyst [Borgwardt et al. **2020**, *J. Phys.*

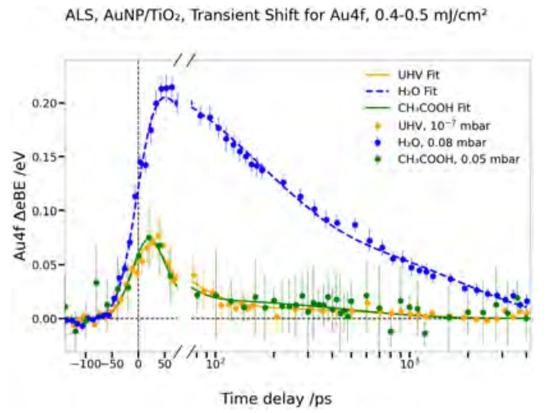

Fig. 2-3: Preliminary picosecond TRXPS data recorded at the ALS. Photo-induced electron transfer from AuNP light absorbers into a TiO_2 substrate leads to transient Au4f photoline shifts to higher apparent binding energies. Exposing the AuNP/TiO_2 interface to different environments, as indicated by the color codes, has a dramatic impact on the carrier lifetimes.

Chem. Lett. 11, 5476]. Building on this expertise, we have significantly extended TRXPS studies of photo-induced charge carrier dynamics in this system toward two main goals: a) understanding the impact of the environment on the interfacial carrier dynamics, and b) gaining a better understanding of the earliest photoinduced dynamics, including the charge-injection process, believed to proceed on femtosecond timescales. Fig. 2.3 shows picosecond time-resolved, transient photo-induced shifts of the effective Au4f binding energies for a AuNP/TiO_2 sample under UHV conditions (orange), as well as under exposure to water (blue), and acetic acid (green). Note the split linear/logarithmic scaling of the optical-pump, X-ray-probe time delay axis. The AuNPs were excited at the peak of the plasmon resonance at 532 nm, leading to hot electron injection into the conduction band of TiO_2. The measurement was performed at BL 11.0.2 of the Advanced Light Source (ALS). The transient Au4f energy shifts provide a direct measure of the time-dependent hole densities on the AuNPs, thus, reflecting the AuNP–TiO_2 electron transfer and subsequent electron-hole recombination dynamics. Fig. 2-3 demonstrates that different environments have a dramatic impact on the charge recombination lifetimes, which needs to be considered when designing photocatalysts for applications. In an upcoming ALS beamtime, we will conduct a series of measurements using a variety of solvent environments to study the impact of the dielectric properties of the solvents on electron-hole recombination times in greater detail, which will allow us to gain a deeper understanding of the underlying physics.

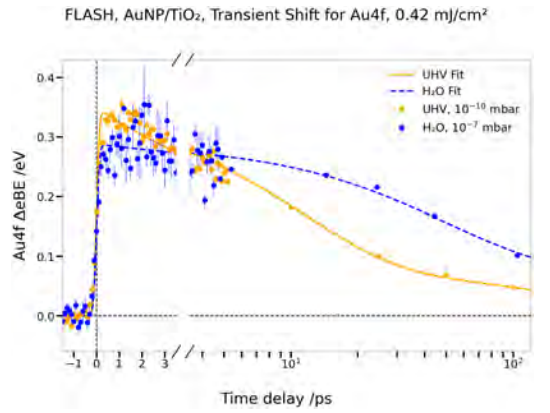

Fig. 2-4: Preliminary TRXPS results on photo-induced charge transfer in AuNP/TiO_2 systems obtained at FLASH. Initial responses are almost identical for UHV (orange) and water exposed (blue) conditions, while notable differences emerge at longer pump-probe delays.

Fig. 2-4 shows results from a femtosecond TRXPS study of the AuNP/TiO_2 system at the FLASH Free Electron Laser in Hamburg. The pump - probe time-delay axis, again, has a split linear/logarithmic scaling. The two curves show the transient Au4f effective binding energy shifts following 515 nm excitation under UHV conditions (orange) and under water exposure (blue). The amplitudes of the two curves for delays shorter than a few picoseconds are almost identical, but depart from another for longer delays, with the water exposed system exhibiting much longer electron-hole lifetimes again. The FLASH measurement clearly demonstrates that the initial electron injection efficiency is essentially the same for the UHV and water-exposed systems, but the much faster recombination dynamics in the UHV system lead to a suppression of the observed amplitudes in the ALS measurement, owing to the much slower temporal response of the ALS TRXPS experiment (~70 ps FWHM).

Future Plans: We will perform additional measurements with a variety of solvent environments at the ALS and continue a detailed analysis of the FLASH and ALS TRXPS experiments. The goal is to gain a better understanding of the mechanisms that drive the injection dynamics and the physics that connect carrier lifetimes with the photocatalyst environment. Interpretation of the experimental results will be aided by *ab initio* calculations in the Qian group (see Subtask 3 and Qian's Early Career Research Program abstract).

XUV Ultrafast Transient Polarization Spectroscopy (X-UTPS)

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 3rd-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 coupled electronic and nuclear 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 this new nonlinear technique, which is based on 3rd-order optical responses, into the XUV and X-ray regime and establish X-UTPS. Accessing inner-shell electronic resonances and absorption edges in X-UTPS is expected to provide 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 3rd order nonlinear response of a system using one excitation pulse and only two probe pulses, instead of three or more probe pulses as in other FWM techniques, which promises good efficiency in the X-ray regime. While the signal and probe are colinear, the near infrared Kerr gate pulse is noncolinear with the probe and signal, like the attosecond-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.

Ultrafast Time-Resolved Dynamics by XUV Nonlinear Spectroscopy and Two-Color Four-Wave Mixing (*Slaughter, Weber*)

Recent Progress: The planned X-UTPS experiments depend crucially on the thoroughly characterized XUV spectrum as well as the spatial and temporal properties of the XUV pulses. Specifically, nonlinear interactions involving two XUV photons require control over the intensity, temporal, and spectral characteristics of the XUV pulse. An optimized parameter set, in order to find and maximize the targeted X-UTPS signals in these intensity hungry XUV pump-probe schemes, is vital. Control over this parameter space requires XUV measurements, not only at the XUV focus in the endstation, but also far-field characterization in the beamline. We, hence, investigated and controlled the set of parameters varying the XUV beam profile at the position of the XUV mirror near the endstation entrance (see the top-left inset of Fig. 2-5). The XUV beam profiles were recorded using an MCP-phosphor-CCD imaging detector, with the integrated charge from the MCP outcoupled to an oscilloscope to measure the XUV yield. One example is shown in the lower-right inset in Fig. 2-5. While increasing the gas pressure in the HHG cell, we measured near-Gaussian XUV profiles that increase in diameter by approximately a factor of two. Specifically, the diameter of the XUV beam increased from 5 mm, at low pressures around a few Torr, to 10 mm at 35 Torr (Fig. 2-5). Using an aluminum filter to exclude the fundamental and low order (hν < 15 eV) photons, the maximum integrated XUV yield was measured at intermediate gas

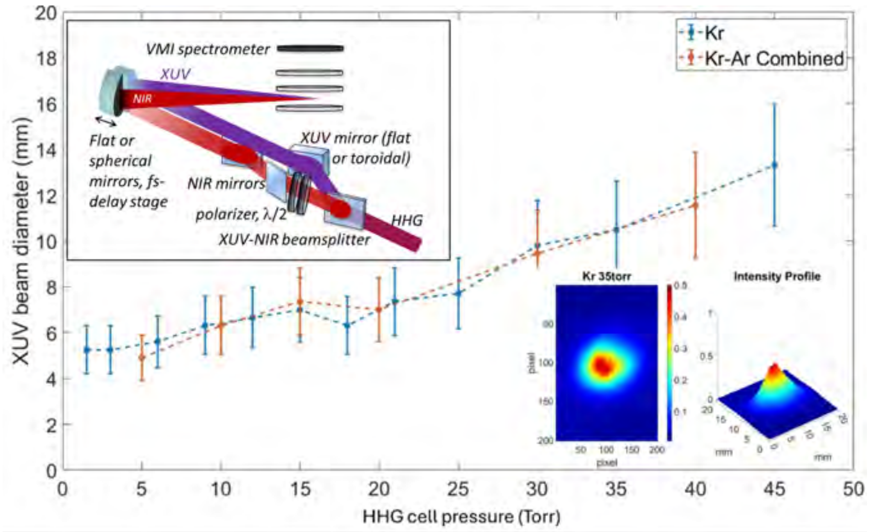

Fig. 2-5: Measured XUV beam diameter as a function of HHG gas and cell pressure (blue symbols: krypton; orange symbols: mixture of argon and krypton). The dashed lines connecting the symbols guide the eye for each series. Insets: schematic experimental setup (upper-left). Near-Gaussian XUV beam profiles measured at the entrance to the endstation, using krypton at 35 Torr (lower-right) as the HHG medium.

pressures around 9 torr. The pulse energies at this pressure are approximately 200 nJ at the source, i.e., around 10^{11} photons per pulse.

These new developments enable the control over the XUV source volume and the resultant spatial properties of the XUV pulse. We anticipate the XUV focal spot size can be varied by a factor of two, and the corresponding intensity can be adjusted by a factor of four, which we will verify with knife-edge scans at the XUV focus. Such control will be vital for optimizing the sensitivity in nonlinear excitation schemes that involve intermediate resonances in molecules in the ionization continuum, while minimizing unwanted background processes such as single-photon photoionization from pump- or probe-only events. Similarly, the Raleigh length, which defines the interaction volume, can be varied by controlling the XUV source volume. These capabilities are crucial for maintaining optimal overlap of two or more pulses, particularly in time-resolved measurements involving multiple XUV photon energies. This innovative and modular configuration enables the delivery of XUV intensities exceeding 100 GW/cm² within the interaction volume, which is crucial for X-UTPS. Using this high intensity, we will first establish XUV-XUV pump-probe schemes in VMI experiments that are sensitive to the beam parameters on a microscopic level at the XUV focus. For this purpose, the endstation is equipped with a 1 kHz pulsed gas jet source and a velocity map imaging (VMI) spectrometer, positioned 4.5 meters downstream from the HHG cell. The focused XUV pulses interact with the molecular beam at the center of the velocity map imaging (VMI) spectrometer, using a back-focusing geometry.

Future Plans: With the new controls to optimize the intensity of the XUV pulses at the focus, we are currently preparing VMI experiments to characterize specific high order harmonics, while directly probing electron-electron correlation effects in fundamental molecular systems. Electronic correlations are crucial in determining the strength of chemical bonds, the motion of electrons and holes, and the lifetimes of electronic states in ionization continua. In the context of ultrafast photochemistry, electron correlation effects are at the core of sub-femtosecond delays observed during photoionization processes. Our recent nonresonant one-color two-photon single photoionization (NOTPSI) studies, utilizing 9.3 eV XUV photons, highlighted the importance of electron-electron correlation in the contributions of autoionizing resonances in NOTPSI of N_2 [Larsen et al. **2020**, *Phys. Rev. A 102*, 063118]. Autoionizing resonances, being electronically quasibound states embedded in the ionization continuum, are expected to resonantly-enhance XUV FWM signals in future X-UTPS experiments, which will be crucial for our planned experiments to probe, for example, the valence and ionic bonding in excited electronic states of CF_3I.

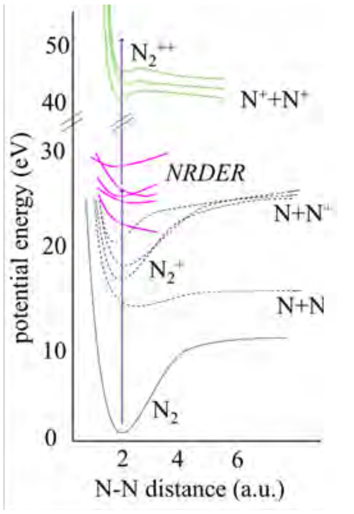

Fig. 2-6: Approximate potential energy diagram of the relevant electronic states of nitrogen, including the non-Rydberg doubly excited resonances (pink curves) in the ionization continuum. Adapted from Furst et al. **2012**, *Phys. Rev. A 86*, 041401(R).

To further explore the coupled electronic and nuclear dynamics that is driven by electron-electron correlations, we plan to set up a resonant two-photon double photoionization scheme at around 25 eV. The goal is to investigate the dissociation dynamics of optically allowed non-Rydberg doubly excited resonances (NRDER, indicated in pink in Fig. 2-6), leveraging the recent and ongoing work of the LBNL theory team (see Subtask 3). These NRDER states, which have ultrashort autoionization lifetimes of approximately 10 fs, exhibit compact orbital configurations involving two excited electrons. These configurations lead to highly correlated motion of at least two electrons, significantly enhancing the effects of electron-electron interactions within these resonances.

The two-color XUV-XUV femtosecond pump-probe scheme using VMI allows the effective energetic separation of photoelectrons produced by solely the pump or probe arms from the photoelectrons that were produced in the double-ionization via the transient NRDER intermediate electronic states. Furthermore, the laboratory-frame angular distributions that will be measured in the planned VMI experiments are expected to be highly sensitive to the symmetries of the NRDER states. Importantly, these experiments will equip us with the capability to realize two-color XUV photoabsorption schemes with our laser and beamline setup and enable us to investigate electron correlation effects of autoionizing states, while establishing the path for future X-UTPS experiments.

Reaction Pathways in Few-Molecule Complexes

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 of weakly-bound, highly-excited molecular complexes. We apply this technique 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 (KER) 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 on Water Dimers: In valence photo double ionization (vPDI) experiments on water dimers at the ALS, employing 60 eV photons for single-photon double ionization, we isolate and investigate the two anticipated reaction channels $D_2O^+ + D_2O^+$ and $D_3O^+ + OD^+$ for ICD dynamics and competing direct double ionization (knock-out) processes. We also find two new 3-body breakup channels, namely $D_2O^+ + D^+ + OD^*$ and $D_2O^+ + D^* + OD^+$, which are not discussed in the literature. The two latter channels likely originate from Proton Transfer Mediated Charge Separation (PTMCS) after single ionization via a Zundel-type intermediate (D_2O—D^+—OD^*). In collaboration with T. Orlando and J. Kretchmer from Georgia-Tech, water dimer cation geometries are identified with real-time (RT-)TDDFT methods to directly simulate the time-dependent dynamics of these competing electronic decay mechanisms in molecular clusters. From these results, KER distributions will be generated, for direct comparisons between the simulations and the experiment.

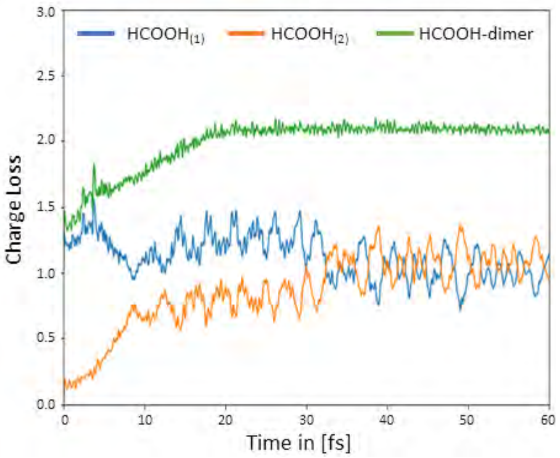

Fig. 2-7: Preliminary RT-TDDFT calculations of the dimer and monomer charge loss as a function of time.

Recent Progress on Formic Acid Dimers: We extended the investigations of ICD dynamics to organic hydrogen-bonding molecules, specifically formic acid dimers. Our DOE-SCGSR student J. Zhong is currently analyzing two competing formic acid dimer reaction channels, namely $HCOOH^+ + HCOOH^+$ and $HCOOH^+ + HCOO^+ + H$ that were recorded at the ALS using 56 eV single photons in a vPDI experiment, to find signatures of ICD in the spectra of electrons that were emitted in coincidence with two ions. He is also conducting RT-TDDFT calculations, in order to model the electron dynamics of the ICD process in real time (see Fig. 2-7). Preliminary results point to an ICD time for formic acid dimers of ~ 15 fs, which is slightly faster than the ICD dynamics of water dimers (on the order of 20 fs) extracted in a previous study. The faster decay time is likely due to the charge density of the double hydrogen bond in formic acid dimer compared to the single hydrogen bond in the water dimer. In order to improve the precision of the charge loss calculation displayed in Fig. 2-7, the next steps in this time dependent computation involve tuning the long-range separation variables to better describe the electron-electron interactions in the decay process of the dimer dication, optimizing the complex absorption potential components, and subsequently comparing the results for relevant geometries of the formic acid dimer.

Future Plans: Applying the developed simulations for water dimers, we will investigate the electron dynamics as a function of the position of the proton and as such determine the relative likelihood of the ICD process at different stages of the proton transfer. For the identified most probable ICD configuration, *ab initio* molecular dynamics calculations will be carried out to predict the final fragmentation structures and the yield of the possible reaction channels, which can then be compared with the experiment. In the next step, the vibration of the hydrogen atom within the dimer complex as an input for the electron dynamics calculation shall be explicitly included. This allows us to investigate how the equilibrium nuclear dynamics can influence the likelihood of ICD and competing electronic decay processes such as electron transfer mediated decay (ETMD).

In the next step we will extend the investigation of ICD dynamics to microsolvated biomolecules. We plan to measure fragmentation channels, branching ratios, as well as electron and ion momenta in water-pyrrole dimers using COLTRIMS and synchrotron X-rays. These experiments in the momentum domain target resonant Auger-Meitner-driven ICD (RA-ICD) processes, which we found to take place in $(N_2)_2$ and $(CO)_2$ dimers [F. Trinter et al. **2014**, *Nature 505*, 664]. We recently performed related measurements with X-rays tuned to excite or ionize the O(1s) orbital in water dimers at the PETRA-III synchrotron in July of 2024, in order to find out how this resonantly enhanced RA-ICD reaction pathway competes with ETMD and PTMCS in dimers with hydrogen bonds. We will complement these investigations with experiments on the microsolvated water-pyrrole system in a recently awarded beamtime at MAX-IV. This project in the momentum domain will be carried out in collaboration with T. Orlando (Georgia-Tech) in November, 2024 and bring us one step closer to the planned X-ray FEL based experiments that will aim to resolve the corresponding dynamics in real-time, using the DREAM endstation at LCLS-II.

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 Ultrafast Photoionization Experiments *(Lucchese, McCurdy, Rescigno)*

To reliably describe ultrafast pump and ionizing probe experiments it is necessary to treat simultaneously the nuclear motion and the correlated electron dynamics of photoionization. The combined treatment of nuclear and electron dynamics can be accomplished if all the bound-bound and bound-continuum transition amplitudes between relevant states of the molecule 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 [Bello et al. **2021**, *Phys. Rev. Res. 3*, 013228, Bello et al. **2023**, *Phys. Rev. A 108*, 033104] that can treat the electron dynamics and one vibrational degree of freedom, and we are extending this approach to include autoionizing (resonant) states and multiple vibrational dimensions.

Recent Progress: 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 reflect that motion. Our first time-dependent calculation, which included two intermediate states of O_2 excited by the absorption of one photon (*B* and *E* states in Fig. 3-1) and four lowest cation states accessed by the second photon, revealed that our previous interpretation of this process was not fully valid. The nuclear motion on the dissociative intermediate state *B* contributes to the 3-5-eV region of the photoelectron spectrum as predicted but the calculated signal is considerably weaker than in the experiment. Furthermore, this calculation that assumes a smooth ionization continuum does not reproduce the prominent peak at the threshold observed in the photoelectron spectrum. We performed extensive scattering calculations using the Schwinger variational method to obtain a more realistic structure of the ionization continuum, see Fig. 3-1. In our preliminary calculations, two autoionizing Rydberg states (broad curves in Fig. 3-1) significantly affect the dynamics and their inclusion reproduces the experiment.

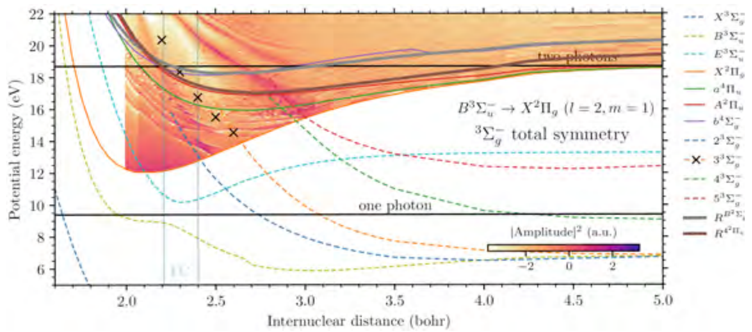

Fig. 3-1: Potential energy curves of O_2 (dashed and broad solid) and O_2^+ (solid). The colormap represents a photoionization amplitude that captures the structure of the electron continuum full of autoionizing Rydberg and doubly-excited states.

Future Plans: In collaboration with Graham Worth (University College London), we employed the Multiconfiguration Time-Dependent Hartree method [Worth **2020**, *Comput. Phys. Commun. 248*, 107040] in the O_2 calculation for the nuclear wave packet propagation, where the continuum energy states can be very effectively treated on a similar footing as the nuclear degrees of freedom. This approach is designed to include multiple nuclear degrees of freedom. In the next step, we plan to study a pump and ionizing probe problem in water or other triatomic molecule in full vibrational dimensionality.

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

Single-photon double ionization of molecules is driven by electron correlation and is particularly sensitive to correlation in the initial state of the neutral molecule. We have studied this problem extensively to develop methods to predict and analyze the data obtained in Subtask 1.

Recent Progress: We have submitted an article "An Orbital Basis Set for Double Photoionization of Atoms and Molecules" to *Journal of Chemical Theory and Computation* together with our collaborator and former postdoc R. Bello (Autonomous University of Madrid) that describes a new method, optimized for time-dependent double photoionization calculations, based on numerical orbitals. In collaboration with F. Yip (Cal State Maritime, LBNL VFP) we have manuscripts in preparation on finished work on (1) a method for extracting polyatomic double photoionization amplitudes that does not require electron-ion scattering wave functions and (2) numerically exact two electron integrals using the infinite range Laguerre Discrete Variable Representation (DVR) that prevents reflections from the end of the grid in time-dependent calculations of ionization.

Future Plans: We will apply both the new numerical orbital and DVR approaches to one photon double ionization of H_2O in the channels in which two electrons are ionized from a single orbital in collaboration with R. Bello and F. Yip. Also, in collaboration with F. Yip, we are finishing an analysis of the effect of initial state correlation in double photoionization of LiH.

Double Photoionization of D_2O by One Photon *(Lucchese, McCurdy, Rescigno)*

Experimental studies on double ionization of molecular systems by single photon absorption necessarily involve the breakup of the doubly ionized molecules. In the case of heavy water at photon energies below 60 eV, a substantial fraction goes into three-body breakup producing $O + D^+ + D^+$. A small but measurable fraction of the breakup goes into the rare $O^+ + D + D^+$ channel, which has been the subject of an ALS experiment led by Th. Weber (see Subtask 1). The analysis of this experiment has been the subject of three published papers, the most recent of which [Iskandar et al. **2024**, *J. Chem. Phys. 161*, 044311] focused on events with high KER_{OD} (> 0.25 eV).

Recent Progress: Absorption of a single photon at 61 eV populates six electronically excited dication states - 1^1A_1, 1^1B_1, 1^3A_2, 1^3B_2, 2^1A_1 and 1^1A_2. We have been able to determine which of these dissociate into the rare $D^+ + O^+ + D$ fragmentation channel. The various pathways involve symmetric stretch as well as both small and large asymmetric stretch via spin-orbit transitions at ~5, ~5.5 and ~7 bohr, respectively. A fast sequential dissociation process via the 1^3A_2 or

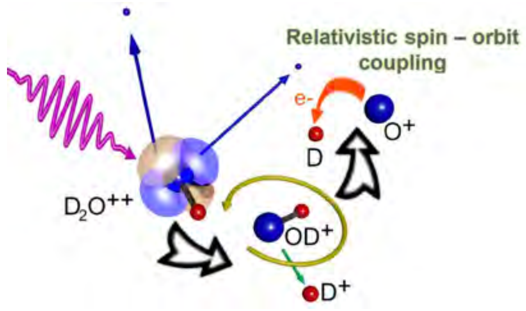

Fig. 3-2: Fast asymmetric dissociation of D_2O^+. Sequential dissociation of 1^3A_2 or 1^3B_2 produces $D^+ + OD^+$ ($A^3\Pi$). A spin-orbit transition can populate the $X^3\Sigma^-$ state of OD^+. Non-adiabatic coupling between the quasi-degenerate A, X and B ($^3\Sigma^-$) OD^+ states at large separations can produce either $D^+ + O + D^+$ or the rare $D^+ + O^+ + D$ fragmentation channels.

1^3B_2 dication states dominates the reaction dynamics. This process is sequential, see Fig. 3-2, involving first a fast dication separation to $D^+ + OD^+(A^3\Pi)$. An atomic spin-orbit transition on O can then populate the ground $X^3\Sigma^-$ state of OD^+ which is energetically close to $A^3\Pi$ at O-D separations beyond ~7 Bohr. At these distances, the X, A and $B^3\Sigma^-$ OD^+ states are all close and non-adiabatic coupling between the X and B states can induce a charge-exchange between X and B resulting in $D^+ + O^+ + D$.

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, $\tau = \hbar \frac{\partial}{\partial E} \arg \left\langle \Psi_k^{(-)} \middle| \sum_i \epsilon \cdot r_i \middle| \Phi_0 \right\rangle$, seek to measure the energy derivative of the phase of the photoionization amplitude. In photodetachment of electrons from atomic and molecular anions the Coulomb phase does not obscure the low energy signatures of resonances or the signatures of the interaction of the emitted electron with the neutral atom or molecule. We are pursuing new physics in both cases as a major focus of our program, as well as exploring the question of how photodetachment delays can be measured within an eV of threshold, where we predict *femtosecond* delays from resonances and threshold scattering laws.

Recent Progress: Our article "Attosecond Time Delays in the Body Frame for Molecular Photodetachment" [Rescigno et al. **2024**, *Physical Review A 110*, 013122] revealed low energy delays of several femtoseconds for core photodetachment and proposed their measurement in the body frame. The article "Attosecond Delays in X-ray Molecular Ionization," with the group of J. Cryan (SLAC) appeared [Driver et al. **2024**, *Nature 632*, 762] describing $O(1s)^{-1}$ time delays in photoionization using angular streaking and found that both a shape resonance and autoionizing resonances were important in describing the measured time delays. In a collaboration with H.-J. Wörner (ETH Zurich), "Attosecond X-ray Core-level Chronoscopy of Aromatic Molecules" has been submitted and compares our Schwinger and Complex-Kohn calculations for $N(1s)^{-1}$ ionization in three azabenzenes with LCLS experiments.

Future Plans: We are continuing our photodetachment studies, turning now to valence photodetachment of the ozone and C_2^- anions. The ozone calculations in collaboration with C. Trevisan (Cal State Maritime, LBNL BLUFF) are exploring the effects of the permanent dipole. The C_2^- calculations will explore the threshold region where the high polarizability of the molecule suggests very large delays will be observed. We have shown formally, using effective range theory, that if *p*-wave scattering dominates an atomic photodetachment, as in the case of the Li^- atom, the threshold value of the delay is finite and is determined exclusively by the static polarizability of the atom. In that case the threshold value is ~1.7 femtoseconds, and near threshold delays are at least a femtosecond. Using established codes for time-dependent *R*-matrix theory we will explore how kinetic energy streaking with IR pulses might measure these large delays in atoms and molecules.

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. We have developed basis set and grid-based methods for the computation of electron-molecule scattering which can yield the needed one-photon amplitudes for photoemission studies. The grid-based methods are not limited to low kinetic energies and can thus study processes such as resonant Auger ionization. As part of our suite of grid-based electron molecule scattering codes we are developing ePolyGrid, which is a new code based on overset grids designed for larger molecules with multichannel capabilities [Greenman et al. **2017**, *Phys. Rev. A 96*, 052706].

Recent Progress: In ePolyGrid, the numerical grids contain 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 non-overlapping sub-grids. We have implemented a new method for partitioning functions which have cusps at nuclear centers that are not at the origin of the central grid. In this method, a function is partitioned into a part on the central grid and a part on the atom-centered sub-grids. In the region of a sub-grid, the part on the central grid will is replaced by a smooth low-order polynomial, known as the "Patch", which can be easily expanded about the origin of the central grid. The remaining part of the function, that is localized on the sub-grids, can easily represent the cusp behavior of the wave functions at the center of each sub-grid. In Fig. 3-3 we show the convergence of the Patch method compared to the original overset grid method, referred to as the "Switch" method, with respect to the number of partial waves needed on the central grid.

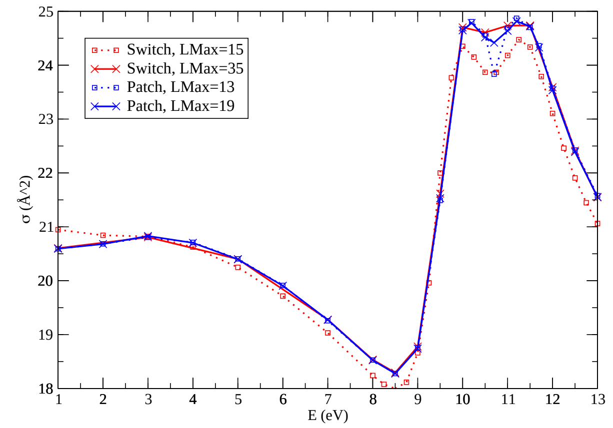

Fig. 3-3: Convergence of the total cross section for *e*-CF_4 scattering with respect to the maximum partial wave (LMax) in the expansion of the central grid.

Future Plans: We will explore methods to accelerate the convergence of the iterative method used to compute the transition matrix elements 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.

Generalization of One-Center Non-Orthogonal Configuration Interaction Singles to Open Shell Singlet Reference States (*Head-Gordon*)

Recent Progress: The Head-Gordon group has reported [Arias-Martinez, Wu, and Head-Gordon, **2024**, *J. Chem. Theory Comput. 20*, 752] a new one-center nonorthogonal configuration interaction singles (1C-NOCIS) theory for the computation of core excited states of an initial singlet state with two unpaired electrons. Fig. 3-4 shows a schematic of the resulting states, with up to 4 singly occupied orbitals. This 1C-NOCIS two-electron open-shell (2eOS) model is appropriate for computing the K-

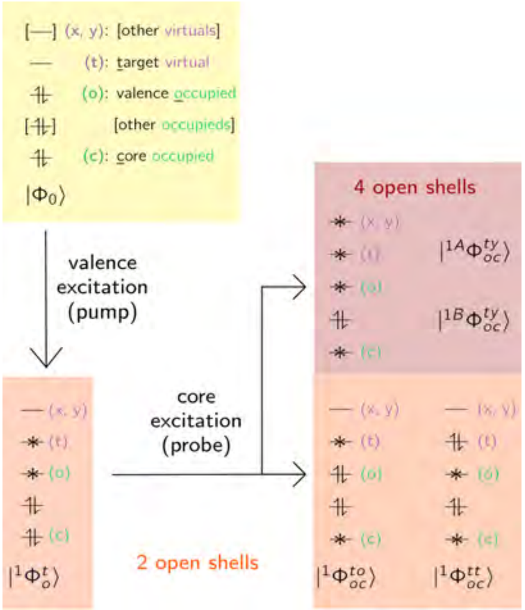

Fig. 3-4: An illustration of the passage from a closed shell ground state (top left) to a one-photon valence excited state with 2 half-occupied orbitals (bottom left) to its core excited states with up to 4 half-occupied orbitals (right). All such configurations are superposed to form the 1C-NOCIS 2eOS states.

edge near-edge X-ray absorption spectra (NEXAS) of the valence excited states of closed-shell molecules relevant to pump-probe time-resolved (TR) NEXAS experiments, such as those being performed in the AMOS program. With the inclusion of core-hole relaxation effects and explicit spin adaptation, 1C-NOCIS 2eOS only requires small shifts to match experiment, is free of artifacts due to spin contamination, and can capture the high-energy region of the spectrum beyond the transitions into the singly occupied molecular orbitals (SOMOs). Calculations on water and thymine illustrate the different key features of excited-state NEXAS, namely, the core-to-SOMO transitions as well as shifts and spin-splittings in the transitions analogous to those of the ground state. Simulations of the TR-NEXAS of acetylacetone after excitation to its π →π* singlet excited state at the carbon K-edge, an experiment carried out recently, showcase the ability of 1C-NOCIS 2eOS to efficiently simulate NEXAS based on nonadiabatic molecular dynamics simulations

Future Plans: While already very useful for small molecules, the present implementation of 1C-NOCIS 2eOS is not scalable to larger molecules due to the high cost of non-orthogonal matrix element evaluation. We are exploring new ideas that promise to dramatically improve its efficiency for large systems by developing new generalizations of the Slater-Condon rules for non-orthogonal determinants that treat the full set of singles that share common orbitals all at once rather than one at a time, as in the present NOCIS code. If successful, this will also greatly accelerate our NOCIS code for evaluating core excitation energies of molecules in their ground states. We are also very interested in the extension of NOCIS and our related orbital optimized DFT (OO-DFT) methods to L edges, and have started to develop the appropriate theory and software implementation.

Femtosecond Core-Level Spectroscopy Reveals Involvement of Triplet States in the Gas-Phase Photodissociation of Iron Pentacarbonyl (*Head-Gordon*)

Recent Progress: Building on the advances represented by NOCIS and its 1C-NOCIS 2eOS extension, and electron affinity TDDFT (EA-TDDFT), the Head-Gordon group collaborated with Ramasesha's experimental group at Sandia to report [Troß, Arias-Martinez, Carter-Fenk, Cole-Filipiak, Schrader, McCaslin, Head-Gordon, and Ramasesha **2024**, *J. Am. Chem. Soc. 146*, 22711] new insights into the dynamics that follow 266 nm photo-excitation of iron pentacarbonyl [$Fe(CO)_5$], a prototypical photocatalyst. It is already well-known that 266 nm photoexcitation causes the sequential loss of two CO ligands in the gas phase, creating catalytically active, unsaturated iron carbonyls. Despite numerous studies, major aspects of its ultrafast photochemistry remain unresolved because the early excited-state dynamics have so far eluded spectroscopic observation. This has led to the long-held assumption that ultrafast dissociation of gas-phase $Fe(CO)_5$ proceeds exclusively on the singlet manifold. Our combined experimental-theoretical study employs ultrafast extreme ultraviolet transient absorption spectroscopy near the Fe $M_{2,3}$-edge, which features spectral evolution on 100 fs and 3 ps time scales, alongside high-level electronic structure theory, which enables characterization of the molecular geometries and electronic states involved in the ultrafast photodissociation of $Fe(CO)_5$. As schematically illustrated in Fig. 3-5, we assign the 100 fs evolution to spectroscopic signatures associated with intertwined

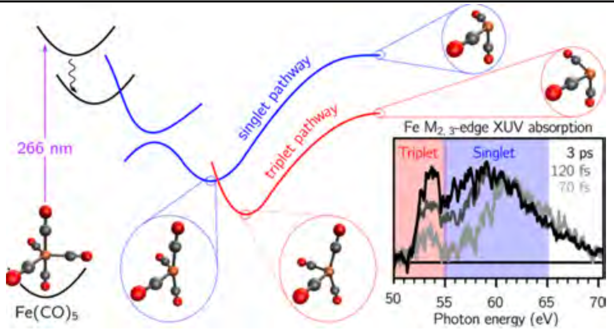

Fig. 3-5: A schematic diagram illustrating the photophysics inferred from simulations and time-resolved XAS experiments for successive loss of 2 carbon monoxide molecules from iron pentacarbonyl after 266 nm excitation, including involvement of triplet states.

structural and electronic dynamics on the singlet metal-centered states during the first CO loss and the 3 ps evolution to the competing dissociation of $Fe(CO)_4$ along the lowest singlet and triplet surfaces to form $Fe(CO)_3$. Calculations of transient spectra in both singlet and triplet states as well as spin−orbit coupling constants along key structural pathways provide evidence for intersystem crossing to the triplet ground state of $Fe(CO)_4$. Thus, our work presents the first spectroscopic detection of transient excited states during ultrafast photodissociation of gas-phase $Fe(CO)_5$ and challenges the long- standing assumption that triplet states do not play a role in the ultrafast dynamics.

Future Plans: The computational methods developed by the Head-Gordon group in the AMOS program for evaluating core-excited states, specifically the NOCIS family of methods, orbital-optimized density functional theory (OO-DFT) and electron-affinity time-dependent DFT (EA-TDDFT) represent a significant step forwards over standard TDDFT methods. We plan to engage in further collaborations that help to better establish the value of these approaches for modeling static and time-resolved X-ray absorption experiments, as well as help to interpret such experiments. In addition, most of these tools are already integrated into the widely used Q-Chem software package, and so can be directly used by other computational modelers and experimental groups as well.

Elucidating the Earliest Electron Dynamics Underlying Interfacial Charge Transfer Processes *(Qian)*

Plasmonic metal nanoparticles (MeNPs), such as AuNPs, can create hot electron–hole pairs upon light absorption that drive chemical reactions [Mukherjee et al. **2013**, *Nano Lett. 13*, 240; Seemala et al. **2019**, *ACS Energy Lett. 4*, 1803]. When the MeNPs are brought into contact with a semiconductor (SC) such as TiO_2, hot electrons can be injected into the SCs by surmounting the metal–SC energy barriers [Neppl et al. **2021**, *J. Phys. Chem. Lett. 12*, 11951]. and propel the downstream photocatalytic water splitting reaction [Linic et al. **2011**, *Nat. Mater. 10*, 911; Kumar al. **2021**, *Trends Chem. 3*, 902]. Understanding the timescales for charge injection is crucial for improving photocatalytic efficiencies [Berdakin et al. **2022**, *Nanoscale 14*, 2816].

We employ a suite of computational tools, such as density of state (DOS), work function (WF), and molecular dynamics (MD), to clarify the details of electron dynamics underlying the ultrafast interfacial charge transfer processes. For validation and comparison with the time-resolved X-ray photoemission spectroscopy (TRXPS) and time-resolved ambient pressure X-ray photoemission spectroscopy (TRAPXPS) experiments described in Subtask 2, we are developing real-space KS-DFT based XPS modules [Xu et al. **2022**, *J. Chem. Theory Comput. 18*, 5471; Liu et al. **2024**, *J. Chem. Theory Comput. 20*, 6134]. These developments, funded by a separate yet synergistic Early Career program (see separate Early Career abstract), will enable *ab initio* prediction of the spectroscopic signatures.

Recent Progress: We are preparing a manuscript reporting the DOS and WF alignment of the AuNP-TiO_2 heterogeneous interface. Using plane-wave KS-DFT as implemented in VASP [Kresse et al. **1993**, *Phys. Rev. B 47*, 558], we report the respective DOS and WF of the individual components - TiO_2 surface, AuNPs, as well as the combined AuNP-TiO_2 system. The WF of TiO_2 has reports of widely different values, varying between 3.5-7.5 eV both theoretically [5.1 eV in Wang et al. **2013**, *J. Am. Chem. Soc. 29*, 10673; 7.5 eV in German et al. **2018**, *Appl. Surf. Sci.*, *428*, 118]; and experimentally [5.0eV in Gautam et al. **2016**, *Phys. Chem. Chem. Phys. 18*, 3618; 4.4 eV in Mansfeldova et al. **2021**, *J. Phys. Chem. C 125*, 1902; 3.5 eV-6.5 eV in Kashiwaya et al. **2018**, *Surfaces 1*, 73]. Meanwhile, reports of the Au bulk WF are consistent between 5.2-5.4 eV

[Brocks et al. **2006**, *J. Phys. Chem. B 45*, 22628]. AuNPs ≤18 nm in diameter exhibit a lower WF (<4eV) and show a size dependence, while allowing for variation in the WF up to 0.2eV for a given particle size [Zhang et al. **2015**, *Nano Lett. 15*, 51]. Mindful of the large variations in the literature values for the TiO_2 WF, we concluded that great care should be taken in modeling the anatase TiO_2 (101) surface. A 1 meV/atom convergence has been achieved using a model size of 5-layer thickness, 2×4 surface area (21.0 Å × 15.3 Å), and 30Å vacuum. A Hubber U value of 6.9 eV has been added to the Ti 3d states to model a realistic band gap, which led to the p-type DOS result shown in Fig. 3-6 a. Upon adding Au_{19} NP to the TiO_2 surface, the system was changed to n-type, where the Fermi energy is near the TiO_2 conduction band. Interestingly, the valence band maximum (VBM) is localized in the Au cluster as a metal plasmon-like state. In contrast, the conduction band minimum (CBM) is localized in the TiO_2 slab as an acceptor state in charge injection. The lowest lying delocalized charge state is 0.1 eV above the CBM, and we show that this delocalized electron state is between the Au_{19} cluster and TiO_2 surface (Fig. 3-6 b-c). This state supports the instantaneous charge injection picture [Long et al. **2014**, *J. Am. Chem. Soc. 136*, 4343], where the charge can be directly injected into TiO_2 due to the density overlap between the AuNP and TiO_2 surface.

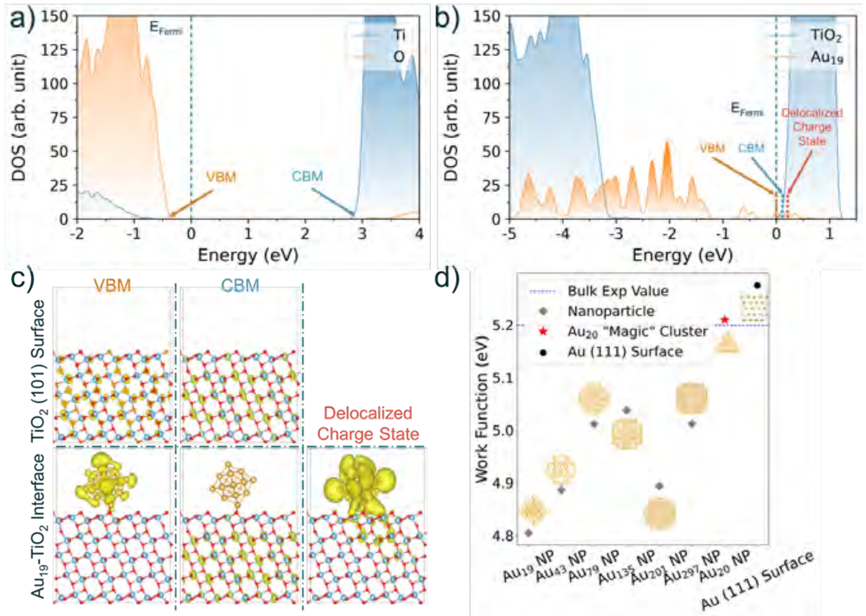

Fig. 3-6: a) Density of states (DOS) of a pristine 2x4x5 TiO_2 (101) surface. The Fermi energy EFermi is set to zero. b) DOS of a Au_{19}-TiO_2 heterojunction. c) The band-decomposed charge densities of the band edge states (VBM & CBM) at the gamma points for isolated TiO_2 surface (top) and a Au19-TiO_2 heterojunction (bottom). The lowest energetic laying delocalized charge state (0.1 eV above CBM) between AuNP and top TiO_2 layers is shown to the right. d) Work Function of AuNPs and Au (111) surface. The bulk experimental 5.2 eV value is shown as a blue dashed line.

We further investigated the AuNP size and shape dependence of the WF (Fig. 3-6 d). The AuNPs were placed within a 25Å vacuum box to avoid periodic images. The WF increases in value with an increase in size up to 135 Au atoms, after which the value decreases and equilibrates to a similar value between 79 and 297 Au atoms. We are currently investigating the kink in the WF of Au_{201} NP. One aspect to consider is the precision of our computational methods. The AuNPs are Wulff constructions resulting in an equilibrium shape that preserves surface symmetry and minimizes surface Gibbs free energy. In comparison, the WF of the Au_{20} "magic" cluster is better aligned to the experimental bulk value of 5.2 eV. This tetrahedral Au_{20} cluster is special due to its high symmetry (T_d), stability, and closed shell nature allowing for better reproduction of bulk properties [Remacle et al. **2007**, *Int. J. Quantum Chem. 14*, 2922]. The Au(111) surface with 5-layer thickness, 2×2 surface area (11.8 Å × 10.2 Å), and 30Å vacuum results in a larger WF than the experimental value. These results highlight the need to adequately address the models used in constructing the Au-TiO_2 heterojunction and resolve the WF discrepancies in the literature due to varying TiO_2 modeling differences such as surface area/thickness and Au size/shape.

Future Work: The current results will set the stage for our future charge injection study. The deep investigation into proper TiO_2 and Au models will allow us to describe the heterojunction interactions more reliably. Our models can now be used within the molecular dynamics framework to investigate and track the dynamic nature of specific states, such as the case when the electrons are localized on the Au (excited metal plasmon state; classic charge injection donor state), localized on the semiconductor (classic charge injection acceptor state), or the delocalized overlap state (plasmon overlap state; instantiations charge injection state) [Long et al. **2014**, *J. Am. Chem. Soc. 136*, 4343; Lewis et al. **2016**, *J. Phys. Chem. Lett. 8*, 1563]. Building on these models, we will also incorporate solvation molecules, such as water, to understand the origins of longer carrier lifetimes seen in a solvated Au-TiO_2 heterojunction. This part of the proposed work is inspired by the most recent TRAPXPS results on H_2O exposed interfaces, described in Subtask 2**.**

Peer-Reviewed Publications Resulting from this Project (2022-2024)

Blue font is used for the authors who are PIs of this FWP, green font is used for students and postdocs supported by the FWP, and red font is used for authors who are PIs of other BES-FWPs at LBNL.

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.

2022

Arias-Martinez, J. E.; Cunha, L. A.; Oosterbaan, K. J.; Lee, J.; Head-Gordon, M., Accurate Core Excitation and Ionization Energies from a State-Specific Coupled-Cluster Singles and Doubles Approach. *Phys. Chem. Chem. Phys.* **2022**, *24* (35), 20728–20741. DOI 10.1039/d2cp01998a

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B. Other publications based on research receiving support from this FWP.

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2023

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

Jin Qian

Chemical Sciences Division, Lawrence Berkeley National Laboratory

1 Cyclotron Road, Berkeley, CA, 94720

jqian2@lbl.gov

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.

In this project, we 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 investigate the electronic structure details of picosecond to nanosecond timescale charge recombination processes at plasmonic nanoparticle (NP) /semiconductor interface. We 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. We also continue our development of a real-space X-ray Photoelectron Spectroscopic (XPS) module so that our computational findings can be validated by ultrafast X-ray spectroscopy experiments.

Recent Progress Building upon our previous success with the 2nd row elements (Xu et al., **2022**, *J. Chem. Theory. Comput.*, 18, 5471) and moving down the periodic table, we have recently enabled real-space KS-DFT XPS prediction capabilities beyond 1s core excitation (Liu et al., **2024**, *J. Chem. Theory. Comput.*, 20, 6134). We report the results for 1s, 2s, and 2p excitation for 3rd row elements Si, P, and S with 0.2 eV accuracy in PP-PBE(B3LYP) level functional, comparing to the experiments (Jolly et al., *At. Data Nucl. Data Tables* **1984**, 31, 433) and high accuracy all electron (AE) results from Martin Head-Gordon (LBNL). The present PP-PBE, PP-PBE(B3LYP) results are plotted against the AE-PBE, AE-SCAN, and experimental data in **Figure 1**.

In this paper we further discussed the implications of periodic boundary condition (PBC) on the challenge of converging the core-excited final states. Two strategies have been proposed for addressing the periodic electrostatic interactions problem due to the presence of the excited core-hole, and both strategies have been exhaustively examined. The first strategy was to subtract an energy correction term (E_{corr}) using the Makov-Payne equation $E_{corr} = \frac{q^2\alpha}{2\epsilon L}$ (*Phys. Rev. B Condens. Matter* **1995**, 51, 4014), where q is the charge of the core-hole and equal to one electron, α is the Madelung constant, ϵ is the dielectric constant of the material, and L is the cell size. The second strategy was to carefully leverage error cancellation and calculate the relative binding energy shift (ΔE_b) within identical supercells by canceling out the Coulomb interactions. We showed that both strategies led to the same, satisfactory results when setting the supercell to a large 25 Å size, but practically speaking, the second strategy is more convenient to adopt.

To illustrate the advantage of the present real-space KS-DFT PP development in simulating large-scale, periodic systems, we turn to ZSM-5 zeolite series which are widely used as catalysts or supports of catalysts for various industrial processes (Hossain et al., *Chem. Eng. J.* **2023**, 475, 146096). The present development enables us to differentiate the key spectroscopic features of Al/Si ratios and the densities of Brønsted acid sites (the protons on the O linking to the framework Al^{3+}).

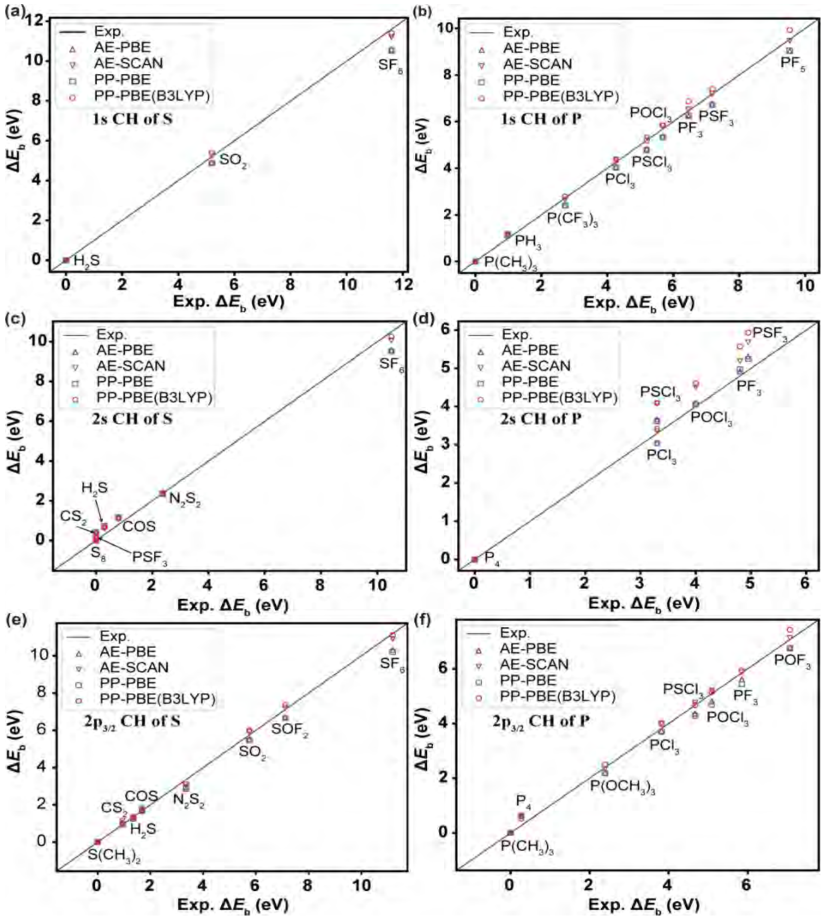

Fig 1. *Binding energy shifts (ΔE_b) of 1s (a, b), 2s (c, d), and 2p3/2 (e, f) core excitations of molecules for S and P elements with respect to the molecules with the lowest E_b in each category: H_2S and $P(CH_3)_3$, S_8 and P_4, $S(CH_3)_2$ and $P(CH_3)_3$, respectively. (Liu et al., **2024**, J. Chem. Theory. Comput., 20, 6134)*

As a separate effort, we have initiated the study of ultrafast charge recombination by coupling constrained DFT (cDFT, Kaduk et al., **2012**, *Chem. Rev.*, 112, 321) with Marcus Theory (Marcus et al., **1964**, *Annu. Rev. Phys. Chem.*, 15, 155) using a small, pilot system of Au_4/TiO_2. This study has been used to support the submission of a DOE SCGSR fellowship application.

Future Plans We will finalize the best cDFT computational setup by deciding on how much charge (likely 0.1 e) is necessary to transfer for accurate charge recombination timescales with our models and comparing cDFT energetics and timescales at different levels of theory (PBE, PBE+U, PBE+U+D3, and PBE+U+D4). To compare with the experiments, our eventual goal will be to build new capabilities for quantitatively predicting the core ionization energies for Au_{4f}, Ti_{2p} by gradually moving down the periodic table. The current cDFT limit is within hundreds of atoms, we will develop real-space KS-cDFT capability to allow for large-scale interfacial charge transfer predictions. We will 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.

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

Liu, L., Cunha, L., Xu, Q., Xin, H., Head-Gordon, M., Qian, J.*, Real-Space Pseudopotential Method for the Calculation of Third-Row Elements X-ray Photoelectron Spectroscopic (XPS) Signatures, **2024**, *J. Chem. Theory. Comput.*, 20, 6134.

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 as well as the Ultrafast Electron Diffraction facility. 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 frontier themes has been reinforced in a several BES workshops and reports. Most recently LCLS released its *Strategic Plan 2023-2028,* which lists "Coupled Dynamics of Energy and Charge in Atoms and Molecules" as one of its primary science priorities.[2] Our PIs have worked directly to develop LCLS-II science opportunities, for example in a "*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.[3] We all contributed as

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

[2] https://lcls.slac.stanford.edu/sites/default/files/2023-12/LCLS%20Strategic%20Plan%202023-2028.pdf

[3] https://conferences.slac.stanford.edu/2020-archives/non-linear-multidimensional-methodologies-studying-chemical-sciences

well to the highly influential 2015 report, New Science Opportunities Enabled by LCLS-II X-ray Lasers.[4] 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*), [5] and also the BESAC 2015 report, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science,*[6] especially the section on *Imaging Matter across Scales*, and *Harnessing Coherence in Light and Matter.* The tasks are also in line with the 2004 report *Directing Matter and Energy: Five Challenges for Science and the Imagination* (a.k.a. *Grand Challenges Report*)[7] 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 and strong-field 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 surface chemistry;
Research Scientist Dr. Thomas Wolf, physical chemistry;
Research Scientist Dr. Adi Natan, AMO physics;
Research Scientist Dr. Amy Cordones-Hahn, chemistry;
Research Scientist Dr. James Cryan, AMO and attosecond 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.

Subtasks: UCS is organized into five tasks. Each has a leader (in bold below). These tasks are

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: Ultrafast Dynamics on Nanoscale Surfaces (Kling)

***Program highlights:* Here are a few recent examples of research progress:**

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[4] https://lcls.slac.stanford.edu/sites/default/files/2023-10/LCLS-IIScienceOpportunities_final.pdf
[5] https://science.energy.gov/~/media/bes/pdf/reports/2018/Ultrafast_x-ray_science_rpt.pdf
[6] https://science.energy.gov/bes/efrc/research/transformative-opportunities
[7] https://science.energy.gov/~/media/bes/pdf/reports/files/Directing_Matter_and_Energy_rpt.pdf

Femtosecond Electronic and Hydrogen Structural Dynamics in Ammonia Imaged with Ultrafast Electron Diffraction: We imaged the hydrogen motion in a photoexcited ammonia molecule, using UED. We observed scattering signatures of the nuclear motion, and also corresponding electronic structure changes resulting from the dissociation dynamics in the time-dependent diffraction. Ab initio simulations of the photochemical dynamics and the resulting diffraction observable confirmed our measurements. The temporal resolution of the UED experiment is insufficient to resolve the dissociation in time, but this is step towards real space and time observations of proton dynamics. [E. G. Champenois et al., Phys. Rev. Lett. 131, 143001 (2023).]

Observation of a Picosecond Light-Induced Spin Transition in Polymeric Nanorods: Spin transitions are candidate for future photoswitchable devices, but their slow material transformations limit device applications. Size reduction could enable faster switching, but the photoinduced dynamics at the nanoscale remains poorly understood. We carried out a femtosecond optical pump x-ray probe study of spin transitions in polymeric nanorods, using both x-ray emission to track the spin transition order parameter, and x-ray diffraction to track the nanorod structure. With sufficient photodoping the spin transition can occur in about 50 ps, or 2 orders of magnitude faster than previously reported for ST compounds, which could promote developments toward spin transition material-based GHz rate photoswitching devices. [M. Reinhard et al., ACS Nano 18, 15468 (2024).]

Floquet engineering of strongly driven excitons in monolayer tungsten disulfide Strong laser fields were used for the Floquet engineering of excitons in tungsten disulfide, and achieved strong-field light dressing of excitons in excess of a hundred millielectronvolts. Transient absorption spectroscopy revealed the formation of a light-dressed sideband from the dark 2p-exciton state. When combined with simulations, the data analysis reveals real-space movies of the exciton dynamics in the strong-field regime, showing the prospect for ultrafast, strong-field device applications of two-dimensional materials. [Y. Kobayashi et al. Nat. Phys. **19**, 171 (2023).]

Awards Prizes, and other Honors this year*:*

Tony Heinz received the Ahmed Zewail Award for Ultrafast Chemistry from the American Chemical Society.

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 assist 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 2024 UXSS was held at SLAC, chaired by UCS PI Shambhu Ghimire.

Attosecond and Femtosecond Atomic and Molecular Physics (AFAM)

Philip H. Bucksbaum, James Cryan
Stanford PULSE Institute, SLAC National Accelerator Laboratory
2575 Sand Hill Rd. Menlo Park, CA 94025
phb@slac.stanford.edu, jcryan@slac.stanford.edu
Participants: *Phil Bucksbaum (PI), James Cryan (co-PI), Taran Driver, Jun Wang, Nick Werby, Emily Thierstein, Ian Gabalski, Erik Isele, David Reis, Todd Martinez, Thomas Wolf*

Project Scope*:* We study the motion of electrons and atoms in molecular systems 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 in 2024:

Attosecond XFEL development [1, 2]*:* together with the group of Agostino Marinelli we continue to develop and characterize attosecond operational modes of the LCLS. We have recently demonstrated a split-undulator scheme that can be used to create two-color attosecond pulse pairs [1]. Using the angular streaking technique, we have characterized the delay between the two pulses. We have further confirmed the application of this technique to a pump–probe measurement in a core-ionized molecular system. We have also demonstrated the generation of terawatt scale isolated attosecond pulses with a two-stage cascaded X-ray free-electron laser [2]. The temporal profile of the pulses was again characterized by angular streaking measurement. This peak power is approximately one order of magnitude higher than previous results. These developments should help to drive nonlinear x-ray matter interactions to better understand ultrafast charge motion.

Photoemission delay for core-level orbitals [3]*:* When x-rays of sufficient photon energy interact with matter, the most probable outcome is the removal of a *K*-shell electron. Measuring the apparent delay between in the photoemission between different *K*-shell orbitals provides a fundamental insight into x-ray matter/interactions. We have observed an unexpectedly large delay, ranging up to 700 attoseconds in NO near the oxygen *K*-shell threshold. Because these measurements were made with an XFEL, we were able to scan the x-ray energy across the entire region near the oxygen *K*-shell threshold to observe the dispersion in photoionization delays in this region. We find the delay spectrum is highly modulated, suggesting several contributions to the delays, including transient trapping of the photoelectron due to shape resonances; collisions with the Auger-Meitner electron that is emitted in the rapid non-radiative relaxation of the molecule; and multi-electron scattering (i.e. multi-configuration) effects. The results demonstrate how x-ray attosecond experiments, supported by comprehensive theoretical modeling, can unravel the complex correlated dynamics of core-level photoionization.

Probing Coherence in Core-Ionized Systems**:** We have used the angular streaking technique to study coherent electronic motion in core-ionized CH_2CF_2 molecules, observing a modulation of the Auger-Meitner (AM) emission with a 0.9 femtosecond period. This modulation reflects partial coherence in the core-excited ion and underscores the sensitivity of attosecond angular streaking to sub-femtosecond electronic motion. This experiment highlights an important aspect of coherent electron motion that has yet to be explored, namely, for the core-level orbitals localized at the non-equivalent carbon-sites we observe the presence of an electronic coherence even with the near absence of modulations of the charge density. Such interference is due to non-local correlations in the electronic wavefunction which can be probed by the Auger-Meitner emission process.

Inference Structures in Strong-Field Ionization [4]**:** In addition to attosecond charge motion probed with X-ray free electron lasers we have also investigated the subcycle intricate electron dynamics involved in strong field ionization, which is encoded as interference patterns in the photoelectron momentum distribution. The interference structures arise from different classes of quantum electron trajectories produced in strong field tunneling. These trajectories, defined by their ionization phases, initial transverse momenta, and the laser field's shape, create observable holograms in strong-field spectra. While the laser field and initial transverse momentum can be measured, ionization phases are difficult to determine experimentally due to multiple contributing trajectories.

Since the earliest days of the semiclassical models of tunneling, optical pulse shaping techniques have been employed to determine the phase at which tunneling occurs. For example, a small phase-shifted second harmonic superposed with the strong ionizing field can enhance the relative tunneling rate over a limited portion of an optical cycle where the strong field and harmonic constructively interfere, so long as those enhancement regions are places in the field cycle where tunneling is indeed taking place. The ionization pattern will change to reflect this enhancement. Such observations have verified several aspects the strong field model.

These pulse shaping methods fail, however, for areas of the spectrum where *two or more* trajectories interfere, since the small additional second harmonic will not generally enhance both tunneling phases at the same time. To address this, two techniques were developed: the time-correlation filter and three-color ionization phase extraction. The time-correlation filter uses differential Fourier analysis of the angle-resolved strong-field photoemission *energy* spectrum to isolate or remove specific holograms based on ionization time correlations, proving effective in revealing new holograms and verifying results against theoretical models. This time correlation analysis is powerful, but only shows trajectory time separations, and not the phases of ionization. Therefore we also developed a new three-color ionization phase extraction method where small amounts of second and third harmonic are superposed with separately controllable phases. The two dimensional phase data allows direct measurement of ionization phases even with multiple trajectories. This technique has shown excellent agreement with theoretical calculations and highlights the potential of three-color laser probes in studying strong-field dynamics.

Time-resolved x-ray absorption: [5]: Attosecond hard x-ray pulses will soon be available at x-ray FELs, and to prepare for this we have improved the methods used in our previous work on femtosecond time-resolved x-ray diffraction. Beyond attosecond-scale electron dynamics we have also studied correlated electronic and nuclear motion in photoexcited molecular systems. Our combined experimental and theoretical TRXPS study of the UV-induced multichannel photodissociation of CS_2 reveals rapid S 2p spectral shifts due to photoexcitation and large-amplitude motion. TRXPS provides detailed insights into the reaction time scales and the complex nature of this reaction, highlighting the limitations of some kinetic models. The technique's sensitivity to multimodal molecular motion and vibrational states is demonstrated, despite challenges in separating spectral contributions from different fragments.

Time-resolved hard x-ray scattering to reveal valence electron dynamics: We have shown previously that hard x-ray scattering can reveal femtosecond interatomic motion with high fidelity. A greater challenge is observing the delocalized electrons responsible for the chemical bonds. This year we observed the changes in valence electron structure of photoexcited deuterated ammonia, by probing the excited molecules with delayed ultrafast hard x-ray pulses and observing scattering. In this case the nuclear motion is largely absent from the time-resolved signal, because the deuterons have no core electrons, and the nuclear charge makes only a negligible contribution. The larges contribution to scattering is due to the component of the electron pair distribution function involving the valence electrons motion with respect to core electrons on the nitrogen.

Future Plans:

Going forward we intend to further probe ultrafast charge motion using the attosecond pump/ attosecond probe scheme described above. We are currently working to understand the discrepancy between our measurements of ultrafast charge motion in the para-isomer of aminophenol and high-level theoretical calculations done by both the group of Fernando Martin (UAM) and separately by Marco Ruberti (Imperial Coll.). We are just now at the point where we can understand and resolve the discrepancy, and inter-channel coupling in the initial ionization is particularly important for modeling the electronic coherence.

Building on this understanding we intend to develop stimulated X-ray Raman scattering (SXRS) as a method to induce ultrafast charge motion induced. In 2020 we demonstrated that SXRS can produce valence excited molecules, moreover the electronic wavepacket produced by SXRS is initially localized near the atomic-site where the x-ray frequency is close to a core- to-valence resonance [6]. Tuning the central X-ray wavelength the initial position of the wavepacket can be controlled. This localization in space and time will provide access to the fundamental physics underlying electron dynamics and photochemical transformations. Using pairs of non-degenerate x-ray pulses to create and probe localized excitations between different molecular sites, and probe coherent redistribution across the molecular backbone.

In addition, we have a confirmed beamtime to explore XFEL pulse shaping to sculpt the coherence induced in core-excited wavepackets. Using the technique first demonstrated by Driver and Li [7], we will measure the quantum beat in the Auger-Meitner emission pattern as we manipulate the spectral phase of attosecond x-ray pulses. Additionally, we have a potential experiment using angular streaking with hard x-ray attosecond pulses to begin developing methodologies to image ultrafast charge motion. The combination of SXR spectroscopic observables and HXR diffractive imaging will provide deeper insight into charge redistribution on attosecond-to-femtosecond timescales.

LCLS Run 24 will commence in FY25, and for this run we have proposed two methods to probe electron motion in strong-field-ionized water. Here strong-field ionization produces doubly charged ions (dications) followed by full three-body dissociation into protons and neutral oxygen atoms in under 20 femtoseconds. The rapid motion of protons that leads to these dissociation channels is driven by rapid electron density changes, which have never been viewed directly; but LCLS-II now gives us the first opportunity to do so. We propose observing this in two ways: hard x-ray scattering at CXI; and soft x-ray absorption at TMO.

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Oliver Alexander, Felix Egun, *et al.* Attosecond impulsive stimulated X-ray Raman scattering in liquid water *Science Advances* **10**, Eadp0841 https://www.science.org/doi/abs/10.1126/sciadv.adp0841

Kareem Hegazy, Phil Bucksbaum, *et al.* Tracking dissociation pathways of nitrobenzene via mega-electron-volt ultrafast electron diffraction *Journal of Physics B: Atomic, Molecular and Optical Physics* **57**, 195101 https://iopscience.iop.org/article/10.1088/1361-6455/ad7431/meta

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CDS (Chemical Dynamics in Solution) Amy Cordones-Hahn, Kelly Gaffney, Adi Natan

SLAC National Accelerator Laboratory, 2575 Sand Hill Rd., Menlo Park, CA, 94025
Email: acordon@slac.stanford.edu, gaffney@slac.stanford.edu, natan@slac.stanford.edu

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. 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 for understanding electronic excited states. 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. The incisive observation of electronic excited state dynamics is an essential step towards this objective.

The CDS sub-task focuses on the development and application of ultrafast x-ray scattering and spectroscopy methods to advance our research agenda. 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 **(1-4)**: 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. 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.

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 these ligand designs provide a promising approach for 1st row metal photosensitizers.

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 Fe L-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 (3). Secondly, we have used simultaneous ultrafast XSS and Fe 1s3p XES to investigate the electronic excited state relaxation mechanisms (1; 2).

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 (3; 4). In our investigations of the Fe-amido and Fe-carbene complexes, the Fe L-edge RIXS has clearly shown that destabilization of the MC excited states is enhanced by covalent delocalization of 3d symmetry orbitals leading to the reduction of the electron repulsive and the Racah B parameter. Thus, we have found tuning metal-ligand covalency provides a systematic approach to influencing the electronic structure and excited state dynamics of Fe photosensitizers.

In parallel we continue to use the established ultrafast XSS and Fe 1s3p XES to follow the electronic excited state dynamics of Fe complexes. We published an ultrafast XES study of the Fe-amido complex this year, where the Fe 1s3p XES definitively shows sub-picosecond formation of the ^{5}MC high spin MC excited state (1). Additionally, this study demonstrated the ambiguity and difficulty interpreting the optical transient absorption measurements and highlighted the value of ultrafast XES. We have also applied ultrafast XES to investigate the photophysics of the mixed Fe-carbene-polypyridyl complex. As seen for Fe-amido, these ultrafast XES measurements require a reevaluation of the electronic excited state relaxation mechanism.

Real-space methods for viewing chemical dynamics in complex chemical environments **(5-7)**: The CDS sub-task has pursued two developments focused on establishing direct structural probes of complex chemical dynamics in solution. We have (1) implemented high-energy (18 keV) XSS to effectively separate the solute and solvation response to electronic excitation in solution and (2) established a model-free approach to invert scattering signals to real space images.

Our development of ultrafast XSS has focused on investigating the photophysical properties of dimeric complexes composed of d^8 square planar metal centers held together with rigid bridging ligands. The investigation of these systems has multiple motivations, including their ability to photocatalytically activate CH bonds. Additionally, they provide model systems for understanding the interplay between attractive dispersion forces and steric strain to assist the development of reliable methods to model metal dimer complexes more broadly. $[Ir_2(dimen)_4]^{2+}$ (dimen = para-diisocyanomenthane) presents a unique case study for such phenomena, as distortions of the optimal structure of a ligand with limited conformational flexibility counteract the attractive dispersive forces from the metal and ligand to yield a complex with two ground state deformational isomers. We use ultrafast 18 keV x-ray solution scattering (XSS) and optical transient absorption spectroscopy (OTAS) to reveal the nature of the equilibrium distribution and the exchange rate between the deformational isomers (6). Our combined experimental and theoretical study provided a critical test of various density functional approximations in the description of bridged d^8−d^8 metal complexes. The results show that density functional theory calculations can reproduce the primary experimental observations if dispersion interactions are added, and a hybrid functional, which includes exact exchange, is used.

While the study of Powers-Riggs *et al.* demonstrated the ability of high-energy XSS to separate solvent and solute contributions to the difference scattering, it did not create real-space dynamics due to the challenges of dealing with distortions created by Fourier inversion of data with limited *Q*-range. To achieve real space dynamics, Natan has developed a model-free inversion method 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 (7). We have used this methodology, in conjunction with molecular dynamics simulations to investigate the photodissociation of $Fe(CO)_5$ and the solvent dependence of the solvation of the electronic excited state of $[Pt_2(POP)_4]^{4-}$ (POP = $(P_2O_5H_2)^{2-}$), and vibrational wavepacket dynamics in I_2.

In $Fe(CO)_5$, we observed for the first time synchronous atomic oscillations and preferential axial CO ligand release post-photoexcitation, alongside correlated rotational motions and a secondary CO release. These processes were mapped using a novel approach that tracks correlated pair density dynamics. Our findings (currently under review) help understand catalytic behaviors by quantitatively detailing energy redistribution across rotations, vibrations and translations, thereby offering an in-depth analysis of the early deterministic and concerted reaction dynamics of a transition metal complex transitioning from coherent to statistical dynamics. In addition, we have successfully integrated coherent control and ultrafast X-ray scattering in a Tannor-Kosloff-Rice excitation scheme with ultrashort hard X-ray probe pulses. These results are supported by numerical solutions of the time-dependent Schrödinger equation, creating spatiotemporal movies of wavepacket evolution, and providing new insights into light-driven quantum dynamics such as wavepacket splitting and delayed dissociation. These advancements, currently drafted for submission, lay the groundwork for studying decoherence in solution environments.

Our studies of the role of substrate-solute structure have focus on electronic excited state solvation studies of 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.

Future Plans

Controlling metal complex excited state properties with metal-ligand covalency: 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. To further the understanding of electronic excited state covalency and the interplay of nuclear and electronic structure, we will be focusing on the development and application of 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. We have our first approved experiment in this direction scheduled from March of 2025 and expect a second experiment in this direction in the Summer of 2025.

Real-space methods for viewing chemical dynamics in complex chemical environments: 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 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.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

1. Reinhard ME, et al. 2024. Time-Resolved X-ray Emission Spectroscopy and Synthetic High-Spin Model Complexes Resolve Ambiguities in Excited-State Assignments of Transition-Metal Chromophores: A Case Study of Fe-Amido Complexes. *J. Am. Chem. Soc.* 146:17908-16
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Gas phase Ultrafast Chemistry (GPUC)

Thomas Wolf, Todd Martinez
Stanford PULSE Institute, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025
thomas.wolf@slac.stanford.edu, toddjmartinez@gmail.com

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 experimental and simulation studies on the ultrafast dynamics of isolated molecules. Together with other leaders in the field of excited state dynamics simulations, we have launched the “Prediction Challenge: Cyclobutanone Photochemistry”, a special issue in the Journal of Chemical Physics. In this issue, we called for studies simulating the photochemical dynamics of cyclobutanone after photoexcitation of the n3S Rydberg state and predicting the resulting ultrafast electron diffraction (UED) observable. The submission deadline was co-timed with a scheduled beamtime at the SLAC UED facility for a complementary experimental study.

Cyclobutanone belongs to the class of organic carbonyls, molecules with relevance to atmospheric photochemistry. The presence of an oxygen atom with lone pairs in these molecules complicates the expected ultrafast photochemical dynamics with respect to unsaturated hydrocarbons. The GPUC subtask previously performed a series of studies on electrocyclic reactions in such unsaturated hydrocarbon compounds combining UED experiments with *ab initio* multiple spawning (AIMS) simulations. These studies demonstrated that AIMS simulations in combination with CASSF electronic structure calculations can quantitatively describe the experimental observations.

The lone pair electrons of the oxygen in organic carbonyls induce the presence of low-lying, spectroscopically dark electronic states with nπ* character, which provide additional relaxation channels for population prepared in spectroscopically bright states through either internal conversion or efficient intersystem crossing to the triplet manifold. These complex reaction landscapes enable a rich photochemistry including Norrish type I and II bond cleavage reactions, hydrogen atom transfer reactions, and roaming reactions. The diversity of reaction channels provide new challenges for both experimental and theoretical investigations. In cyclobutanone, the Norrish type I reaction pathway leads to a ring-opening reaction of an initially highly rigid structure. Additionally, there is previous evidence from secondary fragmentation processes.

The special issue received a high level of attention in the community with a total of 16 submitted manuscripts including a contribution from the theory part of this subtask. The complementary experimental study was successfully performed by the experimental part of the subtask. Preliminary analysis of the experimental results suggests the ring-opening reaction taking place within the first 500 fs and secondary fragmentation process happening within few ps.

Additionally, we performed a complementary study to our previously published UED investigation of the photodissociation of ammonia using ultrafast X-ray scattering at LCLS. While electrons scatter off the Coulomb potential of a molecule with contributions from both the nuclei and the electrons, X-rays scatter off the electron density of the molecule. The resulting differences in the information content of the two observables are subtle in many cases, since the contributions from the electrons are typically dominated by the high electron density at the nuclear positions. However, the hydrogen atoms in ammonia do not possess tightly bound electrons. Therefore, our X-ray scattering study, complemented by *ab initio* simulations of the dynamics and the resulting scattering signatures, provides an unprecedented view on the changes in the valence electron density induced by the photoexcitation and the ensuing adiabatic and nonadiabatic dissociation dynamics.

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 to target heteroatom-containing model systems exploiting the new capabilities enabled by the LCLS-II upgrade. We were awarded beamtime at LCLS-II to study the photochemical dynamics of cyclobutanone with soft X-ray transient absorption spectroscopy at the oxygen edge. Other than in the previously discussed UED study, we will target the photochemical dynamics after excitation to the nπ* state. This state has an extremely low absorption cross-section but has the highest relevance for atmospheric photochemistry due to its overlap with the solar spectrum. The low cross-section makes the dynamics extremely challenging to investigate by time-resolved spectroscopy, since sufficient excited state population must be generated while avoiding multiphoton excitation. The high repetition rate of LCLS-II enables photoexcitation at high average photon flux but low peak intensity, combined with the element and site specificity of soft X-ray probing of the induced dynamics.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

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Sub-task: Ultrafast Dynamics on Nanoscale Surfaces (UDNS)

Matthias F. Kling
2575 Sand Hill Road, Menlo Park, CA 94025
mfkling@slac.stanford.edu

Project Scope

Nanoscale physics bridges the atomic/molecular and bulk condensed matter regimes, exhibiting unique phenomena. [1] This distinctive nature has driven the widespread application of nanomaterials in catalysis, offering a promising avenue for efficient light-to-chemical energy conversion. [2–4] While catalytic activity can occur without external electric fields, the optical (plasmonic) response of nanoparticles (NPs) significantly enhances reactions through electric field localization and amplification at or near the NP surface. [5] Furthermore, the generation and migration of surface charges are critical drivers of photocatalytic reaction pathways. [6] Our momentum-resolved charged particle imaging technique provides high spatiotemporal resolution and chemical specificity. Strong incident fields and the resulting charge buildup lead to dissociative ionization of molecular fragments. By measuring the momenta of emitted charged fragments, we establish a one-to-one mapping from momentum space to real space on the nanosurface, as demonstrated in our studies with solid nanoparticles [A] and liquid droplets [B]. In this program, we aim to extend this method, along with other advanced spectroscopic measurements, to provide insight into the primary photocatalytic reaction channels occurring at the nanoscale.

Recent Progress

Surface Charge Dynamics

We have recently investigated the ultrafast nanoscale surface charge dynamics on individual dielectric nanoparticles, focusing on SiO_2, using a novel time-resolved reaction nanoscopy technique. [I] By employing a two-color pump-probe scheme, we achieved four-dimensional spatiotemporal visualization of surface charge redistribution with

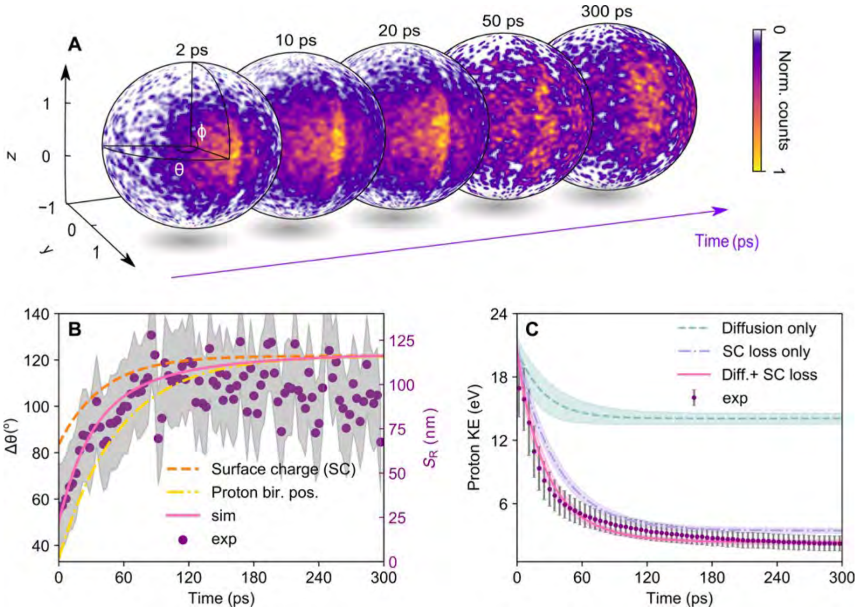

Figure 1. (**A**) 3D angular proton momentum distribution snapshots at various time delays, showing surface charge distribution spread changes. (**B**) Delay-dependent Δθ values from Gaussian fits of time-sliced theta distributions in (A). Gray area shows fitting errors. (**C**) Simulated mean proton kinetic energy values over time with different parameters, compared to experimental data. (Adapted from [I])

femtosecond temporal and nanometer spatial resolution. Through this method, we mapped the momentum distribution of emitted protons, which serve as indicators of surface molecular reactions influenced by localized surface charge. The experiments revealed a biexponential decay in proton kinetic energy, providing insight into the redistribution of surface charges following strong-field irradiation. Our analysis uncovered two distinct timescales: a fast redistribution phase occurring within ~10 picoseconds, followed by a slower decay over ~70 picoseconds, with the timescales varying depending on the nanoparticle size. These observations were further corroborated by semi-classical simulations, which suggested that the charge dynamics are governed by a combination of diffusion and charge loss mechanisms. Figure 1 illustrates these findings, showing the time evolution of the angular proton momentum distribution (Panel A), the measured and simulated angular broadening (Panel B), and kinetic energy decay (Panel C), confirming the strong agreement between experimental data and our theoretical model. The observed timescales reveal a two-step process for the proton emission. The pump pulse first generates positive surface charges aligned with the laser's polarization-sensitive near-fields. As these charges redistribute, they weaken surface bonds that can later be broken by broken by the probe pulse. We were able to theoretically corroborate such bond softening with our newly developed multiscale framework based on quantum dynamical simulations described below. By tracking these dynamics in real time, we were able to demonstrate how localized surface charges influence both chemical reactivity and molecular dissociation. This study advances our understanding of charge-mediated processes on nanoparticle surfaces, shedding light on their broader implications for catalysis and nanomaterials design.

Development of Multiscale Quantum Dynamical Simulation Framework

To elucidate mechanisms and timescales involved in the ultrafast surface chemistry of ionized dielectric nanoparticles we developed a multiscale approach based non-adiabatic quantum molecular dynamics (NAQMD). [J] Our simulations demonstrated the role of hole localization and charge transfer between the ionized nano surface and surrounding molecular environment in driving molecular fragmentation. An example simulation of such ultrafast charge transfer processes and resulting molecular fragmentation is highlighted in figure 2. Our simulations revealed how charge transfer from a highly ionized silica nano surface in a wetted environment to surrounding water molecules can drive a $H_2O^{2+} + H_2O \rightarrow OH^+ + H_3O^+$ reaction on a ~150 fs timescale. This was just one possible reaction channel, and many other fragmentation pathways were explored in our approach. Overall, through

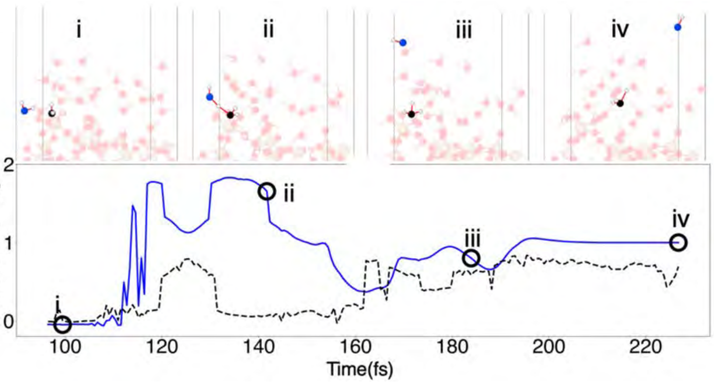

Figure 2. Molecular charge evolution and trajectory snapshots. **Bottom:** Mulliken charges of OH^+ and H_3O^+ fragments over time, with four key points labeled. **Top:** Corresponding trajectory snapshots showing (i) initial uncharged molecules, (ii) two-hole localization on a single water molecule, (iii) charge transfer and dissociation, and (iv) OH^+ ejection from the surface. (Adapted from [J])

utilization of this multiscale simulation framework we were able to elucidate critical electronic processes driving molecular fragmentation and estimates of their timescales. These timescales are critical for next generation experiments to resolve ultrafast catalytic processes induced by ionized nanoparticles in water, which we describe in our future plans.

X-ray Induced Reactions on Nanosurfaces

Building upon our prior optical investigation [7], we have made significant strides in understanding the unique optical properties of nanoscale structures and their potential in catalysis and energy conversion. We have now extended our studies to the X-ray regime by an employing a novel multi-modal method, in which we can simultaneously capture single-shot 3D momentum-resolved ion emission spectra, X-ray photoelectron spectroscopy, and coherent diffraction imaging patterns from individual nanoparticles. We have demonstrated this approach with the SQS instrument at EuXFEL, where we were able reconstruct nanoparticle morphology and explore the role of X-ray ionization surface dynamics crossing multiple intensity regimes.

In the low intensity regime, we explored the role of X-ray ionization to drive chemical reactions on the nanoscale, enhancing catalytic potential and reaction yields. As fluence increases, we observe a transition to plasma generation. Figure 3 illustrates a 2D map the kinetic energy (KE) of emitted silicon ions calculated from the time of flight versus the intensity of the X-rays incident on the nanoparticle. The KE increases from right to left, with higher energies corresponding to shorter flight times. Notably, a kink in the curve indicates a transition to a warm dense matter state with an energy density around 1 MJ/kg. This feature marks a shift to the plasma regime is reached, underscoring our technique's ability to distinguish different intensity regimes – from low-fluence catalytic processes, mid-fluence surface charge buildup, to high-fluence plasma formation. By developing this new multi-modal measurement technique, we can infer nanoparticle morphology, study X-ray ionization driven surface chemistry, and distinguish between various intensity regimes.

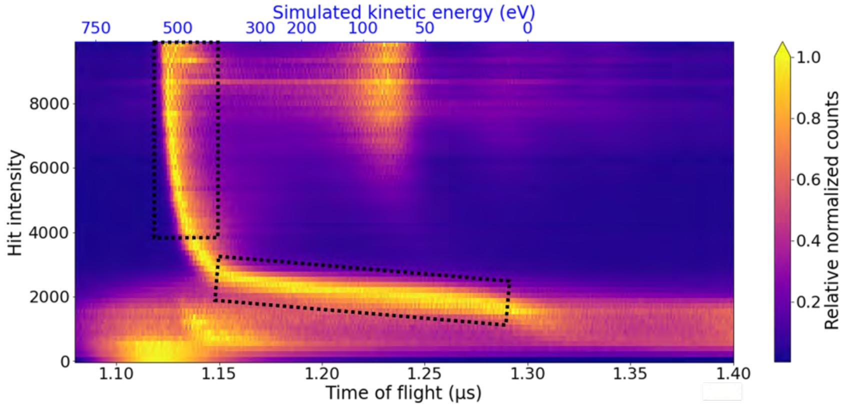

Figure 3. Time of flight spectrum in terms of hit intensity for the silicon ion channel emitted towards the detector.

Future Plans

Effects of Facets on Catalytic Activity

Our project aims to explore the relationship between nanoparticle morphology and site-specific catalytic surface activity, focusing on the role of facets and surface defects. We will leverage our developed multimodal method combining diffractive imaging and momentum-resolved spectroscopy to perform time-resolved experiments of catalytic behavior driven through laser induced ionization. A key experiment is scheduled at the SwissFEL facility's Maloja instrument, using X-ray coherent diffractive imaging and momentum-resolved photo-ion spectroscopy. This experiment will employ a pump-probe approach with an 800 nm optical laser pump and a 1 keV X-ray probe, examining spherical, cubic and octahedral dielectric (silica) and metallic (gold) nanoparticles. By integrating momentum-resolved ion imaging with X-ray coherent diffractive imaging, we aim to uniquely tag chemical reaction dynamics to nanoparticle composition and morphology with nanometer resolution. This research is expected to provide crucial insights into how facets augment photo-catalytic reaction pathways. [8,9]

Nanoparticle-Mediated Charge Transfer Dynamics in Liquid Environments

We aim to utilize ChemRIXS at LCLS to examine interactions between dielectric (polystyrene) or metallic (gold) nanoparticles, and surrounding water molecules, employing time-resolved Resonant Inelastic X-ray Scattering (RIXS) at the oxygen K-edge. This works builds upon recently published results on strong-field photo-electron emission from plasmonic AuNPs. [C] We intend to capture the water splitting process at the surface through time-resolving the formation and evolution of ionic species including hydronium ions (H_3O^+) and hydroxyl (OH) radicals. These species are of significant interest as they play a key role in a wide range of biomedical, chemical and environmental processes, including environmental remediation [10,11], radiation processing [12,13], and radiotherapy [14,15]. Furthermore, comparing the dynamics between dielectric and metallic nanoparticles will provide deeper insights into the mechanisms driving catalysis.

Further studies will focus on charge transfer from ionized gold nanoparticles to sulfur ligands using time-resolved X-ray Absorption Spectroscopy (XAS) at the sulfur K-edge, aiming to characterize the ligand-nanoparticle bond under optical photoexcitation. This approach serves as a sensitive surface probe, providing critical insights into ultrafast surface ligand charge and energy transfer, as well as dissociation processes. The findings would shed light on charge-driven dynamics at the nanoscale, which are paramount for advancing technologies in fields like targeted drug delivery [16], solar energy conversion [10], and molecular electronics [17].

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Peer-Reviewed Publications Resulting from this Project (2022-202

A) Zhang *et al.*, *Optica* **9**, 551 (2022)	B) Rosenberger *et al.*, *Nanophot.* **12**, 1823 (2023)
C) Saydanzad *et al.*, *Nanophot.* **12**, 1931 (2023)	D) Altwaijry *et al.*, *Adv. OM* **12**, 2302490 (2024)
E) Mitra *et al.*, *Opt. Exp.* **32**, 1151 (2024)	F) Wong *et al.*, *Nano Lett.* **24**, 5506 (2024)
G) Altwaijry *et al.*, *APL ML* **2**, 026124 (2024)	H) Mitra *et al.*, *Nature* **628**, 752 (2024)
I) Dagar *et al.*, *Sci. Adv*. **10**, 1890 (2024)	J) Linker *et al.*, *JACS* (2024), published online

Ultrafast Electron Dynamics in Extended Systems

Shambhu Ghimire, Tony Heinz, David Reis
SLAC National Accelerator Laboratory
2575 Sand Hill Rd, Menlo Park, CA, 94025
shambhu@slac.stanford.edu; theinz@slac.stanford.edu; dreis@slac.stanford.edu

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

Controlling and optimizing the HHG process in 2D-crystals: In the gas phase, high-order harmonic generation (HHG) process has been scrutinized as a sensitive probe of the structure and dynamics of the target molecule. The sensitivity arises from the microscopic generation mechanism, which is often described in semiclassical approximation using three steps: strong-field assisted tunnelling, driven laser field acceleration, and re-combination to the parent ion

[Corkum1993]. Both tunneling and recombination rates depend strongly on the geometrical shape of participating electronic orbital therefore HHG can provide structural information. In a typical experiment, isolated molecules are aligned/oriented by a pump laser, and high-harmonics are produced from a probe laser as a function of the pump-probe delay and the orientation of the molecule [Itatani2004]. One of the efforts of this sub-task is to extend these techniques to condensed matter systems such that (i) the fundamental strong-field response of the extended periodic system can be understood, (ii) solid-state HHG process can be conceptualized as a novel ultrafast all-optical probe of solid media such as surfaces, interfaces, or nano-scale two-dimensional crystals, and (iii) efficiency of the HHG process can be optimized.

In previous funding cycles, we have shown that crystal symmetry and special features of the electronic band structure such as Dirac cone are imprinted in harmonic spectra. It includes the observation of orthogonally polarized even-order harmonics in monolayer MoS_2[Liu2017] and anomalous ellipticity response from Bi_2Se_3[Baykusheva2021], attributed to broken inversion symmetry and the non-trivial topological properties, respectively. The crystal structure of MoS_2 is such that, in a side view, Mo atoms are sandwiched by S atoms (see figure 1), and the material is a direct band-gap semiconductor. In this funding cycle, we used monolayer MoSSe, where one set of the S atoms is replaced by a set of Se atom. The replacement not only changes the inversion asymmetry but also markedly modifies the electronic band structure. In the 1T' phase the valence and conduction bands cross each other making this material topologically non-trivial.

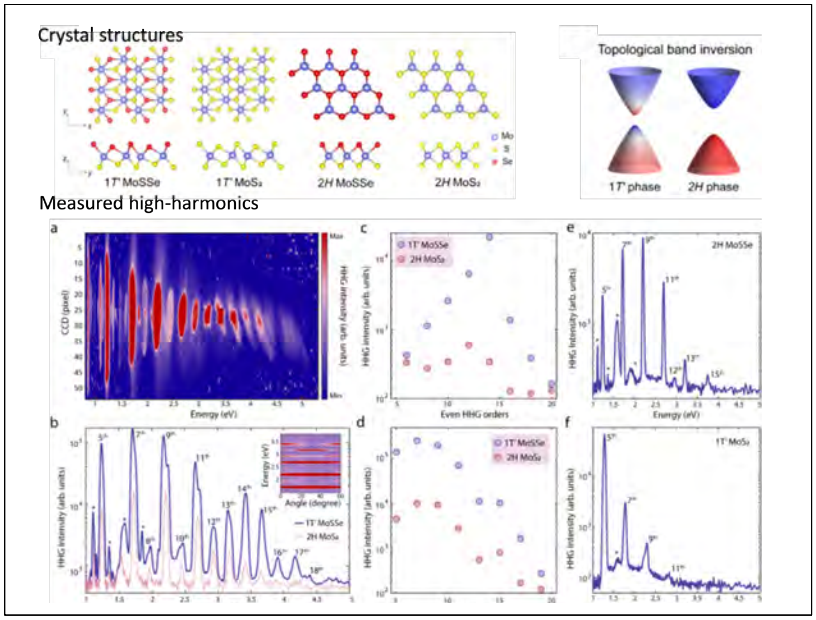
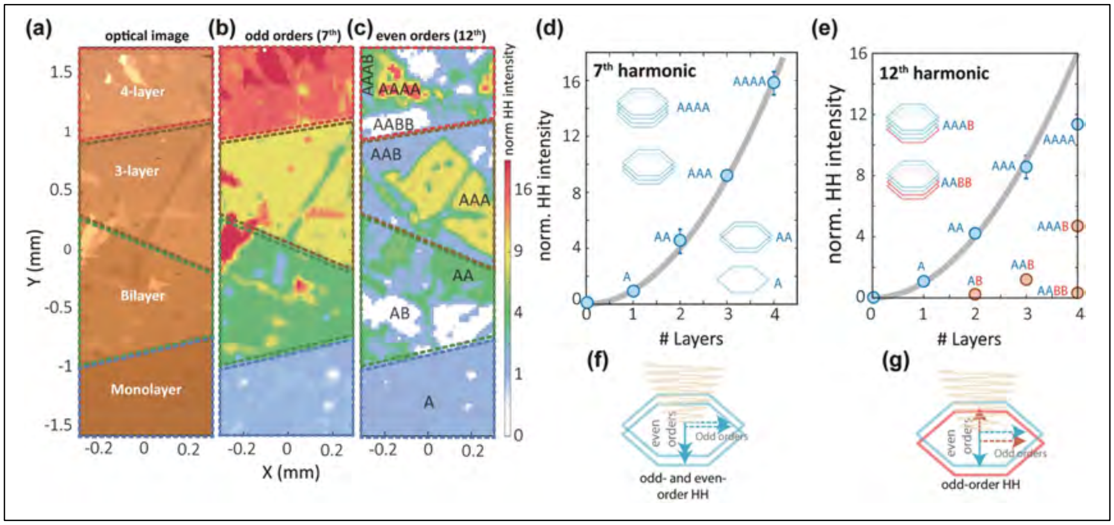


Figure 1: Manipulation of crystal structure to enhance efficiency of high-order harmoic generation process. Top-left figures show the crystal structures of MoSSe and MoS_2, top-right images show the corresponding topological band inversion as the real space picture goes from 2H phase to 1T' phase. Bottom figures show measured high-harmonic spectra and their comparisions. Adapted from *Shi et al., Nature Communications* 14, 4953 (2023)

We find that for the same mid-infrared excitation, 1T' MoSSe produces high harmonics much more efficiently than 2H MoSSe and 2H MoS_2. In experiments, high-order harmonics extending to about 18th order are produced. The enhanced efficiency is attributed to higher degree of inversion asymmetry in the real-space and the topological band inversion in the band structure. The band inversion is around the gamma point, where it provides strong inter-band transition dipole. The results are published in Nature communications.

We performed a systematic study of the HHG response of WS_2 monolayers, as a function of the number of layers and their relative orientation. We find a coherent buildup of the harmonic intensity that depend quadratically on the number of layers for the lower harmonics. The efficiency of 5th and 7th order harmonics increase quadratically as a function of the number of stacked layers, while the above band-gap harmonics exhibit deviations from quadratic scaling (see figure 2). We also find that when we stack the layers in an "AA" configuration we see both even and odd order harmonics, consistent with the absence of inversion symmetry, while in the natural "AB" stacking sequence, only odd order harmonics care produced. Results are published in Nanophotonics.



(a) Optical image WS_2, indicated regions of different layer thickness have been identified by optical contrast measurements. (b and c) high harmonics mapping for HO 7 and HO 12, as representative even and odd-orders (d) For AA stacking, we find quadratic scaling (gray line) of HO 7 as a function of layer thickness. (e) Similarly, quadratic scaling of HO 12 as a function of layer thickness is found, with some deviation for samples with four layers. As a result of the sensitivity to inversion symmetry, the even-order harmonic response is distinct for AA and AB stacking. (f and g) Illustration of even and odd-order harmonic generation for AA stacking in (f) and AB in (g), respectively. Adapted from Nanophotonics 2023

These examples show that material synthesis capabilities can be exploited to control and optimize the solid-state HHG process. Our recent review article titled, "Ultrafast high-harmonic spectroscopy of solids" Nature physics 2024 summarizes the latest updates of this rapidly growing field.

Probing exciton interactions and dynamics in 2D materials. Our research seeks to understand the nature of excited states and their dynamics in 2D semiconductors. These materials have emerged as models for understanding electron correlation effects, the role of localization, interfacial interactions and charge transfer, and the role of electron-electron and electron-phonon interactions in determining relaxation pathways and dynamics. In addition to their intrinsic interest, these systems provide a model for addressing general questions about electronic excited states and their dynamics in reduced dimensions. In particular, it has been well established that the strong electron interactions lead to tightly bound excitons as the optically excited states in these systems. In addition, the ability to stack different 2D semiconductors one on another has created the opportunity to construct model layered systems where interfacial charge transfer is driven by offsets in the energy levels of the two materials. The ability to control the twist angle between the layers alloys access to different degrees of hybridization between the layers and to study of the role of moiré potentials that are created for slight misalignment of the two relevant lattices.

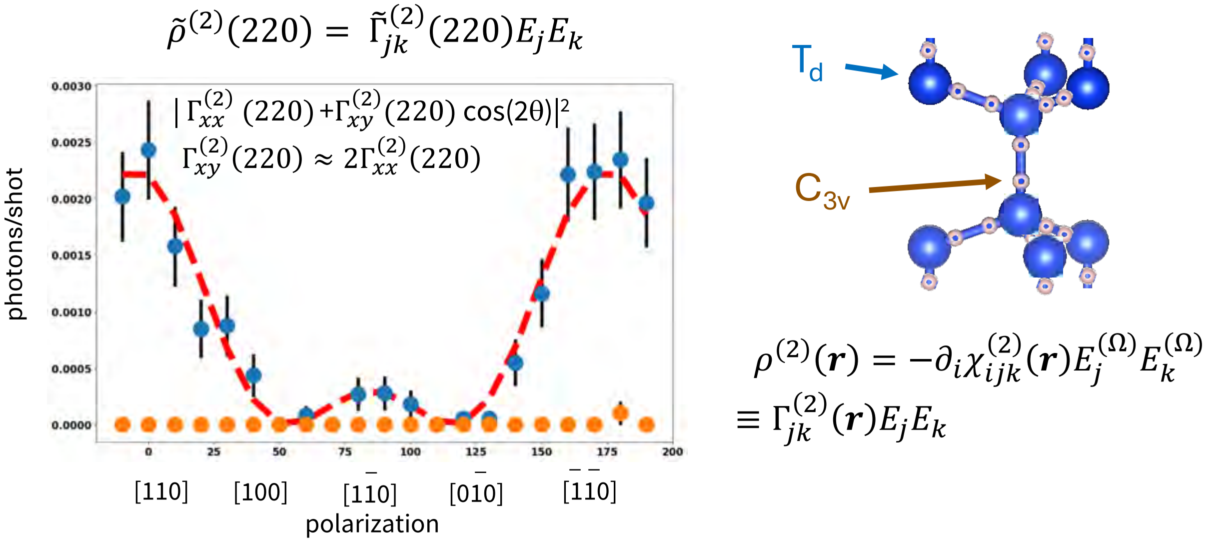
Our recent investigations have made significant strides in gaining a detailed understanding about the excited states in semiconductor heterostructures and their dynamics. We have examined heterostructures formed from two different monolayers in the transition metal dichalcogenide family that exhibit 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. They are termed interlayer excitons since strong electron-hole correlations persist for these states, just as for the intralayer excited states.

Recent progress has reflected advancement in two new experimental techniques to investigate these ILX state. Time- and angle-resolved photoemission spectroscopy (tr-ARPES) studies were carried out in collaboration with the group of K. Dani at OIST in Japan. These results, published in *Nature* [Karni 2022], demonstrated our capability of imaging both the electron and hole components associated with interlayer excitons, with characterization in momentum space of both the electron and hole distributions. 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, as well as the influence of the moiré potential on confinement of the ILX. A complementary study, published in *Science* [Barre 2022], demonstrated how electromodulation techniques could be applied to directly measure the relatively weak ILX transitions in absorption spectroscopy. This investigation yielded new information about the intrinsic radiative rate of the ILX states. A comparison with photoluminescence measurements also revealed that the lowest lying ILX, visible in photoluminescence measurements, was indirect in momentum space, as well as spatially indirect.

During the past year we have continued our investigations in these systems, focusing our attention on the nature of many-body interactions in the regime of high excitation density. In particular, in the tr-ARPES measurements, we have characterized excitons in momentum space in a regime of high exciton density, where a transition to unbound carriers in expected through their mutual screening by a Mott transition. This important quantum phase transition has yet to be characterized in the precise fashion provided by dynamic imaging in momentum space.

A second related effort, carried out in collaboration with the group of Libai Huang at Purdue University, has probed exciton-exciton interactions as they occur in the presence of free charge carriers created in a semiconductor monolayer by electrostatic doping. In the regime of isolated excitons, the lowest-lying excitations in the presence of these charges can be described either as three body trion states or, at higher carrier densities, as attractive Fermi polarons where one exciton interacts with several charges. The behavior with increasing exciton density has been the subject of theoretical attention, with intriguing prediction of different phases, such as Bose polarons in the limit of exciton densities exceeding the carrier density. We have obtained new data for the spectroscopy and spatio-temporal dynamics in the regime of elevated exciton density using ultrafast pump-probe spectroscopy. In our measurements, we record the spatially and spectrally resolved response as a function of delay time. The initial results have revealed a significant enhancement of exciton-exciton interactions in the presence of charge carriers. Quantitative analysis of the results yields an effective area of dressed excitons in the presence of charge carriers that far exceeds the intrinsic size of the neutral exciton.

Imaging valence electron motion with x rays. Much of the chemical and materials properties of matter is determined by the structure and dynamics of valence electrons which are determined by the eV energy and Angstrom spatial scales of the chemical bond. Just as how femtosecond, time-resolved x-ray diffraction has allowed us to study ionic motion on the time-scale of the making and breaking of chemical bonds, attosecond x-ray diffraction will allow us to study the motion of valence electron within a chemical bond. Similar information can be obtained using frequency domain, phase-matched nonlinear x-ray and optical wavemixing (XOM), which can be considered as optically modulated x-ray diffraction. By analyzing the energy and momentum side-bands to ordinary elastic scattering, we obtain information on the spatial and temporal Fourier components of the driven valence electron density. Even with the high brightness of x-ray free electron lasers, these experiments are challenging due to the relatively small efficiencies and large backgrounds associated with diffraction from the more delocalized electrons even if they are driven far from their equilibrium position, combined with the absence of direct phase information. Under AMOS support, we have designed and commissioned a custom monochromator and analyzer on LCLS that yields high efficiency and background suppression. Using this apparatus we have demonstrated how measurements of higher-order sidebands can give information on the local symmetry that help us localize the driven valence electron density even without direct phase information, as we have shown in the case of silicon. Even though silicon has macroscopic inversion symmetry, microscopically there is a second-order nonlinear optical response due to both higher order multipole and local symmetry breaking due to the tetrahedral bonding. Furthermore, by looking at the second-order sideband to the 220 Bragg peak, we are able to separate the nonlinear response of the interstitial electrons which have even lower symmetry that the tetrahedral symmetry about the atomic sites. We find that the response comes predominantly from electrons with C_{3v} symmetry characteristic of the sp^3 bonding with negligible mutipole contributions. Furthermore we were able to determine the relation between three of the four unique components of the micrsocopic second order susceptibility tensor, $\chi_{11}^{(2)}(220) \approx 2\chi_{12}^{(2)} \approx -2\chi_{15}^{(2)}$. The results are in good agreement with first-principles Bloch-Floquet calculations from our collaborator Daria Gorelova.



$$\tilde{\rho}^{(2)}(220) = \tilde{\Gamma}_{jk}^{(2)}(220)E_j E_k$$

$$\rho^{(2)}(\boldsymbol{r}) = -\partial_i \chi_{ijk}^{(2)}(\boldsymbol{r}) E_j^{(\Omega)} E_k^{(\Omega)}$$
$$\equiv \Gamma_{jk}^{(2)}(\boldsymbol{r}) E_j E_k$$

Figure 4. *(Left) Polarization dependence of the second-order XOM signal in silicon. 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 and shows the C3v symmetry of the interstitial bonding electron density (Right). When combined with a geometry where we can also vary the laser polarization along (001), we are able to constrain three of the four independent tensor components,* $\chi_{11}^{(2)}(220) \approx 2\chi_{12}^{(2)} \approx -2\chi_{15}^{(2)}$ *in Voigt notation.*

It would still be valuable to determine the phase of the Fourier components of the induced charge/microscopic polarization. In a recent beamtime, we have demonstrated for the first time a method for determining the phase difference between two sidebands, using the interferometric sensitivity of multi-beam diffraction, extended to the nonlinear wavemixing regime. Here we simultaneously phase match to two different Bragg peaks corresponding to reciprocal lattice

vectors $\vec{G}$ and $\vec{K}$, which are then coupled by elastic scattering of the sum-frequency signals using a third Bragg peak, $\vec{H} = \vec{G} - \vec{K}$. We then vary the relative intensity and phase of our interferometer through the polarization and angular dependence of the scattering.
The method we described above is useful for perfect crystals such as bulk diamond and silicon. To measure imperfect and reduced dimensional crystals, we have modified our instrumentation to use a backscattering analyzer which gives better angular acceptance and increased energy resolution. With this we have performed proof-of-principle experiments using the seeded hard x-ray beam at PAL-XFEL to look at valence electron motion in strongly-driven MgO crystals (under conditions where we measure strongly anisotropic high-harmonic generation). Here we successfully measured the first order side band about a single Bragg peak.

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].

We have an upcoming beamtime at the LCLS to test Al_2O_3, collaboratively with Matthias Kling's team. The driven solid-state 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 study the strongly driven dynamics in dielectric media including in the correlated electron system NiO. Our past 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. Attosecond 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.

Imaging valence electron motion: We are currently revising our back-scattering analyzer in advance of a second beamtime on MgO scheduled for this December. We are also finishing up our manuscript on the 2nd order response in silicon, and analyzing results from the our interference measurements. Despite these our important advances in frequency domain XOM, we are still very interested in developing methods for attosecond measurements. Recent advances in hard x-ray attosecond pulse generation on LCLS should make this possible, so long as we can mitigate the deleterious effects of timing jitter. In collaboration with PULSE PI Kling, we have submitted a beamtime proposal to explore various time-tool and multi-pulse measurement to make this possible. Combined with the high-rep-rate of LCLS-II-HE, such time domain measurements will allow us to scale the technique to smaller samples (including single layer 2D materials). Combined with complementary time-resolved ARPES (angle-resolved photoemission spectroscopy) and transient absorption measurements this approach will provide some of the most detailed views of driven electron dynamics with atomic-scale momentum/position and time/energy resolution.

Peer-reviewed publication resulting from this project (2022-2024)

1. Ultrafast High-harmonic Spectroscopy of Solids, C. Heide, Y. Kobayashi, S. R. Haque, and S. Ghimire, Nature Physics accepted/ in press.
2. Book: High-order Harmonic Generation in Solids, chapter 1: *Probing topological phase transition using high-order harmonic generation*; by Shambhu Ghimire, and Foreword by David Reis and Shambhu Ghimire, Worldscientific, pp. 1-15, https://doi.org/10.1142/9789811279560_0001, (2024)
3. Jiaojian Shi, Haowei Xu, Christian Heide, Changan HuangFu, Chenyi Xia, Felipe de Quesada, Hongzhi Shen, Tianyi Zhang, Leo Yu, Amalya Johnson, Fang Liu, Enzheng Shi, Liying Jiao, Tony Heinz, Shambhu Ghimire, Ju Li, Jing Kong, Yunfan Guo, Aaron M Lindenberg, *Giant room-temperature nonlinearities from a monolayer Janus topological semiconductor*, Nature Comm 14, 4953 (2023)
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Early Career: Atomic View of Molecular Photocatalysis using X-Ray Lasers

Amy Cordones-Hahn
SLAC National Accelerator Laboratory
2575 Sand Hill Rd., Menlo Park, CA, 94025
acordon@slac.stanford.edu

Project Scope:

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

Nickel-based hydrogen-evolving catalysts with 'non-innocent' ligands, known to actively participate in the electron and proton transfer reactions of the catalyst, 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 the important role of x-ray spectroscopy methods in pinpointing the local active site of a catalyst, 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 recently demonstrated S 1s3p Resonance Inelastic X-ray Scattering (RIXS) measurements as a probe of both the energy and ligand contributions to the valence electronic excited states of Ni and Cu bis(dithiolene) complexes (Larsen, 2024). By employing a theoretical approach based on time-dependent density functional theory to interpret the RIXS spectra, we reveal how metal-ligand covalency influences the excited state energies and covalencies. We identify the low energy excited states as having the same symmetry as the nominal 'ligand field' or 'd-d' excited states that dominate the photophysics of 3d metal complexes, but with significant metal-ligand charge transfer character dictated by their covalency. Specifically, we identified ligand-to-metal charge transfer character in the lowest lying 'ligand field' excited state and we found that increasing the degree of metal-ligand covalency (by changing metal or oxidation state of the complexes) increased the energy of that state. The results suggest that strong metal-ligand covalency can be used to influence the charge-transfer photochemistry of first row transition metal complexes.

While the RIXS measurements characterize the valence excited states in the ground state geometry, we have also performed ultrafast Ni K-edge and S K-edge XAS (at the LCLS and SwissFEL facilities, respectively) 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. By comparing the species-associated spectra of each state with ab initio calculations (based on RASCI and TDDFT methods) we confirm the identities of each excited state. We find that the initial excited state has ligand-to-metal charge transfer character and observe that this state is quickly depopulated (~0.3 ps) to form a highly delocalized 'ligand field' state that undergoes a tetrahedral structural distortion in ~1.4 ps. The lowest energy excited state has the same HOMO-LUMO excitation character as that described above by our RIXS studies, but we find that the tetrahedral distortion significantly lowers the metal-ligand covalency in this state by about a factor of two. This result not only characterizes the excited state covalency for this class of molecules, but also demonstrates the structural coordinates that control the degree of orbital hybridization.

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. For example, a parallel photochemical mechanism is observed in that data, which results in a charge transfer from solvent, generating the reduced $[Ni(mpo)_2]^-$ photoproduct. The yield of this process is found to be quite high considering the short lifetime of the reactive excited state, which implies pre-association of the surrounding solvent molecules. We are currently analyzing the geometry and electronic structure of the reduced complex, which represents an important intermediate in photochemical proton reduction catalysis.

In addition, we have started to modify the ligand design in metal-dithiolate complexes to generate mixed metal-ligand to ligand charge transfer excitations. We are exploring how modifying the metal-ligand orbital hybridization influences the excited state energies, dynamics, and relaxation mechanisms. We find that by changing ligand design, we can tune the excited state energies by close to an eV. We intend to explore how the dynamics and relaxation mechanisms are tuned by the same systematic ligand changes. We will do this with a combination of ultrafast optical and x-ray spectroscopies

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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.

Larsen, C. B.; Ledbetter, K.; Nascimento, D. R.; Biasin, E.; Qureshi, M.; Nowak, S. H.; Sokaras, D.; Govind, N.; Cordones, A. A. Metal-Ligand Covalency in the Valence Excited States of Metal Dithiolenes Revealed by S 1s3p Resonant Inelastic X-ray Scattering. *J. Am. Chem. Soc.* **2024**, *Accepted.*

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

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

Program Scope

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

Much of the difficulty surrounding singlet fission involves describing the intermediate triplet-pair states that are populated during the conversion of the initial photoexcited singlet 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 (tr-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 can 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 made significant progress on disseminating our work over the past year. We have completed the analysis of our data on fluence-dependent pseudospin dynamics in graphene, and published the results in *Nano Letters* [1]. We have also written a longer SPIE conference paper describing time-resolved photoemission in 2D materials systems in general, and surveying our work in this area [2]. An invited perspective article for *APL Photonics* is in preparation [3] and will be posted to the arXiv in October. Over the past year, we have presented this work in invited talks at Photonics West, Purdue University, Friedrich-Alexander-Universität in Erlangen, Germany, the Ultrafast Surface Dynamics conference in Göttingen, Germany, and the International Conference on Internal Interfaces in Marburg, Germany.

In the lab, it has been a year of substantial investment in the tr-ARPES beamline and supporting infrastructure. Since our first paper in 2018 [4], two common critiques of our cavity-enhanced HHG approach have been: (1) the very high repetition rate of the experiment may be too high for studying samples with excited-state lifetimes exceeding the 16.4 ns between pulses, and (2) how do you make tunable wavelength pump pulses starting with only $\sim$1 μJ pulses from the laser? This isn't enough to pump an optical parametric amplifier (OPA)? In August 2023, we embarked on a major upgrade of the laser system to solve both problems, and now we have successfully concluded this effort and resumed taking tr-ARPES data. Now, starting with an Er:fiber frequency comb at 1550 nm, we are able to produces seed light both for the high-power Yb:fiber system [5] and an OPA based on periodically-poled lithium niobate, similar to that described in Catanese et al. [6]. Incorporating a new polarization modulation scheme in the erbium-doped fiber amplifier (EDFA)/highly-nonlinear fiber (HNLF) assembly lets us produce OPA seed pump pulses at *arbitrary* (0-61 MHz) repetition rate, such that now the only limit on repetition rate is what the sample can handle. We presented the work on the polarization-modulated EDFA/HNLF scheme at CLEO [7] and both this work and results from the OPA are described in detail in Michael Wahl's Masters dissertation [8], available on the Allison lab website. We are preparing a publication on this for submission to *Optics Letters*.

In another major step forward, we have now developed the capability at Stony Brook to make and characterize our own 2D materials samples suitable for ARPES measurements. We have established two optical microscopy setups, one with a heated stage for doing dry transfer of exfoliated flakes, and a second one for performing optical characterization (photoluminescence, Raman, SHG, reflectance contrast) using various laser and broadband light sources. Figure 1a) shows an example of an optical image of a home-made WSe_2/WS_2 heterostructure, and figure 1b) shows photoluminescence spectra of the monolayer and heterostructure regions. We expect the ability to make our own samples with less than $\sim$1 week turnaround will dramatically increase our scientific productivity, since this allows us to fully exploit our advantage over the competition in data rate.

We have now recorded signficant tr-ARPES data from $MoSe_2/WS_2$ heterostructures. Previous work has interpreted splittings in photoluminescence spectra of this system as a consequence of hybridized excitons [9, 10], with the electron shared between the two layers and the hole localized in the $MoSe_2$ layer. However, recently this assignment has been disputed [11]. Figure 2 shows momentum maps of the exciton signals for $MoSe_2/WS_2$ bilayers with twist angles of 40.2° and 58.0°, recorded 1 ps after photoexcitation of the sample with 517 nm light. The boundary of the first Brillouin zones for $MoSe_2$ and WS_2 are sketched in red and blue, respectively. For the 40 deg. twist angle, the populations in the different layers are readily discernible, with approximately 5 times larger signal from the $MoSe_2$ layer. In time-resolved measurements, the exciton dynamics we record in the bilayer are very similar to those recorded in $MoSe_2$ monolayers, regardless of twist angle, further supporting the conclusion of the excitons in this system actually being intralayer excitons with both the electron and hole confined to the $MoSe_2$ layer. We are in the process of performing control experiments on samples with the layer orientation reversed (i.e. $WS_2/MoSe_2$)

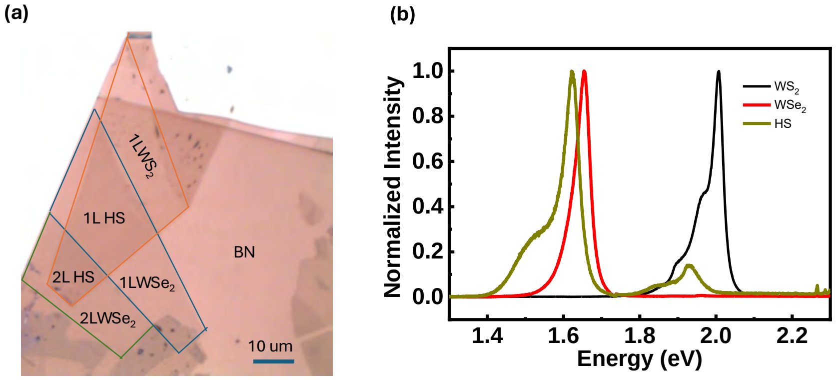

Figure 1: **Sample fabrication at SBU.** a) Optical image of a WSe_2/WS_2 heterostructure assembled at Stony Brook with different sections of the sample labeled. b) Room-temperature photoluminescence recorded from regions of monolayer WS_2 (black), WSe_2 (red), and the heterostructure (gold). The broad spectral feature observed in the heterostructure, extending to 1.4 eV, is due to interlayer excitons.

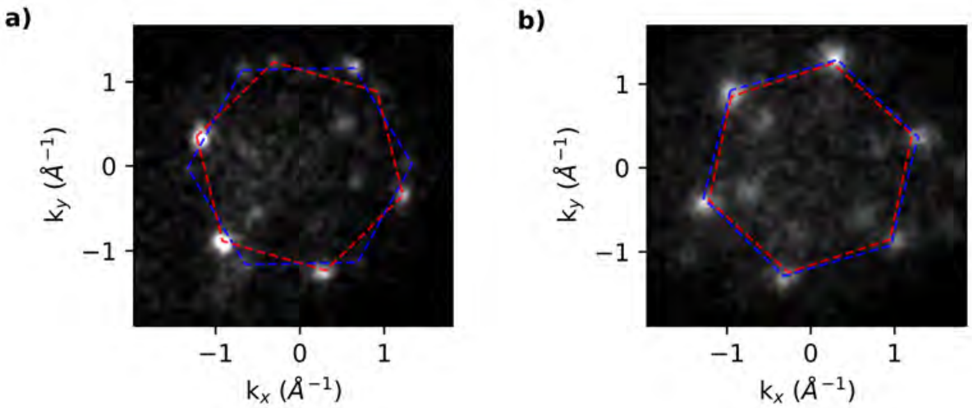

Figure 2: **$MoSe_2/WS_2$ bilayer results.** Exciton signal measured at 90K for $MoSe_2/WS_2$ twisted heterobilayers at twist angles of a) 40.2° ($h\nu_{probe}$ = 27.6 eV) and b) 58.0° ($h\nu_{probe}$ = 25.2 eV). Red (blue) dashed lines indicate the $MoSe_2$ (WS_2) Brillouin zone.

and comparing our results with GW calculations from the group of Diana Qiu at Yale, and we anticipate submitting a publication on this by the end of the calendar year.

Future Plans

We will continue work on tr-ARPES experiments in 2D materials. After publishing the $MoSe_2/WS_2$ work, we plan to shift to WS_2/WSe_2 bilayers. There are many things to study in this system, including the effect of moiré potentials on the exciton transport [12] and strong correlations [13, 14]. Our first experiments will focus on the temperature dependence of dark excitons in the bilayer, which has been inferred from fitting temperature-dependent optical spectroscopy data [12], but not directly measured. With tr-ARPES, we can directly measure the dark state population [15, 16]. In general, our beamline is still "oversubscribed" with a backlog of samples from many collaborators still to measure. 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 [17]. 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 (2022-2024)

- 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).

- J. Bakalis, S. Chernov, Z. Li, A. Kunin, Z. H. Withers, S. Cheng, A. Adler, C. Corder, M. G. White, G. Schönhense, X. Du, R. K. Kawakami, and T. K. Allison. "Momentum-space Observation of Optically Excited Non-Thermal Electrons in Graphene with Persistent Pseudospin Polarization." *Nano Lett.* 24, 9353 (2024).

- T. K. Allison, Z. H. Withers, Z. Li, J. Bakalis, S. Chernov, S. Cheng, G. Schönhense, X. Du, R. Kawakami, A. Kunin. "Ultrafast dynamics in 2D materials and heterostructures visualized with time- and angle-resolved photoemission." Proceedings of SPIE Volume 12884, Ultrafast Phenomena and Nanophotonics XXVIII, 128840A (2024).

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[1] Jin Bakalis et al. “Momentum-Space Observation of Optically Excited Nonthermal Electrons in Graphene with Persistent Pseudospin Polarization”. *Nano Letters* (July 2024).

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

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Vadym Apalkov (PI)

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

E-mail: vapalkov@gsu.edu

1. Program Scope

The program is aimed at theoretical investigation of a wide range of phenomena induced by ultrafast laser-light excitation of nanostructured or nanosize systems. The program is concentrated on finite nanopatches of two-dimensional materials and large polycyclic molecules. The program is specifically focused on 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. Resent Progress and Publications

The recent progress covers the period of 2022-2024 and is illustrated by publications [1-13].

2.1 High harmonic generation in graphene quantum dots: elliptically polarized pulse [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 placed in the field of an elliptically polarized pulse. The nonlinear electron dynamics results in generation of high field harmonics, the spectra of which are sensitive to ellipticity of the incident pulse. In this case, the ellipticity of the pulse can be used as a tuning parameter to change the generation of high-order harmonics in QD systems. We considered two types of graphene QDs: hexagonal and triangular QDs, which have D_{6h} and D_{3h} symmetries, respectively. The radiation spectra of such QDs show strong sensitivity to the ellipticity of an optical pulse when its polarization becomes close to a circular one. Such sensitivity is visible as the suppression of some high-order harmonics in the radiation spectra. The orders that are suppressed are determined by the symmetry of the QD; for a triangular QD, every third harmonic, while for a hexagonal QD, every sixth harmonic is suppressed. While for small field amplitudes, the suppression of the corresponding harmonics is realized mainly for a circularly polarized pulse, for large field amplitude, the suppression occurs also for an elliptically polarized pulse with ellipticities that are in some range close to a circularly polarized pulse. Also, for a hexagonal QD, which has inversion symmetry, all even-order harmonics are suppressed for all ellipticities of an optical.

Interaction of an elliptically polarized pulse with graphene QDs also generates elliptically polarized radiation. The ellipticities of the corresponding high-order harmonics depend on the parameters of the incident pulse, and in some cases, for large enough harmonic orders or large intensities of an incident pulse, the corresponding polarization ellipse of high-order harmonics is effectively rotated by 90^0 compared to the polarization ellipse of the incident pulse.

2.2 Ultrafast high harmonic generation in transition metal dichalcogenide quantum dots [10]

We study theoretically interaction of short optical pulses with transition metal dichalcogenides (TMDC) disk-shaped quantum dots. The electron systems of such QDs are described within a massive Dirac type effective model with infinite mass boundary conditions. The high harmonic spectra are characterized by the intensities of the generated high harmonics and the cutoff frequency, i.e., the maximum harmonic order that can be generated. Generation of high-order harmonics in low dimensional QD systems upon interaction with an ultrafast optical pulse presents the possibility of controlling the nonlinear optical response of such systems. The high harmonics generation can be tuned by changing either the QD size or the parameters of a pulse, i.e., its amplitude, frequency, and polarization. The strongest high harmonics are generated for a linearly polarized pulse, while for a circularly polarized pulse, the high-order harmonics are strongly suppressed. Such a suppression, observable as a function of ellipticity of the incident pulse, shows a very sharp dependence near ellipticity 1 (circularly polarized pulse) for the third harmonics, and for the higher order harmonics, i.e., the fifth and the higher, intensities of the corresponding harmonics smoothly decrease with the ellipticity of the incident pulse. Also, the elliptically polarized pulse generates elliptically polarized high harmonics with the ellipticity that is usually less than the ellipticity of the incident pulse.

The radiation spectra of TMDC QDs also depend on the QD size. The strongest dependence

is realized for the frequency of the pulse that is less then the QD bandgap. In this case, the optical response is determined by the properties, e.g., the density of states, of the valence band and the conduction band edge states of TMDC QD. The number of such states strongly depends on the QD size, which results in strong dependence of the radiation spectra on QD radius. With increasing the QD size, both the intensity of high harmonics and the cutoff frequency increase, which is due to a larger number of QD levels that contribute to the generation of high harmonics. When the frequency of the pulse is above the bandgap of the corresponding QDs, the cutoff frequency shows the saturated behavior for the QDs with the radius close to 15 nm. No such saturated behavior is observed for the frequency of the pulse that is below the bandgap.

The radiation spectra of TMDC QDs also depend on QD material. Out of three considered TMDC materials [10], WS_2 and WSe_2 QDs generate the strongest high harmonics, while the corresponding intensities of MoS_2 QDs is a few orders of magnitude smaller. At the same time, the cutoff frequency of radiation spectra has a weak dependence on the material of QDs.

The high harmonic generation in the quantum dots of TMDC materials holds potential in novel optoelectronic applications utilizing the nonlinear response of such finite nanoscale systems.

2.3 Ultrafast field-driven valley polarization of transition metal dichalcogenide quantum dots [13].

In transition metal dichalcogenide materials with two inequivalent valleys, the valley degree of freedom can be controlled by an ultrashort optical circularly polarized pulse, which brakes the time reversal symmetry of the system. The valley polarization, induced by such a pulse, can be also tuned by introducing spatial confinement of the carries, i.e., by considering QDs of TMDC materials. The QD size controls the bangap of the system and effective average density of states, which finally affects how an external optical pulse interacts with the material. We considered TMDC QDs of a circular shape, for which the controllable parameter is the QD radius, R. The dependence of the valley polarization on R is not universal and strongly depends on the TMDC materials. For some TMDC materials, the valley polarization is almost insensitive to the QD size, while for other materials, the valley polarization shows strong non-monotonic dependence on R with a local maximum at a finite radius.

The valley polarization in TMDC QDs can be generated by an optical pulse with a relatively small field amplitude (<0.15 V/nm), and, as expected, within this amplitude range, monotonically increases with the amplitude reaching a saturated value at the large pulse intensity ~ 0.05 V/nm.

Among studied TMDC materials, very high valley polarization (~90%) can be induced in WS_2 and WSe_2. The fact that such a high valley polarization can be induced by relatively low-intensity pulses and the ability to control the valley polarization by changing the QD radius, provides an effective way to control the valley degree of freedom in transition metal dichalcogenide quantum dot systems.

3. Future Plans

We plan to develop the 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 a periodic potential on the generation of high harmonics in 2d systems. We also plan to study theoretically the interaction effect on generation of high harmonics in quantum dot systems.

4. Peer-Reviewed Publications Resulting from this Project (2022-2024)

[1] 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).

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

[3] 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).

[4] 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).

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

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

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New correlated numerical methods for attosecond molecular single and double ionization

Luca Argenti

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

University of Central Florida, Orlando, FL32816

e-mail: Luca.argenti@ucf.edu; website

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. When this project started, most of the fundamental quantities needed to carry out this program (hybrid integrals and high-order transition density matrices) were not available yet. Computing and incorporating them in scalable programs, therefore, was a major theoretical and computational goal. We have made significant progress towards these goals, bringing us closer to directly imaging correlated motion in matter, a necessary step to expand attosecond science.

Recent Progress

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

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

iv) 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) Completed ASTRA's single-ionization CC sector, integrating points ii) and iv) **[Ref. 8]**.

vi) Validated ASTRA with an *ad hoc* CIS code for the N_2 molecule **[Ref. 8]**.

vii) The XCHEM code, of which the PI is a co-developer, is a benchmark for ASTRA modules. Rewritten scattering solver, Hamiltonian diagonalization, wave packet projection on scattering states, calculation of the molecular-frame photoelectron angular distributions (MFPADs). The new changes have been tested on the channel-resolved MFPADs of the CO molecule **[Ref. 2, 5, 9]**.

viii) Tested the ASTRA CC code to compute bound-states observables in the N_2 molecule, with both uncorrelated and correlated ions, and resonance parameters in neon **[Ref. 7]**.

ix) Developed decoherence models for the strong-field N1s core ionization of the N_2O 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.

x) Developed a model for the direct photoemission recoil and intramolecular photoelectron scattering recoil in the C 1s ionization of the CO molecule control ionic vibrational coherence **[Ref. 4]**. This study is a precursor to *ab initio* study we will do with ASTRA.

xi) 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. **[Ref. 8]**.

xii) Implemented two-photon double-ionization (TPDI) virtual-sequential model for pump-probe double ionization of atoms and molecules. The method has been applied to helium **[Ref. 6]** and neon (see Fig. 1) **[Ref. 10]**.

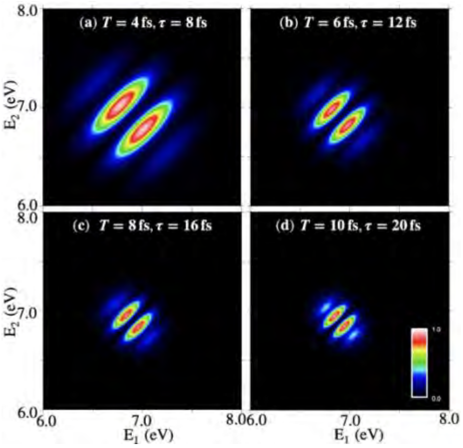

Fig. 1: Joint photoelectron distribution of the pump-probe TPDI of neon, in the Ne^{2+} $2p^4$ (^3P) channels, at four delays. The destructive interference at equal energy sharing reflects the antisymmetry of the photoelectron pair spatial part under exchange. Different panels show that the phenomenon is observable not only with ultrashort pulses, but also with longer pulses, as long as the photoelectron detector has sufficient resolution **[Ref. 10]**.

xiii) Implemented the calculation of the transient-absorption spectrum (TAS) in fixed-nuclei approximation, and applied it on the O_2 and CO molecules *[manuscript in preparation]*.

xiv) 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.

xv) Implemented scattering states in ASTRA, to compute partial PICs and MFPADs for both stationary regime and pump-probe processes (see Fig. 2) *[manuscripts in preparation]*.

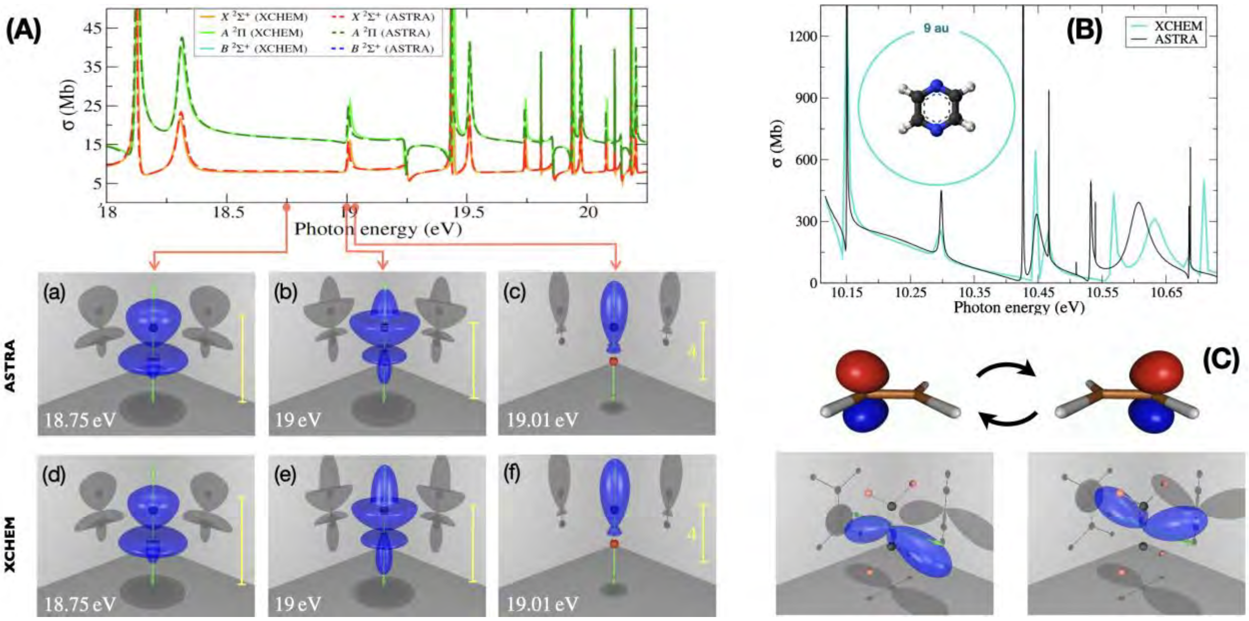

Fig. 2: A) Comparison between partial cross sections and MFPADs for the single ionization of the CO molecule in different ionic channels, using ASTRA and XCHEM. B) Total ionization cross section of pyrazine, a comparatively larger molecule. Thanks to its exact treatment of exchange, ASTRA converges better for larger molecules. C) Time-dependent MFPADs from a coherently excited ethylene molecule.

xvi) The late Barry Schneider and his collaborator completed the implementation of mono and bi-electronic integrals in the new hybrid-integral library (see i). The library is currently being interfaced with ASTRA. Preliminary calculations show excellent agreement with results obtained with GBTOlib. The new library, however, can handle large photoelctron angular momenta, requires a fraction of the memory and time, and converges rapidly also for off-center nuclei. This is a major achievement that will enable ASTRA to compute core photoionization spectra.

xvii) Implemented TDSE solver in essential state basis to reproduce molecular ATAS spectra in fixed-nuclei approximation. The calculations for selected resonant ATAS spectrum of CO and O_2 have been finalized. A manuscript with two graduate students is in preparation.

xviii) Implemented TDSE solver in the full CC basis, as well as projector on scattering states.

xix) Implemented Mask functions in the TDSE solver, which allow us to reproduce long pulses even in comparatively small quantization boxes.

xx) Computed multiphoton ionization yield for the XUV-pump IR-probe double ionization of C_2H_4, based on $C_2H_4^+$ surface-hopping trajectories. ASTRA successfully reproduced the ion yield maximum observed experimentally at 15fs delay *[manuscript in collab. w. S. Nandi & M. Vacher]*.

xxi) Developed a python-based graphical-user-interface prototype for ASTRA, meant to simplify the use of this program for new students and experimental collaborators.

Future Plans

Complete manuscripts on the MFPADs, ATAS, valence ionization of CH4, and photoionization of Mg-Py. Complete integration of hybrid numerical library with ASTRA. Apply ASTRA to study core-ionization processes (targets of particular interest are C_2H_2 and SF_6). Implement the finite-pulse TPDI method in molecules and test it against existing experimental results. Integrate in ASTRA the exterior-complex-scaling method for a better convergence of resonance parameters, for the consistent calculation of perturbative multiphoton matrix elements, and for the efficient *ab initio* study of molecular double-ionization processes.

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Published Peer-Reviewed Papers from this Project (Sep2021-2024, 10 + 1 in proceedings.)

1. H. Gharibnejad, N. Douguet, B. I. Schneider, J. Olsen, L. Argenti, *A multi-center quadrature scheme for the molecular continuum*, CPC **263**, 107889 (2021).
2. V. J. Borràs, J. González-Vázquez, L. Argenti, F. Martín, *Molecular-Frame Photoelectron Angular Distributions of CO in the Vicinity of Feshbach Resonances: An XCHEM Approach*, J. Chem. Th. Comput. **17**, 6330 (2021).
3. Nariyuki Saito, N. Douguet, H. Sannohe, N. Ishii, T. Kanai, Y. Wu, A. Chew, S. Han, B. I. Schneider, J. Olsen, L. Argenti, Z. Chang, J. Itatani, *Attosecond electronic dynamics of core-excited states of N2O in the soft x-ray regime*, Phys. Rev. Res. **3**, 043222 (2021).
4. B. Ghomashi, N. Douguet, L. Argenti, *Attosecond Intramolecular-Scattering and Vibronic Delays*, Phys. Rev. Lett. **127**, 203201 (2021).
5. V. J. Borràs, J. González-Vázquez, L. Argenti, F. Martín, *Attosecond Photoionization Delays in the Vicinity of Feshbach Resonances*, Science Advances **9**, eade385 (2023).
6. S. Chattopadhyay, C. Marante, B. I. Schneider, L. Argenti, *TPDI with finite pulses: Application of the virtual sequential model to helium*, Phys. Rev. A **108**, 013114 (2023).
7. N. G. Puskar, Y.-C. Lin, J. D. Gaynor, M. C. Schuchter, S. Chattopadhyay, C. Marante, A. P. Fidler, C. L. Keenan, L. Argenti, D. M. Neumark, S. R. Leone, *Measuring autoionization decay lifetimes of optically forbidden inner valence excited states in neon atoms with attosecond noncollinear four-wave-mixing spectroscopy*, Phys. Rev. A **107**, 033117 (2023)
8. J. M. Randazzo, C. Marante, S. Chattopadhyay, B. I. Schneider, J. Olsen, L. Argenti, *ASTRA: a Transition-Density-Matrix Approach to Molecular Ionization*, Phys. Rev. Res **5**, 043115 (2023); Springer Proc. Phys. **300**, 115 (2024).
9. V. J. Borràs, P. Fernández-Milán, L. Argenti, J. González-Vázquez, F. Martín, *PICs and PADs of molecules with XCHEM-2.0*, Comp. Phys. Commun. 296, 109033 (2024).
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Ultrafast Atomic and Molecular Dynamics Driven by Ultrashort Intense Laser Pulses

(Award No. DE-SC0001771)

Principal Investigator: Andreas Becker
JILA and Department of Physics, University of Colorado at Boulder,
440 UCB, Boulder, CO 80309-0440
andreas.becker@colorado.edu

Project Scope

The quest 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 experiments. Controlling the electron dynamics over a sub-cycle of the driving laser pulse allows for the emission of coherent light at extreme ultraviolet and soft X-ray wavelengths on the attosecond time scale, through the process of high-harmonic generation (HHG). This progress made it possible to probe electron dynamics in atoms, molecules, and solids. 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.

The goal of our projects is 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 intense complex light fields. A focus is 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 this area of research

Recent Progress

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

A. Generation of elliptically polarized high-order harmonics

High harmonic generation (HHG) provides the opportunity to produce ultrashort pulses of extreme ultraviolet (XUV) and soft x-ray radiation. For a long time, experiments generated and applied linearly polarized harmonics, only recently several methods have been demonstrated to overcome this restriction. The ability to generate elliptically polarized ultrashort light pulses is important since it enables applications in various areas, from studying molecular chirality to the observation of magnetic interactions.

Perhaps, one of the simplest configurations to implement the generation of elliptically polarized harmonics 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.

However, HHG in this configuration entailed an important open question. While in a recent experiment a surprisingly large ellipticity in the generated harmonics has been observed [1], theoretical predictions based on the reflection symmetry of the set-up for long pulses indicated that only linearly polarized harmonics should be generated [2].

We have provided new insights into the feasibility of generating elliptically polarized high harmonics at the cut-off with cross-polarized bichromatic laser pulses and addressed the controversy between experimental observations and previous theoretical predictions [DOE1]. Using solutions of the time-dependent Schrodinger equation we have shown that indeed highly elliptically polarized harmonics from atomic hydrogen as well as atomic argon can be generated. This confirms the experimental observations [1], including the result that the ellipticities of the generated even harmonics are in general larger than those of the odd harmonics. We were able to provide a picture in which the pulse at 2ω acts as a perturbation after the birth of the electron in the continuum by the fundamental field. Furthermore, we have shown that the amount of ellipticity can be controlled via the relative phase between the two pulses, their intensity ratio and the pulse durations of the two pulses. Specifically, we have shown that high ellipticities can be only achieved for a small range of short pulse durations, while for long pulses the harmonics are linearly polarized, in agreement with the earlier theoretical predictions [2].

More recently, we have extended our theoretical studies to further analyze the features for the generation of elliptically polarized harmonics in this set-up. To this end, we have complemented our ab-initio numerical computations by the development of model calculations based on the strong-field approximation for ultrashort pulses. Numerical results from the two approaches are in good agreement and confirm the existence of an optimum short pulse overlap between the pulses as the key parameter in the generation of elliptically polarized harmonics. This optimum overlap can be achieved either by adjusting the pulse durations or by controlling the time delay between the two pulses, as it was done in the experiment [1]. We are currently in the process of determining trends for the optimum pulse overlap as a function of the parameters of the two cross-polarized laser pulses.

B. Interaction with short circularly and elliptically polarized laser pulses

In previous years 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 [3,4]. 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 [5].

Recently, we extended these studies in different directions. First, we performed numerical simulations of photoelectron energy spectra in the interaction of a rare gas atom with circularly and elliptically polarized laser pulses [DOE3]. In agreement with recent observations in circularly polarized fields [1,2] the photoelectron energy spectra for counter-rotating electrons peak at lower kinetic energy than those for co-rotating electrons. We have shown that this difference can be interpreted as being due to the additional pathways to ionization that are available for the counter-rotating electrons only, as predicted by us. Furthermore, our results showed, in agreement with earlier work [6,7], that the off-set angle by which the emission of electrons is rotated in an elliptically polarized field increases with each successive ATI order and is larger for the emission from counter-rotating states as compared to that from co-rotating states. A simple model based on the interference and relative phase difference between just three continuum states provides remarkable agreement and once again emphasizes the importance of the additional ionization pathways available for the counter-rotating electrons.

Next, we presented an alternative way of calculating the Keldysh amplitude, i.e., the length-gauge form of the ionization amplitude in the strong-field approximation. The amplitude is evaluated exactly by expanding it in Fourier components and partial waves [DOE2]. Comparisons of this 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.

Currently, we are investigating 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 [8]. Our initial results confirm experimental observations but also show for longer pulses a transition from symmetric emission at small wavelengths to an asymmetric emission at longer wavelengths. Our preliminary analysis of the results indicates a dependence of the asymmetry on the number of available ionization channels.

C. Photoabsorption time delays in attosecond streak camera

Several techniques have been developed to time-resolve attosecond electron dynamics, including the attosecond streak camera technique [9]. This method employs an isolated attosecond XUV pulse to photoionize the target and a few-cycle, carrier-envelope-phase stabilized pulse to probe the motion of the photoelectron in the combined fields generated by the Coulomb potential of the ion and the electric field of the few-cycle pulse. By varying the delay between the two pulses a streaking trace can be produced which mapping time information onto the final momentum of the photoelectron. In this project we have analyzed the observed so-called streaking time delay in the past [10], including the proposal of observation of an absorption time delay in two-photon ionization [11].

We have now extended our previous studies and proposed a self-consistent method to account for the potential-laser coupling effect and extract the intrinsic absorption time delay, without invoking an implicit assumption of a constant continuum correction made in previous streaking studies [DOE4]. The concept is based on an iterative technique starting from an initial guess of the absorption time delay and using classical electron trajectories to consistently remove the coupling-induced momentum shift to the streak signal. We have shown that the self-consistent iterative algorithm converges quickly and is robust against different initial guesses. The method is then applied to laser-induced ionization of atoms to obtain the absorption time delay in resonant two-photon ionization and to explore possible time delays in above-threshold ionization. The results confirm that the previously proposed absorption time delay linearly dependent on the ionizing pulse duration in resonant two-photon ionization. The method is also shown to perform better than conventional methods and to identify a small negative absorption time delay (less than 2 attoseconds) in above-threshold ionization.

Future Plans

We will continue our studies concerning the asymmetric emission of photoelectrons in few- and many-cycle circularly polarized laser pulses. Goals in these studies are to unveil the physical mechanisms behind the observations and, potentially, to image the motion of the photoelectron in the continuum from the asymmetry in the photoelectron angular distributions. Furthermore, we will extend our studies concerning the generation of elliptically polarized high-order harmonics from bichromatic cross-polarized pulses to bielliptical pulses.

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Peer-Reviewed Publications Resulting from this Project (2022-2024)

[DOE1] B. Ghomashi, S. Walker, and A. Becker, *Enabling elliptically polarized high harmonic generation with short cross polarized laser pulses,* Scientific Reports **13**, 012843 (2023).

[DOE2] S. Walker, B. Ghomashi and A. Becker, *Partial-wave decomposition of the Keldysh ionization amplitude*, Physical Review A **108,** 053102 (2024).

[DOE3] Y. Gebre, S. Walker, and A. Becker, *Photoelectron spectra in circularly and elliptically polarized laser pulses*, Physical Review A **109,** 023120 (2024).

[DOE4] Y. Gao, H. Ni, A. Becker, and J. Wu, *Self-consistent extraction of photoabsorption time delays in attosecond streak camera,* Science China **67**, 124203 (2024).

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

Award # DE-SC0023270

Uwe Bergmann
Department of Physics
University of Wisconsin-Madison, Madison, Wisconsin 53706
Email: ubergmann@wisc.edu

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 with pulse pairs in the sub 0.5 - 5 fs time window.

II. Recent Progress

In last year's report, we described our initial progress in understanding our observed large spatial and spectral inhomogeneities as well as large spectral broadening (beyond what is expected for any multiplet splitting or spectator core-hole generation) of single-shot S-XES spectra. Since the last report we have been able to add new data from a beam time at SACLA (May 2024) using a copper gain medium (in addition to manganese). We were also able to complete our theoretical understanding of the observed phenomena, and our findings are currently under review and can be found on arXiv [1]. Implementing the 3D Maxwell-Bloch theory recently developed by our collaborators [2], we were able to establish that the spectra exhibit the strong-lasing phenomena of filamentation and Rabi cycling [3-6]. While the spatial inhomogeneity arises form formation of hotspots during gain guiding driven focusing and filamentation, the large energetic broadening analogous to super-continuum generation is driven through Rabi cycling, i.e., the periodic modulation of populations in two-level systems within a time-varying field [6]. While in the optical regime Rabi cycling is found in many applications from photonics [7] to quantum computing [8], this phenomenon had not yet been observed in the Angstrom wavelength regime. 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. Crucially, our simulations show that the resulting S-XES pulses are extremely short, in some cases shorter than 100 as. This property can be exploited for hard x-ray attosecond experiments.

When combined with pump pulses that exhibit two strong SASE spikes, these extremely short pulses can also be employed for our proposed pulse-pair spectroscopy applications [9]. The fact that each pulse is much shorter than 1 fs, enhances the temporal range to pulse spacings to below 1 fs opening the door to x-ray coherent attosecond pulse-pair spectroscopy (X-CAPPS). Following the first experiments by graduate student Zain Abhari in the fall of 2023 as part of her student internship at SACLA, we carried out a beamtime at SACLA in March 2024 to test and commission our proposed X-CAPPS spectrometer. Figure 1 (top) shows the schematics of the experimental setup. The incident SASE pump pulse is focused to ~ 100 nm diameter by the SACLA KB optics generating strong lasing in our copper gain medium. If the SASE pulse contains two strong spikes, a pair of coherent S-XES pulses at the Cu Kα_1 line is generated. The pulse pair first passes through a thin (20 µm) Si (440) Bragg crystal (Analyzer 1) resulting in an interference spectrum at Detector 1 that provides the temporal spacing of the x-ray pulse pair. Most of the signal intensity passes through Analyzer 1 before transmitting the sample and impinging on the second Si (440) Bragg crystal (Analyzer 2) for analysis in Detector 2. If the sample modifies both pulses equally, the fringe contrast does not change. Changes to the sample transmission that happen between the two pulses, will reduce the fringe contrast measured in Detector 2 compared to Detector 1.

The aim of our beam time was to commission our proposed X-CAPPS instrument. Figure 1 (bottom) shows a pair of interference spectra (without a sample) measured in Detectors 1 and 2, respectively. The spectra exhibit fringe spacings of ΔE ~ 2.4 eV corresponding to a pulse-pair spacing of Δt = 1.7 fs. Comparison of the two spectra shows a precise agreement, demonstrating that our experimental design for X-CAPPS works. We were able to obtain fringe spacings ranging from ΔE = 8.69 - 0.85 eV corresponding to pulse pairs ranging from Δt = 0.48 - 4.9 fs. We also measured several X-CAPPS spectra with various samples inserted into the beam path. No pump pulse was employed and therefore no change in fringe contrast expected, and we are currently analyzing the date. We are working on a publication describing the X-CAPPS method and instrument. X-CAPPS opens a new window into the sub-10 fs X-ray double probe regime currently not accessible at XFELs. The approach will work for any coherent pulse pairs if they have the same photon energy. Recent advances in better control of SASE pulses including single spike SASE [10] and two-pulse SASE is compatible with our X-CAPPS instrument.

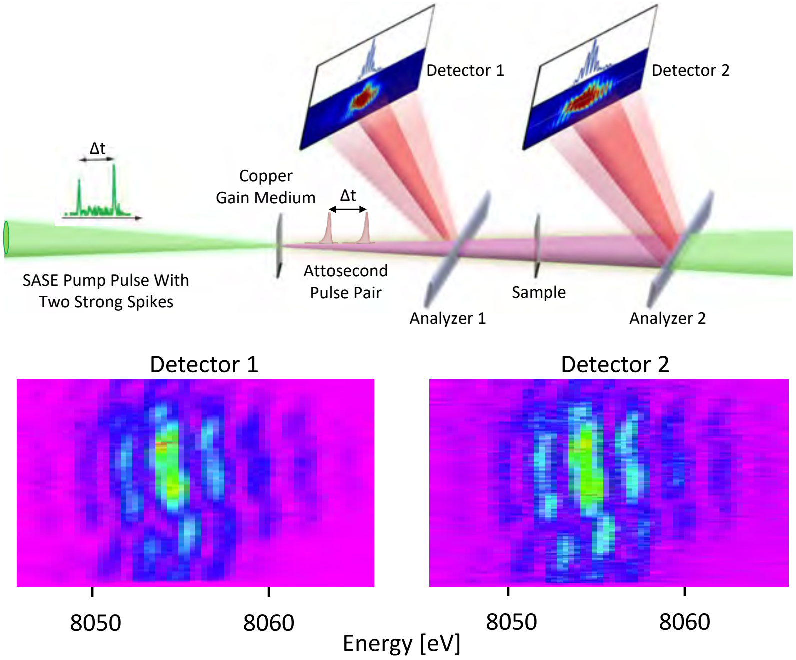

Figure 1 X-CAPPS. Top: Schematics of the X-CAPPS setup. A SASE pump pulse with two strong spikes impinges on the copper gain medium, generating a coherent pulse pair of Kα stimulated emission. The pulse pair is analyzed by Si (440) Bragg crystals (Analyzers 1, 2) and the interference spectrum is recorded in Detectors 1,2. A sample (that can be pumped with an excitation pulse) is placed between the two Bragg analyzers. Bottom: Measured interference spectra resulting in fringes with 2.4 eV spacing corresponding to a pulse pair with a temporal spacing of 1.7 fs. The measurement was performed without a sample resulting in two nearly identical spectra in Detectors 1 and 2, respectively. The measurement demonstrates the sensitivity and validity of the X-CAPPS approach.

To test the sensitivity of S-XES we have measures seeded $K\alpha_1$ S-XES from two Mn compounds with different multiplet structures. We have previously reported updates on these experiments, but we have encountered several challenges that needed to be addressed before submitting the work for publication. Recently, we have been able to address these issues, and the analysis for this work is complete, and we are doing the final edits before submission. One of the compounds, $NaMnO_4$ is a formally d0 transition metal that is expected to have only one strong resonance at the $K\alpha_1$ emission. In our seeded S-XES spectra we confirmed this, however, we did observe a small shift of this resonance to lower and higher energies, depending on whether the seed pulse was below or above the resonance. Based on the theoretical analysis based on the code developed by our collaborators, we now understand that this small shift is due to an effect called frequency pulling, a well-known phenomenon in laser spectroscopy. Such frequency pulling needs to be considered in the application of seeded S-XES to chemical analysis.

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9. Zhang, Y. et al. **Generation of intense phase-stable femtosecond hard X-ray pulse pairs**. *Proc. Natl. Acad. Sci.* **119**, e2116021119 (2022).

10. Franz, P. et al. **Terawatt-scale attosecond X-ray pulses from a cascaded superradiant free-electron laser.** *Nature Photonics* 18, 698 (2024)

III. Future Plans

- In May 2024, we have received a beam time at SACLA to carry out the research on the phenomenon of superradiance in S-XES. The beam time was successful, and we have started the data analysis.
- Explore potential applications of the recently observed spectral phenomena (filamentation, Rabi oscillations). We are exploring to use this phenomenon to obtain extremely short 8 keV pulses (10s of attoseconds) when combining S-XES with single-spike SASE pump pulses. A corresponding beam time proposal has been submitted to LCLS.
- Analysis of the results from three successful SACLA beam times (November 2023, March 2024 and May 2024).
- Dissemination of results at conferences, meetings, and in peer-reviewed journals

IV. Peer-Reviewed Publications resulting from this Project (2022-2024)

Bergmann, U; **Stimulated X-ray Emission Spectroscopy**, *Photosynthesis Research,* (2024) https://doi.org/10.1007/s11120-024-01080-y

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: Erratum**, *Optica* **10**, 1602-1604 (2023) https://doi.org/10.1364/OPTICA.510641

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

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

Project Scope

The goal of our research program is to investigate *fundamental interactions between ultrafast FEL pulses 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 timescales, 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 European 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 the results completed this past year and plans for the immediate future.

Recent Progress

1. Unveiling hidden isomers in ultrafast molecular processes using time-resolved photoelectron spectroscopy with the LCLS high repletion rate FEL.

We led in the spring of 2024 the ultrafast isomerization experiment in acetonitrile (CH_3CN) since calculation by the group of Fernando Martin (Spain) predicted that upon excitation, this linear molecule undergoes isomerization into cyclic and more complex linear conformers before reaching its final state. Proof of the existence of the predicted isomers has not been reported in earlier experiments. Using time-resolved X-ray photoelectron spectroscopy and spectral domain ghost imaging techniques, we planned to resolve the isomeric states temporally and spectrally and as a result, hope to determine the timescales of the underlying process. The LCLS delivered successfully 8.3 kHz high repetition rate, which combined with precision spectroscopic methods offered an ideal means to investigate such novel processes. We performed the first LCLS high-rep rate time-resolved X-ray photoelectron spectroscopy measurements in acetonitrile using an IR pump −X-ray probe. Specifically, CH_3CN was irradiated by an intense IR pulse (800 nm), which created an ionic state in the molecule. The acetonitrile cation can go next through different isomeric states. A time-delayed X-ray probe pulse ($h\nu$=525 eV) was used to directly ionize N(1s) electrons, allowing us to examine the chemical shifts from isomerization on the specific elemental site. Our experiment, conducted with James Cryan's team, was very successful! The data is currently being analyzed by my student and postdoc with the state-of-the-art analysis tools such as spooktroscopy developed at the SLAC PULSE institute. Our collaboration with James's Cryan team is essential since they are guiding my UConn team with the use of the new analysis tool.

2. Fragmentation dynamics of fullerenes upon extreme electronic excitation near the giant resonance with XUV free-electron laser pulses.

Fullerenes are paradigmatic in understanding energy absorption and dissipation in large molecules which often exhibit complex interplay of single- and many-body phenomena. Their strong coupling between dense electronic states and phonon modes leads to complex energy absorption and relaxation pathways. To explore these processes, we leveraged the collective resonance of C_{60} to deposit a large amount of energy through intense XUV radiation over ultrashort timescales. Using a single-color pump-probe scheme, energy redistribution in the system was measured through the kinetic-energy spectra of both light and heavy ionic fragments as a function of the pump-probe delay. We carried out the experiment using the FLASH-II XUV FEL pulses paired with a COLTRIMS.

Our investigation of the relaxation and fragmentation dynamics of gas-phase C_{60} allowed us to measure kinetic energy spectra of the ionic fragments as a function of the pump-probe delay, revealing the intricate interplay between Coulombic and molecular forces following intense energy absorption over ultrashort timescales via the giant plasmon resonance. The fragmentation dynamics are governed by a transient nanoplasma whose formation is corroborated by molecular dynamics simulations. Our theoretical modeling revealed the formation of a transient nanoplasma, which explains the distinctive delay dependence of the doubly charged carbon yield and is also consistent with the Wigner threshold behavior observed in the kinetic-energy distributions of monomer and dimer ions.

The underlying model also identifies the total number of absorbed photons, which amounts to over half a keV of electronic energy. We expect that the features identified in this work and the underlying mechanisms to be of a rather general nature when a substantial amount of energy is deposited into a large molecular system over a short time. This is particularly important for heterogeneous systems where the excess energy can efficiently be transferred to lighter fragments. Additionally, the photon-energy regime near the ionization threshold is particularly interesting, albeit challenging, from a theoretical perspective since the highly excited electrons and nuclear dynamics take place on roughly the same time scales. Similar phenomena are expected in larger molecular systems consisting of heavy and light atoms. Our submitted manuscript is under review with Phys. Rev. Lett.

<u>Future Plans.</u>

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 between molecular dissociation and ring opening in 2-bromothiophene (C_4H_3BrS) as a function of UV excitation wavelength, probed by UED. **2.** Analyze the data from the first LCLS experiment using the high repetition rate of 8.23 kHz. The experiment consisted of revealing in CH_3CN hidden isomers using time-resolved photoelectron spectroscopy. **3)** Finish the analysis of the time-resolved experiment we conducted during our granted FEL beamtime at the FERMI FEL facility. The experiment consisted of investigating intermolecular interactions of molecular iodine solvated in small water clusters. **4)** We had planned to carry out an experiment to map out the UV-induced dissociation of water molecules and measure the hydroxyl radical formation in real time using the EUXFEL's COLTRIMS in May 2024. Our beamtime proposal was accepted, however, the side of the COLTRIMS spectrometer important for the experiment was not working when we arrived at XFEL. Instead, we were able to conduct another experiment we had proposed which was also accepted. This experiment consisted of unraveling electronic and nuclear dynamics through X-ray resonance enhanced multiphoton ionization (X-REMPI) of several molecules such as CO, CO_2 and O_2. We capitalized on site- and element-selective spectroscopy to study molecular multiphoton ionization, fragmentation and charge redistribution, not explored previously. This experiment was successful. It also prepared us to use, the high rep rate and the COLTRIMS named DREAM at LCLS-II.

Peer-Reviewed Publications Resulting from this Project (2022-2024).

1. E. Wang, N. G. Kling, A. C. LaForge, R. Obaid, S. Pathak, S. Bhattacharyya, S. Meister, F. Trost, H. Lindenblatt, P. Schoch, M. Kubel, A. Rudenko, T. Pfeifer, S. Dıaz-Tendero, F. Martin, R. Moshammer, D. Rolles, and N. Berrah, "Probing ultrafast roaming mechanisms in ethanol: electron transfer versus proton transfer", J. Phys. Chem. Lett. 14, (18), 4372–4380 (2023).

2. Taran Driver, Miles Mountney, Jun Wang, Lisa Ortmann, Andre Al-Haddad, Nora Berrah, Christoph Bostedt, Elio G. Champenois, Louis F. DiMauro, Joseph Duris, Douglas Garratt, James M. Glownia, Zhaoheng Guo, Daniel Haxton, Erik Isele, Igor Ivanov, Jiabao Ji, Andrei Kamalov, Siqi Li, Ming-Fu Lin, Jon P. Marangos, Razib Obaid, Jordan T. O'Neal, Philipp Rosenberger, Niranjan H. Shivaram, Anna L. Wang, Peter Walter, Thomas J. A. Wolf, Hans Jakob Wörner, Zhen Zhang, Philip H. Bucksbaum, Matthias F. Kling, Alexandra S. Landsman, Robert R. Lucchese, Agapi Emmanouilidou, Agostino Marinelli & James P. Cryan, "Attosecond delays in X-ray molecular ionization", Nature, 632, 762, (2024).

3. Zhaoheng Guo, Taran Driver, Sandra Beauvarlet, David Cesar, Joseph Duris, Paris L. Franz, Oliver Alexander, Dorian Bohler, Christoph Bostedt, Vitali Averbukh, Xinxin Cheng, Louis F. DiMauro, Gilles Doumy, Ruaridh, Forbes, Oliver Gessner, James M. Glownia, Erik Isele1, Andrei Kamalov, Kirk A. Larsen, Siqi Li, Xiang Li1, Ming-Fu Lin, Gregory A. McCracken, Razib Obaid, Jordan T. O'Neal, River R. Robles, Daniel Rolles, Marco Ruberti, Artem Rudenko, Daniel S. Slaughter, Nicholas S. Sudar, Emily Thierstein, Daniel Tuthill, Kiyoshi Ueda, Enliang Wang, Anna L. Wang, Jun Wang, Thorsten Weber, Thomas J. A. Wolf, Linda Young, Zhen Zhang, Philip H. Bucksbaum, Jon P. Marangos, Matthias F. Kling, Zhirong Huang, Peter Walter, Ludger Inhester, Nora Berrah, James P. Cryan, and Agostino Marinelli, "Experimental Demonstration of

Attosecond Pump-Probe Spectroscopy with an X-ray Free-Electron Laser" Nature Photonics, Nature Photonics, 18, 691–697 (2024) 18ISSN 1749-4885 DOI: https://doi.org/10.1038/s41566-024-01419-w · OSTI ID:2340110

4. Oliver Alexander, Felix Egun, Laura Rego, Ana Martinez Gutierrez, Douglas Garratt, Gustavo Adolfo Cardenes, Juan J. Nogueira, Jacob P. Le, Kaixiang Zhao1, Ru-Pan Wang, David Ayuso, Jonathan C. T. Barnard, Sandra Beauvarlet, Philip H. 5 Bucksbaum, David Cesar, Ryan Coffee, Joseph Duris, Leszek J. Frasinski, Nils Huse, Katarzyna M. Kowalczyk, Kirk A. Larsen, Mary Matthews, Shaul Mukamel, Jordan T. O'Neal, Thomas Penfold, Emily Thierstein, John W. G. Tisch, James R. Turner, Josh Vogwell, Taran Driver, Nora Berrah, Ming-Fu Lin, Georgi L. Dakovski, Stefan P. Moeller, James P. Cryan, Agostino Marinelli, Antonio Picón Jonathan P. Marangos, "Attosecond Impulsive Stimulated X-ray Raman Scattering in Liquid Water" (in press Science Advances").

5. Niels Breckwoldt, Sang-Kil Son, Tommaso Mazza, Aljoscha Rörig, Rebecca Boll, Michael Meyer, Aaron C. LaForge, Debadarshini Mishra, Nora Berrah, and Robin Santra, "Machine-learning calibration of intense X-ray free-electron-laser pulses using Bayesian 2 optimization" Phys. Rev. Research 5, 023114 22 May (2023). DOI: 10.1103/PhysRevResearch.5.023114.

6. A. R. Abid, S. Bhattacharyya, A. S. Venkatachalam, S. Pathak, K. Chen, H. Van Sa Lam, K. Borne1, D. Mishra, R C. Bilodeau, I. Dumitriu, A. Rudenko, N. Berrah, M. Patanen, D. Rolles, "Hydrogen migration in inner-shell ionized halogenated cyclic hydrocarbons" Scientific Reports, 13, 2107 (2023). https://doi.org/10.1038/s41598-023-28694-x

7. C. LaForge, J. D. Asmussen, B. Bastian, M. Bonanomi,C. Callegari, S. De, M. Di Fraia, L. Gorman, S. Hartweg, S. R. Krishnan, M. Kling, D. Mishra, S. Mondal, A.Ngai, N. Pal, O. Plekan, K. C. Prince, P. Rosenberger, E. Serrata, F. Stienkemeier, N. Berrah, and M. Mudrich, "Relaxation dynamics in excited helium nanodroplets probed with high resolution, time-resolved spectroscopy", PCCP 24, 28844 (2022).

8. N. Berrah, "Probing C_{60} Fullerenes From Within Using Free Electron Lasers", Atoms, 10, 75 (2022).

9. Siqi Li,Taran Driver, Philipp Rosenberger, Elio G. Champenois, Joseph Duris, Andre Al-Haddad, Vitali Averbukh, Jonathan C. T. Barnard, Nora Berrah, Christoph Bostedt, Philip H. Bucksbaum, Ryan Coffee, Louis F. DiMauro, Li Fang, Douglas Garratt, Averell Gatton, Zhaoheng Guo, Gregor Hartmann, Daniel Haxton, Wolfram Helml, Zhirong Huang, Aaron C. LaForge, Andrei Kamalov, Jonas Knurr, Ming-Fu Lin, Alberto A. Lutman, James P. MacArthur, Jon P. Marangos, Megan Nantel, Adi Natan, Razib Obaid, Jordan T. O'Neal, Niranjan H. Shivaram, Aviad Schori, Peter Walter, Anna Li Wang, Thomas J. A. Wolf, Matthias F. Kling, Agostino Marinelli, James P. Cryan, " Real-time Observation of Coherent Electron Motion by Attosecond Streaking of Auger-Meitner Decay", Science 375, 285–290 (2022).

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

Award Number DE-SC0014170

PI: Martin Centurion
Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588-0299
martin.centurion@unl.edu

Program Scope or Definition

This project aims to investigate photochemical reactions at the molecular level by observing how the molecular structure changes upon light absorption. The project relies on ultrafast electron and X-ray diffraction to image photo-induced reactions in isolated molecules with atomic resolution. A sample of molecules in the gas phase is excited by a femtosecond laser pulse, and the structure is probed by a femtosecond electron or X-ray pulse. The scattering pattern contains information on the structure of the molecule, which reveals the nuclear motions triggered by the laser excitation and captures 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 user facility at SLAC National Lab. This RF photoelectron gun produces femtosecond electron pulses in an energy range between 2 MeV and 5 MeV, with a repetition rate of 360 Hz. At the initial stages of the facility development we collaborated with the SLAC team in the development of the instrument. 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. 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 provides very high temporal resotluion and will be complementary to the UED measurements.

Recent Progress

Over the last year of this project, we have carried out two UED experiments at UNL and one X-ray scattering (XRS) experiment at LCLS. We performed a UED experiment on aligned photoexcited trifluoroiodomethane (CF_3I) molecules. In this experiment we demonstrate, for the first time, the capability to pre-align molecules with an IR laser pulse, then excite them with a UV pulse, and probe the structural dynamics with an electron pulse. Carrying out an align-pump-probe experiment has been a long-standing goal, as it has the potential to provide much more information about the structural dynamics than standard UED experiments from randomly oriented molecules. We also continue working towards extending our UED technique to study ionized molecules and carried out first measurements on the dynamics of dicyclopentadiene following ionization. These experiments are currently ongoing. We successfully carried out an X-ray scattering experiment at LCLS on the photodissociation of diiodomethane (CH_2I_2). The beam time provided high quality data at two different excitation wavelengths which is currently being analyzed. In addition to the experiments, we have continued to work on a genetic algorithm structure retrieval code. We published the results of a prior experiment on o-nitrophenol and are currently writing manuscripts for publication on two other experiments on stilbene and brommocyclopropane. We are also continuing the data analysis and interpretation of an experiment carried out last year on iodobenzene.

Align-pump-probe UED measurement. We have previously shown that diffraction from aligned molecules provides significantly more information than diffraction from randomly oriented molecules, and that three-dimensional structural information becomes accessible. A goal for some time has been to add alignment to UED studies of photoexcited molecules. We have carried out a proof-of-principle align-pump-probe experiments on the UV photodissociation of CF_3I. The molecules were first impulsively aligned using an IR femtosecond pulse. A second pulse arrives after a time delay of approximately 600 fs, when the alignment is reaching its peak value. A crucial point here is that by using impulsive alignment, we guarantee that the IR pulse is no longer present when the molecules are photoexcited by the UV pulse. The UV pulse in this experiment triggers the photodissociation of into CF_3+I. We carried out three measurements: IR only to characterize the alignment dynamics, UV-only as a reference measurement, and IR+UV. The IR+UV shows a higher excitation percentage compared to the UV-only measurement with the same UV laser power. This is due to pre-alignment of the transition dipole moment of the molecule with the polarization direction of the UV laser pulse. We also see a significantly stronger difference signal in the angularly dependent pair distribution function in the case of alignment, which is a key for retrieving three-dimensional structural information. The analysis and interpretation of this experiment is still on-going.

X-ray scattering at LCLS on the photodissociation dynamics of CH_2I_2. The photodissociation of this molecule as previously been studied using UED and transient absorption spectroscopy (TAS)[1,2]. The TAS measurements at 330 nm excitation observed changes in the signal that were interpreted as the formation of a CH_2I-I isomer through roaming of the iodine atom. The UED experiments, carried out at an excitation wavelength of 266 nm, did not observe the formation of the isomer. The discrepancy can be explained in multiple ways. It is possible that the UED measurement did not capture the isomer formation due to limited time resolution (150 fs), or that the roaming channel does not have a significant yield at 266 nm. Another possibility is that the spectral changes captured in the TAS data, which is not directly sensitive to structure, are not due to the formation of the isomer. The goal of our XRS experiment is to resolve shed light on the initial dynamics of the reaction, for which XRS is ideally suited since it has a high time resolution of ~50 fs and is directly sensitive to the nuclear motion. Our preliminary analysis of the data reveals a fast dissociation as the main channel, in good agreement with theoretical calculations from the group of Todd Martinez. The data analysis is still ongoing to determine if there are other minor channels in addition to the direct dissociation, which seems to be the dominant channel.

UED on the structural dynamics and fragmentation of ionized dicyclopentadiene. We have carried out first time-resolved measurements to captured the dynamics of dicyclopentadiene after ionization. This sample was previously studied by the Dantus group using time-resolved mass spectrometry, which revealed pre-fragmentation dynamics on the time scale of several hundred femtoseconds[3]. The goal of this experiment is to determine the nuclear motions that take place before the molecule breaks apart. The sample has a low vapor pressure and is a liquid (gel) at room temperature. This required some modifications of our sample delivery manifold to operate a higher temperatures, and the introduction of a cold trap below the nozzle to minimize sample contamination of the target chamber and the detector. We have reached stable operating conditions for sample delivery, captured static diffraction patterns, established the excitation conditions and acquired preliminary time-resolved data on the picosecond time scale. The data acquisition for time-resolved data on the femtosecond scale is on-going.

Hybrid Genetic Algorithm fitting for structure retrieval. We have previously demonstrated the use of a genetic algorithm (GA) for retrieving structural dynamics [see JPF Nunes et al, PCCP 2024 in the publication list below]. However, the standard GA method is mostly limited to reactions with a single reaction channels. For the case of multiple reaction channels and/or multiple end-products, the standard procedure is to use fitting methods that rely on theoretical structures to produce basis functions. These methods can capture the relative yield of end products and determine the time at which different products appear. However, they have two main limitations due to the use of calculated end-product structures as basis functions: i) It is challenging to capture the nuclear motions in the transition state since the transient structures do not match the basis functions, and ii) It can potentially miss structures not predicted by the calculations. We are currently developing a hybrid method where we combine theoretically predicted diffraction signals of end-product structures with a GA to identify the early time dynamics and to determine the presence of products not predicted by the calculations.

Progress in other projects: Our work on the structural dynamics of o-nitrophenol was published and featured on the cover of the journal Phys Chem Chem Phys. We are drafting a manuscript on the results of two prior MeV-UED experiments carried out at SLAC. The first is on the dynamics of stilbene after a 2-photon excitation with a UV pulse into an ionic state. The second is on the investigation of the photodissociation of bromocyclopropane, where we have determined that the reaction produces mostly a ring-closed end-product, in good agreement with theory. We are also continuing with the data analysis and interpretation of the UV dissociation of iodobenzene, after acquiring carrying out the UED experiment UNL last year. In this experiment we are observing mostly a slow dissociation channel with a lifetime of several hundred femtoseconds.

Future plans

We have received beam time to carry out an X-ray scattering experiment at LCLS in December/2024 to study the photochemistry of bromoform. Prior UED experiments at SLAC led by the group of Oliver Gessner at LBNL have observed the formation of a long lived iso-$CHBr_3$ structure. The goal of the XRS experiment is to capture the structural dynamics leading to the formation of this product which could not be time-resolved during the UED experiment. We will complete the UED experiments on dicyclopentadiene at UNL and carry out the data analysis. We will complete the data analysis and prepare manuscripts on the projects described in the previous section.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

1. M. Centurion, T. J.A. Wolf, J. Yang, "Ultrafast Imaging of Molecules with Electron Diffraction" *Annual Review of Physical Chemistry* 73 21 (2022). DOI: https://doi.org/10.1146/annurev-physchem-082720-010539

2. Y. Xiong, K. J. Wilkin, S. K. Saha, S. B. Muvva, H. Zhao, M. Centurion, "Retrieval of the molecular orientation distribution from atom-pair angular distributions" *Physical Review A* 106, 033109 (2022). DOI: https://doi.org/10.1103/PhysRevA.106.033109

3. W. O. Razmus et al, "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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5. Y. Liu et al., "Rehybridization dynamics into the pericyclic minimum of an electrocyclic reaction imaged in real-time" *Nature Commun.* 14, 2795 (2023). DOI: https://doi.org/10.1038/s41467-023-38513-6

6. E. G. Champenois, et al, "Femtosecond Electronic and Hydrogen Structural Dynamics in Ammonia Imaged with Ultrafast Electron Diffraction" *Phys. Rev. Lett.* 131, 143001 (2023). DOI: https://doi.org/10.1103/PhysRevLett.131.143001

7. J. P. F. Nunes, M. Williams, J. Yang, T. J. A. Wolf, C. D. Rankine,R. Parrish, B. Moore, K. Wilkin, X. Shen, Ming-Fu Lin, K. Hegazy, R. Li, S. Weathersby, T. J. Martinez, X. J. Wang, and M. Centurion, "Photo-induced structural dynamics of o-nitrophenol by ultrafast electron diffraction" *Phys. Chem. Chem. Phys.* 26, 17991 (2024), DOI https://doi.org/10.1039/D3CP06253H

8. K. Hegazy et al., "Tracking dissociation pathways of nitrobenzene via mega-electron-volt ultrafast electron diffraction" *J. Phys. B*. 57 195101 (2024), DOI 10.1088/1361-6455/ad7431.

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

Award number DE-SC0020276

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

[1]Department of Physics and Astronomy, University of Nebraska, Lincoln, NE 68588-0299, *martin.centurion@unl.edu*
[2]Department of Chemistry, Brown University, Providence, R.I. 02912
[3]Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford OX1 3QZ
[4]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803
[5]J.R. Macdonald Laboratory, Department of Physics, Kansas State University, Manhattan, KS, 66506

Program Scope or Definition

This project, which started on August 15, 2019, is in collaboration with the groups of Daniel Rolles and Artem Rudenko at Kansas State University, Peter Weber and Adam Kirrander at Brown University, and Kenneth Lopata at Louisiana State University. A series of ultrafast photo-triggered ring-opening and ring-closing reactions are investigated, with the goal of developing general rules that can be applied to understand and predict the outcome of a large class of reactions. We 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 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. The third and last two-year period focuses on investigating methylated cyclopentadienes and carrying out additional experiments and calculations to resolve unknown aspects of the reactions investigated so far. 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. In order to support our time-resolved studies of the interconversion reaction, which we performed in the last cycle (specifically the TRPES experiment at FERMI, whose results, combined with extensive ab initio electronic structure and dynamics calculations, are now published [Pub. 9]; and the MeV-UED experiments summarized below in section I.2), we have investigated the UV and XUV absorption spectra of NB and QC using high-resolution Fourier transform absorption spectroscopy at the SOLEIL synchrotron.

I.1 High-resolution UV and XUV absorption spectra of norbornadiene and quadricyclane

The key experimental results from the SOLEIL measurement, including absolute photoabsorption cross sections and the assignments from our supporting calculations, are shown in Fig. 1. The experiment yielded rich information on the valence-shell electronically excited states that were crucial for interpreting our time-resolved data and for guiding our electronic structure calculations. The absorption spectrum of NBD exhibits sharp structure associated with transitions into Rydberg states, superimposed on several broad bands attributed to valence excitations. Similar transitions into Rydberg states, although much less pronounced, and broad valence-excitation bands also appear in the absorption spectrum of QC. Assignments have been proposed for some of the absorption bands using calculated vertical transition energies and oscillator strengths for the electronically excited states of NBD and QC [Pub. 8].

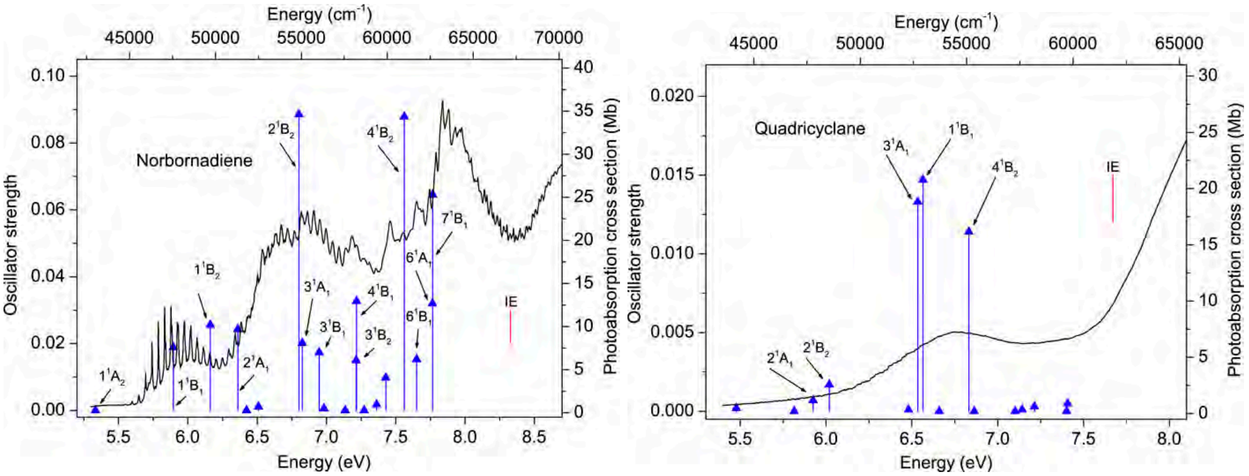

Figure 1: High-resolution absorption spectra of NBD (left) and QC (right) measured at the SOLEIL synchrotron. The absolute photoabsorption cross sections (right-hand scale) are shown together with the theoretically predicted electronic transitions, plotted as vertical sticks using the calculated vertical excitation energies and oscillator strengths (left-hand scale). The adiabatic ionization energies (IE) for each molecule are also indicated. Figure adapted from Pub. 8.

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. Over the past year, we have completed the analysis of the UED data and we are currently drafting a manuscript. The UED data captured a signal at low scattering angles corresponding to excitation to states with Rydberg character, which decays on a time scale of a few hundred femtoseconds. This electronic signal provides an experimental time-zero and thus allows us to accurately determine the time delay between excitation and nuclear motions. Interestingly, the structural changes are delayed with respect to excitation by several hundred femtosecond and coincide with the time at which the electronic signal decays. Through comparison with simulations and the previous TRPES measurements, we interpret this as the molecule undergoing the conversion from QC to NBD only as it traverses the CI and reaches the ground state. The timescale for structural changes matches the slower dynamics identified in the TRPES measurements.

Both the TRPES and MeV-UED experiments have captured data at longer delays up to approximately 100 ps. These data show that the signal continues to change, most likely due to fragmentation of the molecules in the ground state. The interpretation of these data has proven challenging due to the large number of possible fragments. We plan to work on the interpretation of these longer time signals over the next year.

II. 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)[Brauman66, VanTemelen71] and tricyclo[2,1,0,02,5]pentane (TP)[Andrews77]. We have expanded this investigation to include also the methylated derivatives tetramethyl cyclopentadient (TMCP) and pentamenthyl cyclopentadient (PMCP). We will investigate how the addition of the methyl groups affects the dynamics and the yield of the ring-closing reaction.

II.1. Ultrafast X-ray scattering of CP. The results of the X-ray scattering experiments were analyzed and published (see Huang et al, JPCA 2024 in the publication list). This experiment determined reaction kinetics over the first few picoseconds and 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$_4$H$_x$ and CH$_{6-x}$.

III.2. UED experiments on CP, TMCP and PMCP. We have successfully carried out UED measurements on all three molecules. CP and TMCP were investigated during a beamtime at the SLAC MeV-UED facility, while the PMCP data was acquired using the UED instrument at UNL. We also have supporting theory on the dynamics of CP and the calculated diffraction observable. Figure 2(a-b) shows the experimental and theoretical difference diffraction signals, respectively. We have found very good agreement between the experimental and calculated patterns. Fitting of the UED data to predicted signals from different end products revealed yields of 0.42±0.20 % for hot CP, 0.50±0.19 % for the formation of BP and 0.07±0.04 % for the formation of a ring-opened product. This compares well with the predicted yields of 55 %, 44% and 0.2% for CP, BP, and the

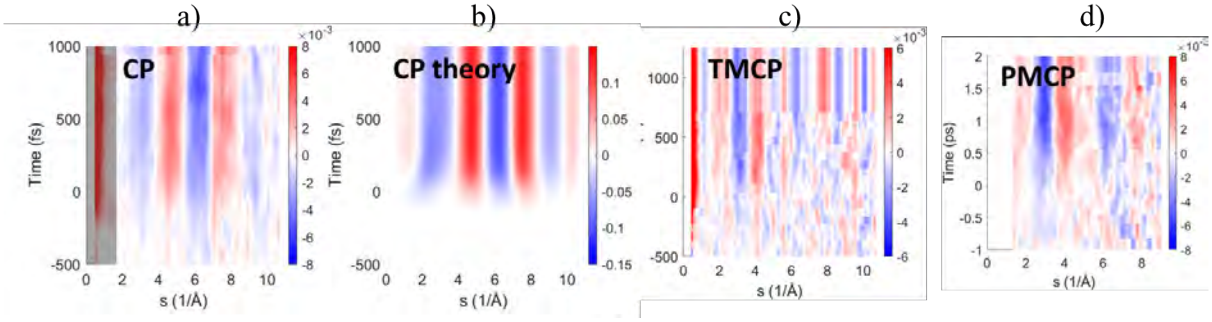

Figure 2: UED difference diffraction signals. a) UED data acquired for cyclopentadiene. b) Theoretically predicted UED signal for cyclopentadiene. c) UED data acquired for tetramethyl-cyclopentadiene. d) UED data acquired for pentamenthyl-cyclopentadiene.

ring-opened product, respectively. Within uncertainties, both experiment and theory capture comparable yields of CP and BP, with only minor contributions from other channels. The calculations showed the ring closing reaction taking place in approximately 50 fs, so the dynamics were not captured due to the limited time resolution of 150 fs.

Figure 2(c-d) shows the difference diffraction signal collected for TMCP and PMCP. The first thing that is obvious from these data is that the dynamics are slower, with the signals changing over several hundred femtoseconds. One could imagine that the higher density of states in the methylated molecules would lead to faster relaxation dynamics, while on the other hand the increased mass and moment of inertia would slow the reaction down. Clearly the former effect is more relevant here as the reaction is significantly slower compared to CP. Our preliminary analysis of these data suggests a ring-closing reaction takes place in TMCP with a yield comparable to CP, but with the nuclear motions slowed down to several hundred femtoseconds. First analysis of the PMCP data suggest that the ring-closing reaction is inhibited by the addition of the fifth methyl group. These are however very preliminary observations and more work is needed before reaching any firm conclusions.

II.3. TRPES measurements on TMCP and PMCP. We have also previously acquired TRPES data on the rection dynamics of TMCP and PCMP at the FLASH FEL facility in Hamburg. These measurements were complemented by time-resolved mass spectrometry at 266 nm at KSU. These data will provide a different perspective on the reaction dynamics and will be analyzed in parallel with UED data.

III. Distinguishing 3D molecular structures with Coulomb explosion imaging

In addition to 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.

III.1 Coulomb explosion imaging of toluene and other C_7H_8 isomers

In the first cycle of our EPSCoR grant, we studied the strong-field induced fragmentation and isomerization of toluene using ultrafast

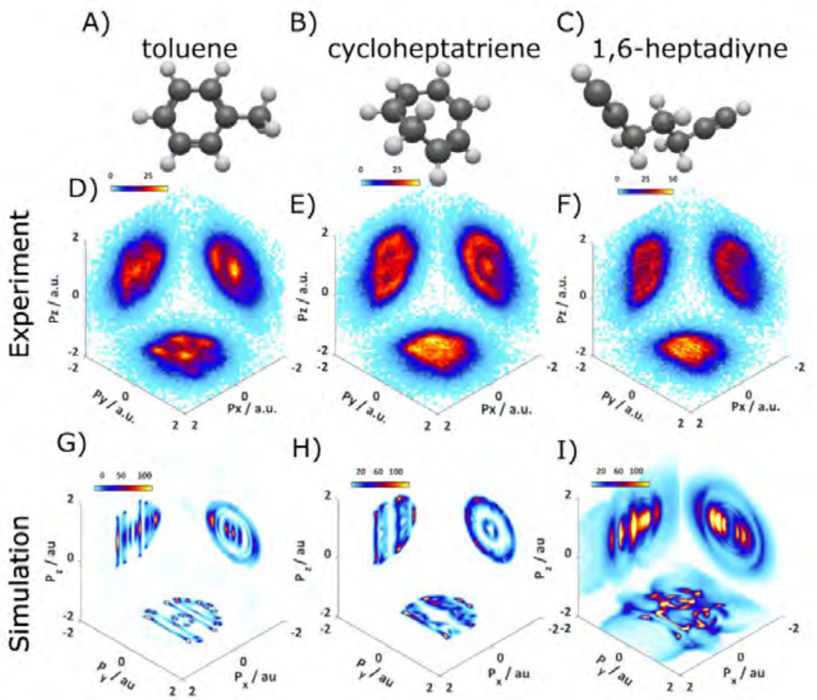

Figure 3: Molecular geometries and Newton plots of toluene (A), cycloheptatriene (B), and 1,6-heptadiyne (C). (D-F) Experimental Coulomb explosion imaging results represented as three-dimensional Newton plots. G-I) Simulated Newton plots, summed over all possible molecular reference frames that are included in the experimental results. Figure taken from Ref. [Borne24].

femtosecond electron diffraction and mass spectrometry [Xiong21]. As a next step, we also performed a Coulomb explosion imaging (CEI) experiment at the European XFEL, with the goal to determine if CEI is able to distinguish toluene from several of its isomers, notably cycloheptatriene and 1,6-heptadiyne (see Fig. 3).

Compared to some of our earlier CEI work on complex molecules, e.g. Pubs. 3 and 20, CEI of toluene and its isomers is complicated by the fact that the molecules only consist of carbon and hydrogen constituents, i.e., they do not include any unique "marker" atoms that can be used for orienting the molecular frame. The "traditional" Newton plots obtained from the experiment are therefore sums over all possible reference frames that can be constructed by using the emission direction of any one carbon as the reference for the x-axis. This situation can be modeled via classical Coulomb explosion simulations, which produce qualitatively similar patterns that are, however, difficult to interpret in terms of molecular geometries. As part of his PhD thesis, graduate student Kurtis Borne from KSU investigated if additional information available from the momentum-resolved ion coincidence experiment can be used to identify fragment ions originating from specific positions in the molecule in order to overcome the ambiguity in the definition of the above Newton plots. We found that sorting the data based on the relative angle between pairs of carbon ion momentum vectors can indeed reduce some of this ambiguity and lead to Newton plots that are easier to interpret, although some averaging over a subset of molecular reference frames cannot be avoided [Borne24].

IV. Quantitative X-ray scattering

X-ray scattering is an almost unique method in that it provides quantitative measurements about molecular electron density distributions. This is because the X-ray scattering signal of a gas phase molecule is only dependent on the number and spatial distribution of its electrons. Consequently, X-ray scattering finds important applications in the measurement of chemical reaction dynamics, the quantitative evaluation of kinetics networks, and the benchmarking of electron density distributions for the verification of computational codes.

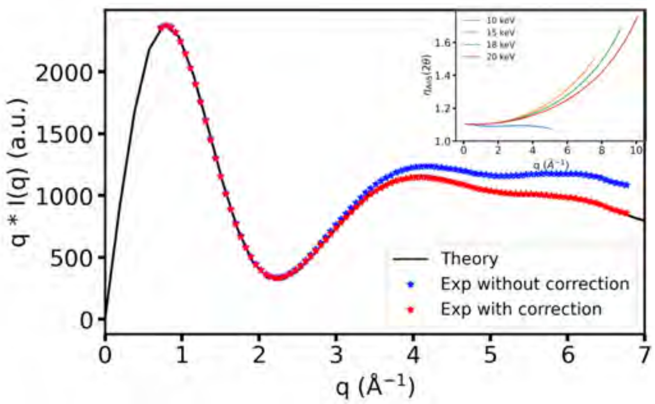

Figure 4: The raw experimental data, blue stars, deviates from the computed scattering patterns especially at large values of the scattering vector. Application of the combined angle-of-scattering corrections, $\eta_{AoS}(2\theta)$, inset, recovers X-ray patterns that can be quantitatively compared to theory. The correction factor depends on the photon energy and is shown for 10, 15, 18, and 20 keV.

But before such quantitative analyses can be conducted, it is necessary to correct the raw data by removing artifacts stemming from the experimental measurement. In a manuscript currently in print [Pub. 1], we derived corrections that need to be applied to the experimental data, including angle-of-scattering effects arising from the geometry of the scattering cell, the effusion of gas through the pinholes through which the X-rays enter and exit the cell, the sensitivity of the detector as a function of the angle of the incident radiation and the transmission of the beryllium window of the scattering cell. Combining these effects results in a substantial correction factor, especially at large scattering vectors, Figure 4. The figure shows the experimentally measured scattering pattern of SF_6 with 15.3 keV photons. Without the corrections, blue data points, there are significant deviations between the measurement and the theory. Application of the corrections results in an excellent agreement between the experimental scattering pattern and the computed one, red, in this molecular system as well as in several other gases.

V. Attosecond X-ray scattering

V.1 Scattering from attosecond electron fluxes

Over the last year we continued our simulation work using hard X-ray scattering to probe attosecond dynamics, in order to motivate potential XFEL measurements of electronic currents during the very fast initial processes involved in ring-opening. Since scattering is most sensitive to time-evolving divergent electron current fluxes, it is an especially useful probe for systems containing rings. It is also well-suited to systems without heteroatoms (purely carbon and hydrogen), which are difficult to measure using inner-shell transient absorption due to the nearly equivalent carbon atoms. Our previously reported results in ultraviolet-pumped carbon monoxide show that scattering peak shifts, intensities, and widths all encode information about the electronic processes, but interpretation of simulated scattering signals is difficult even in the diatomic case. More complex systems we studied, like core-hole pumped oxazole, benzene, and aminophenol, are even more challenging due to the complex spatial short and long-range current flows in the molecule.

In the last year, we focused on determining the specific origins of scattering pattern shifts in terms of the instantaneous currents, i.e., electrons moving in what region(s) of a molecule cause these scattering shifts? To reduce the prohibitively large amount of storage required for storing 4D (x,y,z,t) volumetric data, we completed development of the “dvis” module in the NWChem computational chemistry package, which allows for computation of densities and currents from a time-dependent density fuctional theory (TDDFT) simulation in parallel. This does calculation of high-resolution densities and currents in parallel (distributed over multiple compute nodes, and over processes per node), as well as analyses such as integration over arbitrary sub-regions, orbital-decomposition, and vector analysis of fluxes, without requiring any volumetric data to be written to disk. Moreover, this allows for density/current grids with $>10^9$ points, which helps remedy artifacts in the scattering due to grid discretization. For the TDDFT, as with our previous studies, we used a UV-like sudden excitation and a time-derivative ansatz for the scattering. Simulations of benzene and derivatives are ongoing, with preliminary results suggesting that computing the scattering arising from different regions of the molecule, as well as from particular molecular orbital contributions (e.g., pi orbitals) are a promising way of interpreting the scattering. Going forward, it is expected that these tools and ideas will be helpful when used in conjunction with an improved description of coherent scattering (in progress).

V.2 Nonadiabatic Transitions

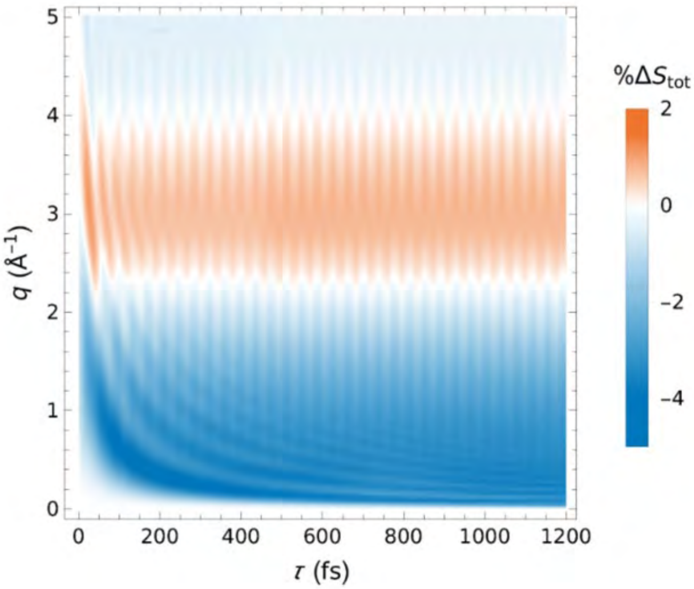

Figure 5. The total percent-difference scattering signals from photoexcited LiF molecules, probed by 10 fs duration hard X-ray pulses as a function of momentum transfer q and pump-probe delay time τ, based on accurate quantum dynamics simulations with quantitative x-ray scattering cross sections.

Nonadiabatic transitions at conical intersections and avoided crossings play a pivotal role in shaping the outcomes of photochemical reactions. Using the photodissociation of LiF as a model, we carried out a theoretical study to demonstrate how gas-phase nonresonant ultrafast x-ray scattering can map nonadiabatic transitions at an avoided crossing, utilizing a part of the scattering signal which probes electronic coherence directly. The predictions are based on numerically exact propagation of the LiF wavepacket and uses two- rather than one-electron densities, to obtain accurate scattering cross sections which inherently account for *all* possible electronic transitions. The results are shown in Figure 5. The calculations provide quantitative predictions of the experimental signals, thereby facilitating future experimental endeavors to observe nonadiabatic effects and coherent electron dynamics with ultrafast x-ray scattering [Pub. 4]. We have also continued to develop our computer codes for the accurate prediction of X-ray and electron scattering cross sections [Pub 25].

VI. Simulations for experiments

In 2023-24, we contributed two papers to the *Prediction Challenge* in the Journal of Chemical Physics for ultrafast electron diffraction measurements carried out on photoexcited cyclobutanone. The first paper demonstrated a new multistate mapping approach (MASH) for surface hopping and included a new electronic structure method known as selected-CI [Hutton24]. The second exploited the *ab initio* multiconfigurational Ehrenfest method for nonadiabatic nuclear dynamics [Makhov24]. We also developed efficient and accurate electronic structure models for the quadricyclane and norbornadiene to match the experimental studies carried out by our team. This included extensive benchmarking of advanced *state-of-the-art* electronic structure methods and the development of a custom basis [Pub. 8]. Furthermore, we have continued to develop inversion and data analysis tools. Recent results, shown in Figure 6, demonstrate how our algorithms can identify the main reaction mechanisms in complex photochemical reactions [Kara24].

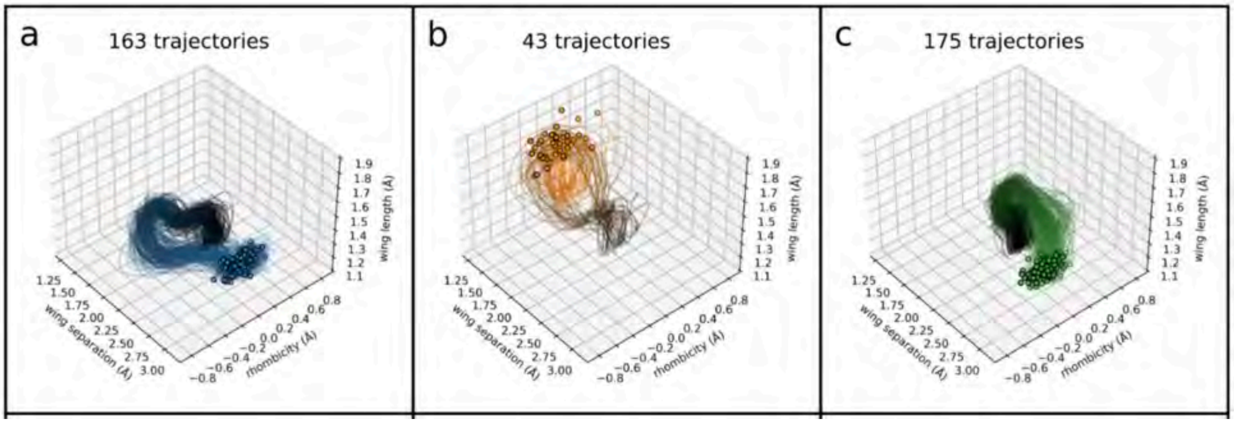

Figure 6. Different classes of trajectories for the nonradiative decay of photoexcited quadricyclane and norbornadiene, automatically identified using new clustering algorithms. These make it easier to recognize the key photochemical mechanisms in the simulations and enable more effective comparison to experimental data. The trajectories are represented in a suitable subspace of internal coordinates.

Future Plans

For the coming year, several experiments are already teed up. In December ’24 we will have one shift of LCLS beam time to explore the chemical dynamics of cyclopentadiene with 200 nm excitation, which will complement our experiments performed at longer wavelengths. In January 2025 we will be back at LCLS to explore ultrafast X-ray scattering experiments with strong field ionization in an effort to experimentally observe coherent mixed scattering signals, which the team has calculated theoretically. Finally, in February 2025, we will attempt a new type of X-ray scattering experiments at LCLS. We induce structural changes and ionization of molecules by a first X-ray pulse, and probe the dynamics with a time-delayed second X-ray pulse using X-ray scattering. While some specificity will be lost in the excitation scheme, the experiment promises to provide a time resolution of better than 10 fs. Our collaboration also submitted several new proposals for LCLS Run 24, some of which will hopefully be scheduled in 2025. We will also submit a proposal for the next gas phase run at the SLAC MeV-UED which is scheduled to start in the Summer of 2025.

In the laboratory at Brown University, work will continue on a new photoelectron spectrometer with an improved time resolution to match the one we aim for at LCLS. This entails commissioning a new spectrometer and generating few-fs light pulses using hollow core fibers. At KSU, a new 100-kHz laser system with a dedicated COLTRIMS end-station was installed and commissioned this summer, which we plan to use for time-resolved Coulomb explosion imaging experiments. The new laser also has a dedicated HHG source that we plan to use for TRPES experiments with superior temporal resolution. Computational and theoretical work will continue to focus on advanced quantum dynamics simulations, accurate prediction of observables, and the development of new data analysis tools.

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2. J. P. F. Nunes et al. “Monitoring the evolution of relative product populations at early times during a photochemical reaction”, J. Am. Chem. Soc. **146**, 4134 (2024). DOI: 10.1021/jacs.3c13046
3. H. V. S. Huynh et al. “Differentiating Three-Dimensional Molecular Structures using Laser-induced Coulomb Explosion Imaging”, Phys. Rev. Lett. **132**, 123201 (2024). DOI: 10.1103/PhysRevLett.132.123201
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6. L. Hutton et al. ‘Using a Multistate Mapping Approach to Surface Hopping to Predict the Ultrafast Electron Diffraction Signal of Gas-Phase Cyclobutanone’. The Journal of Chemical Physics (2024) 160 (20): 204307. https://doi.org/10.1063/5.0203667.

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

DOE Grant No. DE-SC0002325

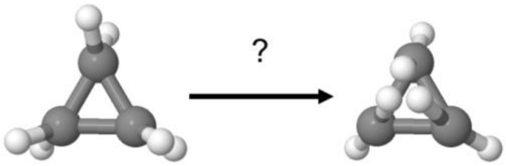
Marcos Dantus, dantus@msu.edu
Department of Chemistry and Department of Physics and Astronomy, Michigan State University, East Lansing MI 48824

Project Scope

Recent advances in our understanding of laser-matter interactions over the past two decades enable us to explore strategies for observing and controlling the various processes and reactions these interactions trigger. Our proposed research focuses on the chemical processes occurring in polyatomic molecules under intense laser excitation and aims to develop strategies for their control. This work aligns with the Grand Challenge questions in recent DOE and NSF-sponsored workshops. Additionally, this project enhances the chemical perspective within strong-field science, by examining interactions with larger molecular systems. During the last period, we collaborated on theoretical and experimental efforts to clarify the mechanism of H_3^+ formation from organic molecules. We focused on complex dissociative ionization processes in which isomerization occurs before fragmentation. To enhance our analysis of dissociative ionization, we introduced two methods: coherence mapping and non-commensurate bichromatic fields. Additionally, we authored invited reviews for *Accounts of Chemical Research* and *Science*. In the upcoming period, we will complete a project focused on the factors, beyond intensity, that control dissociative ionization using shaped laser pulses. We will also begin a project aimed at controlling the nascent wave packets on the dissociative continuum of IBr, to create interference at the avoided crossing that leads to the formation of I + Br and I + Br*. Preliminary experiments will be conducted at MSU, with additional experiments planned at LCLS, where X-rays will be used to image the dissociation process. Finally, we intend to investigate how wavelength and intensity affect the extent of multiphoton ionization and ionization resulting from tunnel ionization followed by inelastic electron rescattering in polyatomic molecules.

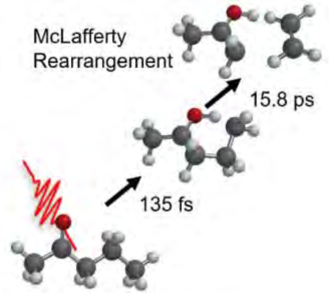
Recent Progress

(a) 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*, **127**, 8633-8638 (2023).



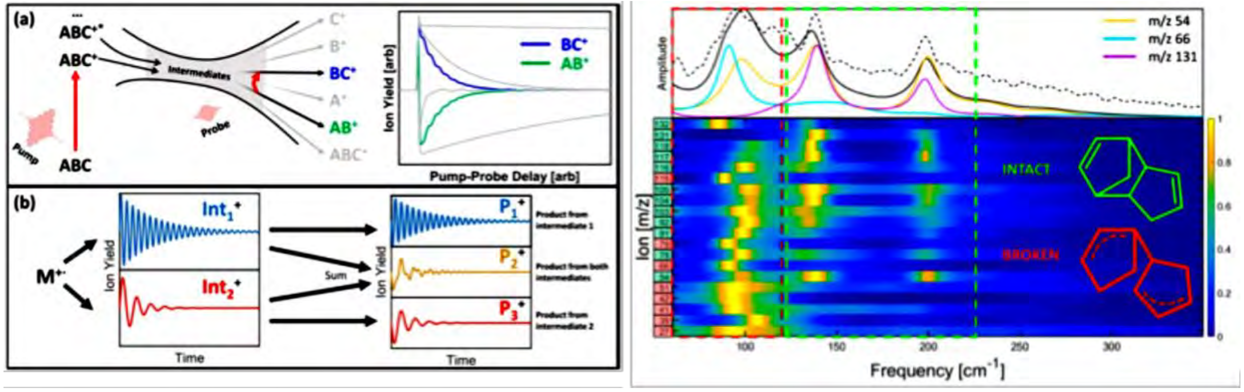
We completed an experimental and theoretical study to determine the mechanism of H_3^+ formation from cyclopropane. We examined a recently proposed mechanism in which three hydrogen atoms in one plane of the cyclopropane dication come together in a concerted 'ring-closing' mechanism to form H_3^+. Our time-resolved measurements indicate the formation time is 249 ± 16 fs, which does not align with the concerted formation. Further measurements on propene, an isomer of cyclopropane, reveal an H_3^+ formation time of 225 ± 13 fs, suggesting a similar timescale for both molecules. *Ab initio* molecular dynamics trajectories on the potential energy surface of these dications support a ring-opening mechanism. Upon ring opening, H-migration and H_2 formation take place. H_2 roams the dication before it abstracts a proton to yield H_3^+. These findings enhance our understanding of complex interstellar chemical reactions and reaction dynamics relevant to electron ionization mass spectrometry.

(b) The Surprising Dynamics of the McLafferty Rearrangement J. Stam, et al. *J. Phys. Chem. Letters,* **14**, 10088-10093 (2023).



The McLafferty rearrangement is a well-known fragmentation mechanism in mass spectrometry. It occurs in radical cations and involves a γ-hydrogen transfer to a double-bonded atom via a six-membered transition state, resulting in beta-bond cleavage and the formation of a neutral olefin. We measured the timescale of the McLafferty rearrangement reaction in 2-pentanone, 4-methyl-2-pentanone, and 4,4-dimethyl-2-pentanone. We found that the proton transfer occurs in 135 fs, while the π-electron rearrangement occurs after 16.5 ps. Examination of AIMD trajectories revealed the molecular wavefunction explores the multidimensional potential energy surface until it finds the transition state responsible for π-electron rearrangement and dissociation into an enol and olefin. This vibrational control of an ostensibly pure electronic motion parallels the Marcus theory of electron transfer. This surprising finding—that electron rearrangement occurs 120 times slower than molecular isomerization—reminds us that while molecular geometry at equilibrium is determined by electronic configuration, far from equilibrium electronic configuration depends on molecular geometry.

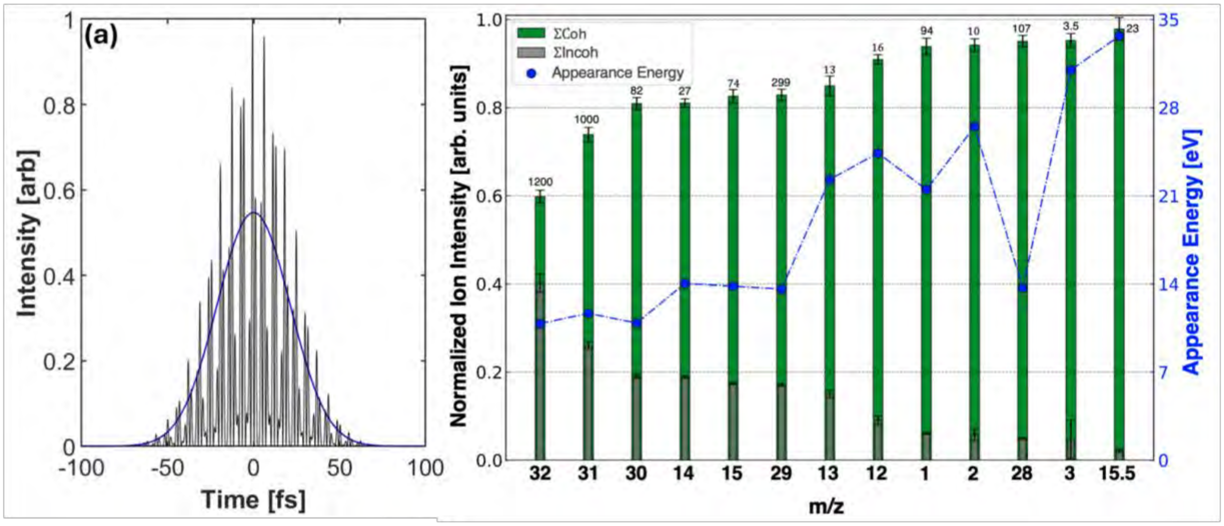
(c) Coherence mapping to identify the intermediates of multi-channel dissociative ionization J. Stamm, S. Kwon, S. Sandhu, J. Sandhu, B. Levine, M. Dantus, *Commun. Chem*. **7**, 103 (2024). During dissociative ionization, it can be challenging to determine whether a product forms via two independent pathways. To tackle this challenge, we introduced the coherence mapping method (see figure below). We isolate the vibrational coherence in the time-dependent data for each fragment ion. By applying the Fourier transform or maximum entropy method (MEM), we obtain a vibrational spectrum for each ion. The vibrational information allows us to create a coherence map, which helps identify short-lived intermediates. We applied this approach to the dissociative ionization of dicyclopentadiene and identified the intermediates leading to each fragment ion.



Coherence mapping for identifying reaction intermediates: (a) Upon ionization the radical cation breaks into tens of different fragment ions. (b) The residual oscillations in the time-resolved ion yields reveal which intermediate(s) a particular product originates from based on the vibrational signatures mapped onto their fragmentation products. (Right) The top panel shows the sum of all maximum entropy method (MEM) spectra (black solid line), the sum of all Fourier transforms (black dotted line), and three specific ion MEMs. The bottom panel shows the MEM spectra for all the ions. Each spectrum has been normalized and labeled with a colored box indicating if its dominant frequencies come from the broken DCPD (red), or a mixture of broken and intact DCPD (green).

(d) Enhanced strong-field ionization and fragmentation of methanol using non-commensurate fields E. Prieto, et al., accepted in *J. Phys. Chem. A*.

When two non-commensurate fields (not integer multiples of each other) with a 25%/75% ratio of 800 and 1400 nm wavelength pulses are overlapped, we observe that, for the same total intensity, the resulting field shows significantly larger peaks in the temporal intensity (see figure below). This occurs due to optical cycles coinciding in phase, leading to constructive interference within the pulse envelope. The intense cycles are spaced ~6 fs apart, which is farther than the 800 nm field cycles, which are spaced 1.33 fs apart. As a result, when applied to methanol, we find ion yield enhancements by more than an order of magnitude for high-appearance energy fragments (see figure), when compared to non-interacting fields.



The temporal intensity profiles of the combined 800 nm (2.5 × 10¹³ W/cm²) and 1400 nm (7.5 × 10¹³ W/cm²) fields (black line) alongside the envelope of a single-color field at a total intensity of 1 × 10¹⁴ W/cm². The NC field reaches a maximum of 3.7 V/Å, while the single-color fields have a maximum of 2.8 V/Å. The bar graph shows selected ions from intensity difference spectra, normalized so that the incoherent sum (grey) plus the coherent sum (green) equals one. The number above each bar indicates the normalization factor for the raw ion yield, and the error bars represent ±1 standard deviation from 64 scans.

(e) H_3^+ Formation from Methyl Halogens and Pseudohalogens J. Stamm, et al., *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 roams the dication until it 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 that the excess relaxation energy released after double ionization of CH_3X molecules combined with substantial geometrical distortion that favors H_2 formation before proton abstraction boosts the generation of H_3^+. Our study provides useful guidelines for examining alternative sources of H_3^+ in the universe.

(g) Tracking Molecular Fragmentation in Electron-Ionization Mass Spectrometry with Ultrafast Time Resolution M. Dantus, *Acc. Chem. Res*. **57**, 033003 (2024). Review of our latest research into inelastic electron rescattering initiated chemical reaction dynamics. It includes a section on future challenges: shorter timescales, tracking neutral fragments, ion pattern prediction.

(h) Ultrafast studies of elusive chemical reactions in the gas phase M. Dantus, *Science* **385**, (2024). Review of challenging time-resolved experiments on reactions initiated by inelastic collisions among molecules or molecules and high-energy electrons and proposed future work.

Future Plans

i. Explanatory Factors for the Control of Molecular Ionization and Fragmentation Using Binary Phase Shaped Strong Fields. We use 80-bit binary spectral phase functions to map the search space and identify pulse parameters that significantly affect ion yield and fragmentation patterns, independent of peak intensity, for triethylamine ($N(C_2H_5)_3$). This search has revealed the role of Rydberg states in controlling chemical reactions in strong fields.

ii. Imaging the Coherent Control of IBr Dissociation via Time-Resolved X-ray Scattering. We plan to shape an excited state wavepacket in neutral IBr to cause interference at the avoided crossing resulting in two photoproduct channels that differ in the bromine's electronic state. Initial experiments will be carried out in our lab, with subsequent measurements at LCLS.

iii. We plan to conduct experiments on various polyatomic molecules to develop guidelines for identifying the predominant strong-field ionization processes. We aim to identify wavelength-dependent resonant enhanced multiphoton pathways and assess the extent of inelastic electron rescattering for each molecule when those ionization pathways are avoided.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

1. B. Jochim, L. DeJesus, M. Dantus, "Ultrafast Disruptive Probing: Simultaneously Keeping Track of Tens of Reaction Pathways," *Rev. Sci. Instr*. **93**, 033003 (2022).
2. S. Li, B. Jochim, J. Stamm, D. Peng, H-C. Shao, J. M. Ngoko Djiokap, M. Dantus, "Pulse shaping in strong-field ionization: Theory and experiments," *Phys. Rev. A* **105**, 053105 (2022).
3. J. Stamm, et al., "Femtosecond intramolecular rearrangement of the CH_3NCS radical cation," J. Chem. Phys. 157, 214304 (2022).
4. S. Kwon, et al., "What is the mechanism of H_3^+ Formation from Cyclopropane?," *J. Phys. Chem. A*. **127**, 8633-8638 (2023).
5. J. Stamm, et al., "The Surprising Dynamics of the McLafferty Rearrangement," *J. Phys. Chem. Lett.* **14,** 10088-10093 (2023).
6. T. Severt, et al., " Initial-site characterization of hydrogen migration following strong-field double-ionization of ethanol," *Nat. Comm*. **15**, 74 (2024).
7. M. Dantus, " Tracking Molecular Fragmentation in Electron-Ionization Mass Spectrometry with Ultrafast Time Resolution," *Acc. Chem. Res.* **57**, 033003 (2024).
8. J. Stamm, et al., "Coherence mapping to identify the intermediates of multi-channel dissociative ionization," *Commun. Chem*. **7**, 103 (2024).
9. M. Dantus, "Ultrafast studies of elusive chemical reactions in the gas phase," *Science* **385**, eadk1833 (2024).

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

AWARD NUMBER: DE-FG-04ER15614

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

1.1 PROJECT SCOPE

The primary focus of the program 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 recollision physics using a new method dubbed Quantum Trajectory Selector. In addition, we have also explored the use of high harmonic spectroscopy in thin liquid sheaths as a potential nonlinear probe of solvation dynamics. 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 organic solutions and (3) attosecond pump-probe experiments using the XLEAP mode of the LCLS.

1.2 PROGRESS IN FY2024

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 separately. 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 release 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 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 $2\omega_{MIR}$ 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.

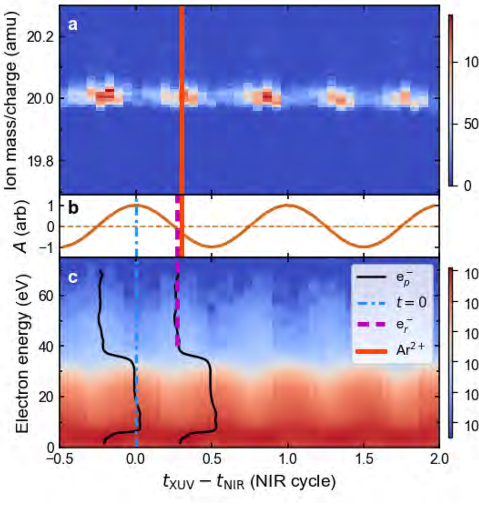


Figure 1: The delay spectrogram for argon atoms. (a) Ar^{2+} ion production and (c) photoelectron yield for argon using the QTS approach. (b) Plot of the fundamental field vector potential calibrated by the streaking of direct electrons. The experiment uses 13 TW/cm^2, 2.4 μm pulses and a XUV pulse with 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 $2\omega_{MIR}$. 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 near 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 in Fig. 1(a) and (c) illustrate the retrieved phases of the double ion (inelastic channel) and rescattered (elastic channel) 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.

Over the last year we have performed TDSE studies to establish the viability of the field calibration procedure. Our simulations, using input from experimental RABBITT and FROG measurements, show that the zero of the field can be extracted with a precision of 0.015 cycles. This clearly establishes QTS as a new attosecond tool for studying recollision processes in atoms, molecules or solids. The manuscript is currently under review at *Phys. Rev. Lett.*

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 are 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.

High harmonic generation (HHG) in liquids has recently been explored revealing characteristic spectral features such as a wavelength independent cutoff energy, in stark contrast to gas phase where the cutoff energy increases as λ^2. These recent studies have largely been restricted to pure solvents mainly consisting of water and various alcohols. We have extended high harmonic spectroscopy (HSS) to liquid phase with an emphasis on studying solutions. We observe evidence of measuring newly formed solvation structure imprinted on the harmonic spectra in the form of a strongly suppressed harmonic order. The suppression is observed in harmonic emission from solutions of different benzene derivatives solvated in methanol (MOH). For low mole concentration (9-14%) of fluorobenzene (PhF) solvated in MOH, it's been observed that there is a strong suppression of an individual harmonic in addition to a broad yield suppression relative to the harmonics from the pure MOH solvent. Our experimental and theoretical studies provide evidence that the harmonic spectra are sensitivity to the local solvation structure of the solution. This work demonstrates the potential of high harmonic spectroscopy in liquids and the ability to extract information about the solvation structure on the sub-angstrom scale in addition to further exploring the mechanisms of HHG in liquid phase.

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 in measuring molecular delays are described in Ref. [7A]. This work was part of a collaboration led by James Cryan, Agostino Marinelli and Taran Driver.

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 and CO 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. A new postdoc from Anne L'Huillier's group, Ann Katherine Raab, will join our group in 2025 as a postdoctoral research associate.

HHG from liquid sheets. We will continue to study binary mixtures. To date, all evidence suggests that the length scale is the key 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 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 further insights over the next year. A new postdoctoral research associate, Larissa Boie (ETH), will join our group in 2025.

LCLS: The group will continue participation in the LCLS Directors Charge Migration Campaign. We also have a proposal pending using the FERMI XFEL (Trieste) for studying molecular delays near the shape resonance in CO_2. The latter is a collaboration with James Cryan and Taran Driver.

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 (2022-2024)

1A. "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.

2A. "Attosecond coherent electron motion in Auger-Meitner decay", Siqi Li *et al.*, Science **375**, 285 (2022). doi: 10.1126/science.abj2096.

3A. "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.

4A. "Kramers–Kronig relation in attosecond transient absorption spectroscopy", V. Leshchenko *et al.*, Optica **10**, 142 (2023). doi: https://doi.org/10.1364/OPTICA.474960.

5A. "Sub-two-cycle gigawatt-peak-power LWIR OPA for ultra- fast nonlinear spectroscopy of condensed state materials", V. Leshchenko, Sha Li, P. Agostini and L.F. DiMauro, Opt. Lett. **48**, 4949 (2023). doi: https://opg.optica.org/ol/abstract.cfm?URI=ol-48-19-4949.

6A. "Experimental demonstration of attosecond pump–probe spectroscopy with an X-ray free-electron laser", Zhaoheng Guo *et al.*, Nat. Photonics **18**, 1 (2024). doi: https://doi.org/10.1038/s41566-024-01419-w.

7A. "Attosecond delays in X-ray molecular ionization", Taran Driver *et al.*, Nature **632**, 762 (2024). doi: https://doi.org/10.1038/s41586-024-07771-9.

8A. "Attosecond Clocking and Control of Strong Field Quantum Trajectories", A. Piper *et al.*, PRL (2024) under review.

Simulating Photo-Induced Electronic Energy and Charge Transfer Dynamics in Complex Molecular Systems and Their Spectroscopic Signature

PIs: Barry. D Dunietz[a], Eitan Geva[b], Maragret Cheung[c]

[a]Kent State University, Department of Chemistry, 800 E Summit, Kent, OH 44242
(bdunietz@kent.edu)
[b]University of Michigan, Department of Chemistry, Ann Arbor, MI
[c]Pacific Northwest National Lab

Project Scope:

A computational approach is developed and employed to guide the design of materials used in energy conversion applications by investigating key structure-function relationships.

Electronic energy transfer (EET) and charge transfer (CT) dynamics play a key role in determining the functionality and efficiency of biological and synthetic energy conversion systems. Our research program focuses on developing new computational methods for simulating EET and CT dynamics in such complex molecular systems. We will investigate the relationships between electronic and molecular structure and EET and CT dynamics, and the role of the molecular environment in determining EET and CT rates and pathways. We will also investigate the signature of those processes on state-of-the-art multidimensional time-resolved spectra.

While our computational approach is general-purpose and expected to be applicable to any complex molecular system, it is developed and tested on an emerging class of bioinspired peptoid-based materials. These novel systems can be tuned by side chain functionalization of energy/charge donors/acceptors at different backbone sites for controlling self-assembly and optoelectronic properties.

The three principal investigators (PIs) combine complementary expertise in state-of-the-art condensed phase electronic structure calculations (Dunietz), quantum rate theory and optical response theory for simulating EET and CT in complex molecular systems and their spectroscopic signature (Geva) and classical molecular dynamics simulations (Cheung).

Recent Progress: N/A

Future Plans:

Mentoring of research staff and setting up the collaborative network is underway. Initial research progress focus on transfer processes within dimers of porphyrinic rings ligating Fe(II) and Fe(III) centers.

Peer Reviewed Publication Resulting From this Project (Start Date: 9/2024): No publications to report

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

Award number: DE-SC0021336
Principle Investigator: Li Fang
Department of Physics, University of Central Florida, 4111 Libra Dr. Orlando FL 32816
Email: Li.Fang@ucf.edu

Project Scope:

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

Recent Progress:

COLTRIMS has been built up and we are currently commissioning the beamline and the spectrometer. There are issues with the spectrometer signal, and we are troubleshooting the delay-line detector. We are also recovering from some detector electronics damages. Our 1μm high-average-power high-repetition-rate laser system is having injection issues at the compression stage and the overall performance of the laser is degraded. This is expected to be fixed within the next few months with the assistance of the laser company. A new graduate student and a new postdoc researcher are participating in this project starting in July and September 2024 and are receiving instrumental and hands-on training.

Future Plans:

We will continue the commissioning of the beamline and the spectrometer and expect to complete the commissioning by the end of 2024, if the replacement parts for the equipment arrive as scheduled. We aim to bring the experimental line to operation by February 2025 and carry out experiments on autoionization of N_2 and/or C_2H_2 starting in March 2025. Attosecond streaking measurement will be performed. The phase measurement apparatus will be set up and commissioned in April 2025. Meanwhile we are participating in collaborative XFEL experiments and are taking a role in data analysis and interpretation, and we plan to participate in-person in a XFEL beam time in 2025. The milestones to achieve include (1) demonstrating operation of REMI spectrometer; (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; (5) obtaining data and scientific outcome in XFEL experiments.

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

Transient Absorption and Reshaping of Attosecond Pulses

DE-SC0010431

Mette B. Gaarde (mgaarde1@lsu.edu), Kenneth J. Schafer (kschafer@lsu.edu)
Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70803

October 2024

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-R3], [1–5]. 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) [5,6].

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-R3], [1–4].

(i) Transient absorption and reshaping of few-fs XUV pulses in He gas: Continuing our collaboration with the Ott/Pfeifer experimental group at the Max Plack Institute (MPI) in Heidelberg, Germany [R1,R3], we have studied several aspects of few-fs XUV pulse absorption and reshaping. (a) In agreement with previous results, we find that the combination of propagation-based reshaping (so-called resonant pulse propagation, RPP) and the Stark shift induced by a moderately intense near-infrared (NIR) laser pulse leads to an absorption spectrum that undergoes a series of changes with increasing density-length product (DLP): starting from a narrow Lorentzian linewidth, the optical density (OD) spectrum broadens and then splits and develops new narrow features on line center [7]. Interestingly, we find that at even higher DLP, the OD lineshape returns to Lorentzian, albeit much broader than in the thin-gas limit. This can be understood by considering the time-domain picture: the macroscopic RPP means that the XUV pulse lengthens and develops a series of sub-pulses in the tail. During propagation, more and more of the pulse energy is concentrated in the tail of the pulse (similar to a dispersion-induced delay). The IR pulse, on the other hand, is unaffected by the XUV resonance and arrives at the same time independent of propagation distance. This means that the IR-induced Stark shift is only imposed on a negligible part of the XUV pulse, so that the XUV pulse becomes insensitive to the IR pulse. The high-DLP lineshape therefore returns to what it would be in the case of ”normal” RPP, in the absence of the IR field, namely a broadened Lorentzian, see Fig. 1. This work is currently under review [3]. (b) We have studied the absorption characteristics of several doubly ionized states in He, and in particular how they change in the presence of a dressing

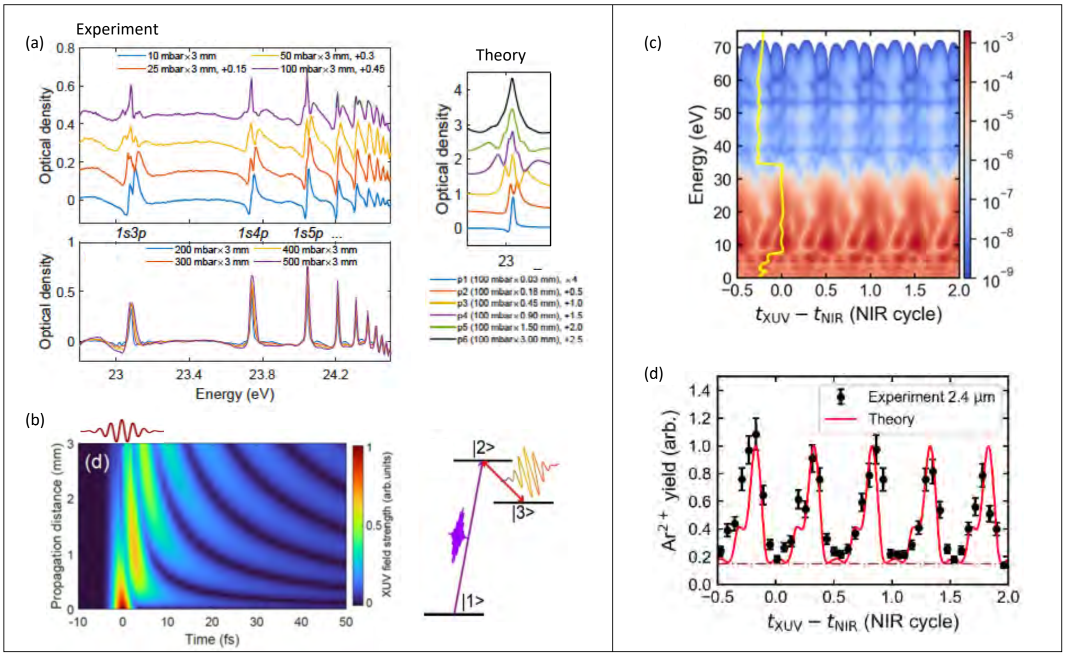


Figure 1: (a,b) A few-fs XUV pulse propagating through a resonant medium is reshaped in time through RPP and the Stark-phase shift induced by an NIR pulse. (a) This manifests as a lineshape change that increases in complexity with the DLP, as shown in experimental and TDSE-MWE-calculated spectra. At the highest DLPs, the lineshapes return to broadened Lorentzians. (b) In the time domain, this happens when XUV pulse reshaping is so severe that the NIR phase change is marginal, illustrated for a three-level model system. Adapted from [3]. (c,d) Quantum trajectory selector: (c) TDSE-calculated photoelectron spectra in argon vs XUV-IR delay, using a 13 TW/cm^2, 2.4 μm NIR pulse and an XUV APT. The yellow line traces the delay that gives maximum electron yield. (d) Double ion yields vs delay time, theory (red line, including convolution of pulse envelope and cross-section), and experiment (black symbols). Adapted from [2].

(ii) Quantum trajectory selection: In collaboration with the DiMauro group at the Ohio State University we have investigated quantum trajectory selection (QTS) [8] applied to non-sequential double ionization (NSDI) in Ar [2]. By using laser fields with a wavelength 1.7- 2.4 μm, intensities can be obtained 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 NSDI [2]. For the QTS to be a true time-resolved measurement, it is necessary to be able to calibrate the delay axis. We hypothesize that this can be done via a measurement of the “direct” electrons (those that do not rescatter). Semi-classical considerations suggest that the highest energy direct electrons are ionized at maxima of the vector potential (the zero points of the electric field). We have carried out extensive TDSE simulations of ionization in argon at the experimental wavelengths of 1.77 and 2.4 μm and have found that for electrons with energies between 2 and 4 U_p, the maximum phase does correspond to zero electric field, to within a small uncertainty. An example of these calculations, which include the full measured attosecond pulse train (APT), including the attochirp, is shown in Figure 1(c).

We have also extended our modeling of QTS to study NSDI in argon using a collisional excitation model that is based on the idea that any electron that is excited by the returning primary electron will be quickly ionized by the laser field. Ar^{2+} yields based on this model, using excitation cross sections from the literature and the calculated returning electron wave packet, are shown in Figure 1(d). The match to experiment is excellent.

(iii) Nonlinear reshaping of intense XFEL pulses in neon gas: Continuing our collaboration with the Young experimental group at Argonne National Lab [5], we are interested in 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). Our calculations are based on a coupled TDSE-MWE solution in which the TDSE is solved for a few-level atom-and-ion system. A study concentrating on the XSRS and its applications is currently under review [1], based on experiments done at the European XFEL facility.

Future Plans

Several projects are in progress:

(i) Nonlinear reshaping of intense X-ray pulses in neon: A second study is based on experiments done at the LCLS, using the XLEAP capacity to generate isolated attosecond X-ray pulses, with photon energies both below and above the neon K-edge. Both experimental and theoretical results indicate that the substantial spectral and temporal reshaping of the attosecond X-ray pulses is predominantly a result of population transfer and coherence in the neon ions, not the neutral neon. Interestingly, we also see evidence that the attosecond XFEL pulses have enough intensity to drive Rabi cycling of population between the ionic states, which leads to an evolution of the XRL spectrum somewhat similar to that illustrated for the lower DLPs in Fig. 1(a). This work is still in progress.

(ii) Intensity dependence on NSDI: We will use TDSE-calculated electron wave packets to study the intensity-dependence of the time-dependent NSDI yield in argon. Initial results indicate that the XUV-NIR phase that maximizes NSDI depends on the NIR intensity, contrary to the simple semi-classical prediction of an intensity-independent maximum phase.

(iii) Condensed-phase ATA: (a) In collaboration with the Leone experimental group, we are studying attosecond transient absorption in an ionic solid with prominent core excitons. We are using a few-level-model solution of the TDSE to identify and characterize the relevant exciton states, similar to what was done in [9]. (b) We are implementing a solution of the semi-conductor Bloch equations across the focal plane of a two-color field consisting of an XUV pulse (to excite out of inner valence bands) and an NIR pulse (to add an intensity-dependent Stark-phase shift). Our goal is to spatially separate, at the macroscopic level, the microscopic response for different crystal momenta.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

R1 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).

R2 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)

R3 Y. He, C. and Ott, T. Pfeifer, and M. B. Gaarde, *Local enhancement in transient absorption spectroscopy by gating the resonance in the time domain*, Phys. Rev. Res. **6**, 013103 (2024).

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[3] Y. He, S. Hu, G. D. Borisova, Y. Zhang, M. Rebholz, M. B. Gaarde, C. Ott, and T. Pfeifer. Coherent control of photoabsorption with intense laser pulses: from optically thin to thick media. 2024 (under review).

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Unraveling ultrafast electron-nuclear dynamics in molecules

Award Number: DE-SC0024182

Nikolay Golubev

Department of Physics, University of Arizona, 1118 E. Fourth St., Tucson, AZ 85721
E-mail: ngolubev@arizona.edu

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.

One phenomenon of particular interest for attosecond science is the process of migration of a positive charge created after ionization of a molecule by an ultrashort laser pulse. The fundamental reason underlying the motion of the created charge is the involvement of multiple electronic states that must be populated coherently during the ionization process. In a difference to atomic systems, where the created coherent superposition can, in principle, exist forever, the electronic coherences in molecules are strongly and unavoidably influenced by the nuclear motion. It was demonstrated in numerous studies that the slow nuclear rearrangement has a dramatic impact on the electronic dynamics, which leads to the fast decoherence of electronic oscillations on a time scale of just a few femtoseconds.

Recently, we demonstrated that a simple semiclassical approach, in which the propagating nuclear wave packets are approximated by Gaussian functions, can be very useful technique for calculating electronic coherences in molecules [1]. We identified several so far unexplored molecules in which the electronic coherences survive the nuclear rearrangement within at least ten femtoseconds making these systems promising candidates for follow-up theoretical and experimental studies [2].

II. Recent Progress

One of the molecules with promising properties we found before [2] is butynal which is composed of a chain of four carbon atoms with an alkyne group at one end and an aldehyde group at the opposite end. While the molecule is already a good candidate for experimental studies, it is interesting to investigate how small variations in molecular structure could influence the charge migration and the lifetime of electronic coherences. We, therefore, studied the influence of the molecular structure on charge migration in three homologous molecules: propynal (1 carbon atom between the aldehyde and alkyne groups), butynal (2 carbons between the groups), and pentynal (3 carbon atoms between the groups).

We identified that all the studied molecules have comparable ionization spectra (see Figure 1, A and B). In all cases, a hole-mixing structure is present between the first and third cationic states. Propynal and pentynal have a planar symmetry and belong to the C_s point group. The mixed cationic states as well as the involved orbitals have an A′ symmetry, whereas the second state belongs to the A″ irreducible representation. In contrast, butynal does not have any symmetry, as the OCCC dihedral angle differs by 30 degrees from the less favorable symmetric conformer. This induces a slight hole-mixing between the second cationic eigenstate and the adjacent ones. However, the charge migration dynamics arising from the possible presence of the additional electronic state in the wavepacket is negligible since the major contribution to the second state is coming from the orthogonal HOMO-1 orbital. It is, therefore, expected that the ionization of these molecules by an ultrashort laser pulse will lead to comparable charge dynamics.

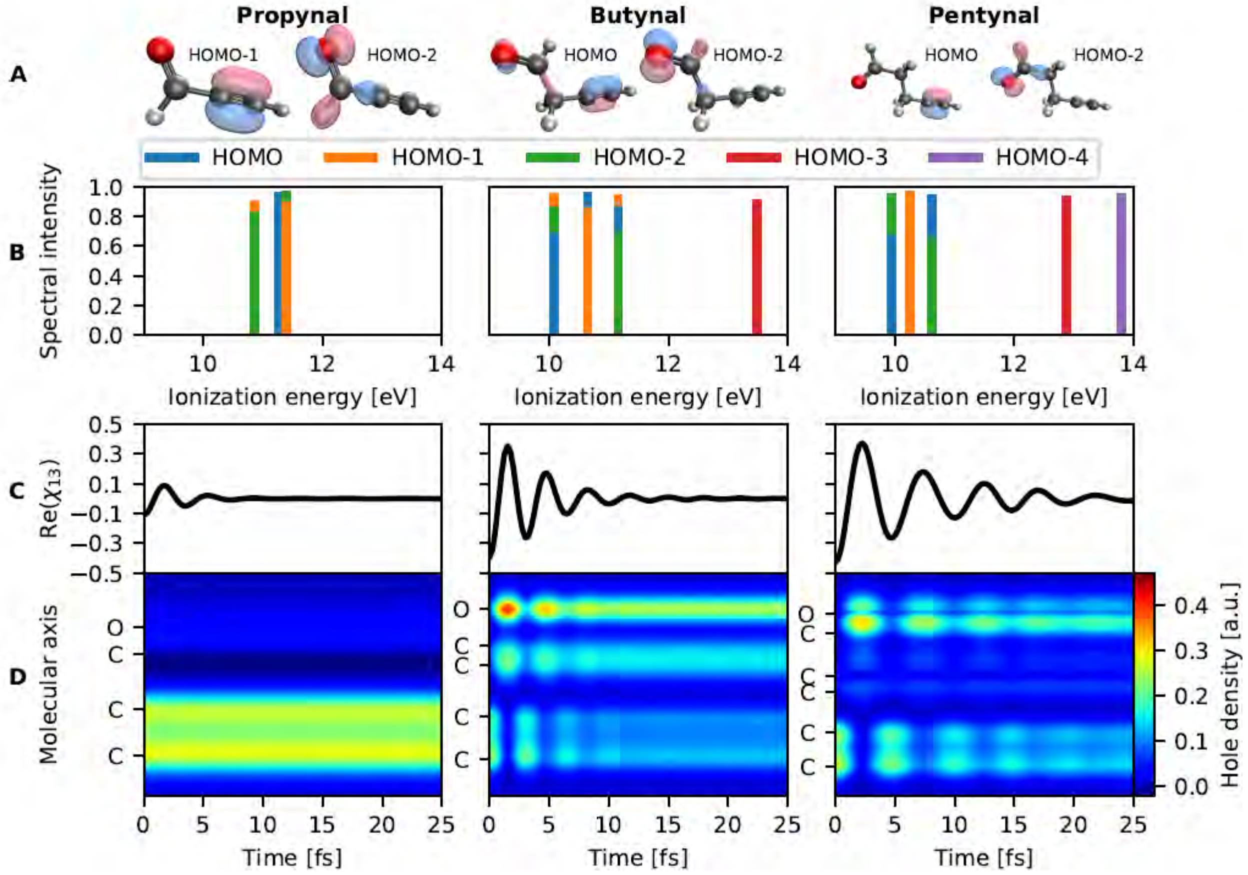

Figure 1: Ionization spectrum and charge migration triggered by ionizing the propynal (left), butynal (middle), and pentynal (right) molecules. (A) Hartree-Fock molecular orbitals involved in the hole-mixing. (B) First cationic states in the energy range of 9 to 14 eV. (C) Time evolution of the electronic coherence between the first and third cationic states created by the ionization. (D) Charge migration projected along the molecular axis passing through the carbon triple bond.

In Fig. 1(C), the real part of the electronic coherence is shown. In propynal, the coherence oscillation has a very small amplitude because of the weak hole-mixing, whereas pentynal has a more pronounced and more persistent coherence oscillation than butynal. This result is remarkable, since adding a carbon atom makes the molecule more flexible and increases the number of vibrational modes, which would be expected to accelerate the decoherence.

The charge migration analysis in Fig. 1(D) shows the hole dynamics after ionization out of the HOMO (HOMO-1 for propynal). Due to the very weak hole-mixing in propynal, the hole remains strongly localized at the triple bond, and no oscillation can be observed. Charge migration is more pronounced in pentynal than butynal due to the disappearance of the hole density at the C-C bond close to the oxygen. This suggests that experimental observation of the hole dynamics with time and spatial resolution might be easier in pentynal.

We, therefore, report quite surprising and interesting result that increasing the size and flexibility of a molecule can prolong the electronic coherence and charge migration. Importantly, the observed enhanced coherence is attributed to a reduction of the decoherence induced by specific internal vibrations when extending the molecular backbone. Exploiting the semiclassical description of the nuclear motion, we found not only which vibrational modes are responsible for the suppression of the charge oscillation, but also through which mechanisms.

III. Future Plans

The coupling between the electronic and nuclear degrees of freedom is not only the source of decoherence that can play pivotal role in laser-induced charge dynamics in molecules. Another very important aspect that has not been fully understood yet is the ionization step itself. We, therefore, will develop appropriate methods permitting explicit description of the interaction of a molecule with a laser pulse and the transition of an ionized electron to continuum. Ultimately, we aim to combine the fully quantum description of the ionization process with our semiclassical description of the nuclear dynamics thus developing predictive theory and corresponding numerical approaches capable of describing the ultrafast charge dynamics following molecular ionization.

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 such as Ehrenfest dynamics and the exact factorization formalism.

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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

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

Project Scope

In atomic and molecular physics, the word *correlations* has historically been used primarily to treat electron-electron correlation phenomena in atoms and molecules. In this project we interpret this word more broadly because there is a far more extensive collection of related phenomena where multiple degrees of freedom are strongly coupled and is in fact nonseparable or entangled in multiple coordinates. Our focus is on 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 problems constitute the focus of much theoretical and experimental interest in this field because the simplest and most common theoretical models, such as the independent-electron model and its improved variants, fail in many cases to provide an adequate theoretical description. Our group develops and applies a somewhat unconventional theoretical toolkit, including hyperspherical coordinate formulations, R-matrix theory and multichannel quantum defect theory, or newly developed time-propagation algorithms for ultrafast processes, to treat increasingly complex dynamical and spectral observations. 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, or both. The work ranges from ultrafast ionization and/or dissociation processes in simple molecules to coherent multiphoton excitation and ionization processes in atoms with two or more 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) Molecular physics and electron collisions

This year our group studied the unusual and exotic weakly-bound $2p\sigma,\ v=1$ state of the simplest molecule H$_2^+$. This state, bound by only about 10^{-8} eV, correlates with a huge proton-hydrogen scattering length in that symmetry, larger than 700 bohr radii. The fragility of this system and its sensitivity to careful treatment of the long-range interactions have posed stringent challenges to theory, and have required previous theoretical treatments to go beyond the conventional Born-Oppenheimer approximation. Our study, published this year in [1], is one of the few that have tackled this system using the adiabatic hyperspherical representation, which has the advantage that the dissociation thresholds are treated essentially exactly, overcoming a major problem with standard Born-Oppenheimer theory. The treatment [1] obtains a quantitative scattering length equal to 765.5(2) a.u., competitive with the best previous results, and showing that an adiabatic hyperspherical treatment is already quite accurate without inclusion of interchannel coupling, despite the fragility and sensitivity of the solution to the long-range interactions.

Significant progress was achieved in two other areas of molecular physics this year, although the manuscripts are not yet quite ready for submission and are in the final preparation stages now. The first is a major new treatment of the most difficult processes in low-energy electron collisions with H_2^+, namely those that result in electron capture and dissociative recombination. For some applications that need the dissociative recombination rate or cross section, it is crucial to get the low energy resonances to near-spectroscopic accuracy. While the theoretical treatments have been able to predict some observables accurately, such as resonance positions and widths in photofragmentation of H_2 and its isotopologues in the final state gerade symmetry, a similar level of accuracy has never been achieved for the dissociative recombination observables. We have now developed a new variant of the energy-dependent vibrational frame transformation theory, integrated with generalized multichannel quantum defect theory, which appears to solve this problem almost completely. A long manuscript in preparation lays out the theory and its first application, with benchmarking that enables a highly sensitive test of its accuracy. The second is a reformulation with significant extensions and improvements over our previous generally successful treatment of dissociative recombination in the simplest polyatomic ion H_3^+ and its isotopologues. This development was motivated in part by the fact that the theory actually gave far worse agreement with experiment performed for the partially deuterated isotopologues H_2D^+ and D_2H^+. A second motivation is the fact that the experimental measurements have now become significantly improved with far lower ion temperatures, thanks to the cryogenic storage ring in Heidelberg that has been used to take the newest data. With a new round of calculations, based now on *ab initio* fixed-nuclei scattering data instead of the original body-frame data that was extracted from bound state potential curves using quantum defect ideas, we expect to have a comparison of state of the art theory and experiment ready for publication in the coming months.

(ii) Multiphoton ionization of strongly correlated atoms

This year saw the completion of a strong theoretical PhD thesis by Miguel Alarcon in our group, and as part of his dissertation research, he developed a major new capability for the group, an implementation of the eigenchannel version of R-matrix theory for the Dirac equation. A first article on that development, containing a test calculation for beryllium photoionization and also with a revised formulation of generalized quantum defect theory for the Dirac Coulomb problem, is currently under journal review. Our goal is to implement this approach to describe single- and multi-photon ionization of more complex atoms (or ions) with two valence electrons, such as radium (or Fr^-).

Progress has been achieved in a collaborative effort with Arvinder Sandhu's experimental group, a collaboration between theory and experiment working towards deepening our understanding and then extending capabilities for 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. 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.[2] One finding published in 2022 [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. Subsequently, our collaboration described a more challenging process (from both a theoretical and experimental standpoint) involving 3 photon absorption, again in a pump-probe scenario that is sensitive to phases acquired during the photoionization process.[2]

A publication in 2022 [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. This has the potential to extend the capability to create SPDC time- and energy-correlated photon pairs to much higher frequencies and shorter time scales, beyond the limitations of current sources.

We also applied our toolkit of variational R-matrix theory and multichannel quantum defect theory to understand the phase lag measurement involving interfering one- and two-photon processes in the barium atom, carried out more than a decade ago by Dan Elliott's group, which had not previously been understood theoretically. [7] That study also extended the barium treatment to make analogous predictions for this type of process in highly-correlated atomic strontium, in a subsequent article [4], not yet studied experimentally.

And, in a collaboration with the groups of Thomas Pfeifer and Christian Ott at the Max-Planck Institute for Nuclear Physics in Heidelberg, this project published an ambitious combined theoretical and experimental study of the simplest above-threshold ionization process in atomic helium, in which the Heidelberg experimentalists 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.

(iii) 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 [3] decisively disproves their contention. Our study confirms that one obtains 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 former PhD student who graduated this summer, Miguel Alarcon, plans to continue 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. In addition, as was mentioned above, our strengthened theoretical treatments aiming to improve the quantitative treatment of dissociative recombination in small, fundamental molecules will be implemented.

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

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DOI: 10.1088/1361-6455/aceb28

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DOI: 10.1103/PhysRevLett.129.183204

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DOI: 10.1103/PhysRevA.105.013113

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DOI: 10.1103/PhysRevLett.128.083001

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

DE-SC0022105

Loren Greenman
Dept. of Physics, Kansas State University, Manhattan KS, 66506
lgreenman@phys.ksu.edu

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

We have completed two studies related to the understanding of photoionization time delays in chiral molecules and we are preparing the manuscripts for these results. These studies are both based on the experiments of Meng Han and Hans-Jakob Wörner, in which COLTRIMS and RABBITT were combined to measure time delays associated with both HOMO-based ionization of methyl oxirane as well as ionization from lower-lying orbitals that could be detected in coincidence with dissociating fragments. The collaborative paper describing the experiments and analysis of the HOMO-based photoionization has been submitted. In Fig. 1, it can be seen that the time-dependent perturbation theory (TDPT) based approach was consistent with the experimental time delays.

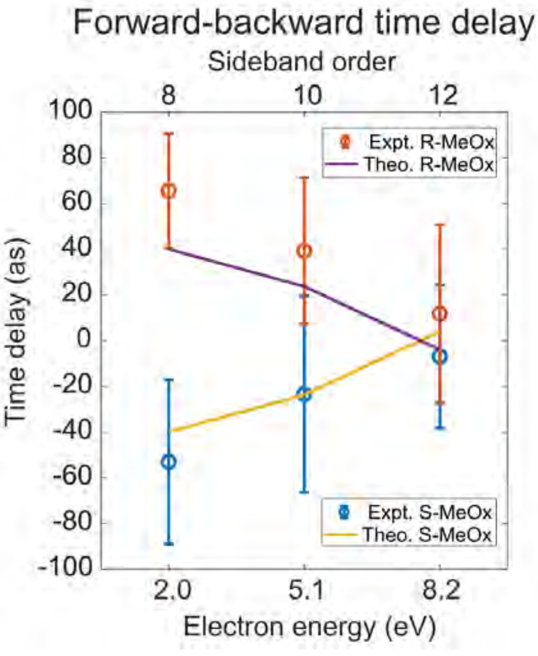

Figure 1: Comparison of experimental and theoretical attosecond time delays for the chiral methyl oxirane.

The agreement in Fig. 1 was obtained only after modifying the calculated virtual orbital energies. This is not surprising, as the virtual orbitals calculated by uncorrelated electronic structure calculations are not expected to be accurate. Furthermore, the nature of the spatial confinement imposed by the Gaussian basis set provided the ability of the system to develop pseudoresonances in the photoelectron spectrum. While we feel that such modification of the virtual energies is justified, it is still desireable to have a completely ab initio method for calculating time delays and other photoionization observables. We therefore undertook two detailed studies of the performance of the model. In the first study, we examined the robustness of our calculations to modifying the parameters such as the virtual orbital energies. In the second, we attempted and succeeded at converging Gaussian basis sets in predicting methyl oxirane time delays.

In Fig. 2, the result of modifying the virtual orbital energies can be seen. The Hartree-Fock virtual orbital energies for a number of basis sets fall in a cone around the values we considered. Linear fits to the orbital energies of various slopes were compared, and this is what is pictured in Fig. 2. It can be seen, in fact, that there are pseudoresonance effects in the various anisotropy parameters ($\beta_{L,M}$). These are especially pronounced in sideband 10, and much smaller in the other sidebands. In fact, there is a large region where these resonance effects can be avoided. These effects are also born out in the photoelectron circular dichroism observable. However, in this particular study we were interested in the underlying parameters that we calculated, which were the β parameters.

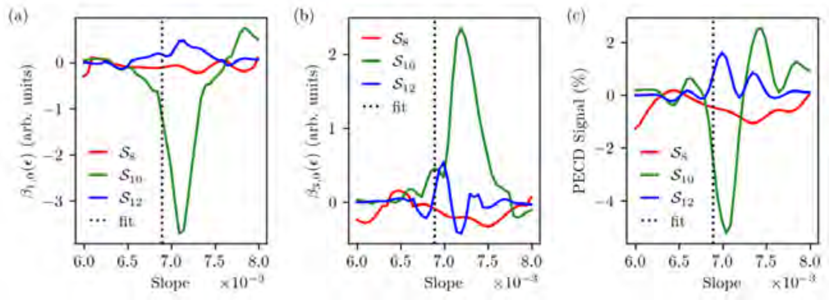

Figure 2: Sensitivity of various β-parameters (anisotropy components) to virtual orbital energies.

Quadratic fits were also explored in this work, and we found that the β parameters were less sensitive to the quadratic fit parameters, at least in the regions where they matched the calculated orbital energies. Sideband 10 was again the most sensitive to changes. Other sidebands showed oscillations in anisotropy with respect to quadratic parameters, but lacked major pseudoresonance effects like those seen above.

Finally, complex orbital energies were used. This is a frequently used tool in similar calculations, where pseudoresonances can be avoided by imbuing the affected states with sufficiently short lifetimes. Again, the tenth sideband was most sensitive to changes in complex part of the orbital energy. The changes of the various observables and the β parameters were each on the order of a few percent. While small, this is comparable to the size of the overall anisotropy effects we are trying to describe.

The most desireable way to perform these calculations would be to use the basis sets directly without any subsequent modification of virtual levels. We explored this option in a separate study. Our main approach was to increase the basis by using diffuse functions centered at the center of mass of the molecule. We modified the basis with up to 8 diffuse functions. Somewhat surprisingly, we found that we were able to converge the results at many of the sidebands.

In Table 1, we show the photoelectron circular dichroism (PECD) of methyl oxirane

PECD	H7	SB8	H9	SB10	H11	SB12	H13	SB14
cc-pVQZ	-0.888	0.0279	-2.34946	0.3557	4.5687	-0.03679	0.10851	-0.00827
aug-cc-pVQZ	-3.50329	-0.0358	-2.42826	-1.3570	4.6535	1.37428	0.11376	0.05599
1 additional diffuse function	-3.47175	-0.0718	-2.347	-0.8819	4.6382	2.37189	0.09239	0.24515
2 additional	-3.43641	0.1779	-2.33762	4.9957	4.6388	1.10862	0.08756	0.37962
4	-3.42526	1.0349	-2.33536	-0.7074	4.6387	0.23431	0.08618	0.47508
6	-3.42432	1.0996	-2.33523	-1.0057	4.6387	0.29664	0.0861	0.46669
8	-3.42427	1.1123	-2.3352	-1.0667	4.6387	0.2369	0.08609	0.48778

Table 1: PECD % at harmonics H7-H13 and sidebands SB8-SB14 for different basis sets at $\theta = 0°$. The red colored digits are the converged digits.

calculated with various amounts of diffuse functions added. The sidebands all converge to at least one digit (which is useful in a PECD calculation). For the lower sidebands, we were able to converge multiple digits with fewer than 8 diffuse functions.

Similar results were obtained also for the anisotropy parameters, suggesting that PECD is not the only observable we can successfully converge using this technique. Even the extremely trick forward-backward time delays for the sidebands were able to be converged. However, convergence did not match precisely what is shown in Fig. **??**. Unsurprisingly, correlated calculations will be required to obtain both a converged result relative to calculation and accurate to experiment.

In addition to our projects exploring the photoionization of chiral molecules, we have also been exploring the excited-state dynamics of iodobenzene. We have found the existence of slow and fast pathways after excitation at 220 nm. We have connected the slow pathways to additional motion in the puckering angle of the iodine with respect to the benzene ring. Our calculations of the nuclear motion have been performed using the SHARC package [1]. We are working with the groups of Martin Centurion and Dan Slaughter to compare these predictions to ultrafast electron diffraction experiments.

Future plans

We are currently preparing explore the Dalgarno-Lewis summation in order to sum intermediate states on the grid directly [2, 3]. 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-

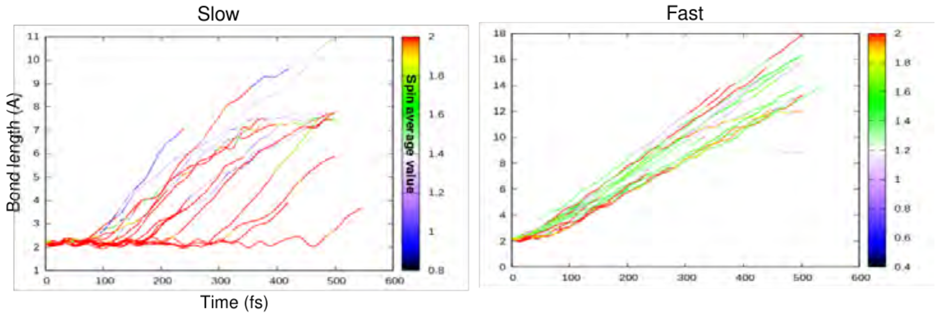

Figure 3: C-I bond length vs time for the slow and fast pathways in iodobenzene.

over-states methods may also lead to more accurate calculations of molecular properties like hyperpolarizabilities.

We also continue to explore the use of "overset grid" in collaboration with the theoretical team at Berkeley National Lab. We believe that these grids are better suited to molecules. We hope to combine correlated calculations of photoionization observables with these grids with the perturbative approaches used to calculate time delays here in the near future.

We plan, as mentioned above, to further compare our iodobenzene calculations to experimental results. We are also engaged in the prediction of transient absorption spectra for small molecules to compare with results from the Shivaram group at Purdue University.

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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

PI: Ryan G. Hadt
Division of Chemistry and Chemical Engineering, California Institute of Technology
1200 E. California Blvd., MC 127-72, Pasadena, CA 91125 rghadt@caltech.edu

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.[2] 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.[3] 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. Developing variable-temperature, variable-field T_1 measurements (VTVH-T_1) to detect new spectroscopic signatures of phonon character in electron spin relaxation.

In previous work, we have demonstrated that anisotropy in the spin lifetime (T_1 anisotropy) contains important mechanistic information.[4] This information can be extracted by measuring T_1 through pulse electron paramagnetic resonance (EPR) at various magnitudes of the applied magnetic field, B_0. Because an EPR spectrum contains natural statistical selectivity for various orientations at various values of B_0, T_1 anisotropy information can be extracted even for randomly oriented powder samples. Here, we are extending this concept into a new dimension by profiling how the anisotropy changes across a variety of temperature regimes. This entails a two-dimensional experimental design against both B_0 and T as independent axes, so we have dubbed this approach "variable-temperature, variable-field T_1" (VTVH-T_1). We find that the powder T_1 anisotropy varies significantly as a function of temperature for two molecular qubit candidates: $Cu(acac)_2$ and CuOEP (**Figure 1A-B**). Factor analysis modeling of the VTVH-T_1 data reveals distinct mechanistic regimes for spin relaxation, characterized by their own unique anisotropy pattern and thermal dependence (**Figure 1C-F**). We have shown that these mechanistic regimes cannot be reliably extracted from traditional temperature-dependent T_1 measurements at a fixed B_0. Finally, single-crystal T_1 anisotropy experiments reveal a change in the symmetry of the spin relaxation tensor between the low-T and high-T mechanistic regimes (crossover at 36 K for $Cu(acac)_2$, 47 K for CuOEP). These changes enable assignment of the low-T regime anisotropy to delocalized phonons, while the high-T regime anisotropy arises from localized molecular stretching vibrations. Thus, VTVH-T_1 provides a new direct spectroscopic probe revealing the character of the nuclear motions that lead to spin relaxation.

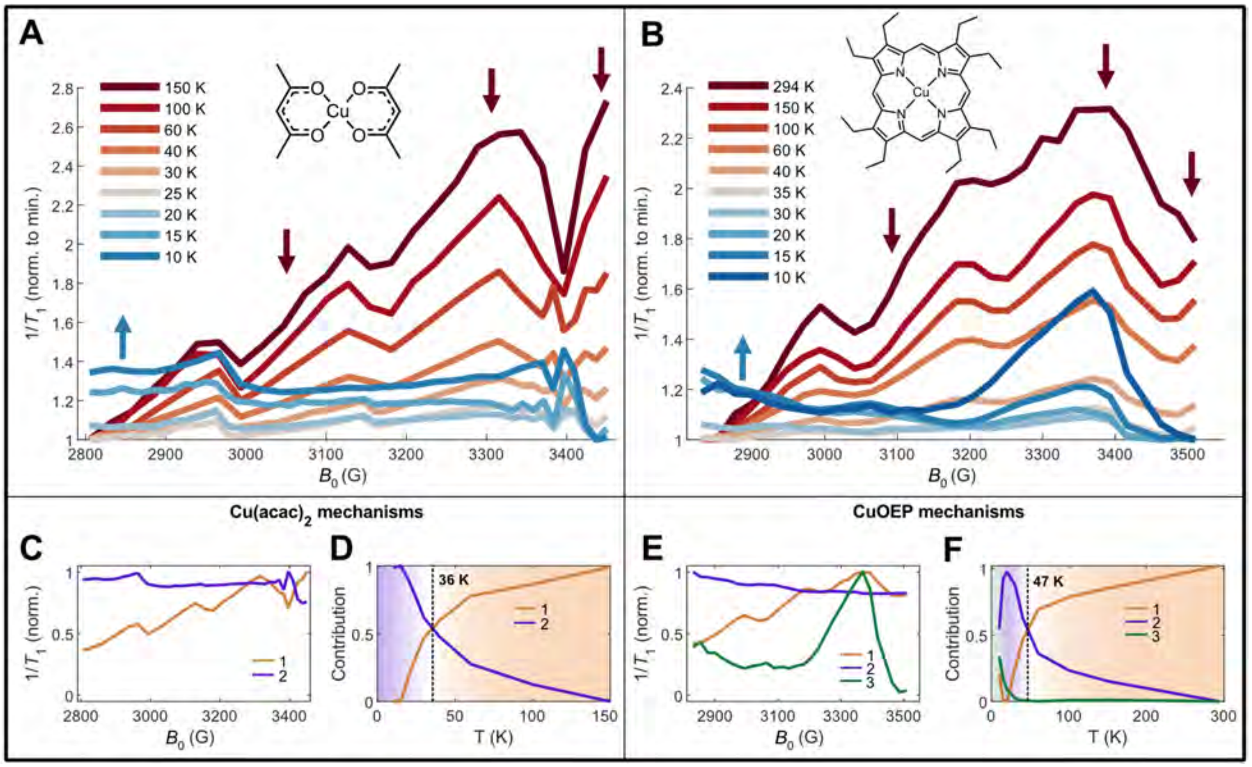

Figure 1. VTVH-T_1 measurements for powder samples of (A) $Cu(acac)_2$ and (B) CuOEP. Factor analysis decompositions enable the extraction of fundamental anisotropy shapes (C, E) with characteristic temperature dependencies (D, F), enabling direct delineation of different mechanistic regimes of spin relaxation.

1.2 Using Time-resolved Faraday ellipticity (TRFE) for all-optical detection of T_2^*.

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 ellipticity (TRFE). 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 "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, inducing probe ellipiticity. By varying the time delay between pump and probe pulses, the spin coherence dynamics are measured through the dynamics of this optical ellipticity change. We have demonstrated this setup can measure spin decoherence rates (T_2*) all-optically on the ultrafast timescale (**Figure 2**). Spin coherence is detectable at room-temperature and in aqueous solution for the compound K_2IrCl_6, with sensitive detection down to ~20 µM. These exciting results suggest that TRFE may provide a rational pathway to all-optical, room-temperature molecular quantum sensing in the very near future, a long-desired goal in molecular quantum information science.

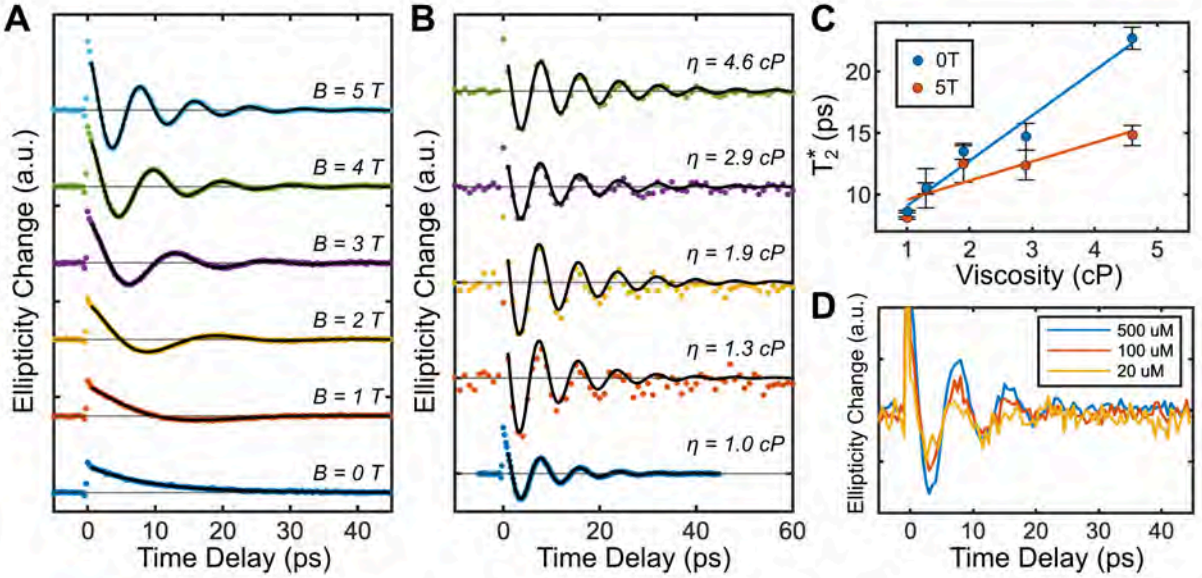

Figure 2. Ultrafast free induction decay at room temperature. (A) TRFE measurements on K_2IrCl_6 dissolved in H_2O at various field strengths with fits shown in black. (B) In water:glycerol mixtures to modify viscosity at 5 T with fits shown in black. (C) Viscosity dependence of T_2* measured at 0 T and 5 T alongside corresponding linear fits. (D) Concentration sensitivity in H_2O at 5 T.

Future Plans

Building on the successes described above, we will continue to develop new 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, and (2) application of MCD to a broad compound scope for interrogation of ligand field strength effects on spin relaxation.

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 high-temperature T_1 anisotropy, the influence of the crystal lattice on optical phonon (i.e., molecular vibrations) spin relaxation has not been fully 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 extend 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. MCD spectroscopy. 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. This allows for quantification of how ligand field strength impacts spin relaxation. The *d-d* transitions are selectively enhanced at low temperature due to the role of spin-orbit coupling in the *C*-term intensity mechanisms.[5] We will extend our preliminary measurements to a systematic scope of twelve square-planar Cu(II) compounds for comparative investigations of ligand field electronic structure (**Figure 3**). The results will be correlated to the absolute rates of T_1, as well as 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. Successful execution could produce a spectrochemical series for spin relaxation, enabling use of this common synthetic principle from inorganic chemistry to augment the performance of molecular quantum bits.

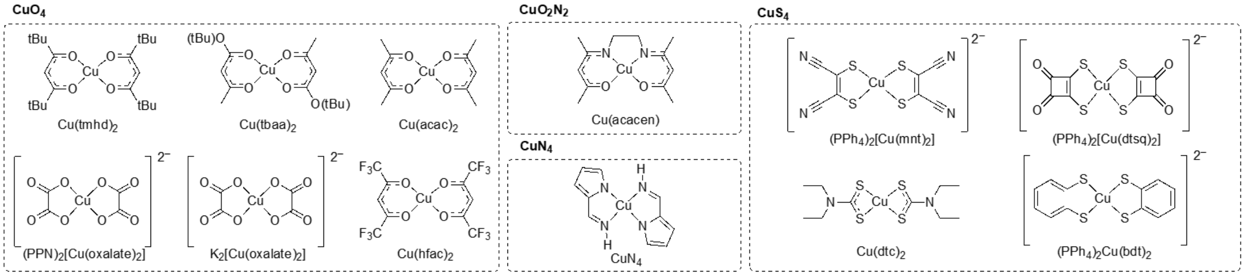

Figure 3. Compound scope for MCD studies of ligand field strength impacts on T_1. Twelve Cu(II) square-planar compounds chosen encompass both room-temperature coherent qubits (e.g. $(PPh_4)_2[Cu(mnt)_2]$) and fast-relaxing complexes (e.g., $Cu(hfac)_2$).

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Peer-Reviewed Publications Resulting from this 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.

Molecular Structural Dynamics and Function at the Fundamental Level

Award Number: DE-SC0002164

Principal Investigator: Ahmad Hosseinizadeh
Dept. of Physics, University of Wisconsin Milwaukee
3135 N. Maryland Ave, Milwaukee, WI 53211

Project Scope

Biological molecules such as proteins undergo structural changes throughout their life cycle with profound effects on their function and mechanism. A comprehensive insight into their real-time structural dynamics has been a dream goal in biophysics and structural biology. This is crucial for several reasons including (i) gaining a deeper understanding of biological mechanisms responsible for many natural events, (ii) expanding our knowledge of the structural basis of genetic and sporadic diseases and therefore developing more effective pharmaceutical drugs for their control, (iii) facilitating the design and fabrication of new materials with exceptional functional capabilities. In this regard, great efforts have been made in the past decades via a variety of experimental, theoretical, and computational methods such as X-ray diffraction, cryogenic electron microscopy, nuclear magnetic resonance spectroscopy, molecular dynamics simulation, and so on. However, they are encountered with significant challenges such as poor data quality as well as algorithmic and data analysis difficulties so that, at best, they can recover a few static pictures of structures far apart in time, but not continuous structural variations in real-time. Accordingly, more experimental and data analytic improvements are still necessary. It is well known that the dynamics of a biomolecule essentially is a series of concerted and continuous structural changes happening in extremely short time intervals. With the invention of synchrotron radiation, and over the past fifty years, time-resolved X-ray crystallography has become the most conventional technique for this purpose. The advent of the X-ray free-electron laser (XFEL) technology in 2009 established a new era in this field because very intense and short XFEL pulses offer the unique opportunity to observe molecular dynamics at femtosecond regimes. However, the standard data analysis tools, which mostly originate from synchrotron radiation-based methods, cannot reach the ultrafast molecular processes due to the aforementioned issues. Therefore, besides modernizing experimental techniques, new theoretical and algorithmic paradigms are required for a full characterization of molecular structural variabilities at the most fundamental level.

Recent Progress

We have continuously been developing innovative data analytical machine learning methods in the past decade, which have been applied to different types of data including XFEL [1-4] and cryo-EM [5-6]. In cryo-EM, we have generated three-dimensional (3D) movies of continuous conformational changes of molecular machines, while traversing their work cycle on their free-energy landscape [5-6]. This paves the way for an in-depth understanding of such molecules in protein synthesis and their operational mechanisms in living cells. We also applied this method to single-particle XFEL data from a virus and captured its biologically related structural changes along its conformational coordinate, which was quite innovative using X-ray data [2]. In the area of time-resolved XFEL, our data-analytical approach can extract the extremely ultrafast dynamics of molecules from noisy spectral snapshots on timescales far below the timing uncertainty involved in data [3]. Moreover, our newest method can find ultrafast structural dynamics of proteins in the presence of severe data incompleteness, timing inaccuracies, and other stochastic artifacts that time-resolved crystallography snapshots confront in XFEL [4]. So far, we have studied the Photoactive Yellow Protein (PYP) by this approach and extracted the femtosecond dynamics of this protein and charge oscillations of the chromophore while passing through a conical intersection [4]. Our algorithm can also identify the key collective variables and trajectories as well as the associated population dynamics (Figure 1) involved in the de-excitation of this complex molecule. This level of detail in structural dynamics cannot be accessed by any conventional techniques in biophysics with X-ray free-electron lasers.

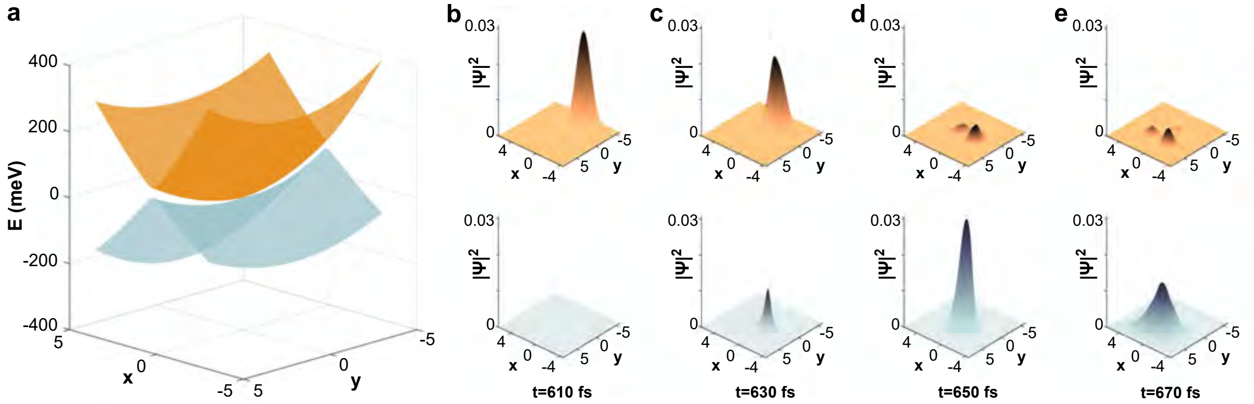

Figure 1: Topography of the conical intersection of the photoactive yellow protein and the associated population dynamics, as deduced from five experimentally determined dynamical trajectories [Ref. 4]. **(a)** Reconstructed potential energy landscape in the vicinity of the conical intersection. The touching of the two potential energy surfaces constitutes the conical intersection. **(b – e)** Time evolution of a Gaussian wave packet on the electronically excited state (top panels) and electronic ground state (bottom panels) in the vicinity of the conical intersection.

Future Plans

Despite all the above-mentioned advancements, however, there are still important questions that need to be addressed. Particularly, two central problems are detailed observation of functionally relevant and important structural motions at high temporal and spatial resolutions, as well as deriving their underlying functional and energy-efficient pathways.

To tackle these problems, we are working on a new generation of our data-analytical algorithms by combining concepts from machine learning, differential geometry, graph theory, diffraction physics, and data science. As an upgrade to our former algorithms, we have shown through simulations that the spatial resolution of a noisy dataset can be boosted by harnessing the geometric relationship amongst a related but less noisy dataset. This proves, in principle, that fusing heterogeneous data enhances our ability to obtain high-quality information from noisy snapshots of biomolecules. To achieve this and further investigate the biomolecular mechanisms, we would like to use a combination of structural and spectroscopic data from proteins. Such data can be collected simultaneously for the same samples at an XFEL with a much lower signal level for spectroscopic data than for structural data.

Furthermore, in our recent studies of photoactive proteins, we have found single-mode femtosecond dynamics, i.e., structural variations along single reaction coordinates, where isomerization and chemical bond breaking occur. However, in addition to that, we would like to visualize the time-dependent 3D structural changes associated with functional states, which will advance our understanding of molecular conformations and dynamics along functional pathways. This goal requires the appropriate combinations of the single-mode dynamics that we have extracted in our earlier investigations. We believe that this study will open new doors to further discover how biological cells and organisms work at the molecular level, which in turn, will enhance our knowledge of the fundamental mechanisms of many diseases that originate from the disruption of functional pathways of biomolecules.

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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, *Sci. Rep.* **13**, 1372 (2023).
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On-Chip Attosecond Metrology of Solid-State High-Harmonic Generation

Award No.: DE-SC0024173

PI: Phillip D. Keathley, Principal Research Scientist, Research Laboratory of Electronics at MIT; **Address:** 77 Massachusetts Avenue, Bldg. 36 Rm. 293, Cambridge, MA 02139; **Email:** pdkeat2@mit.edu

1 Project Scope

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, using field-resolved time-domain spectroscopy. While HHG from atomic and molecular systems has been investigated extensively, many open questions remain. In particular, questions 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, field-resolved measurements of the HHG radiation from solids in the time domain. For our measurments, we will leverage nanoscale petahertz electronic devices developed and fabricated by our team. These devices will uniquely provide the ∼MV/m field sensitivity needed to study the harmonics in time, in addition to polarization polarization sensitivity for full polarization and time-domain electric field waveform characterization of solid-state high-harmonic radiation spanning the visible to near-infrared. To compliment our experimental efforts, we will also use comparison to theory and computational models such as time-dependent density functional theory to understand the underlying physics [1].

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 anticipate these methods will have impact beyond the studies of HHG in solids by enabling the general study of attosecond- to femtosecond-scale electron dynamics in complex media.

2 Recent Progress

In the last year we have made progress in the following areas.

2-µm Few-Cycle OPA Development and Experimental Test Station The experiments in this program will be driven using a home-built, few-cycle 2-µm optical parametric amplifier (OPA). As discussed in our work in Ref. [1], for adequate spectral coverage in waveform measurements using waveform measurments similar to that described in Refs. [2], [3], it is essential to use an adequately short gating pulse (between 2-3 cycles full-width at half maximum or less). Furthermore, adequate total energy on the order of several micro-joules is needed for driving both the high harmonics as well as the field-resolved waveform measurements.

We have finalized the implementation and characterization of an OPA source that meets these requirements. A critical part of this effort was the design and use of customized chirped mirrors to ensure a near transform-limited duration between 2 to 3 cycles. The system reliably generates microjoule-level pulses between 2-3 cycles in duration at a center wavelength of 2.5 µm. In addition to the OPA, we have also implemented the experimental test station (not shown) and are currently transitioning our focus to experimental testing.

Completion of studies of temporal and spectral mixing properties of lightwave electronic currents for field-resolved waveform measurements. As we set out to investigate harmonic radiation using our nanoscale lightwave-electronic devices, it is critical that we understand the temporal properties of the emitted currents and their impact on the characterization of temporal and spectral properties of the solid-state HHG fields of interest. To this end, we have completed two sets of work.

The first is a study of the properties of the nanoantenna devices when used as harmonic frequency mixers for the analysis of harmonic waveforms. This work showed how harmonic fields information is obtained through a harmonic-frequency mixing process in the generation of current from the nanoantenna structures similar to what is often used at lower frequencies for RF signal analysis using more conventional nonlinear electronics. We showed analytically how both amplitude and phase information of harmonics is preserved in this process. Importantly we clarified that CEP-stabilization is in fact not required to retrieve accurate phase information of harmonics down to an absolute offset phase. For experimental demonstration, we showed how the first and second harmonic waveforms are accurately retrieved using a single gate at the fundamental frequency. This work is critical to the measurements we want to pursue in this program as it confirms experimentally that CEP stabilization is not required, relaxing the experimental complexity. It also serves as the first experimental confirmation that the TIPTOE approach [4] we plan to use can be extended to the characterization harmonic field waveforms in the time-domain (this had only been theorized by prior work). This work has now been published in Science Advances [3].

The second is a study of how the lightwave electronic currents from the nanoantenna devices reshape the spectral response of the waveform characterization process over a single harmonic passband. By using a multicycle gate pulse to excite the antennas we ensure that each harmonic passband is narrower than the bandwidth of a 1.5-cycle supercontinuum which is used as the signal waveform. This allows us to investigate the intrinsic bandwidth limitations of the photocurrent response for each harmonic. Our work shows remarkable agreement between the experimental data and simulations based on both quasi-static tunneling models as well as more complete solutions of the time-dependent Schrödinger equation. This strong fit to both models allowed us to further explore the time-domain emission response under the experimental conditions used. More broadly, this work confirms the accuracy of the quasi-static Fowler-Nordheim tunneling models for simulating gold device response in the optical-field emission regime. Importantly for this program, it ensures the accuracy of our earlier simulations of device performance for the study of solid-state HHG, and that we can trust more simplified quasi-static models to design and analyze the device response for the extraction of the precise amplitude and phase properties of the incident harmonic signals we wish to measure. A manuscript describing this work is now completed and we will be submitting it for publication in the coming weeks.

For these two manuscripts, initial data was collected with support of an AFOSR program that has ended. Given the significant importance of these works to the specific aims of this program, all work in completing these studies including analytical analysis, simulations and their analysis, and manuscript writing has been fully supported by this program.

Design of two-channel devices for accurate vectorial field measurements. We have continued the development of devices having polarization-sensitive response for tracing time-domain vectorial fields from solid-state HHG. Original concepts aimed to use devices having a meandering pattern of electrically-connected cross-polarized devices with alternating **x**- and **y**-polarized devices for measuring the **x**- and **y**-polarized signal fields respectively. However, further experimental work combined with simulations has shown that due to coupling between the connected nanoantenna pairs, cross-talk occurs between devices oriented in each polarization state. This means that when excited with a signal containing only one polarization state, for instance **x**-polarization, erroneous information can be coupled into the orthoganally-polarized antenna creating a spurious measurement of **y**-polarized signal. The degree of this coupling is highly sensitive to the precise device geometry as fabricated. Given tolerances in fabrication, we have found it is nearly impossible to ensure reliable removal of this coupling in electrically-connected arrays.

To solve this issue, we have developed two-channel devices having disconnected arrays of devices for measuring two different orthogonal polarizations. One device array is designed to measure waveforms polarized along **x**, while the other to measure waveforms polarized along **y**. These two sets of arrays are placed adjacent to one another so that the incident signal waveform is split in half spacially, with one half for measuring **x**-polarized light and the other for measuring **y**-polarized light. This approach ensures complete decoupling of the two polarizations in measurement for accurate vectoral analysis of harmonic fields.

Initial two-channel devices have been fabricated and testing is planned for the upcoming months to ensure accurate vectorial signal readout.

3 Future Plans

HHG studies. With the characterization of our experimental test bed complete, in the next year we plan to pivot towards experimental measurements of HHG fields. We will start with perturbative harmonics in bulk media like fused silica and silicon among others, examining simultaneous second and third harmonic generation at lower intensities. We will then transition to generating and characterizing higher-order harmonics focusing on how the nature of the harmonic radiation changes as intensity is increased going from a perterbative to a non-perturbative response. The aim of these studies will follow our initial proposal to investigate the various contributions of inter- and intraband charge dynamics on the harmonic radiation under various excitation conditions for different materials.

In addition to bulk materials, we are also working with collaborators to explore harmonic radiation from other materials of interest, such as flakes of transition metal dichalcogenides (TMDCs) [5] or graphene [6]. For the TMDCs we aim to investigate the impact of exciton dynamics and charge-transfer on the generated harmonics. For this work Dr. Christian Heide, a postdoc working with Prof. Tony Heinz and David Reis at Stanford, will visit from October to November of 2024 to take part in a measurement campaign at MIT. We intend to continue measurements on these materials and their analysis after this visit.

Continued development of devices for vectorial field measurements. Now that we have designed and begun fabricating two-channel devices for vectorial field measurments, in the next year we intend to verify their operation. For this we will confirm the ability of the devices to accurately measure waveforms of various ellipticity in the time-domain.

Publish manuscript describing studies of temporal and spectral mixing properties of lightwave electronic currents for field-resolved waveform measurements. We anticipate this manuscript will be published within the next year.

Publish manuscript detailing our custom 2-μm **OPA.** We will draft and submit a manuscript for publication about our custom 2-μm OPA system built for this work.

4 Peer-Reviewed Publications Resulting from This Project (2022-2024)

Yeung, M., Chou, L.-T., Turchetti, M., Ritzkowsky, F., Berggren, K.K., Keathley, P.D., 2024. Lightwave-electronic harmonic frequency mixing. Science Advances 10, eadq0642. https://doi.org/10.1126/sciadv.adq0642

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Attosecond Physics with XFEL sources

Award number: DE-SC0022093

Principal Investigator: Alexandra Landsman

191 West Woodruff Avenue
Ohio State University
Columbus, Ohio 43210
Email: Landsman.7@osu.edu

PROJECT SCOPE

In the past 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 descriptions of both strong field ionization and single photon ionization relying on analytical and numerical approaches. 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.

We work closely with experimentalists at SLAC and the Ohio State University (OSU) to interpret measurements at LCLS using attosecond X-ray sources. Theoretical developments will be made both independently, and when possible, hand-in-hand with our experimental collaborators at SLAC and OSU, resulting in increased relevance, rigor, and higher impact.

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*. This has resulted in several products, published [i,ii], accepted [iii], and submitted (see Reference [5]), which are summarized below. Note that Roman numerals are reserved for products in the last section ("Peer Reviewed Publication Resulting from this Project"), while Arabic numbers are from the "References" section.

Strong field interactions:

We recently investigated strong field interactions between X-ray radiation produced by XFELs and atoms [iii]. This study delves into the relatively uncharted territory of Above Threshold Ionization in atoms, triggered by intense X-ray radiation fields. The conditions we examined are similar to those currently achievable at LCLS. At these frequencies, the energy of a single photon far exceeds the ionization potential of valence electrons in atoms and molecules. Under such high-frequency scenario, the onset of strong field ionization requires a shift away from the traditional quasi-classical approach. We therefore developed an analytical model to characterize how the field-free ionization potential, ponderomotive energy, and photon energy govern the transition to this regime, all accounted for by means of the Keldysh and Reiss parameters. The Keldysh parameter, $\gamma = \omega\sqrt{2I_p}/F$, depends on ionization potential, laser frequency and field strength (given by I_p, ω and F, respectively.) The Reiss parameter, given by $\mathrm{Z} = U_p/\hbar\omega$, relates the ponderomotive energy of the free electron to the photon energy. We show that both of these parameters are needed to capture the onset of strong-field behavior due to both bound state and continuum state properties. At higher X-ray intensities, we find that ionization rates deviate from the linear intensity scaling expected from lowest order perturbative processes, corresponding to channel closure and higher-order photon absorption processes.

Attosecond Ionization Delays in Atoms and Molecules:

In products [i,ii,5], we focused on ionization delays. In particular, [ii] 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. 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. One interesting conclusion is that at low energies, the separation of the Coulomb-Laser coupling (CLC) time from the Wigner time breaks down and the interpretation of experimentally measured streaking delays becomes more difficult.

In publication [i], we collaborated with a large experimental effort, led by James Cryan to investigate attosecond delays in X-ray molecular ionization of Nitric Oxide (NO). This experiment used attosecond X-ray pulses produced by LCLS to ionize from the K-shell of the oxygen and nitrogen atoms, respectively. There relative delays were subsequently probed by the circularly polarized infrared field, using the attoclock principle. The experimental measurements showed significant delays at certain energies, highlighting the complex many-body dynamics of inner-shell photoionization. Our group contributed to the interpretation by introducing a new Coulomb-Laser coupling (CLC) delay, which can be substantially different from the currently used linear CLC delay. We also performed simulations using our previously developed Classical Wigner Propagation (CWP) method, performed within the single active electron approximation. This approach was not able to account for significant bumps in delay at certain photon energies, highlighting the need for developing a many-body theory of inner-shell photoionization.

Product [5] is another collaboration with the experimental group of James Cryan, analyzing RABBIT measurements led by Anna Wang-Holzen during her PhD study. This work, currently under consideration, investigates relativistic effects in molecules due to spin-orbit coupling. In particular, the RABBIT experiment measures relative delays between two neighboring spin-orbit states of the valence orbitals of methyl iodide. The experiment observed substantial variation in delays, which could not be explained using standard molecular theory. We were able to explain the dip observed in the experimental data using relativistic atomic simulations. In particular, the dip in the measured delay was explained as due to the interplay between relativistic spin-orbit activated interchannel coupling (SOIAIC) and spin-flip transitions. There was an unexpectedly large delay observed in the region known for high-density two-electron transitions, which we are currently working to explain. There is currently no known theoretical approaches that describe relativistic two electron transitions in molecules (including time-delays), and therefore new theoretical developments are necessary.

FUTURE PLANS

We will continue to build on the above-described results involving (a) strong field interactions between high frequency radiation and matter (see publication iii); (b) developing proper descriptions of Coulomb-Laser coupling delays for circular streaking experiments, such as currently conducted at LCLS (see publications i and ii); and developing models to account for many-body dynamics in the photoionization process (see product iv). We also plan to extend our theory of strong field ionization with high frequency pulses to the multi-electron systems, such as neon. The idea is to make predictions which can be tested in the future LCLS experiments or other XFEL facilities around the world.

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PEER REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2022-2024)

[i] T. Driver, et al, “Attosecond delays in X-ray molecular ionization", *Nature* 632 (8026), 762-767, (2024)

[ii] L. Ortmann and A.S. Landsman, “Understanding attosecond streaking" *Reports on Progress in Physics* 87 (8), 086401, (2024)

[iii] S. Walker, A.S. Landsman, “Above-threshold ionization with X-ray free-electron lasers" *Communications Physics (Springer, Nature)* accepted

[iv] 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)

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

Tracking multi-electron dynamics in molecules at the attosecond timescale

Award Number: DE-SC0024383
Guillaume Marc Laurent (PI)
Department of Physics, Auburn University, Auburn, AL, 36849
Email: glaurent@auburn.edu

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 fully completed the development of the experimental system required for this project, which combines a source of shape-controlled attosecond pulses and a multi-particle imaging system (reaction microscope or COLTRIMS) for electron/ions coincidence measurements. 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, a COLTRIMS, and an EUV photon spectrometer [1]. The COLTRIMS spectrometer is now routinely used in our laboratory, and we currently are performing our first time-resolved measurements at the attosecond timescale.

In addition, we have also completed a study initiated in our previous DOE project related to the characterization of the spectral components of attosecond pulse trains generated by a two-color field. This study was motivated by the needs of tailored attosecond pulses with well-defined temporal profile for our attosecond experiments. A systematic study of the dependence of the temporal profile of such pulses on the various parameters controlling the high harmonic generation process was crucial for our project, as COLTRIMS measurements are too time-consuming for allowing pulse-shape optimization experimentally.

1 - Completion of the reaction microscope.

Over the past year, the major development has been the completion of our reaction microscope [2, 3]. In order to perform a complete measurement of the coupled electronic and nuclear dynamics in molecules proposed in this project, we have added a second multi-hit detector for the detection of ions and molecular fragments. We now have the capability to carry out coincidence measurements of the 3D-momentum distribution of all the emitted charged particles. The system has been custom-designed by us, and recently fully assembled and tested. It combines a modulable charged-particles spectrometer and two multi-hit detectors. 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 magnetic field, both the photoelectrons and photo-ions are steered toward the detector with a (quasi) 4π solid angle collection for kinetic energies up to tens of eV. From both the time of flight and the impact position, the complete momentum vector of each charged particles is reconstructed and the energy deduced with a resolution ($\Delta E/E$) of about 5%.The capability of our system is demonstrated in figures 1 where we displayed the photoelectron momentum distribution (a), the photo-ion time-of-flight (b), and the photo-electron/photo-ion coincidence spectrum (c) of photoelectrons and photions generated from argon by absorption of an attosecond pulse train (APT) made of odd harmonics.

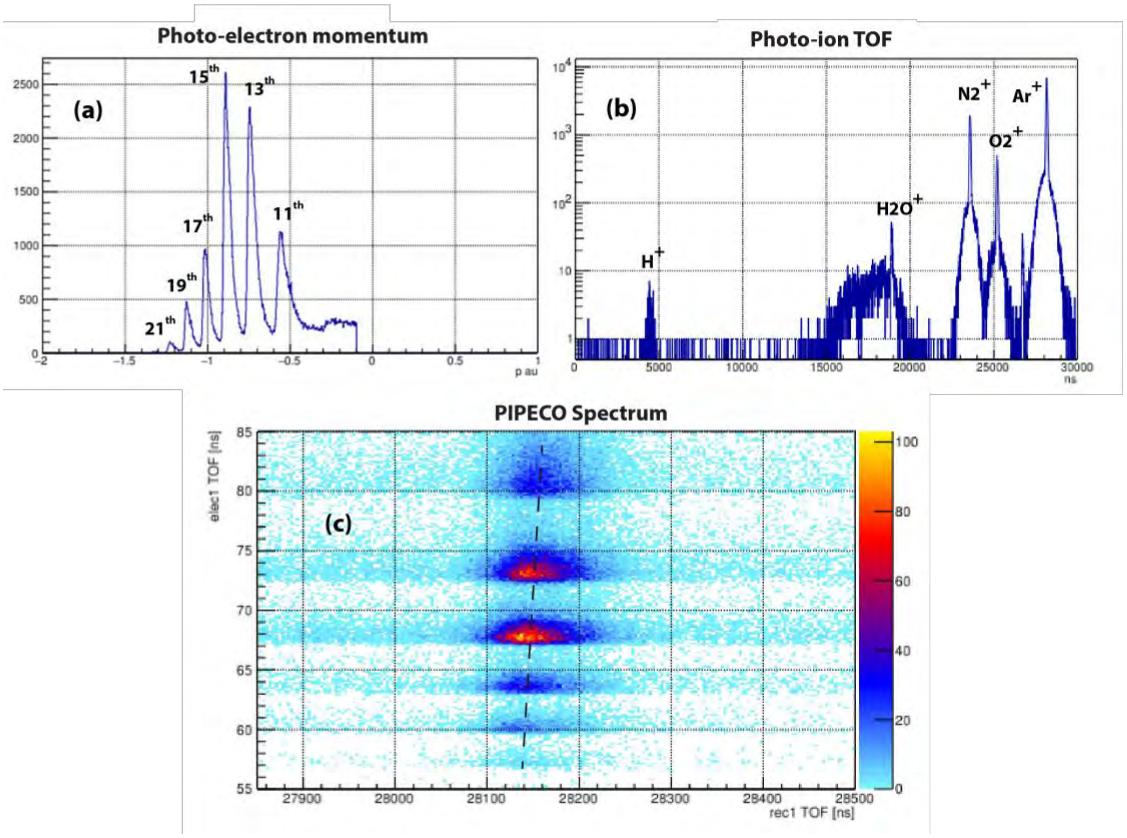

Figure 1: Current capability of our reaction microscope: (a) photo-electron momentum distribution, (b) photo-ion time of flight, and (c) photo-electron/photo-ion coincidence spectrum (PIPECO) of photoelectrons and photo-ions generated from argon by absorption of an attosecond pulse trains (APT).

2 - Characterization of the spectral components of attosecond pulse trains generated by a two-color femtosecond laser fields.

The development of attosecond light sources based on the high-harmonic generation (HHG) process has offered new possibilities to probe dynamics in matter down to the natural timescale of electron motion. Attosecond measurements are generally performed through the generation of an electron wave-packet by absorption of the attosecond pulse. The dynamics under scrutiny is then unraveled from the attributes of the wave-packet assuming that the spectral components of the attosecond pulse encoded in the measurement are known. The spectral characteristics of attosecond pulse trains (APTs) generated by an one-color driving field have been reported extensively in the literature. In particular, it is well known that the frequency-dependence of the spectral phase limits the achievable level of synchronization of the frequencies making up the pulse [4]. On the contrary, studies on the spectral phases of APTs generated by a multi-color field have been sparse so far, despite the potential such APTs could have for attosecond experiments.

In this project, we have performed a comprehensive study of the spectral phases of APTs generated by intense two–color femtosecond fields ($\omega+2\omega$), and we have shown how they can be tuned by varying both the intensity ratio and the relative phase between the two components of the driving field. We have found that the spectral phases exhibit high tunability for an intensity ratio between the two colors of the driving field in the range of 0.1 to 5%, as shown in Figure 2. In particular, we have shown that the spectral phases can be manipulated in order to produce either one or two attosecond pulses per optical cycle of the driving field. A manuscript summarizing the main results of this study is in preparation.

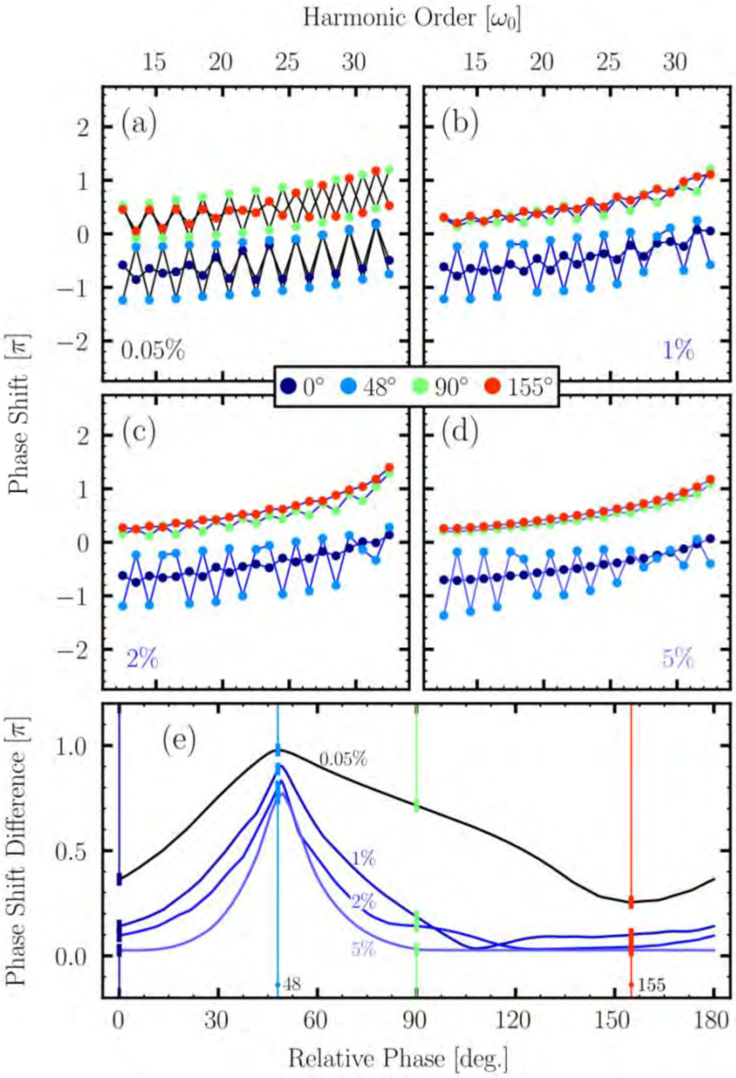

Figure 2: Quantum orbit calculations for various intensity ratios and relative phases between the two components of the field. (a-d) Phase shift between consecutive odd and even harmonics. (e) Average of the absolute difference between consecutive phase shifts over the harmonic plateau region

Future Plans

In the next year, we plan to use our recently built experimental capability to study 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. The number of parameters which could be varied to unravel the electron dynamics in this system 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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Peer-Reviewed Publications Resulting from this Project (2022 - 2024)

No publications to report.

Towards imaging time-resolved non-equilibrium molecular structures with ultrafast intense laser pulses

Award number: DE-SC0023192

Principal Investigator**:** Anh-Thu Le
Department of Physics, University of Connecticut, 196A Auditorium Rd, Storrs, CT
email**:** thu.le@uconn.edu

I. Project Scope

The purpose of this project is to theoretically and computationally study the dynamics of 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.

II. Recent Progress

1. New progress in development of the strong-field Herman-Kluk simiclassical method

Last year we reported a new semiclassical method that combines Herman-Kluk propagator with strong-field formalism for atoms in intense lasers. We showed that our method, the strong-field Herman-Kluk (SFHK), provides very accurate two-dimensional (2D) photoelectron momentum distribution (PMD) [1]. This method has now been successfully extended to molecules. As an illustration, we show in Fig. 1 photoelectron yields vs scattering angles at momentum $p = 3.5$ au from a chiral molecule (CHFClBr) in a typical 1,200-nm intense laser pulse. We found that our method extends the LIED technique beyond the Quantitative Rescattering (QRS) theory and the independent atom model. Furthermore, due to its semiclassical nature, this method can provide insightful interpretations for various effects found in rescatteing physics. A major advantage is that the method is based on classical trajectories that can be calculated independently

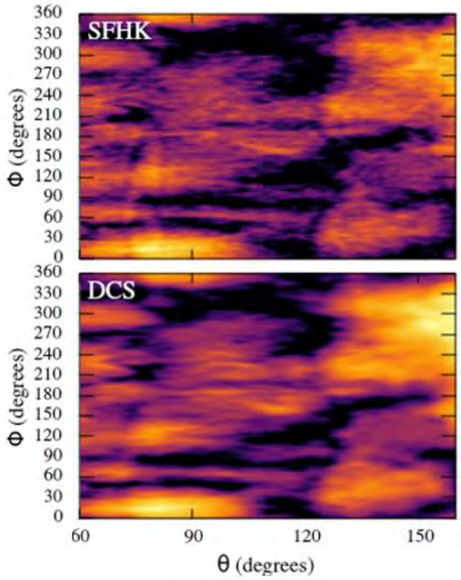

Fig. 1. Comparison of the PMD at $p = 3.5$ au obtained with the SFHK and the DCS as function of scattering angles for CHFClBr.

by solving classical Newton equations such that primitive parallelization can be conveniently employed to accelerate the calculations.

We have also extended the SFHK method to elliptically polarized lasers. Our intention is to use the method to probe chiral molecules, especially in the rescattering region, where the chiral sensitivity is expected to be strong (see Sec. III below). As a first application, we investigated the 3D PMD in low energy region for atoms in an intense elliptically polarized laser pulse. By using a relatively long pulse, separate above-threshold ionization (ATI) shells in 3D momentum space can be clearly identified. For hydrogen atom, we confirmed the earlier experimental results [2] that the offset angle increases with increased ATI ring, which has been attributed as due to the nonadiabaticity in strong-field ionization. We have also extended this analysis to the states with magnetic quantum numbers of $m=+1$ and $m=-1$ in Ar and show that the exact numerical solutions of the time-dependent Schrodinger equation (TDSE) can be accurately reproduced by the SFHK. By using the SFHK, we have identified the effect of the ring currents directions as due to the initial "kick" along (or opposite) to the electric field rotation direction. These results were reported at the DAMOP 2024 meeting, and a draft of our paper is under preparation [3].

2. XUV + IR scheme for time-resolved laser-induced electron diffraction imaging

We extended the LIED imaging technique by adding a relatively weak XUV pulse to the driving IR or midIR laser pulse to control and enhance the LIED signals. The XUV pulse prepares an electron wave-packet near the ionization threshold. The ionized electron is driven predominantly by the IR. We have carried out detailed investigations using numerical solutions of the TDSE and showed that accurate elastic electron-target ion scattering differential cross section (DCS) can be retrieved within this scheme. More importantly, with the control of the electron emission time provided by the XUV pulse, not only the temporal resolution of the measurement can be improved, but the LIED signals can also be increased by two orders of magnitude, as compared to the standard LIED technique. An additional advantage of this scheme is that a relatively weak IR pulse can be used, thereby overcoming the difficulties associated with the depletion of the target ground state. A draft of our paper is under preparation [4]. Note that this scheme has been used earlier in HHG by K. Schafer and M. Gaarde group at LSU and A. L'Huillier group. For the LIED, experimental investigations have also been proposed by L. DiMauro.

3. Ring interlocking in 3D photoelectron momentum distribution at low energies

We have collaborated with Prof. C. Trallero experimental group on 3D PMD from atoms in intense elliptically polarized lases. The high-quality experimental 3D data for the PMD revealed interesting features, most notably the ring interlocking which resembles the formation of electron vortices that has been reported earlier using a different experimental setup. Our TDSE calculations showed excellent agreements with the measured PMDs. With the rotation of the center of mass from ring-to-ring signals (the offset angles) being well understood (see also Sec.II.1), we now focused on the interlocking feature in the first ATI ring. To understand its origin, we have carried out detailed analyses of our SFHK and TDSE results. We found that the main features of the experiments can be reproduced by using nonadiabatic ionization within the SFHK method, but they cannot be obtained by using the adiabatic ionization. Furthermore, the interlocking can be interpreted as vortices in the momentum space formed by electrons with different final orbital angular momenta. These electrons were "born" at different times under different initial distributions. These results were reported at the DAMOP meeting and Gordon

Conference on multiphoton processes (2024). A draft of our paper is under preparation while another manuscript was submitted to Physical Review Research [5].

4. Accurate HHG simulations for atoms and molecules, including macroscopic propagation.

We have recently developed a very efficient numerical method for solving the TDSE for polyatomic molecules within the single-active-electron approximation. For atomic targets, the method is so fast that it allows us to solve the coupled Maxwell-Schrodinger equations numerically for a gas-cell setup in which the intense driving lasers is modified during its propagation in the medium with a typical length of 1 cm. This is of practical interest since other methods such as the TDDFT and the QRS have their own difficulties (high demanding computational resources for the former and inaccuracies for below threshold harmonics for the latter). We have been collaborating with the group of Dr. Predrag Ranitovic (University of Belgrade) to compare our results with their measurements. Our joint paper is under preparation.

5. Interferometric harmonic spectroscopy and APT phase retrieval

Motivated by recent experimental advances in interferometric harmonic spectroscopy [6], in collaboration with Prof. C. Trallero we have investigated the interferometric transient absorption spectroscopy (iTAS) technique which we apply to electron dynamics imaging and APT phase characterization. In contrast to the ATAS, which gives access to the imaginary part of the refractive index, an interferometric phase measurement gives information of its real part. Specifically, we theoretically analyzed experimental phase at the XUV frequencies of interfering electromagnetic radiation arising from two spatially separated arms when an argon sample in one arm is subject to an APT whereas a similar sample in the second arm is subject to a replica of the APT in combination with a weak IR of adjustable intensity. By comparing a full scheme involving numerical solution of the coupled Maxwell-Schrodinger equations against a perturbative treatment for the propagating radiation, we identified the different photoexcitation pathways imprinted in the real part of the refractive index. We then retrieved the APT spectral phase based on the interferometric phase measurements. Furthermore, we also analyzed the effects of spin-orbit interaction and macroscopic propagation on the APT phase retrieval. These results were reported at the DAMOP (2024). Our joint paper is under preparation.

III. Future Plans

We plan to further develop our semiclassical method, the SFHK, for applications in strong-field processes. An extension of the method to the HHG process would seem quite natural and we plan to use hydrogen and argon as test cases to benchmark our method against the TDSE solutions. Here care should be taken so that the transition dipoles (associated with the photo-recombination) can be calculated accurately and efficiently within the coherent states basis used in the SFHK method. It would be interesting to see how the SFHK performs for below-threshold (or near-threshold) harmonics. Based on our experience with the PMD calculations (see Sec. II.1), we expect that the SFHK for HHG can be extended to polyatomic molecules in a straightforward manner.

Next, our main effort will be devoted to including nuclear motion in the simulations of LIED and HHS. Within the SFHK, the classical motions of nuclei can be included in the calculations. We plan to try this approximation first. Note that this level of approximation is quite common for simulations of Coulomb explosion processes. In principle, the quantum nature of nuclear motion can be accounted for by including the nuclear degrees of freedom semiclassically in the SFHK in the same manner as the electronic degrees of freedom. In the simplest case of one nuclear degree of freedom, we expect that this would lead to about 30% increase in computer time as compared with the frozen nuclei approximation. This should be manageable, and therefore, we plan to study LIED and HHS within the pump-probe scheme for dissociating molecules within the SFHK. Alternatively, we can also simulate by using the time-dependent nuclear wave packet obtained from the solution of the coupled channel equations 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 QRS.

Many theoretical and computational tools developed in this project are also relevant to other time-resolved spectroscopic techniques such as ATAS and time-resolved photoelectron spectroscopy (TRPES). We therefore plan to perform simulations for other related techniques of current interest to the research community, including the ATAS and TRPES. Together with LIED and HHS, these techniques provide complementary information on molecular structure. Finally, we plan to use the tools developed here to probe chiral sensitivity in chiral molecules within the LIED and HHS schemes.

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V. Peer-Reviewed Publications Resulting from this Project (start date: 08/2022)

1. L. He, C. H. Yuen, Y. He, S. Sun, E. Goetz, A.-T. Le, Y. Deng, C. Xu, P. Lan, P. Lu, and C. D. Lin, *Ultrafast picometer-resolved molecular structure imaging by laser-induced high-order harmonic*, Phys. Rev. Lett. **133**, 023201 (2024).
2. P. Zhang, V.H. Hoang, C Wang, T.T. Luu, V Svoboda, A.-T. Le, H.J. Wörner, *Effects of Autoionizing Resonances on Wave-Packet Dynamics Studied by Time-Resolved Photoelectron Spectroscopy*, Phys. Rev. Lett. **130** (15), 153201 (2023).
3. L. He, Y. He, S. Sun, E. Goetz, A.-T. Le, X. Zhu, P. Lan, P. Lu, C. D. Lin, *Attosecond probing and control of charge migration in carbon-chain molecule*, Adv. Photonics **5**, 056001 (2023).

Beating electronic decoherence (DE-SC0020994)

Wen Li, Wayne State University (wli@chem.wayne.edu)
H. Bernhard Schlegel, Wayne State University (hbs@chem.wayne.edu)

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 the time domain. (2) devising atomistic schemes that can suppress decoherence and produce long-lived electronic coherence in molecular systems.

Recent Progress

1. Phase-resolved attoclock

Two-electron angular streaking (*2e-AS*) was recently developed to study electronic motion in atomic and molecular systems for the first few femtoseconds of the excitation. The carrier-envelop-phase (CEP) dependence of the photoelectron momentum distributions was used to differentiate the two ionized electrons arising from the double ionization processes. Recently, the

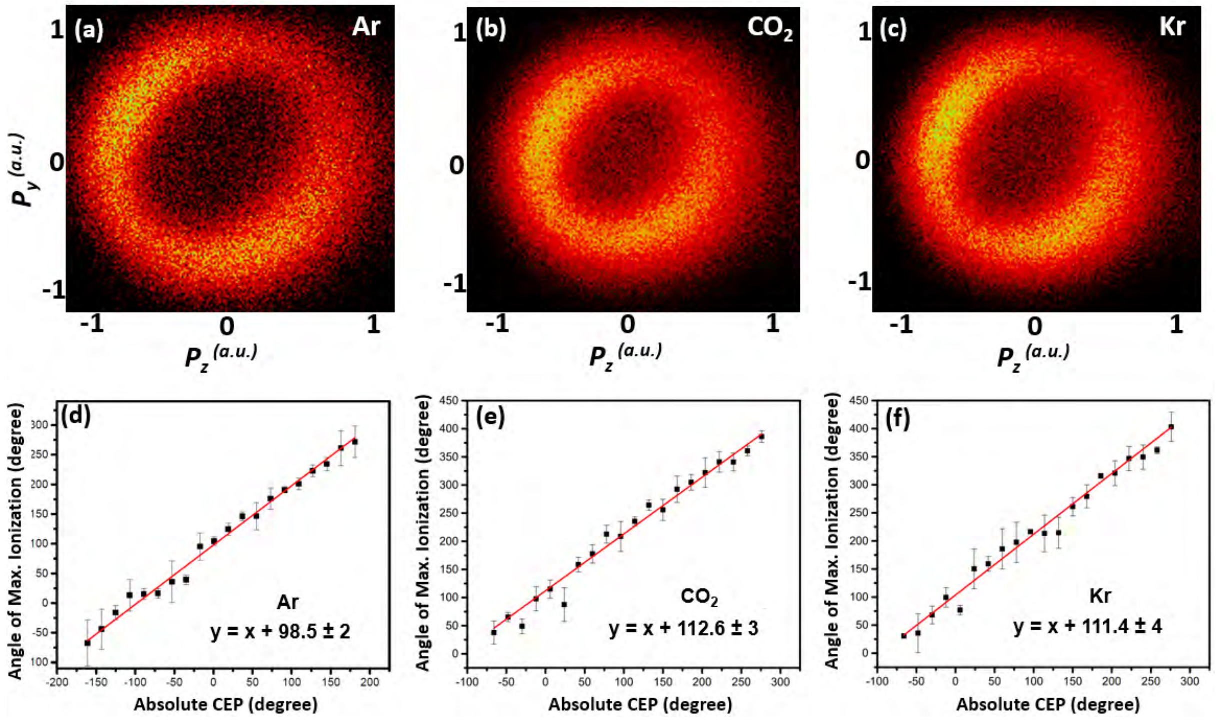

Fig. 1 Experimentally obtained photoelectron momentum distributions of (a) argon (b) carbon dioxide and (c) krypton. All three images are CEP averaged. The ellipticity is 0.9. (d)-(f) are the corresponding correlation plots between the angle of maximum ionization and the absolute CEP. The intercepts of the linear fittings give the attoclock deflection angles for circularly polarized light in various atomic and molecular systems.

Li group has developed a normalization procedure that can retrieve the deflection angle in angular streaking experiments for few-cycle circularly polarized pulses, for the first time. It exploits the carrier-envelop-phase dependence of angular streaking. The method avoids the ambiguity inherent to the elliptical attoclock. The results also show that the attoclock deflection angles are solely sensitive to the ionization potentials of targets and tunneling delay is a minor effect. The manuscript is currently under review in Physical Review Letters.

2. Reducing the cost of TD-CI simulation of strong field ionization

Strong field ionization of molecules by intense laser pulses can be simulated by time-dependent configuration interaction (TD-CI). In this approach, the wavefunction is written as a linear combination of time-dependent coefficients with time-independent states of the field-free Hamiltonian. A complex absorbing potential (CAP) is used to remove the outgoing electron and the ionization rate is obtained from the decrease in the norm squared of the wavefunction. A wavefunction consisting of the ground state and all singly excited configurations (CIS) is suitable for the ionization of a neutral molecule. For ionization of a cation to dications, we use a CISD-IP wavefunction consisting of singly ionized determinants and singly excited, singly ionized determinants constructed from the orbitals of the neutral molecule. Standard molecular basis sets used for these wavefunctions must be augmented with several sets of diffuse functions for effective interaction with the CAP. This dramatically increases the number of configurations and the cost of the TD-CI simulations as the size of the molecules increases. The cost can be reduced by eliminating those virtual orbitals that make negligible contributions to the strong field ionization rate. This can be determined from the matrix elements of the absorbing potential and the TD-CI coefficients from test simulations. Compared to a simple 3 hartree cut-off in the orbital energies, this reduces the number of virtual orbitals by 20% - 35% for neutral molecules and 5%-10% for cations. As a result, the cost of simulations is reduced by 35% - 60% for neutral molecules. The number of virtual orbitals needed can also be estimated by second-order perturbation theory without the need for test simulations. The number of virtual orbitals can be reduced further by adapting orbitals to the laser field using natural orbitals derived from test simulations. This is particularly effective for cations, yielding reductions of more than 20%. This work was published in the Journal of Physical Chemistry A.

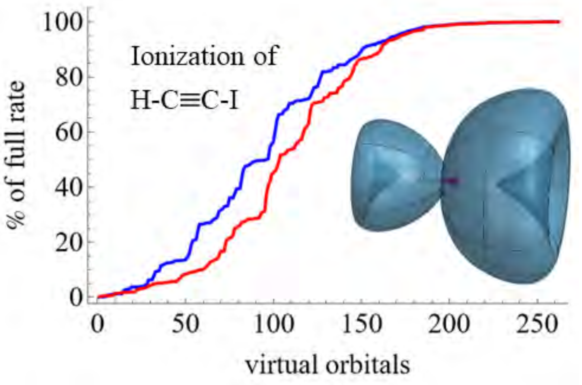

Fig. 2 Cumulative contribution to the total strong field ionization rate as a function of the number of virtual orbitals determined from test simulations (red) and by perturbation theory (blue).

3. Developing a new multi-hit and multi-mass 3D momentum imaging system

In 2023, the Li group demonstrated a simple two-camera imaging system to slice 3D ion Newton spheres arising from strong field ionization of molecules. The technique can achieve massive multi-hit capability. One shortcoming is the relatively low time resolution (8.8ns). This resolution is good enough for slice ion imaging but inadequate for obtaining the full 3D ion momentum when the time-of-flight spread of the ions is limited. Recently, we have resolved this issue by adopting a simple scheme to correct the camera shutter jitter, which is the main factor limiting the system time resolution. By using a light-emitting diode (LED) to monitor and correct the camera shutter, the TOF resolution has been improved to better than 2ns. Furthermore, we also show that the technique can detect two ions with different masses simultaneously by utilizing both the rising and falling edges of the camera shutter. The technique will be quite useful in ion imaging and covariance measurements. Further implementation with electron imaging is also possible. This work was published in Review of Scientific Instrumentation.

4. Future Plans

The Li group will continue to study the electronic decoherence/revival dynamics using both the *2eAS* method and the strong field pump-probe method. We are incorporating phase-resolved attoclock into *2eAS* to study electronic coherence. We recently obtained interesting data on different iodine-containing compounds. The Li and Schlegel groups are currently working on the interpretation of experimental data.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

1. G. Basnayake, Y. Ranathunga, S. K. Lee and W. Li, 3D Velocity Map Imaging: From Technique to Application, J. Phys. B **2022**, 55, 023001
2. H. B. Schlegel, P. Hoerner and W. Li, Ionization of HCCI Neutral and Cations by Strong Laser Fields Simulated with Time Dependent Configuration Interaction, Frontier Chem. **2022**, doi.org/10.3389/fchem.2022.866137
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4. G. Stewart, D. Debrah, P. Hoerner, S. K. Lee, H. B. Schlegel and W. Li, Carrier-envelope phase controlling of ion momentum distributions in strong field double ionization of methyl iodide, J. Phy. Chem. A., **2023**, 127, 870
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7. Durden, A. S.; Schlegel, H. B.; Reducing the Cost of TD-CI Simulations of Strong Field Ionization. *J. Phys. Chem. A.,* **2024**, 128, 7440-7450
8. E. Orunesajo, S. Abubakar, B. Oguh, S. K. Lee and W. Li, A multi-mass and multi-hit two-camera 3D ion momentum imaging system, *Rev. Sci. Instrum.* **2024**, 95 073302

Triggering and Probing Attosecond Dynamics with X-rays

Award number: DE-SC0024484

Kenneth Lopata
Department of Chemistry, Center for Computation and Technology
Louisiana State University, Baton Rouge, LA 70803
klopata@lsu.edu

Project Scope

Driven by advances in ultrafast science, observing the attosecond motion of electrons in molecules and solids has become the focus of intense interest. These poorly understood sub 5-fs processes are predicted to underpin a range of applications such as energy conversion/storage, optical breakdown, and photochemistry. Soft X-rays transient absorption is one especially promising technique for measuring these dynamics, 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. Since many ongoing and planned experiments use soft X-rays as pumps for the dynamics (e.g., in a soft X-ray pump/probe configuration), it is also important to understand how different types of core-holes induce attosecond valence dynamics [Kuleff2016, Bruner2017].

To address this challenge, this project uses quantum chemistry simulations to shed light on a two key questions related to triggering probing coherent dynamics with soft X-rays: (i) What is the relationship between time-evolving electron density and the corresponding transient inner-shell absorption spectra, and how general is this for a wide range of molecular and solid systems? (ii) How do core-holes created via soft X-ray pulses actually induce valence electron dynamics, and how do the dynamics depend on the character (heteroatom) used and the shape (edge) of the core-hole? We made progress over the last year towards answering these questions, with details supplied in the following sections.

Recent Progress

Inner-Shell Probed Attosecond Metallization

Attosecond experiments on solids offers unique insights into important processes such as dielectric breakdown and band tunneling. Transient inner-shell spectroscopy is well-suited, especially in a IR pump/XUV configuration, and interpreting delay-dependent modulations benefits from first-principles simulations. In the past year, we completed work on using basis-set time-dependent density functional theory (TDDFT) for simulating transient metallization and inner-shell transient absorption in silica and diamond. This was a continuation of work conducted in the PI's previous Early Career Award. Our approach draws on previously reported techniques including all-electron hybrid functional TDDFT with spectra computed via accelerated transforms of the dipole moment [Chen2020], a filtered dipole operator to remove intruder peaks [Yang2023], and uses bulk-mimicking finite cluster models [Darapaneni2020]. These make it well-suited to pump-probe

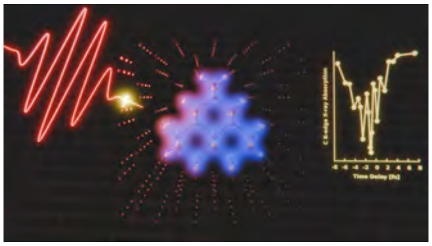

Figure 1: Schematic of a IR pump/X-ray probe of transient metallization in diamond. Our simulations use time-dependent density functional theory simulations with bulk-mimicking clusters.

simulations involving inner-shell states (see Fig. 1). Our diamond K-edge results demonstrate that using soft X-ray energies for measuring attosecond band processes in dielectrics is promising, since the instantaneous modulations in XAS optical density can be related to the transient population of the conduction band from the IR field. These findings have been submitted and are under review/revision.

Core-Holes as Triggers of Attosecond Dynamics

One major question related to resonant soft X-ray pump experiments is: how do the induced valence dynamics depend on the specific core-hole used as a trigger? To help address this, in the previous year, we focused on simulating the effects of different types of heteroatom core holes for various conjugated aromatic compounds, including: fluorobenzene, chlorobenzene, bromobenzene, phenol, thiophenol, pyridine and phosphorine. These compounds were selected as a representative group for functionalized benzene derivatives, which are known to support attosecond electronic dynamics in the π system faster than most Auger-Meitner decays or nuclear motion.

To simulate this process, we used TDDFT (def2-TZVP/B3LYP), and a sudden ionization approximation to emulate resonant X-ray ionization via an attosecond pulse. To quantify the dynamics we analyze the time-dependent number of electrons by integrating the electron density over particular regions of the molecule, e.g., half of the ring.

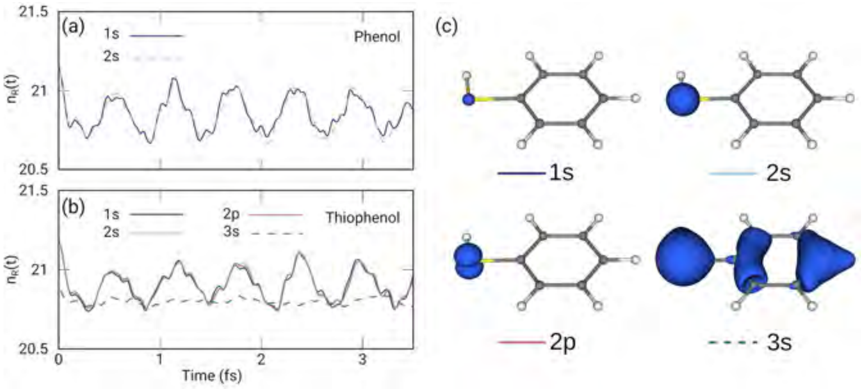

Figure 2: Simulated time-dependent number of electron on the right half of the rignt for phenol (a) and thiophenol (b) for various O/S core-holes. Solid lines denote inner-shell ionization, and dashed-lines denote inner-valence shell. Panel (c) shows the corresponding initial hole densities in thiophenol. The 1s, 2s, and 2p holes are all atomic-like (localized) and induce similar dynamics, whereas the 3s hole is molecular-orbital-like (delocalized) and does not trigger ring oscillations.

As a example, we present the result of phenol and thiophenol, which are examples of core-holes indirectly inducing π electron dynamics. Fig. 2(a) shows the charge on the right half of the ring in phenol following ionization of an electron from either a 1s (purple) or a 2s (cyan) orbital on oxygen. Both of these core-holes cause the electron density to oscillate at a the same main frequency. Fig. 2(b) shows the dynamics in thiophenol, where all inner-shell S core-holes (1s, 2s, 2p) induce similar valence dynamics. In contrast, the 3s inner-valence hole does not cause π dynamics (dashed green). This can be understood by considering the shape of the initial hole density (Fig. 2(c)). The 1s, 2s and 2p core-holes are essentially localized and atomic-like, thus they all shield the valence electrons from the nucleus by a similar amount. The 3s hole, however, is more molecular orbital like rather than atomic-like, and does not induce π electron dynamics.

Similar results were obtained for all molecules studied, from which we concluded a simple heuristic: the type of core-hole used to launch attosecond dynamics does not generally affect the dynamics, provided the core-hole is inner-shell (localized) and not inner-valence (delocalized). This has many implications for the design of X-ray pump/probe experiments, such as at XFELs, where often particular edges are more practical to ionize at. We have a draft manuscript detailing these results that will be submitted shortly.

1ω/2ω X-ray Pump/Probe in Chlorocinnamaldehyde

Soft X-ray pump / soft X-ray probe schemes, which are promising for triggering and probing attosecond dynamics, are now becoming possible at X-ray free electron laser (XFEL) facilities such as LCLS. In the previous year, we focused on simulating 1ω/2ω pump/probe transient absorption in conjugated molecules, where the system is ionized at the chlorine L_2 (2p) edge and probed at the O K-edge via transient absorption spectroscopy (TAS). This work was done in collaboration with the Rudenko and Rolles groups at KSU. Using this modality has multiple advantages. First, the pump and probe atoms (Cl, O) are located at different regions of the molecule, meaning the pump creates a local excitation in the valence density on one end of the molecule, and the probe measures the time-varying local density on another. Secondly, a 1ω/2ω scheme is convenient for practical experiments, such as at LCLS. Finally, the Cl 2p core-hole Auger-Meiter has an especially long decay time of ~40 fs, which means this process is not expected to substantially influence the sub 10-fs dynamics.

One system studied on was 4-chlorocinnamaldehyde (C_9H_7ClO), which is a planar conjugated molecule with a Cl on one end, and an O integrated into the other conjugation at the other end. We used TDDFT (def2-[T/Q]ZVP/B3LYP) and a sudden ionization approximation to simulate the electronic dynamics by removing an electron from a Cl 2p orbital. As shown in Fig. 3(a), this causes a regular oscillation with a period of ~1 fs. The corresponding computed Bader charges around the oxygen atom (b) show a modulation of ~12% of an electron charge at the same frequency. The difference density snapshots (c) shows that these dynamics correspond to a long-range oscillation of electron density along the π-backbone of the molecule. This motion is conceptually similar to the benzene derivative case (previous section), but is more complicated, since it involves a ring, an alkene, and a terminal aldehyde.

The X-ray attosecond transient absorption spectra are computed by Fourier transform of dipoles generated from time-delayed weak broadband probe fields [Chen2020]. Fig. 3(e), shows simulated spectra for the delays, corresponding to maximum and minimum electron density on oxygen. It is observed that when there is extra electron density around the O atom (time τ_1), the optical density (OD) at the O $1s \rightarrow \pi^*$ peak decreases (purple curve), and when there is less electrons around the O (τ_2) the

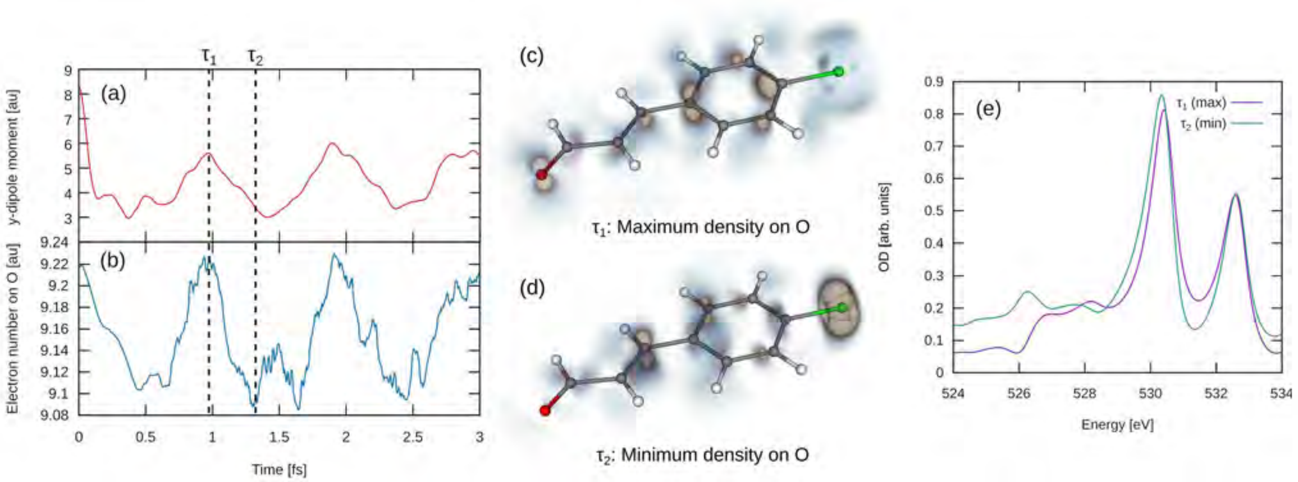

Figure 3: Simulated electronic dynamics after Cl 2p ionization of 4-chlorocinnamaldehyde. (a) The timedependent dipole moment. (b) The corresponding time-dependent electron number density on the oxygen atom. (c,d) Difference electron density snapshots for the delays corresponding to maximum (c) and minimum density on the vicinity of the oxygen atom. (e) The calculated transient absorption signal (optical density OD) below the oxygen K-edge for the delays corresponding to maximum (magenta) and minimum (green) electron density on oxygen.

OD increases (green curve). These simulations demonstrate the potential viability of a 1ω/2ω (Cl/O) pump-probe scheme for inducing and probing attosecond electron dynamics.

Going forward, our results formed the basis for a recently accepted beamtime proposal to carryout this 4-chlorocinnamaldehyde Cl 2p / O K-edge transient absorption experiment at LCLS using the XLEAP pump-probe capabilities. Currently, LCLS is the only light source in the world that can provide this type of two-color attosecond X-ray pulse pair. The experiment is scheduled for March 2025, and will be carried out by the Rudenko and Rolles groups, in conjunction with teams of Taran Driver and James Cryan at SLAC.

Future Plans

In the coming year, we will begin work on simulating transient metallization in silicon, using a similar bulk-mimicking cluster approach to our previously reported SiO_2 and diamond work. This will involve the use of spin-orbit TDDFT, which is necessary to adequately describe the Si L-edge for this system. Additionally, we will continue work on simulating the effect of core-hole on attosecond dynamics, including larger and more complicated molecules. We will also validate and go beyond the sudden-ionization approximation by using explicit X-ray pulses and complex absorbing potentials. Finally, we will incorporate Auger-Meitner decay phenomenologically to our simulations in order to determine if/how the lifetime of a core-holes affects the sub 5-fs dynamics. For the 1ω/2ω project, the near-term focus will be on simulations to support the planned LCLS experiment, including averaging over pump and probe polarizations, incorporating pulse width effects, and averaging over initial states. Additional studies will be also performed for other Cl/O functionalized organic molecules, as molecules with other heteroatoms, to further assess the viability of transient X-ray absorption, and to identify other candidate molecules for such studies. Other 1ω/2ω modalities using different heteroatoms/X-ray edges will be studied.

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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
Steven T. Manson, Principal Investigator
Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303
(smanson@gsu.edu)

Project Scope

The goals of the research program: to further understand 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; to seek out new phenomenology, especially for 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; interchannel coupling effects in the vicinity of inner-shell thresholds, and dynamical properties of atoms endrohedrally confined, primarily in C_{60}. Flexibility has been maintained to respond to opportunities as they arise. The program is on a no-cost extension and will terminate in the next year,

Recent Progress

Various aspects of the dynamics of electrons in the photoemission process have been explored. 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} [1] and Mg@C_{60} [2]. Confinement resonances [3], 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 [4]. The photoionization of endohedral atoms in nested fullerenes makes the confinement resonances considerably more complicated [5]. These effects carry over to the photodetachment of fullerene (and nested fullerene) cations which exhibit large resonances and a variety of unexpected properties [6]. And calculations taking full account of the molecular symmetry [7] have revealed a wealth of detail on valence and core photoionization of C_{60} and are the most accurate calculations to date. In particular, at the higher energies, it has been found that the various model potentials which do not specifically include the 60 carbon nuclei, can be grossly incorrect even at photon energies of 100 eV, by orders of magnitude. The difficulty is a result of the need for conservation of momentum which is problematic in the model potentials at high energy owing to the lack of any nucleii to recoil.

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 [8], 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 [9]. 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 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. Stimulated by our calculations, an experiment was performed at SOLIEL, the French synchrotron, in late 2023 and the results are still being analyzed.

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 [10,11]. 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. In addition, a study of Cooper minima of *ns* states (where the nonrelativistic Cooper minimum splits into two minima corresponding to $ns \rightarrow \varepsilon p_{1/2}$ and $ns \rightarrow \varepsilon p_{3/2}$) of high-Z atoms has found that relativistic effects can be huge and lead to rather different phenomenology from nonrelativistic predictions [12]. For example, in a nonrelativistic formulation, the trajectory of the Cooper minima eventually moves below threshold with increasing Z. Relativistically, on the other hand, certain of the minima move out to higher energy with increasing Z. This leads to huge splittings in the relativistic minima from a given subshell, as large as 3 keV for the 6s subshell of the superheavy element, Z=118. This occurs because of the spin-orbit interaction which can be attractive or repulsive, depending upon the total angular momentum *j*. And the splittings of the Cooper minima lead to significant effects on cross sections and, most importantly, of the photoelectron angular distributions, The initial studies were restricted to ns states, but have now been extended to np photoionization [13] that is even more complicated owing to the initial state spin-orbit splitting and the nonrelativistic Cooper minimum is split into three relativistically, leading to a significantly more complex phenomenology is. Of note here is that experimental studies of superheavy atoms are now possible [14,15].

Double K-shell photoionization had been investigated [16] in for Ne in conjunction with experiment. Double photoionization is of particular interest because it can only occur *via* correlation, since the photon interacts with only a single electron. Using an updated version of the Belfast R-matrix code with pseudostates, we were able to mock up the two-electron continuum and obtain quite good agreement with experiment over an extended energy range, thus demonstrating that the important correlations involved in the double ionization process were included in our R-matrix calculation. In addition, using data from other systems, we were able to put together a scaling law for the ratio of double to single photoionization as a function of Z. We expect this law to be tested for higher Z in the near future.

The near-threshold photoionization of the Na atom, 3s photoionization, has long been a difficult problem for theory. Using an extremely large configuration basis in a calculation using R-matrix with pseudostates, we have provided the most accurate cross section to date [17]. A number of consistency checks were made to ensure accuracy. The position of the Cooper minimum is in excellent agreement with experiment. Our theoretical results away from the minimum are found to be lower than the experimental data, and we make the case that the experimental magnitudes are an overestimate. The dipole cross section dips to a very low value at the minimum, but not zero owing the separate contribution of the two relativistic components, ns→$\varepsilon p_{1/2}$ and ns→$\varepsilon p_{3/2}$. The dipole cross section is so low, however, that the quadrupole cross section is then competitive with the dipole value. We have performed both dipole and quadrupole calculations [18] and, it is found, that at the dipole Cooper minimum, the quadrupole cross section is approximately a factor of two larger than the dipole; the quadrupole dominates over an approximately 40 meV energy range around the minimum. This is an excellent venue to study nondipole photoionization experimentally.

Future Plans

This project will be terminating at the end of the no-cost extension period. During this period, we will write up the remainder of the unpublished research and see to the graduation of the graduate students involved,

Peer-Reviewed Publications Resulting from this Project (2022-2024)

● "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).
● "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).
● "Energy variation of double K-shell photoionization of Ne," S. H. Southworth, S. Li, D. Koulentianos, G. Doumy, L. Young, D. A. Walko, R. Püttner, D. Céolin, R. Guillemin, I. Ismail, T. Marchenko, O. Travnikova, M. N. Piancastelli, M. Simon, S. T. Manson, and T. W. Gorczyca, Phys. Rev. A **107**, 023110-1-9 (2023).
● "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).
● "Quadrupole effects in the photoionisation of sodium 3s in the vicinity of the dipole Cooper minimum," Nishita Hosea, Jobin Jose, Hari R Varma, Pranawa C. Deshmukh, Steven T. Manson, ATOMS **11**, 125-1-13 (2023).

- “Attosecond Time Delay in Atomic Photoionization: Angular-Dependent Transition from Dipole to Quadrupole and Spin-Flip Dynamics,” Rezvan Khademhosseini, Pranawa C. Deshmukh and Steven T. Manson, Phys. Rev. A **108**, 063107-1-6 (2023).
- “Photoionization of Atomic Sodium Near Threshold,” T. W. Gorczyca, C. P. Balance, M. F. Hasoğlu, N. R. Badnell, S. T. Manson and D. W. Savin, Phys. Rev. A **109**, 053102-1-7 (2024).
- “Cooper minima in high-Z atoms: Effects of correlation and relativity on *np* photoionization,” S. Baral, J. Jose, P. C. Deshmukh and S. T. Manson, J. Phys. B **57**, 135001-1-12 (2024).
- “Measurability of Wigner time delay in a photoionization experiment,” Pranawa C. Deshmukh, Sourav Banerjee and Steven T. Manson, Canadian J. Phys. (in press). doi.org/10.1139/cjp-2023-0226
- “Interchannel Coupling Effects on Atomic Photoionization: Correlation in the Continuum,” Steven T. Manson, Canadian J. Phys. (in press). doi.org/10.1139/cjp-2023-0270

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Relativistic and Many-Body Effects in Attosecond Time Delay and Other Processes and Free and Confined Heavy and Open-shell Atoms And Molecules

Award number: DE-SC0025316

Steven T. Manson, Principal Investigator
Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303
(smanson@gsu.edu)

Project Scope

This theoretical research program is concerned with understanding the complexity of the electron dynamics inherent in the photoionization of atoms and molecules broadly with a particular focus on the dynamics of electrons at the ultrafast, attosecond level, the natural timescale of electron motion in atoms and molecules. The theoretical calculations include both the correlated motion of these electrons, many-body interactions, and relativistic effects. A series of calculations will be performed that explore the correlation and relativistic effects on the photoionization process in various cases and explore the attosecond time delay. The understanding gained will allow the accurate prediction of the details of these complex processes and, using this understanding, to control them. We shall study time delay in heavy atoms, where relativistic effects are crucial, and open-shell atoms which have not been explored as of yet. In particular, we shall look at inner shells, the x-ray region, since the inner shells of atoms behave pretty much as the inner shells of molecules and atoms provide a simpler “laboratory” to study time delay.

We shall also look at molecules with two aims. The first is to spotlight the differences in time delay in inner-shell photoemission between the free atom and the atom in a molecule. The second is to do calculations on a molecule containing atoms in non-equivalent sites to probe the site sensitivity of time delay and to learn what information this might give of chemical significance.

Another objective of the research program is the photoabsorption of confined atoms and molecules, e.g., confined in fullerene molecules, such as C_{60}, or quantum dots. Emphasis shall be placed upon how the confinement alters the properties of free atoms and molecules. Specifically, a focus shall be on how the conditions of confinement affect attosecond time delay and how the confinement can be used to control the electron dynamics at the attosecond level.

Many of the theoretical investigations will be performed in collaboration with experimental and theoretical groups in the U.S. and internationally. The results will provide further insight into the nature of these fundamental atomic processes that are of importance in plasma physics and controlled thermonuclear research, atmospheric, solar, and astrophysics, radiation and radiological physics and therapy, and for studies of x-ray laser mechanics. Furthermore, the understanding of the properties of confined atoms and molecules could lead to new classes of devices for use in various applications, e.g., quantum computing, quantum control, drug delivery and ultrafast switching. Finally, it is important to note that atoms molecules are the elementary particles of the macroscopic world. The properties of these complex systems often reflect atomic and molecular phenomena. This gives further impetus to the study of the properties of free and confined atoms and molecules.

Peer-Reviewed Publications Resulting from this Project (August 2024 – present)

Nothing to report.

Resolving femtosecond photoinduced energy flow: capture of nonadiabatic reaction pathway topography and wavepacket dynamics from photoexcitation through the conical intersection seam (DE-SC0020141)

Principal Investigator: Jeffrey Moses

School of Applied & Engineering Physics, Cornell University
142 Sciences Dr./223 Clark Hall, Ithaca, NY 14853

email: moses@cornell.edu

Project Scope

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

Pauli-blocking spectroscopy measurement of graphene

During this reporting period we began the important step of benchmarking our novel instrument for hyperspectral 10-fs-resolved transient absorption spectroscopy by observation of ultrafast Pauli blocking during hot electron relaxation in graphene [8]. As a graphene sample is much easier to handle than rhodopsin and the spectroscopy signal will have a relatively high SNR, this is a relatively simple, scientifically interesting benchmarking experiment, providing insight into the phenomenon of ultrafast electron-electron scattering during initial relaxation after ultrafast laser pumping of a semiconductor to a non-thermal, high-energy distribution.

In May, PhD student Connor Davis traveled to Politecnico di Milano to perform an experiment on graphene with our collaborators Dr. Eva Pogna and Prof. Giulio Cerullo and PhD students. This experiment served as an important training opportunity in femtosecond optical transient absorption of graphene for Davis, using a visible pump (~0.5 μm wavelength) and mid-IR probe (~3 μm wavelength), each with few-hundred fs duration. This experiment allowed measurement of slower (0.1-10 ps timescale) electron-phonon scattering dynamics during hot electron relaxation by the Pauli-blocking spectroscopic approach.

The initial relaxation after photoexcitation, however, is mediated by electron-electron scattering, which takes place over only ~50 fs. Thus, our hyperspectral 10-fs-resolved transient absorption spectroscopy apparatus at Cornell University is uniquely capable of capturing these dynamics via a Pauli-blocking signal (near-IR pump/mid-IR probe). PhD student Davis is completing the spectroscopy setup. Graphene samples are currently being prepared by Dr. Camilla Coletti as part of our collaboration with Politecnico di Milano. This experiment is a key stepping stone towards our major program goal of ultrafast transient absorption experiments of the rhodopsins and DNA.

Rebuild of the optical source

During this reporting period (since November 2023), we also began the important and necessary step of rebuilding our entire laser front-end and optical source for spectroscopy. Our existing Amphos laser system, which drove our spectroscopy source, failed during the summer of 2023. This laser had failed several times during our grant period of performance, and we determined that its further use is too risky for continued progress. Therefore, we decided to completely rebuild the optical spectroscopy system using a newly acquired Pharos laser. Given the significantly shorter duration of the new laser's pulses (400 fs vs. 2 ps for the Amphos system), we have had to redesign and fully rebuild our white-light generation, noncollinear optical parametric amplifier, and adiabatic frequency conversion stages. PhD student Connor Davis has nearly completed the work, and is in the process of a final characterization of the 11-fs pulses.

Preparation of publications

We completed a manuscript on our novel method for frequency shifting 11-fs pulses to via adiabatic frequency conversion with intrinsic dispersion management. This manuscript reports efficient conversion of an 11.2-fs near-IR pulse to an 11.6-fs mid-IR pulse in a single-crystal device, and that nearly any custom dispersion function can be written intrinsically using our method (see Fig. 1). As dispersion management is among the most challenging aspects of optical systems used for ultrafast spectroscopy when approaching the single-cycle limit, this technique will help to push the boundaries of temporal resolution in ultrafast optical spectroscopy, generally, and help to bring about the new capability of 10-fs resolution in hyperspectral studies. A draft was posted to the *arXiv* earlier this year [9]. The final manuscript will be submitted to a *Nature* journal.

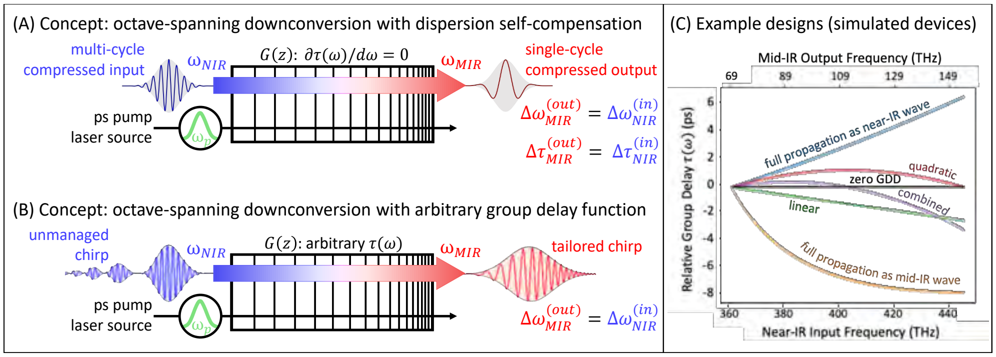

Fig. 1: Concepts of demonstrated novel frequency conversion device: a downconversion (or upconversion) device for octave-spanning pulses that can (A) emit a frequency shifted pulse with no change in duration, down to 10 fs, by self-compensating its own material dispersion and thereby exhibiting zero group-delay dispersion (GDD), or (B) emit a frequency shifted pulse with arbitrary dispersion function. (C) Example arbitrary dispersion functions that can be obtained through chosen device design. Taken from [9].

Analysis of future studies enabled by our technique

The PI visited the groups of Prof. Marco Garavelli and Prof. Ivan Rivalta of U. Bologna to discuss ongoing collaboration on rhodopsin and DNA, as well as future uses of our experimental methods for collaborative work. Ideas include: (1) Study of S1/S2 coupling during photorelaxation, which can create a barrier on S1 that can affect non-adiabatic dynamics. This hypothesis can be tested by our unique spectroscopy apparatus, as our 10-fs mid-IR and near-IR pulses correspond to the effective level spacing of 0.1-1.0 eV. (2) Study of unprotonated Schiff base rhodopsin, the so-called “UV rhodopsin”, to test the hypothesis that UV-induced proton transfer begins the conformational change.

Future Plans

During the final project year, we will focus on the following tasks, in order of priority:

- Completing the 10-fs resolved near-IR pump/mid-IR probe Pauli-blocking spectroscopy measurement of electron-electron scattering dynamics during the first 50-fs following photoexcitation; data analysis; and preparation of a manuscript with collaborators at Politecnico di Milano.

- Adding the additional stages of the 10-fs resolution transient absorption spectroscopy instrument as shown in Fig. 2 (in boxes with dashed-lines).
- Preparation of experimental samples of channelrhodopsin and initial studies of electron wavepacket dynamics.

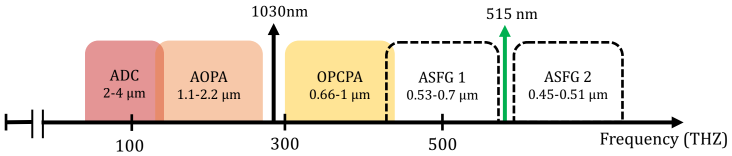

Fig. 2: Using intrinsically dispersion-managed adiabatic frequency converters, the planned five-channel source for hyperspectral 10-fs-resolved transient absorption spectroscopy. Included realized stages for near-IR and mid-IR sources by OPCPA, adiabatic downconversion (ADC), and adiabatic OPA (AOPA), as well as designed stages for the visible range employing adiabatic sum-frequency generation (ASFG).

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

P. Margules, J. Moses, H. Suchowski, and G. Porat, “Ultrafast Adiabatic Frequency Conversion,” J. Phys. Photonics **3**, 022011 (2021).

Modeling of Multidimensional X-ray Probes of Chemical Processes and Dynamics in Molecular Systems

DE-SC0022225 (previously DE-SC0019484)

Shaul Mukamel, University of California, Irvine, (Lead Principal Investigator)
Sergei Tretiak, Los Alamos National Laboratory (Co-PI)
Niranjan Govind, Pacific Northwest National Laboratory (Co-PI)
Marco Garavelli, University of Bologna (Co-PI)

Project Scope

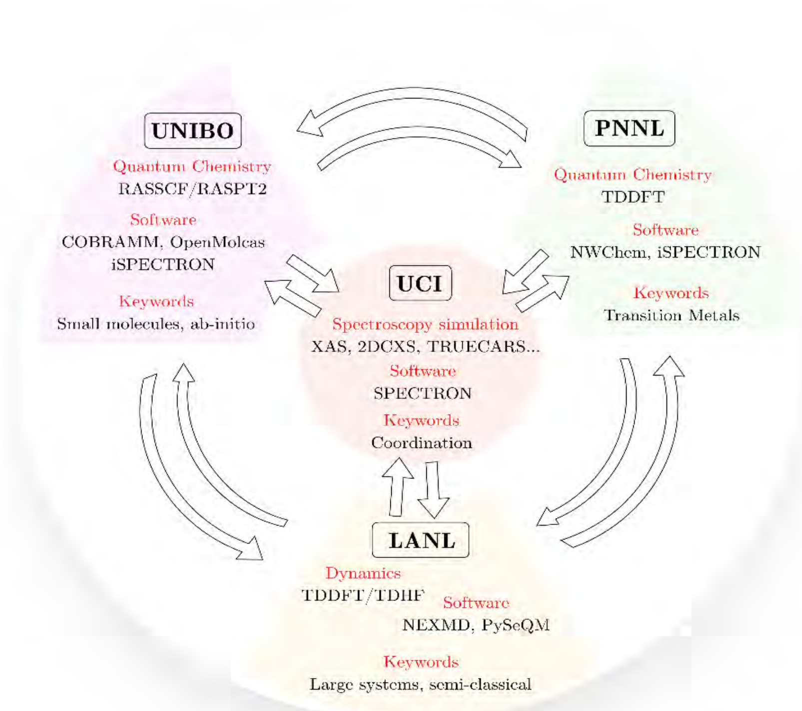

Figure 1: Sketch of the interplay between the different institutions participating in the proposal.

Emerging X-ray free electron laser (XFEL) sources offer unique probes of matter with unprecedented spatial and temporal resolutions. XFEL-based multidimensional nonlinear techniques, which combine sequences of X-ray and possibly optical pulses, provide a unique experimental toolbox for probing the dynamics of core and valence electronic excitations, vibrational motions, as well as molecular structure. These experimental advances provide unparalleled insights into the motions of electrons and nuclei, charge and energy transfer in molecular systems and must be combined with predictive theoretical methodologies and computational tools to shed light onto the underlying electronic and structural dynamics and for the simulation and interpretation of the relevant X-ray signals. The current research effort (Figure 1) focuses on the development of cutting-edge simulation tools for nonlinear multidimensional X-ray/optical spectroscopies and their application to molecular systems, aiming at fundamental chemical dynamics. Our program addresses key questions in “Priority Research Opportunities” 1 *(Probing and controlling electron motion within a molecule)* and 3 *(Capturing rare events and intermediate states in the transformation of matter)* as mentioned in the BES Roundtable Report “*Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science*”. The current effort extends time-resolved methodologies widely used in the visible and the infrared regimes to tackle the molecular response in the X-ray regime. Applications include multidimensional stimulated

Raman signals, three- and four-wave mixing, as well as time-resolved X-ray and electron diffraction, X-ray sum-frequency generation, time-, frequency-, and wavevector-resolved diffraction, novel chiral signals with circularly polarized X-ray pulses, and quantum phase-sensitive imaging using entangled X-ray photons.

This project aims at streamlining the modeling, simulation, and prediction of XFEL-based multidimensional spectroscopies, providing fundamental insights into ultrafast molecular processes ,and guiding the design of new XFEL experiments. The research is carried out by a multi-disciplinary four-institution research team (Figure 1), 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. It is delineated into three interconnected thrusts: methodology and protocol development (THRUST 1), design of novel nonlinear X ray signals (THRUST 2), and applications of these methods to a broad range of molecular systems and chemical processes (THRUST 3). Experimental probes at XFEL facilities were planned. Methodology developments and simulations were carried out and deployed via open-source codes (NWChem, OpenMolcas, NEXMD, and SPECTRON) and made available to XFEL facility users, both experimentalists and theorists.

The program primarily aims at creating modeling capabilities to support existing and inspire new cutting edge XFEL experiments in molecules. Key measurements that demonstrated the capabilities of FELs include femtosecond diffraction of nano-crystalline samples, mapping molecular vibrations mediating bond formation, possibilities of performing stimulated X-ray emission and Raman spectroscopy, generating phase-locked pulse pairs and performing four-wave-mixing measurements at seeded FELs, and resolving coherence effects in transient absorption. By probing the electronic structure and nuclear dynamics of molecules through their response to sequences of short optical and X-ray pulses with variable time delays, multidimensional techniques offer a versatile experimental toolbox for probing the dynamics of core and valence electronic excitations, nuclear motions and structure. Novel X-ray pulse sequences and experiments that probe core and valence electronic excitations were designed . Efficient simulation protocols for multiple-core excited state energetics and dynamics and for the interpretation of their spectroscopic signatures were developed.

A key component of the proposed program is a flexible integration, application, and further development of codes for computing spectroscopic signals based on the UCI SPECTRON package (including the newly developed iSPECTRON simulation interface) and an exhaustive variety of quantum chemical packages (including NWChem, OpenMolcas, and NEXMD). The latter provide atomistic electronic structure information necessary for spectroscopy simulations at different levels of fidelity (ranging from RASPT2 to TDDFT and to reduced complexity semiempirical models), allowing for simulations of a variety of chemical systems and photoinduced non-adiabatic dynamics at different levels of sophistication. Our toolbox for simulating non-Born-Oppenheimer dynamical processes includes mixed quantum-classical trajectory surface hopping (TSH), semi-classical ab initio multiple cloning (AIMC), multi-configuration time-dependent Hartree (MCTDH) and exact quantum dynamics methodologies. All software developments were released as open source to the research community. *Applications were made to a variety of biological and functional molecular systems, targeting fundamental processes of charge and energy transfer, complex coherent dynamics and conical intersection passages, photocurrents, chiral signals,* *chemical dynamics initiated by core-hole excitations near transition elements and emerging polaritonic probes of many-body physics. These applications target parameter regimes accessible in modern ultrafast X- ray facilities and in near-future developments. Some of these studies were performed in collaboration with ongoing experiments at XFEL facilities.*

Recent Progress

Design and Applications of Novel Signals Tailored to XFEL Experiments

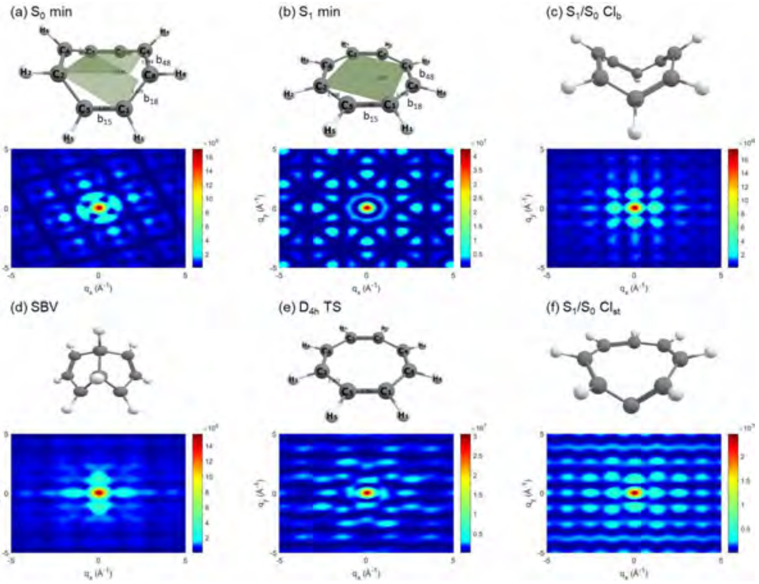

Figure 2. The two-dimensional TRXD elastic scattering pattern for optimized geometries of COT (a) S_0, (b) S_1, (c) CI$_b$, (d) SBV, (e) D$_{4h}$ TS (TS$_{RI}$), (f) CI$_{st}$.

(i) Vibronic coherences and molecular aromaticity in photoexcited cyclooctatetraene (COT) with 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 time-resolved CI dynamics remains a formidable experimental challenge. We have simulated the photoinduced non-adiabatic dynamics of a prototypical photoswitch, COT molecule, involving multiple CIs, achieving good agreement with experimental relaxation times. The possibilities of probing CI passages with off-resonant X-ray Raman spectroscopy (TRUECARS) and time resolved X-ray diffraction (TRXD) were explored. We found that these signals sensitively monitor key chemical features during the ultrafast dynamics involving aromatic and non-aromatic electronic configurations of COT. The TRUECARS technique is capable of distinguishing different CIs along the complex photoexcitation relaxation pathway. TRXD, where X-ray photons scatter off electron densities, resolved ultrafast changes in the aromaticity of COT (Figure 2). For TXRD from an all-atom perspective, the signal computation was derived and implemented within the AIMC framework, adding the capability to the NEXMD and NWChem software packages. [P2]

(ii) X-ray and optical circular dichroism as local and global ultrafast probes of chirality (PNNL + LANL + UCI): Optical Circular Dichroism (OCD) is a well-stablished technique that probes the overall chirality of molecules in the UV-visible regime without distinguishing local chiral features. X-ray Circular Dichroism (XCD) enabled by recent advances in X-ray sources is more sensitive to the structure in the vicinity of the resonantly probed atom. Helicenes are examples of systems displaying a fascinating interplay between global and local chiralities. During its racemization, the molecule can be globally achiral while retaining a local handedness of some segments (Figure 4a). We have used this system to assess the capabilities of OCD and XCD as

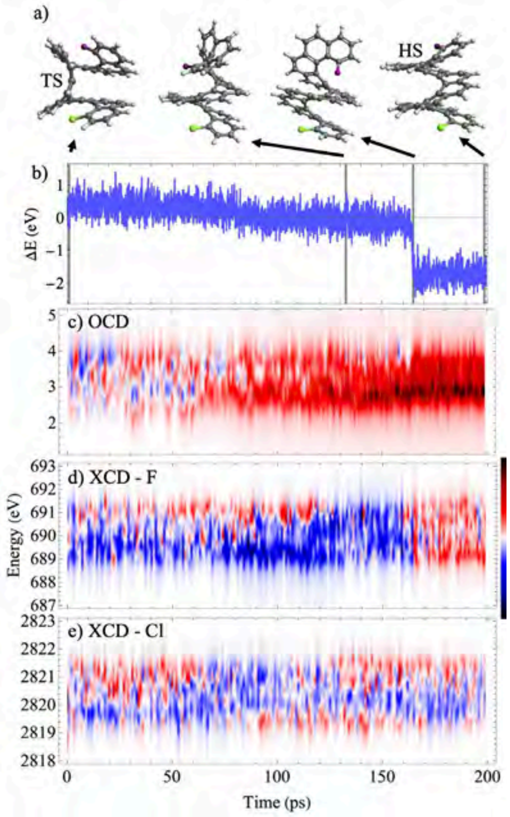

Figure 3. Racemization of [12]helicene (a and b) probed by OCD (c) and XCD (d and e).

time-dependent probes for global and local chiralities, respectively. Figure 3 shows the time-dependent OCD and XCD signals on the F and Cl sides along the [12]helicene racemization pathway. These simulations provide the basis for using XCD signals as local windows for the dynamics of chiral systems at XFEL and synchrotron facilities. They were enabled by combining semi-empirical ground state dynamics with the NEXMD code and with TDDFT calculations with NWChem of the core excitations and XCD spectra along the thermal racemization pathway of helicene. [P4]

(iii) Ultrafast energy transfer (ET) in photoexcited water solvated nicotinamide-adenine heterodimer (NADH) (UNIBO + UCI): A 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 were modeled at different spectral windows,ranging from the VIS/UV (time-resolved PP, TR-PES) to the X-ray (TR-XANES and TR-XPS, at the N-Kedge) (Figure 4). The different techniques were compared to discern which is most suited for monitoring the charge-transfer mediated ET dynamics. TR-XPS shows the largest spectral shift when the CT state is transiently populated, due to a sudden change of the partial charges on N atoms in the two moieties. We have developed an accurate and practical approach for computing spectroscopic signals of molecules subject to impulsive interactions with an incident electromagnetic field. It incorporates the effect of ultrafast nonadiabatic quantum dynamics by means of explicit numerical propagation of the nuclear wave packet. The fundamental expressions for the first- and higher-order response functions were recast in a general form that can be used with any quantum dynamics code, capable of computing the overlap of nuclear wave packets evolving on different states. These expressions were evaluated within the

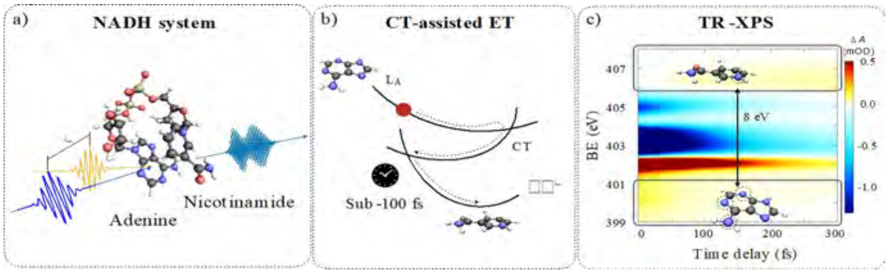

Figure 4. a) Nicodinamide adenine dinucleotide system, together with a sketch of the VIS/UV pump X- ray probe process simulated; b) Schematic of the proposed charge-transfer assisted energy transfer process: the pump-induced populated adenine LA state undergoes energy transfer to the nicotinamide $\pi\pi\pi\pi^*$ state, passing through an intermediate CT state. Such charge redistribution strongly affects the N K- edge signals; 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.

MCTDH framework with electronic structure calculations performed at the CASPT2 level of theory [P8, P9, P15].

Methodology and Protocol Developments for X-ray Spectroscopies

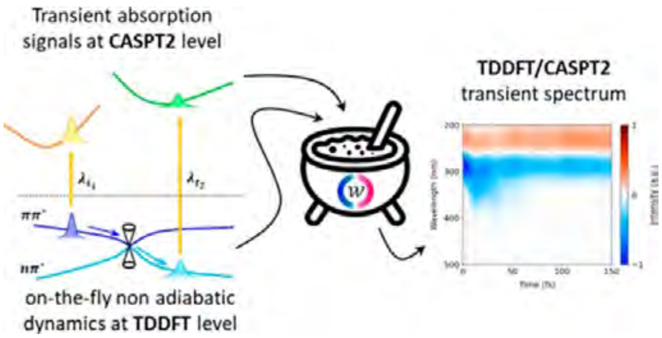

Figure 5. WFO computational protocol blends electronic structure methods of different fidelity.

(i) X-ray/optical spectroscopy analysis tools at different levels of theory (LANL + PNNL + UNIBO + UCI)*:* Extending our X-ray/optical spectroscopies analysis capacity, requires matching the signal from different levels of theory (CASSCF/CASPT2, TDDFT and semi-empirical). To that end, it is necessary to have a 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 at different levels of theory. The acetylacetone system was used 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 5). Such delineations and identification of states is critical for indirect validation of excited state molecular dynamics calculations with lower-level theories. The WFO script has been incorporated in the UNIBO code COBRAMM, eventually allowing to test it on non-adiabatic molecular dynamics performed with different software packages, including NWChem, NEXMD, Molcas, etc. [P19]

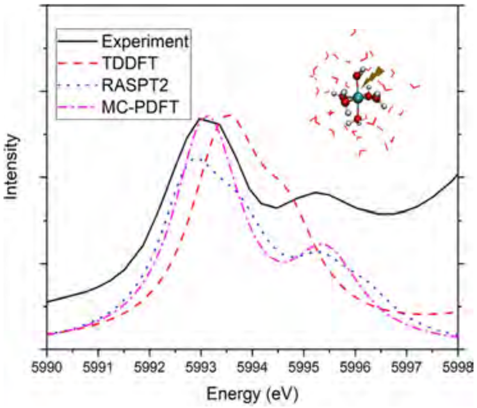

Figure 6. 1s–3d pre-edge spectra for Cr3+ from computation and experiment. The calculated spectra have been aligned with experiment.

(ii) Combining wave function and density functional theory towards the simulation of K-edge X-ray absorption near-edge spectroscopy (PNNL + UCI): We have developed a computational protocol based on multiconfiguration pair-density functional theory (MC-PDFT) for X-ray absorption spectra and applied it to calculate the metal K pre-edge features of aquated 3d transition metal ions in common oxidation states. The results were compared with experiment and analyzed against restricted active space second-order perturbation theory (RASPT2) and TDDFT. 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 (Figure 6). 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

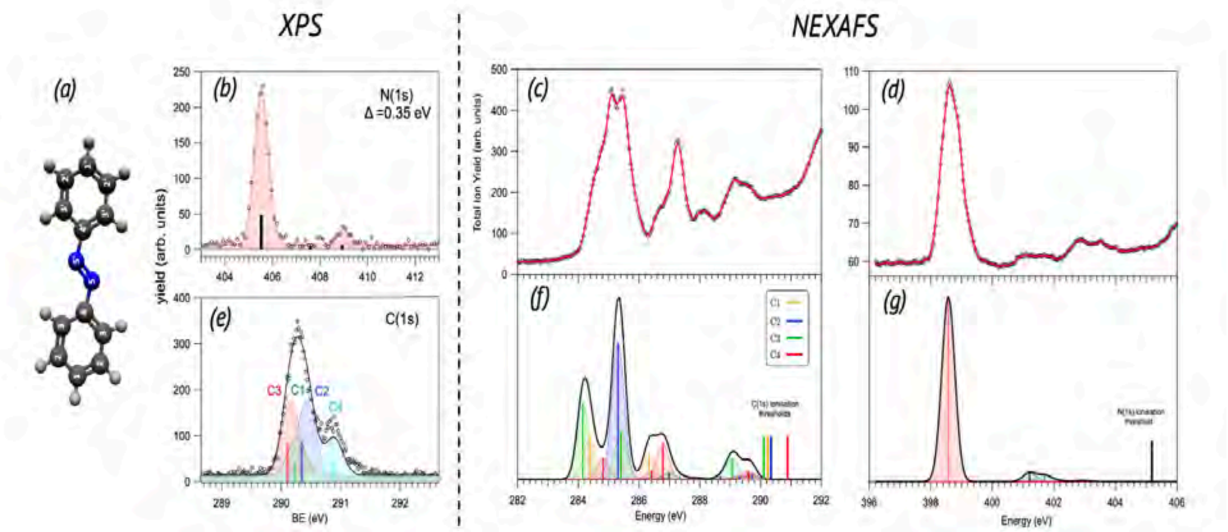

Figure 7. Electronic spectroscopy of *trans*-azobenzene (a) in the core shell: the nitrogen (b) and carbon (e) experimental 1s XPS spectra (reported here with open dots) are compared with the theoretical RASPT2 predictions (vertical bars). The experimental fits (full areas) are also reported in (b) and (e). Experimental carbon K-edge (c) and nitrogen K-edge (d) NEXAFS spectra are here compared with the corresponding RASPT2 simulations (f and g respectively).

results demonstrate that MC-PDFT performs equally well with a significantly lower computational cost and is a viable approach for X-ray spectroscopies [P3].

(iii) Extending the CASSCF/CASPT2 XAS approach to larger molecules (UNIBO): The recently developed protocol [P12] for core level CASSCF/CASPT2 spectroscopy simulations has been extended to larger/complex molecular systems.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 7) [P10]. Through 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 them with measurements performed at the BEAR beamline.

(iv) Software Releases (LANL + PNNL + UNIBO): Novel implementations in the software developed by our team (Figure 8) are being continuously released to the user community. In 2023 we have released major updates in three computational packages. In particular, the NEXMD v2.0 code [P7] now implements Ehrenfest and Ab-Initio Multiple Cloning (AIMC) types of non-adiabatic dynamics, along with several 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 including many-body Green's function methods, exact two components relativistic methods, the real-time equation-of-motion coupled cluster cumulant formalism, advanced non-adiabatic molecular

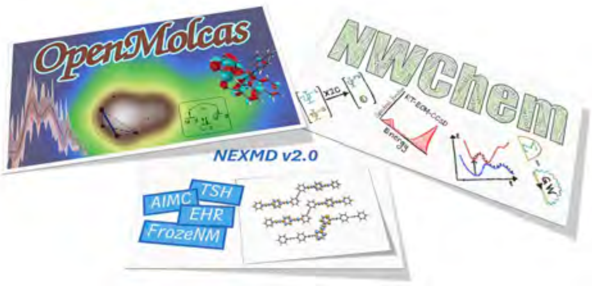

Figure 8. Software developed by our teams showcasing recent capabilities.

dynamics methods, and improvements to existing methods already present in NWChem. A roadmap review on real-time electronic structure methods was also published. The OpenMolcas package updates 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. [P5, P6, P7]

Future Plans

Extending Single Excitation Methods to Tackle Conical Intersections: Traditional TDDFT and TDHF approaches cannot be used to capture conical intersections between ground- and excited-states due to the lack of doubly excited configurations since singly excited configurations do not couple with the ground state. A potential low-cost solution of this deficiency is diagonalizing the Hamiltonian in a basis of singly excited configurations with an added conical intersection correction. This establishes a coupling between the ground state reference and the first excited state and addresses an important conical intersection topology. We have implemented this approach in the NWChem code within the TDDFT framework and are validating the results by comparing our results with high fidelity wavefunction-based approaches. We are currently working on implementing the analytical gradients using this approach, which will allow us to compute non-adiabatic couplings. This approach will also be implemented in the semi-empirical NEXMD packages.

Improving Model Hamiltonians within the Developed MCTDH/Spectroscopy Platform for X-ray Signals: The Multi Configuration Time Dependent Hartree (MCTDH) protocol constitutes one of the most accurate standards for efficient quantum dynamics modeling. It works within a diabatic representation and when employing harmonic potentials it can handle tens (or even hundreds) of modes for sized molecular systems. We have a diabatic multi-dimensional MCTDH framework that allows to parametrize the quantum dynamics Hamiltonian within a harmonic linear vibronic coupling model by employing experimentally accurate state-of-the-art RASPT2 energy inputs. The protocol capabilities were demonstrated for challenging benchmarks and were extended to model nonlinear pump/probe spectroscopic signals covering a broad spectral window, ranging from the visible to the Xray [P8, P9, P15]. However, photochemical processes, that involve bond-breaking/bond-forming events, and their underlying conical intersections, do involve highly anharmonic reaction coordinates . MCTDH can also deal with generally anharmonic potentials that have been efficiently implemented in the Quantics code. Together with available tools for the generation of kinetic operators for general curvilinear coordinates, we are extending the platform for nonlinear spectroscopy simulations based on multidimensional MCTDH quantum dynamics, to explicitly handle the non-harmonic reactive modes involved in the description of photoinduced reactions, yet being able to describe non-perturbatively their coupling to the remaining degrees of freedom of the system described as a bath of harmonic modes. Eventually, this allows the modelling photoinduced bond-breaking/bond-forming processes as well as the underling transient signals following UV/VIS pump, X-ray probe (both resonant and non-resonant).

Probing Electronic Coherences at Conical Intersections with Four-Wave Mixing Techniques: This project is a collaboration with the Leone/Neumark group at UC, Berkeley, and the Keefer group at the MPI (Mainz). Experimentally, the CH_3I is being studied using an attosecond extreme ultraviolet optical table-top approach and theoretically, using high-level quantum chemistry and quantum dynamics approaches.

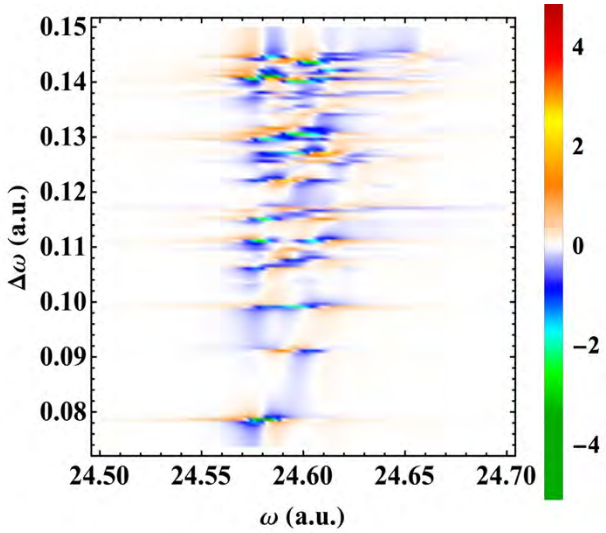

Figure 9. Proof-of-principle simulations of XROA signal with a scattering angle of $\frac{\pi}{2}$ for the transition state of [12]Helicene in the F-atom K-edge region.

Modeling of Time dependent X-ray Raman Optical Activity: Evaluation of time-dependent XROA signals requires on-the-fly calculations of transition dipole moments between excited states. This capability was recently implemented in the NWChem code enabling computation of transition dipoles among multiple excited states, which makes it particularly appealing for modeling XROA signals in time-domain. As an initial molecular target we shall use the racemization pathway of [12]Helicene, where two distinct X-ray chromophores track independently the time evolution of the local chirality of the molecule at different sites. Figure 9 shows our preliminary evaluation of the XROA signal with a scattering angle of π/2 for the transition state of [12]Helicene in the F-atom K-edge region.

Time- and Angular- 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 an earlier work by our group, where we had directly probed the CI responsible for the internal conversion of photo-excited uracil. Its extension to the X-ray regime adds element/site specificity providing sensitivity to the molecular environment, such as photoinduced bond/breaking formation. 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

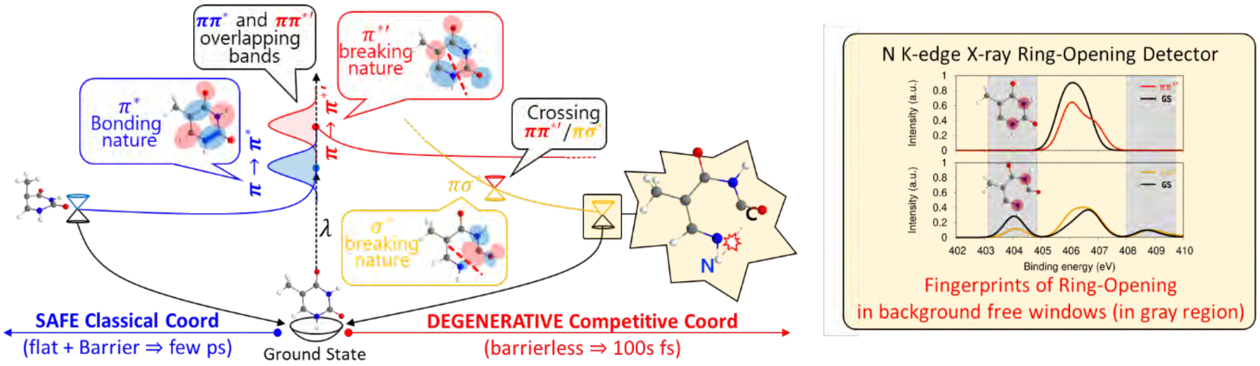

Figure 10. (left) Schematic representation of two competitive relaxation pathways in gas-phase thymine. (right) X-ray photoelectron spectroscopy at the N K-edge comparing ring-closure and ring-open product.

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 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 CI in molecules. Our preliminary electronic structure calculation at the Franck-Condon region indicates that part of the $\pi \rightarrow \pi^{*\prime}$ excitation is enabled, responsible for the ring-opening decay pathway due to its anti-bonding character between the N and C atom (Figure 10). Along with a well-known pyrimidine dimerization, such ring-opening relaxation constitute a source of DNA damage, resulting in skin cancer. We will extend tr-PES into X-ray regime at the N and C K-edges to provide a real-time probe of photoinduced ring opening.

Double-Core-Hole X-ray Spectroscopy: Novel developments in X-ray free-electron laser (XFEL) sources has enabled the creation of double core holes (DCHs) simultaneously at the same or different atomic sites in a molecule. DCH X-ray emission is a new form of X-ray nonlinear spectroscopy that can be studied with a XFEL. By utilizing a TDDFT-based protocol we have developed in NWChem, we will compute the DCH VtC-XES signals for a series of homo- and hetero-nuclear dinuclear octahedral *3d* transition metal complexes linked by hydrogen bonds. We will compare the simulated DCH VtC-XES signals with conventional single core hole (SCH) XES signals. Two distinct sites DCH (ts-DCH) and single-site DCH (ss-DCH) will be compared. ts-DCH is a more sensitive probe of the local chemical environment of the excited atoms compared with ss-DCH. We hypothesize that the energy shifts and intensity changes of the DCH emission lines with respect to the corresponding SCH-XES features are fingerprints of the coupling between the second core hole and the occupied orbitals around the DCHs that contain important chemical bonding information of the complex. We will also compute the XANES signals in the presence of SCH and DCH states. In the dinuclear transition metal systems we plan to study, the creation of a SCH at one transition metal center will induce ultrafast charge migration across the hydrogen bonds of the dimer complex and the XANES probed at the other transition metal center will report on the *d-d* correlations between the two metal centers. We will also compare our results with higher order wavefunction approaches. We will collaborate with Uwe Bergmann (University of Wisconsin, Madison), who will design experiments at current XFEL sources to explore these spectroscopies.

X-ray Probes of Solvent Modulation of Excited States in Mixed-Valence Donor-Bridge Acceptor Metal Complexes: Our objective is to understand how the solvent influences the electronic structure and the charge delocalization between linked metal atoms in mixed-valence donor-bridge acceptor metal complexes. We are studying the Ru(III)Os(II) complex in high donor number solvents (i.e. solvents that can form strong hydrogen bond interactions) and Ru(II)Os(III) complex in low donor number solvents. We are investigating mechanisms for 1) how the solvent stabilizes one oxidation state configuration with respect to the other, and 2) the competition between solvent reorganization energy and electronic coupling between the metals in dictating delocalization. To connect with experiment, we are collaborating with Dr. Elisa Biasin at PNNL and beamline scientists at SLAC from the Gaffney group.

Metal-Ligand Covalency in the Valence Excited States of Metal Dithiolenes Revealed by S 1s3p RIXS: This work was performed in collaboration with Cordones-Hahn group at the Stanford PULSE Institute at SLAC. Metallo dithiolene complexes with biological and catalytic relevance are well-known for having strong metal-ligand covalency, which dictates their valence electronic structures. Resonant sulfur Kβ (1s3p) x-ray emission spectroscopy for a series of Ni and Cu bis(dithiolene) complexes will be used to reveal the ligand sulfur contributions to both the occupied and unoccupied valence orbitals. We have identified the low energy excited states as having the same symmetry as the nominal 'ligand field' or 'd-d' states that typically dominate the photophysics of 3d metal complexes, but with significant metal-ligand charge transfer character dictated by their covalency. Preliminary results suggest that strong metal-ligand covalency can be used to influence the charge-transfer photochemistry of first row transition metal complexes. [P20]

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Theory and Simulation of Nonlinear X-ray Spectroscopy of Molecules

Shaul Mukamel
University of California, Irvine, CA 92697
smukamel@uci.edu
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Program Scope

Nonlinear x-ray spectroscopy experiments which use sequences of coherent broadband X-ray pulses, are made possible by new ultrafast X-ray free electron laser (XFEL) and high harmonic generation (HHG) sources. These techniques provide unique windows into the motions of electrons and nuclei in molecules and materials, and offer 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.

Recent Progress

X-ray and optical circular dichroism as local and global ultrafast probes of chirality

Optical Circular Dichroism (OCD) is a well-stablished technique that probes the overall chirality of molecules in the UV-visible regime without distinguishing local chiral features. X-ray Circular Dichroism (XCD) enabled by recent advances in X-ray sources is more sensitive to the structure in the vicinity of the resonantly probed atom. Helicenes are an example of systems displaying global chirality where electric and magnetic allowed transitions are distributed across the entire molecule due to the high conjugation. During its racemization, the molecule can be globally achiral while retaining a local handedness (Figure 1a). We used this system as a model to assess the capabilities of OCD and XCD as time-dependent probes for global and local chiralities, respectively [1]. Figure 1 shows the time-dependent OCD and XCD signals on the F and Cl sites along the [12]helicene racemization pathway. These simulations provide the basis for using XCD signals as local windows

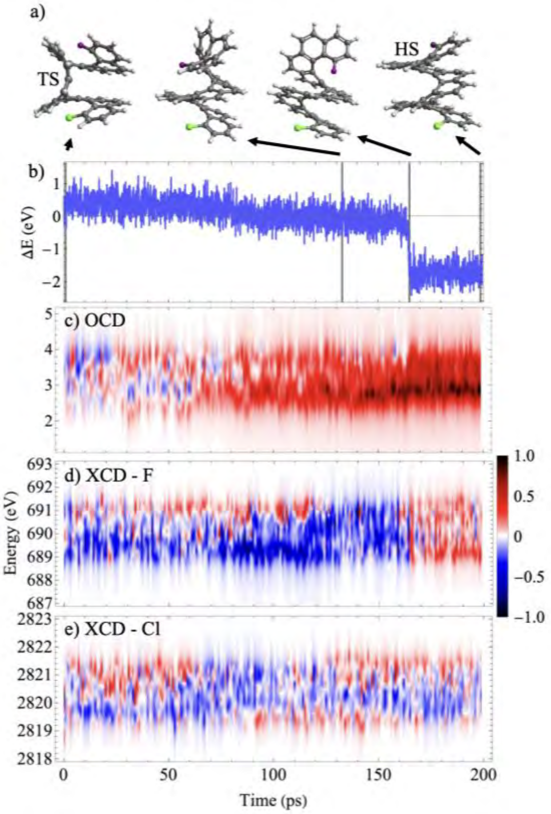

Figure 1. Racemization of [12]helicene (a and b) probed by OCD (c) and XCD (d and e).

for the dynamics of chiral systems at X-ray free electron laser and synchrotron facilities. These simulations were enabled by combining semi-empirical ground state dynamics with the NEXMD code and with TDDFT calculations with NWChem of the core excitations and XCD spectra along the thermal racemization pathway of helicene.

Single-Electron Self-heterodyne Diffractive Imaging of Ultrafast Electron Dynamics

A self-heterodyne electron diffraction technique based on single electron pulses was proposed to directly image the time-evolving molecular charge densities ⟨σ⟩ on atomistic scale and at femtosecond resolution [2], in contrast to traditional ultrafast electron diffraction which images ⟨σ^† σ⟩. The probing electron is split into two beams, one passes through the sample and its interference with the second beam produces a heterodyne diffraction signal that images the charge density (Figure 2a). The diffraction pattern reflecting the charge density in momentum space can potentially be used for producing real space charge density when combined with phase shifting measurements. This proposed signal is applied to probing the ultrafast electronic dynamics in Mg-phthalocyanine. A circularly polarized pump pulse excites the molecule and creates the coherence of electronic excited states in the range of 2 eV to 4 eV. After the pump pulse, the coherent evolution causes the charge density redistribution within the molecule, e.g., concentrate more on the left and right phenol ring, and then concentrate more on the higher and lower ring and back and forth. The single electron pulses follow the optical pump pulse at time delay T, probing the time resolved self-heterodyne electron diffraction pattern, depicted in Figure 2. The charge density redistribution is reflected in the change of the diffraction pattern (Figure 2b). This simulation demonstrates the potential of this technique for imaging chemical dynamics.

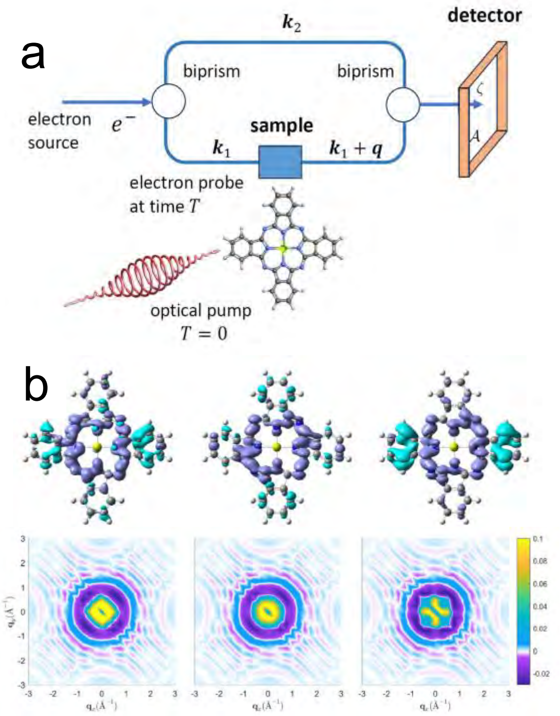

Figure 2. a) Self-heterodyned ultrafast electron diffraction set up. b) First row: real space charge density at time delays T=2.1, 8.1, 17.1 fs minus the charge density at the initial time. Second row, diffraction corresponding at the corresponding time delays.

Chemical bond reorganization in intramolecular proton transfer revealed by ultrafast X-ray photoelectron spectroscopy

Monitoring fundamental chemical reaction events in real time is an essential goal of ultrafast chemistry. Excited-state intramolecular proton transfer (ESIPT) is one of the elementary reactions in photochemistry and biophysics. It has been widely applied to sensors, light generations and photo-switching devices. Local observation of the associated hydrogen donor and acceptor atoms undergoing bond breaking and forming processes is therefore of special interest. Conventional optical spectroscopies usually detect the delocalized features of the entire molecule. X-ray light

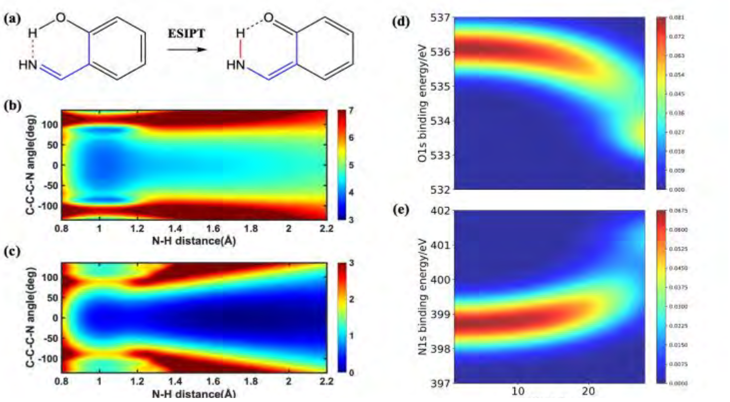

Figure 3. (a) Excited-state intramolecular proton transfer in 2-(iminomethyl)phenol. The selected nuclear degrees of freedom are marked in red (N-H distance) and blue (C-C-C-N dihedral angle). (b) and (c) show the adiabatic potential energy surfaces of S1 and S0 in the two-dimensional nuclear space marked in (a). (d) and (e) are TR-XPS signals for 1 fs probe pulses for the oxygen 1s ionization and the nitrogen 1s ionization.

pulses from free-electron lasers provide novel tools to study chemical reactions in real time by core excitation. Time-resolved X-ray photoelectron spectroscopy (TR-XPS) is promising for monitoring the ultrafast dynamics. Due to the local nature of the core ionization, TR-XPS can track atom-specific excited-state chemical shifts in real time, providing local bonding dynamics of atoms in molecules. This is a time-domain extension of the classical electron spectroscopy chemical analysis (ESCA). We have simulated the TR-XPS signals to monitor the ESIPT process between oxygen and nitrogen atoms in 2-(iminomethyl)phenol. As illustrated in Figure 3a, b, and c, we have performed exact nuclear wave packet dynamical simulations in a reduced nuclear space of the N-H distance and the C-C-C-N dihedral angle [3]. The TR-XPS signals at the oxygen 1s and the nitrogen 1s levels are depicted in Figure 3c, and d. The signal of the donor oxygen atom shows significant intensity change and rapid red shift of ionization energies. The signal of the acceptor nitrogen atom, in contrast, yields a rapid blue shift. The unique local features of the proton transfer process are therefore revealed. We demonstrate the sensitivity of TR-XPS signals for local chemical environments of the probed atoms in molecules. The time evolution of the chemical shifts provides a novel access to local bonding dynamics. TR-XPS is a potential tool of atom-specific probe for not only proton transfer, but a wide range of ultrafast reactions.

Time-resolved enantiomer-exchange probed by orbital angular momentum of X-ray light

A novel technique, time-resolved helical dichroism (tr-HD), was proposed for monitoring ultrafast molecular chirality using X-ray beams carrying orbital angular momentum (OAM). By employing a bias pump near the Franck-Condon point, the asymmetric wavepackets in the ground and excited states exhibit different dynamics. This technique demonstrates how OAM-carrying X-rays can be used to monitor enantiomeric excess in the time domain and across different potential energy surfaces (PES).

Future Plans

Using X-ray Orbital Angular Momentum (OAM) as an ultrafast probe

A charge migration triggered in a molecule generates a characteristic fluorescence. Depending on the structure of the electronic motion, the emitted light carries a distribution of OAM that can be characterized in an OAM-resolved technique. An intuitive description of the OAM interaction with matter requires the calculation of transition current densities present in the molecular structure. This will be performed for [12]helicene in the NWChem code, where the vector potential can be obtained using the far field approximation. The vector potential can then be projected onto the OAM basis to obtain the corresponding contributions. This system is expected to have interesting emission properties, such as circularly polarized luminescence or light with OAM.

Extending single excitation methods to tackle conical intersections.

TDDFT and TDHF approaches, as constructed, cannot be used to capture conical intersections between ground- and excited- states due to the lack of doubly excited configurations since singly excited configurations do not couple with the ground state. A potential low-cost solution of this deficiency is diagonalizing the Hamiltonian in a basis of singly excited configurations and an added effective doubly excited configuration. We will implement this approach in both ab initio NWChem and the semi-empirical NEXMD packages. The results will be refined and validated with high fidelity wavefunction-based approaches. Core-level spectroscopic signals will be computed at the conical intersection geometries. We expect that this hybrid approach will provide a numerically efficient and flexible protocol for simulating X-ray signals in extended molecular systems.

Peer-Reviewed Publications Resulting from the Project (2023-2024)

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6- Matthias Kizmann, Shaul Mukamel, “Impulsive stimulated Raman spectroscopy with frequency correlated entangled photons”, Optica Quantum (submitted 1/24/24).
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Structured VUV, EUV and Soft X-ray Light for Probing Quantum Systems

Margaret M. Murnane and Henry C. Kapteyn
JILA and Department of Physics, University of Colorado at Boulder
Phone: (303) 210-0396; E-mail: Margaret.Murnane@colorado.edu

Project Scope

The goal of this research is to develop novel short wavelength quantum light sources, and use them to to understand 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 15 peer-reviewed papers published, accepted or in review in top journals since 2021. Recent graduates from our group went to DOE Laboratories (Sandia (3), Los Alamos (3), 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

Bright VUV Source via Four-Wave Mixing and Cascaded Mixing of Widely-Spaced Colors in Photonic Crystal Fibers [4,7]: The deep and vacuum-UV (DUV, VUV) spectral regions span the ionization energies of most molecular and solid-state systems, making it an ideal spectroscopic probe using time- and angle-resolved photoemission spectroscopy (trARPES), ultrafast photovoltage spectroscopy (UPS), Photoionization Mass Spectroscopy (PIMS) and more. Additionally, nuclear clocks using the lowest known energy nuclear isomer in ^{229}Th require resonant excitation in the VUV (~8.3 eV). Vacuum UV light can be generated using discharge lamps or synchrotrons; however, many applications benefit from bright pulsed (i.e.) coherent sources. To date, generating bright VUV light with high flux has been challenging: High Harmonic Generation (HHG) requires lasers with high peak intensities ($>10^{14}$ W/cm^2), thereby limiting the achievable repetition rates.

In past AMOS research, we demonstrated nonlinear upconversion of near-IR lasers using cascaded four-wave mixing (CFWM) in gas-filled anti-resonant hollow core fibers (ARHCFs) can access the VUV spectral region through a series of $\chi(3)$ four-wave mixing steps, generating combs spaced in energy by the difference of the two driving harmonics (ω and 2ω). ARHCFs enable long interaction lengths (~centimeters) with low-loss confinement of modes smaller than achievable by standard unstructured capillaries, further reducing the threshold peak intensity. CFWM requires two orders of magnitude less peak intensity than HHG ($>10^{12}$ W/cm^2) and enables the use of high repetition rates. *In very recent AMOS research*, we enhanced the VUV flux by orders of magnitude to demonstrate bright coherent tabletop VUV beams with linewidths <20 meV. We achieved this by driving the process with the fundamental and fourth harmonic of a ytterbium-based laser, to generate the 7th harmonic (147 nm, 8.4 eV) in a *single* four-wave mixing step ($4\omega + 4\omega - \omega \rightarrow 7\omega$) with a narrow linewidth (<20 meV), ultrafast pulse duration (<70 fs), and high efficiency (>0.1%). As shown in Fig. 1, theory predicts that this bright VUV source extends to >20 eV, while the low laser intensity is compatible with MHz repetition rates. This makes it a truly ideal source for a host of applications in photoelectron spectroscopies and nuclear-referenced clocks.

Enhancing soft X-ray high harmonic sources using structured waveguides [3]: We also used gas-filled photonic crystal waveguides for high harmonic generation, 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 in the mid-IR region compared with the simple capillary waveguides, enabling 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 ~10mJ in past work). Figure 1 shows the excellent stability and beam quality of the resultant soft X-ray HHG beams.

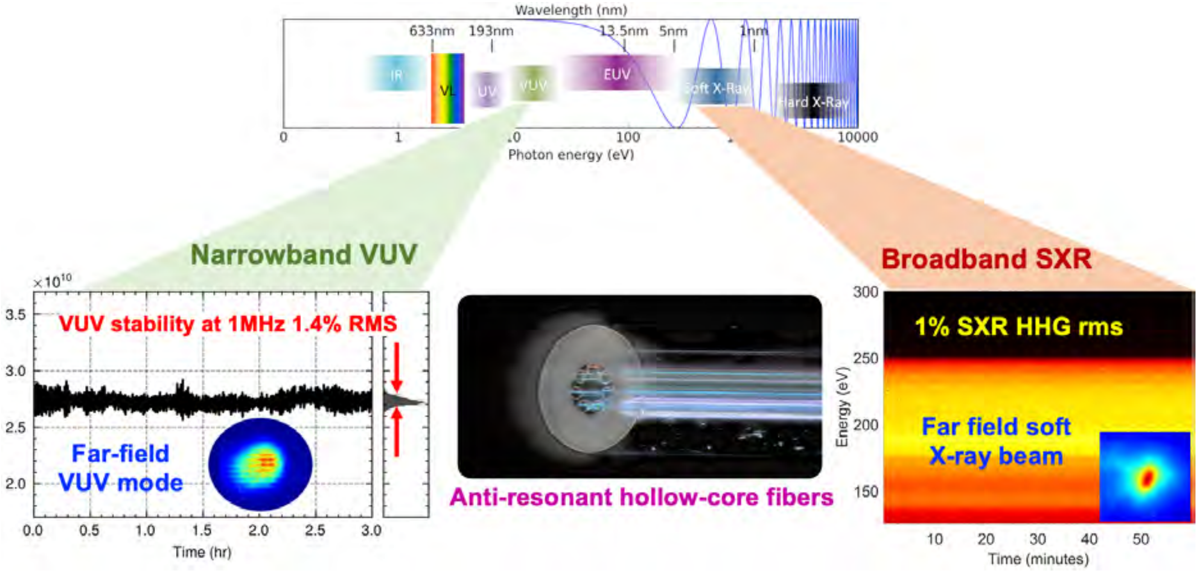

Fig. 1. Enhancing VUV and soft X-ray sources using anti-resonant hollow-core waveguides. Their small diameters and photonic structures guide the driving laser light, enabling high-stability VUV and soft X-ray beams with high beam quality.

Tailoring the Spectrum and Structure of Extreme-Ultraviolet and Soft X-Ray Beams via SAM and OAM [1-3,5,6]: The extreme nonlinear optical process of high-harmonic generation 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 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 applications.

Very recently we overcame a long-standing challenge by developing schemes that can generate bright 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 for the first time, by using more precise, robust and stable pulse shapers and lasers.

Future work

We are extending bright structured high harmonic beams from the EUV into the soft x-ray regions of the spectrum. We also implementing pulse shaping of mid-IR lasers to enhance soft X-ray HHG. 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, that have broad applications in transient grating spectroscopies and quantum sensing of molecules and materials. Continuously tunable VUV sources are also being explored.

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4. *Bright Tabletop Vacuum-Ultraviolet Source via Single-Step Four-Wave Mixing in Photonic Crystal Fibers*, J. Thurston, L. Weiner, D. Morrill, T. Kafle, M. Murnane, H. Kapteyn, in prep. (2024). (Two-page peer-reviewed summary will appear online soon, Optica Frontiers in Optics, Paper FTu6E.3).
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4. *Necklace-structured high harmonic generation for low-divergence, soft X-ray harmonic combs with tunable line spacing*, L. Rego*, N. Brooks*, Q. Nguyen, J. San Roman, I. Binnie, L. Plaja, H. Kapteyn, M. Murnane, C. Hernandez-Garcia, Science Advances **8**, eabj738 (2022). DOI: 10.1126/sciadv.abj7380
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DYNAMICS OF TWO-ELECTRON ATOMIC AND MOLECULAR PROCESSES

Principal Investigator: **Jean Marcel Ngoko Djiokap**, Award Number: **DE-SC0021054**
The University of Nebraska, Department of Physics and Astronomy
855 North 16th Street, 208 Jorgensen Hall, Lincoln, NE 68588-0299
Email: marcelngoko@unl.edu

PROGRAM SCOPE: This project develops or modifies 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 study 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****:* 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. In collaboration with the Dantus group, experiments on Ar, H_2O, N_2 and O_2 are carried out 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 [P1] in the list of publications below.)*

B. ***Reversible electron spiral by chirped attopulses at zero-time delay:*** A novel class of linear, spiral phenomena is reported in the photoelectron momentum distribution (PMD) when examining 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 [P2] in the list of publications below.)*

C. Time-delay control of reversible electron spirals using arbitrarily chirped attopulses: We revisit the study [P2] by demonstrating how varying the pulse chirp rates and time delay provide a way of manipulating the linear and quadratic spectral phases of the photoelectron responsible for this phenomenon. Our prediction has been confirmed experimentally in 2023 by the Wollenhaupt group in the femtosecond regime. Potential applications include masking the timing information in photoionization such as Ramsey or Wigner delay. *(See [P3] in the list of publications below.)*

D. Ouroboros-like electron spirals by synchronous crossed laser pulses: Atomic photoionization by crossed linearly and circularly polarized pulses linearly chirped at zero-time delay was studied. In this scheme, spirals [1-3] cannot occur for transform-limited pulses. We forecasted 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. *(See [P4] in the list of publications below.)*

E. ***Asymmetric photoelectron momentum distribution of carbon monoxide:*** Photoionization of the HOMO and HOMO-1 in CO for a variety of orientations of light polarization vector with respect to the molecular axis is reported. It is found that the asymmetry in the HOMO is reflected in the PMD, which is sound for a linear process. *(See [P5] in the list of publications below.)*

F. Electron vortices creation by atomic ionization using a few-cycle circularly polarized laser pulse: Electron vortices in the amplitude of atomic ionization by an isolated few-cycle circularly polarized pulse are analyzed in the multiphoton regime. We show that the number of vortices, as well as their position and strength are determined by the relative magnitudes of the dynamical amplitude parameters corresponding to sequential photon absorption. It is shown that the phase maps of the ionization amplitude in the momentum space exhibit spiral structures, which are signatures of the Coulomb scattering phases. *(See [P6] in the list of publications below.)*

G. Orientation-dependent production of normal Archimedean and dynamical spirals for revealing orbital symmetries in small heteronuclear diatomic molecules: The basic Einstein's photoelectric effect in multi-electron and multi-orbital aligned diatomic molecules is investigated using a sequence of counter-rotating circularly polarized broadband attopulses. It is shown that multi-orbital ionization leads to multiplexed molecular-frame PMD, hiding thus any molecular orbital structure information. Only when the molecular orientation is to use to manipulate some ionization channels that one can identify and isolate a robust channel where the asymmetric HOMO is imparted to the PMD. Our results are extremely important for the correct analysis of molecular imaging techniques. *(See [7] in the list of publications below.)*

H. ***Transformation by Rabi oscillation of the photoelectron spectra produced by oppositely circularly polarized laser pulses*****:** We report on the potential of coherent Rabi-type dynamics and formation of the Aulter-Townes doublet to dramatically transform the patterns emerging in the PMD from resonant two-photon ionization of H atom. As the superposition of two quantum states is the basis of charge migration activities in matter, this spirals-asunder results provides an avenue for revealing charge migration in complex molecules. *This work was submitted to Phys. Rev. A, July 2, 2024 (under review), see [7] in the list of references below.*

I. ***Chirp-induced anisotropy on the angularly resolved electron spectra of hydrogen negative ion by a few-cycle laser pulse*****:** We use the strong-field approximation (SFA) method to study theoretically the photo detachment of the H negative ion by a linearly polarized few-cycle laser pulse, which is linearly chirped. Besides the pulse carrier-envelope-phase and duration, we show that the angularly resolved electron distributions are very sensitive to the pulse chirp, creating novel forward-backward anisotropic features. *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 two years:

(a) **Nuclear motion effects on attosecond processes**: Stimulate and guide the first experimental observation by the UConn group led by Carlos Trallero of in-plane chiral attosecond electron phenomena, including the molecular symmetry mixed dichroism [5] and dynamical vortices [4] produced by double photoionization in hydrogen molecule. In contrast to H_2 molecule, the HeH^+ molecule has only one dissociative potential curve. Thus, we plan to include this target in this project and investigate also the process of single ionization for all these targets.

(b) Photoemission time delay study between electrons originating from the ground state of hydrogen and helium using reversible spirals and attosecond streaking. We plan to be broader by also considering both homonuclear and heteronuclear diatomic molecules since our results [P7] show clearly that spirals can be formed when pulling an electron out from HF, CO, H_2.

(c) **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., [6]) for resonant harmonic generation (HHG) 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?

(d) Spiral traces from ionization of NO by circularly polarized XUV or soft X-ray attopulses seeded by an X-ray free-electron laser to guide any experiment planned by the Primoz Rebernik Ribic group at the Fermi Free- Electron Laser in Trieste, Italy in collaboration with the SLAC group (led by Marinelli, Kling, and Cryan). The plan is to use the numerical RMT code, successfully applied to treat photoionization of CO and HF (closed-shell) molecules, to tackle the more challenging case of NO molecule, which is an open-shell molecule.

(e) **Interaction of arbitrarily polarized attopulses with achiral and chiral heteronuclear molecules:** Interaction of circularly polarized laser pulses with chiral molecules or achiral targets. Our initial plan was to consider H_2O_2, the simplest chiral molecule, and then the 1-Chloro-1-fluoroethane. On top of this, because the group of Meng Han (an investigator funded by the DOE AMOS physics program) from Kansas State University can manipulate the chiral molecule of propylene oxide molecule, this target will also be considered and the numerical code to be used for such study will be the multi-configuration time-dependent Hartree (MCTDH). 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.

(f) ***Time delay effects in resonant HHG of He or Be:*** Control of the multiphoton regime plateau structure [8] will be studied for driving laser pulses delayed in time at resonant frequencies.

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PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2022-2024)

[P1] Shuai Li, Bethany Jochim, Jacob Stamm, Dian Peng, Hua-Chieh Shao, Jean Marcel Ngoko Djiokap, and Marcos Dantus, "*Pulse shaping in strong-field ionization: Theory and experiments*," Phys. Rev. A **105**, 053105 (2022).

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[P3] M.A.H.B. Md Yusoff, and J. M. Ngoko Djiokap, "*Time-delay control of reversible electron spirals using arbitrarily chirped attosecond pulses,*" Phys. Rev. A **109**, 023107 (2024).

[P4] L. Pedersen and J.M. Ngoko Djiokap, ``*Ouroboros-pattern-like electron spirals by synchronous crossed chirped laser pulses*," Phys. Rev. A **109**, 033114 (2024).

[P5] H. B. Ambalampitiya and J.M. Ngoko Djiokap, ``*Asymmetric photoelectron momentum distribution of carbon monoxide*," Phys. Rev. A **109**, 043108 (2024).

[P6] M. A. H. B. Md Yusoff, J.M. Ngoko Djiokap, A.V. Meremianin, and N.L. Manakov, ``*Electron Vortices Creation by Atomic Ionization using a Few-Cycle Circularly Polarized Laser Pulse*," Phys. Rev. A **110**, 023102 (2024).

[P7] H. B. Ambalampitiya and J.M. Ngoko Djiokap, ``*Orientation-dependent production of normal Archimedean and dynamical spirals for revealing orbital symmetries in small heteronuclear diatomic molecules*," Communications Physics, (Accepted, September 2024).

"Low-Energy Electron Interactions with Complex Interfaces and Biological Targets"

Thomas M. Orlando
School of Chemistry and Biochemistry and School of Physics,
Georgia Institute of Technology, Atlanta, GA 30332-0400
Thomas.Orlando@chemistry.gatech.edu, Phone: (404) 894-4012

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 the formation of holes, ejection of low energy secondary electron and the formation 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.

Recently, we have developed a simulation methodology to calculate the explicit electron dynamics on the atto- to femtosecond timescale during intermolecular Coulombic decay (ICD). The methodology utilizes real-time time-dependent density functional theory (RT-TDDFT) in conjunction with a complex absorbing potential (CAP). The presence of the CAP allows for the removal of the secondary ionized electron during the simulation. In comparison to previous methodologies, we showed that the combination of RT-TDDFT utilizing a tuned long-range corrected functional (LC-PBE) in conjunction with a CAP accurately simulates the ICD process in a variety of non-covalent bonded dimers [1]. Specifically, we showed excellent results for the water dimer, the HF dimer, and Ar-H_2O. However, there was a breakdown in the methodology for the weakly bound Ne-H_2O and Ar-Ne dimers, which we attribute to the inability of DFT to accurately capture the coupling between monomers in such weakly bound systems. The benefit of the presented real-time methodology is that it provides direct time-dependent population information without necessitating any a-priori assumptions about the electronic relaxation mechanism. As such, the RT-TDDFT/CAP simulation protocol provides a powerful theoretical approach to differentiate between competing electronic relaxation pathways following inner-valence or core ionization.

As an example, Fig. 1(a) plots the time-dependent charge-loss on each monomer for the Ar-H_2O dimer along with the population of a few key molecular-orbitals (b) as a function of time. The charge-loss dynamics are clearly indicative of an over-all ICD process in which the Ar is initialized to a cationic state (blue-curve) and remains in a cationic state, while the water decays from a charge-neutral state to a cationic state (red-curve). However, the real-time dynamics show additional dynamics prior to and subsequent with the ICD process associated with charge transfer back and forth between the Ar and water.

Further insight into the complex dynamics is provided in Fig. 1(b), which presents the time-dependent molecular orbital populations. The initial hole on the Ar 3s orbital (orange) first exhibits Rabi oscillations associated with hole transfer to the water $2a_1$ MO (black), consistent with the charge transfer observed in Fig. 1(a). The Ar 3s orbital is then re-populated from electron density relaxing from the valence Ar 3px (blue) and 3pz (green) orbitals, simultaneous with ionization of the valence water $3a_1$ MO (red). *In this context, we observe hole-transfer competing with the expected ICD process.* The discovery and investigation of such competing pathways illustrates the major benefit of real-time methodologies, especially in more complex systems.

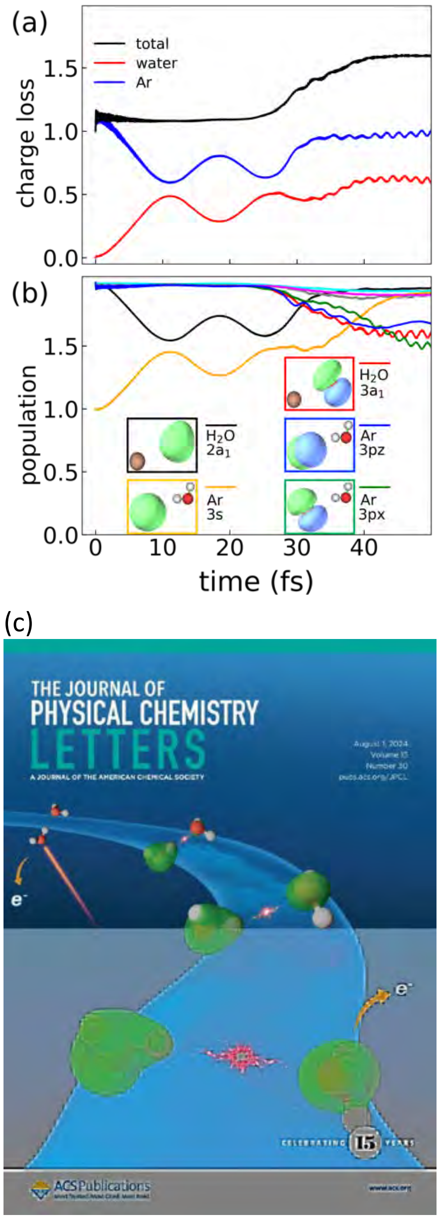

Figure 1: (a) The time-dependent charge-loss on Ar (blue) and water (red). The total charge-loss of the Ar-H_2O dimer (black) corresponds to the sum of the blue and red curves. (b) The time-dependent population of the key molecular orbitals participating in the ICD. dynamics. (c.) Cover article image highlighting this work.

Task 2a: The dynamics of ICD in the water dimer

In collaboration with the Lawrence Berkeley National Laboratory Atomic, Molecular and Optical Physics group, we have been examining fragmentation of the water dimer using computational methods. Specifically, we are using *ab-initio* molecular dynamics (AIMD) to first sample the initial distribution of water dimer nuclear configurations at 30 K. From this distribution, we've randomly selected 28 geometries to run subsequent AIMD simulations on various dicationic states that could be generated from the ICD process. We have run AIMD simulations on the ground, as well as the first 10 excited, dicationic states in both the singlet and triplet configuration; in principle both the singlet and triplet are allowed as they arise from the original doublet single cationic state used to initialize ICD. These states are calculated using the LC-PBE/aug-cc-pVDZ level of theory using linear-response TD-DFT. Intriguingly, our initial results indicate that only the first and fifth dicationic excited states lead to a Coulomb explosion of the dimer, while the dimer remains intact in all other states. Furthermore, we observe that for the first excited state, the singlet configuration leads to proton transfer prior to fragmentation, such that the final fragmentation products correspond to H_3O^+ and OH^+. In comparison, the triplet configuration leads to straight Coulomb explosion of the water dimer, such that the final fragmentation products correspond to H_2O^+ and H_2O^+. The fifth excited state only fragments in the triplet configuration and similarly fragments into H_2O^+ and H_2O^+. Along with the AIMD calculations, we are also performing the RT-TDDFT calculations using our developed methodology on the same geometries used to initialize the AIMD calculations. These calculations will be used to identify which of the dicationic states are most likely to contribute to the downstream fragmentation process. *Combining, this computational analysis with extensive experimental measurements of the fragmentation branching ratio and KER obtained by the LBNL group will yield a comprehensive picture of ICD and fragmentation in the water dimer.*

Task 2b: The dynamics of ICD in the formic acid dimer

Mr. James Zhong, a recipient of a DOE SCGSR fellowship, carried out studies on ultrafast energy exchange and charge transfer in hydrogen-bonded dimers and solvated biomolecules at LCLS-II. During his time at SLAC, he was mentored by Drs. Thorsten Weber (LBNL), Dan Slaughter (LBNL) and James Cryan (SLAC) on calculating the dynamics and analyzing existing data on the dissociative ionization of the formic acid dimer. The data was previously obtained using the Advanced Light Source and the COLTRIMS apparatus. Using the above mentioned RT-TDDFT/CAP simulation, we carried out preliminary calculations on HCOOH dimer. This dimer is bonded together with two hydrogen bonds. These preliminary calculations show interesting electron dynamics that suggest an ICD time of ~ 20 fs, which is faster than the water dimer. This is likely due to the double hydrogen bond in the formic acid dimer vs a single hydrogen bond in the water dimer. The next steps involve tuning the long range separation variables, the complex absorption potential components, and looking at additional configurations of formic acid dimer. Zhong has also been involved in assisting in EuXFEL data analysis of an ongoing experiment on “Imaging the Ultrafast Photochemistry of a Prototypical Carbonyl”.

Task 3: Virtual photon dissociation in the Ar:H_2O system

Theory predicts rapid electronic energy exchange and up to 10^5 gain in the photodissociation cross section due to the interaction of the virtual photon produced after excitation of the rare gas neighbor [2]. Cross-sections for virtual photon-induced dissociation (VPD) have been calculated for N_2, H_2O and CH_4, with rare gas atoms Ar, Kr and Xe acting as neighbors. We have initiated experiments to exam VPD from sub-monolayer coverages of D_2O on Ar multilayers. The Ar $3s^23p^54s \rightarrow 3s^23p^6$ transition occurs at 11.8 eV and overlaps with the high lying dissociative sates of water from below 180 nm to above the ionization threshold at 98 nm (12.65 eV). Preliminary data using 2+1 REMPI detection of the D atom yield and velocity distributions using an incident electron energy of 50 eV shows a larger yield and narrowing of the velocity distribution for D_2O on Ar but not near the magnitude predicted. This is likely due to the fact that the excitation energy is where the ICD channel leading to ion ejection via Coulomb explosions dominate [3]. Work at lower energies, where VPD is more likely to dominate, is on-going.

Future Plans

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. The AMOP group at ANL was awarded beam-time at the EuXFEL in June 2024 to begin examining energy exchange with the solvent shell for simple NaOH and NaCl ionic solutions. Orlando and DOE supported members of the IDREAM2 EFRC were involved in this effort. A LCLS-II beam-time proposal with the Argonne AMOP group has also been submitted using x-ray pump probe experiments.

Time resolved ICD in gas-phase dimers

The collaboration with the LBNL group will continue on multiple projects with the expectation of joint publications involving graduate student James Zhong and GT theory colleagues, Prof. Josh Kretchmer and Dr. Y-S Wang. The first paper will focus on the dynamics of ICD in water dimers and the second on the dynamics of ICD in formic acid dimers. In addition, the collaboration with LBNL will help commission the Dynamic REAction Microscope (DREAM) at LCLS-II to directly observe ICD in momentum- and time-resolved fashions. This will involve interrogation of dimers such as $(N_2)_2$, $(CO)_2$, H_2O-CO, and H_2O-rare gases, in accordance with the current instrumental limitation of low repetition rate (33 kHz) during the startup phase of LCLS-II. The original effort was scheduled for the summer of 2024 but this has been postponed by the LCLS-II administration. In addition, Orlando was a Co-I on two beam time proposals submitted to the LCLS-II on examining ICD, ETMD and molecular elimination in methanol dimers and core hole localization in CF_4 molecules using x-ray-x-ray pump probe.

ICD and VPD in adsorbed over-layers

The search for VPD in N_2, CH_4 and H_2O co-adsorbed with rare gases Ar, Kr and Xe will continue using REMPI and by working at lower incident electron energies (6-20 eV). We will also utilize frequency tripled and up converted light to carry out VUV 10 – 15 eV photoexcitation. Once experiments with these simpler systems are complete, we will carry out work with more complex hydrocarbons such as formic acid (to be compared to the gas-phase work done at Berkeleyy), tetrshydrofuran and pyridine. The latter polyatomic molecule has recently shown to undergo an unusual photo-activated 3-center ICD process [4].

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Recent publications acknowledging support from this program (2022-2024)

1. Y.-S. Wang, J. Zhong Manis, M. Rohan, T.M. Orlando, and J. Kretchmer "Modeling Intermolecular Coulombic Decay with Non-Hermitian Real-Time Time-Dependent Density Functional Theory" submitted, *J. Phys. Chem. Lett.* April 10, 2024. https://doi.org/10.26434/chemrxiv-2024-60ngs.
2. S . Kundu, H. Hu, X. Li, M. Schaible and T. M. Orlando, "Electron Scattering with Ethane Adsorbed on Rare Gas Multilayers: Hole transfer, Coulomb Decay and Ion Dissociation", *J. Chem. Phys.* (2022) https://doi: 10.1063/5.0099594

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1. J. Kretchmer, "Real-time simulations of non-equilibrium electron dynamics", University of South Carolina, Columbia, SC, 04/2024
2. J. Kretchmer, "Real-time simulations of non-equilibrium electron dynamics, University of Washington, Seattle, WA, 02/2024
3. J. Kretchmer, "Real-time simulations of non-equilibrium electron dynamics, PNNL, Richland, WA, 02/2024
4. J. Kretchmer, "Real-time simulations of non-equilibrium electron dynamics, Machine Learning, Embedding, and Dynamics of Many-Electron States in Molecules and Materials, CUNY Graduate Center, New York, NY, 10/2023
5. T. M Orlando, "Probing energy-exchange at surfaces with attosecond x-ray pulses", LCLS-II Workshop and User's meeting. Sept. 26, 2023.

Control of Molecular Dynamics: Algorithms for Design and Implementation

Herschel Rabitz and Tak-San Ho
Princeton University, Frick Laboratory, Princeton, NJ 08540
hrabitz@princeton.edu, tsho@princeton.edu

A. Project Scope:

Achieving control of molecules with lasers is a long-standing goal going back to 1960s. Advents in ultrafast laser technology along with powerful pulse shaping capabilities have enabled a rapidly increasing number of successes in the control of broad varieties of chemical and physical phenomena. The subject is now open for development at an advanced level, 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. The control of chemical dynamics opportunities offered by simulations will continue to be a focus of our research. 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 computational 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 2023 to August 2024, 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 values 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 2023 to September 2024, a broad variety of research topics were pursued in the general area of understanding and controlling quantum dynamics phenomena. A summary of these accomplishments is provided below:

[1] Quantum Optimal Control of Driven Dissipative Two-Level Systems: This work investigated the dynamics of a two–level system coupled to a super–Ohmic boson bath, which is the so–called driven spin–boson model. Using the polaron transformation we derived the Bloch vector of a master equation where the bar tunneling parameter was used as the basis for a perturbation expansion. Our method was based on the canonical quantization provided by the Bloch–Redfield formalism. We applied quantum optimal control theory to the realization of a quantum Z–gate and also the coherent destruction of tunneling (CDT). To solve the optimal control problem, we used the techniques of automatic differentiation (AD) as an alternative to Pontryagin's minimum principle (PMP). The latter is less straightforward since the master equation is complex.

[2] Ultrafast control of the LnF^+/LnO^+ ratio from $Ln(hfac)_3$: This work studied the photo-induced dissociative ionization of lanthanide complexes $Ln(hfac)_3$ (Ln = Pr, Er, Yb) using ultrafast shaped laser pulses in a time-of-flight (TOF) mass spectrometry setup. Various fluorine and Ln-containing mass fragments were observed, which can be interpreted by the photo-fragmentation mechanistic pathway involving C–C bond rotation processes proposed previously. A set of experiments used pulse shaping guided by closed-loop feedback control to identify pulses that optimize the ratio of LnF^+/LnO^+. In agreement with previous studies in which very little LnO^+ was observed, broad pulses were found to maximize the LnF^+/LnO^+ ratio, which involves metal–ligand bond-breaking followed by bond rotation and bond rearrangement. In contrast, a transform limited pulse favored the formation of LnO^+. Finally, the recently developed experimental control pulse slicing (CPS) technique was applied to elucidate the dynamics induced by fields that either maximize or minimize the LnF^+/LnO^+ratio, which also indicates that longer laser pulses facilitate LnF^+ formation during the C–C bond rotation dissociative-ionization process**.**

[3] Exploiting Automatic Differentiation for Quantum Optimal Control of Driven Dissipative Two-Level Systems: In this work, we considered the optimal control problem of a driven spin-boson model system and determined the response of the system to the variation of the control by the master equation and the equation of motion for the propagator of the coherent system dynamics. We have adopted a powerful technique of automatic differentiation, which in principle amounts to doing calculus on the fully discretized form of the optimal control problem. Automatic differentiation tools can be viewed as black boxes taking as input a program computing the cost functional and giving as output another program computing its gradient. Specifically, we obtained the Born–Markov master equation for the polaron transformed Hamiltonian using the Bloch–Redfield formalism. By combining the latter with automatic differentiation we were able to implement the Z–gate and coherent destruction of tunnelling with high fidelity. Optimization of a dissipative quantum gate poses a more complex numerical problem. Since it should occur independent of the input state. To overcome this difficulty, we applied optimal control to the master equation which is the generalization of quantum unitary evolution operator in case of dissipative dynamics.

[4] Entanglement Propagation in Integrable Heisenberg Chains from a New Lens: In this study, we obtained the exact single-magnon entanglement evolution in Heisenberg chains using the Quantum Correlation Transfer Function (QCTF) formulation. A dual frequency and time-domain analysis showed that the transient dynamics of individual spins' entanglement is described via a Bessel function of the first kind. Through QCTF, we bypassed the evaluation of the full system's state for the purpose of obtaining entanglement. Although it was known that the observable entanglement edge can be formed by the arrival of a stream of quasi-particles that travel with the maximum group velocity, we showed how the early quasi-particles travel faster than the maximum group velocity of the chain and contribute to entanglement production. Our results can be extended to the multi-magnon regime, therefore making available the means to better interpret equilibration dynamics and thermodynamics in Heisenberg chains.

[5] Discrete real-time learning of quantum state subspace evolution of many-body systems in the presence of time-dependent control fields: In this study, we developed a method for discrete real-time learning (DRTL) of the evolution of a many-body quantum state in the presence of time-dependent control fields. This method was based on the recent adoption of the Artificial Neural Network (ANN) ansatz within the framework of the time-dependent variational Monte Carlo (t-VMC) method in learning large-scale quantum many-body dynamics. The method leveraged accurate short-time quantum state propagation with the Schrödinger equation and the efficient stochastic quantum natural gradient descent algorithm in machine learning and may be considered as a synergism between the time-dependent Schrödinger equation and the ANN quantum states. Specifically, this method minimizes the normed distances between the time-dependent variational ANN ansatz and a set of partial quantum states over a sequence of stochastically sampled subspaces that are connected to each other in small discrete time steps. We have demonstrated the high accuracy and stability of the DRTL method for the spin excitation dynamics of 4 × 4, 6 × 6, 8 × 8 and 10 × 10 2D Heisenberg spin-1/2 lattices driven by time-dependent control fields applied to a corner spin along with strong exchange coupling between the nearest-neighbored spins. It was found that the number of ANN parameters for properly following the dynamically occupied subspaces approximately increases quadratically with the number of spins in the system. This finding provides a basis for future work to perform quantum optimal control simulations of 2D spin lattices and other multiparticle systems.

[6] Optimal control simulations of many-body quantum systems by a synergism of Neural Network Quantum States and Quantum Optimal Control Theory: In this work, we considered a self-consistent algorithm for optimal control simulations of many-body quantum systems. The algorithm featured a two-step synergism of Neural Network Quantum State (NQS) training using a machine learning technique and Quantum Optimal Control Theory (QOCT) applications to the time-dependent Schrödinger equation. Specifically, in step 1 the NQS was trained over small time steps to identify the working space for the time evolution of the many-body quantum system in the presence of a training field and in step 2 the QOCT was applied to find the underlying optimal control field for a chosen control objective. Steps 1 and 2 were iterated until a self-consistent control objective value was reached such that the resulting optimal control field yields the same objective value when the corresponding working space was enlarged. We have demonstrated the high efficiency and fidelity of this two-step self-consistent NQS-QOCT method by considering the optimal control simulations of the time evolution of the strongly interacting 1D and 2D Heisenberg spin systems under the local control condition that only a single spin is driven by the time-dependent control fields. Particularly, it was found that the dimensionality of the compact working space scales only quasi-linearly with the number of spins.

[7] Orthogonal Bootstrap Monte Carlo: In this work we introduced the novel bootstrap Monte Carlo method based on the notion of orthogonal dice applied to a family of discrete uniform distributions. The orthogonal bootstrap method was implemented to generate random samples using non-identically distributed uniform random variables. As a result, we were able to yield mean estimators with notably reduced variance compared to conventional techniques. In particular, we have obtained a $O(1/n^2)$ rate of convergence of the variance of the mean estimator and showed it to be within a constant factor of two of the optimal bound implied by the Koksma-Hlawka inequality. This study demonstrated the efficacy of the orthogonal bootstrap in Monte Carlo integration, showcasing its performance across various examples.

C. Future Plans:

In the coming period, we plan to draw on our current progress using special artificial neural network (ANN) tools to deal with large-scale quantum problems for accelerating simulations for many-body quantum dynamics under control. Our current research indicates that a suitable synergism of the dual use of ANN and the 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 render comfortable polynomic scaling by exploiting the compressed quantum dynamics working space. In addition, we plan to study the dispersion and volume of saddles in control space to reveal their nature and significance upon quantum control performance for a better understanding of fundamentals of quantum optimal control. 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 carefully examine, both theoretically and numerically, the top of quantum control landscapes corresponding to where a primary physical objective achieves its optimal value. Particularly, we plan to perform mechanism analysis utilizing algorithms customized to quantum control applications. Our current 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 that account for the prior determined optimal control and ideally interpret the encoding/decoding 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 (2022-2024):

[1] Selective photoexcitation 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).

[2] A Generalized Kernel Method for Global Sensitivity Analysis, J. Barr and H. Rabitz, J. Uncertainty Quantification, 10, 27-54 (2022).

[3] 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).

[4] 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).

[5] Chemically Sensitive Fluorescence Imaging of Colliding Microdroplets, Z. Quine, A. Goun, F. Laforge, H. Rabitz, and C. K. Law, Phys. Fluids, 35, 052002 (2023).

[6] Kernel-Based Global Sensitivity Analysis obtained from a Single Data Set, J. Barr and H. Rabitz, Reliability Engineering & System Safety, 235, 109173 (2023).

[7] 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).

[8] 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 127, 4224 (2023).

[9] Quantum tracking control of the orientation of symmetric top molecules, A. B. Magann, T.-S. Ho, C. Arenz, and H. Rabitz Phys. Rev. A 108, 033106 (2023).

[10] Ultrafast control of the LnF^+/LnO^+ ratio from $Ln(hfac)_3$, J. Chen, X. Xing, R. Rey-de-Castro, and H. Rabitz, Phys. Chem. Chem. Phys., 26 15850, DOI: 10.1039/d4cp0337c (2024).

[11] Exploiting Automatic Differentiation for Quantum Optimal Control of Driven Dissipative Two-Level Systems, H. Jirari and H.Rabitz, Euro. Phys. Lett. (2024) accepted.

[12] Entanglement Propagation in Integrable Heisenberg Chains from a New Lens, Peyman Azodi and Herschel Rabitz, J. Phys.Commu. (2024) accepted.

[13] Quantum optimal control of the driven dissipative two-level system, H. Jirari and H. Rabitz, Phys. Rev. A, (2024) accepted.

“Atoms and Ions Interacting with Particles and Fields”
Award No. DE-SC0012193

F. Robicheaux
Purdue University, Department of Physics and Astronomy,
525 Northwestern Ave, West Lafayette IN 47907
(robichf@purdue.edu)

Program Scope

This theory project focuses on the time evolution of systems subjected to either coherent or incoherent interactions represented by fields and particles, respectively. This study is divided into three categories: (1) correlations between two electrons in highly excited states or in double continua, (2) processes for one electron in time dependent or non-separable potentials, and (3) the interaction of atomic electrons with strong electromagnetic fields. Some of the techniques we developed have been used to study collision processes in ions, atoms, and molecules. In particular, we have used these techniques to study the correlation between two (or more) continuum electrons and electron impact ionization of small molecules.

Recent Progress (Publications 10/2023-9/2024)

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. The results were published in Phys. Rev. E.

There was one graduate student supported by this grant during the past year. Mohamed Eltohfa started research in January 2023 working on the thermalization in lineland project. He finished that project which was published in Phys. Rev. E. In addition, two undergraduates were supported, Xinghan Wang and Colton Griffin, who worked on an early state of the lineland thermalization project.

Future Plans

N/A

Peer-Reviewed Publications Resulting from this Project (2022-2024)

[1] Akilesh Venkatesh and F. Robicheaux, “Simulations for x-ray imaging of wave packet dynamics,” Phys. Rev. A **106**, 033125 (2022).
[2] M. Eltohfa, Xinghan Wang, Colton M. Griffin, and F. Robicheaux, “Simulations of classical three-body thermalization in one dimension,” Phys. Rev. E **110**, 014114 (2024).

Light-induced couplings to study and control electronic interactions and electron-nuclear dynamics

Award Number: DE-SC0018251
PI: Arvinder Sandhu
Department of Physics and College of Optical Sciences
The University of Arizona
Tucson AZ 85721
asandhu@arizona.edu

Project Scope

This project employs light-induced couplings to investigate and control the correlated and coupled electron and nuclear dynamics in atoms and molecules. The objectives of this research project are to 1) To demonstrate optical control of electronic processes including relaxation dynamics; 2) To study the strong field modification of the electron-nuclear dynamics; 3) To observe and steer coherent electronic oscillations and charge migration. These goals will be achieved through systematic studies that employ tunable near to mid infrared optical pulses along with XUV or soft-x-ray pulses to probe and control the light-induced couplings between electronic states. Diagnostics techniques such as attosecond transient absorption spectroscopy (ATAS), four-wave-mixing (FWM), and velocity map imaging (VMI), are utilized on this project to obtain complementary information on the real time evolution of electronic processes.

Recent Progress

We made progress along study of multielectron excitations and control of autoionization dynamics using multi-wave-mixing and transient absorption spectroscopies. We conducted photoelectron interferometry to understand the impact of short-range electron-core interactions on the quantum beats in spin-orbit split continuum channels and how it impacts the anisotropy parameters. We continued work towards control of coherent wavepacket motion and conical intersection dynamics. Collaborations with theory groups from Central Florida, Purdue, and Arizona have been vital in this project.

Probing the evolution of multielectron excited states:

Radiative nonlinear four-wave mixing processes arising from the interaction of extreme-ultraviolet attosecond pulse trains and tunable strong-field infrared pulses can monitor the evolution of electronic wavepackets and capture the light-induced couplings between excited states. We used this approach to investigate the dynamics of multielectron excited states in Krypton. Specifically, there are several doubly excited states around 27 eV, interspersed between singly excited states $4s^{-1}np$ states. This opens the opportunity of real-time monitoring of two-electron dynamics in an autoionizing transient wave packet in krypton. While the singly excited states are well-known (red labels on the top of Fig. 1), the identification of the doubly excited configurations (blue labels on the top of Fig. 1) is non-trivial and requires elaborate R-matrix calculations.

We excited a coherent superposition of two Fano resonances and probed them through tunable FWM with a delayed IR pulse. In the FWM signal around 25 eV (Figure 1), we observe a quantum beat corresponding to interference between one- and two electron excitation paths, and this is superimposed on a slower decay corresponding to autoionization of the wavepacket.

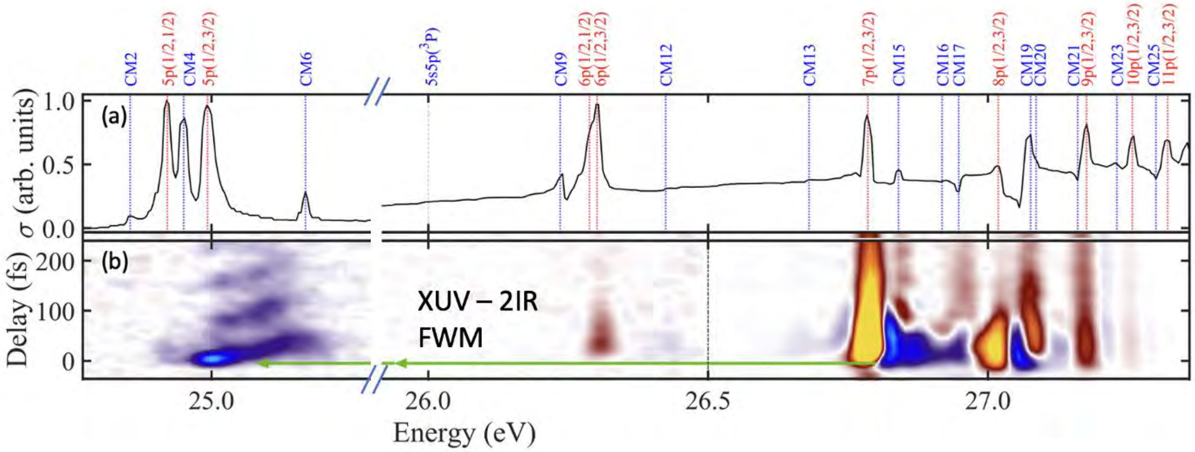

Fig. 1 (a) Spectrum of Krypton showing doubly excited states (blue labels) and singly excited 4s^{-1}np states (red labels). (b) Background-free FWM emission from interference between the singly and doubly excited states show beats with energy dependent phase structure.

The observed interference signal exhibits interesting spectral and temporal characteristics, which are also dependent on the frequency of the probe, yielding control over the emission characteristics from the time-evolving Fano wavepacket. We are working with Chris Greene on a model that captures the time and energy structure of the FWM in terms of the mixing between one electron and two electron configurations.

__Four-wave-mixing emissions from laser-coupled autoionizing states__:

We investigated the optical response of argon to a multi-pulse sequence consisting of an extreme ultraviolet (XUV) pulse, an overlapping collinear IR pulse, and an angled delayed IR pulse (Figure 2). Absorption of an XUV and an IR photon from the collinear beams excites, sequentially, the 3s^{-1}4p bright state and the 3s^{-1}3d/5s dark states. The subsequent absorption of an IR photon from the non-collinear beam results in an angled XUV emission whose delay dependence encodes the coupling between autoionizing states and the dynamics of dark state. Ab-initio predictions by Luca Argenti's group for the angled FWM signal are in excellent agreement with our experimental result. Both predict a double-peak structure (Figure 2), which we attribute to the interference between contributions from 5s and 3d intermediate dark states. We find that the population in each intermediate state shows large Rabi oscillations, and for a specific arrival time of the angled optical pulse, the amplitudes of oscillations for two intermediate states have opposite sign, corresponding to a dip in the observed FWM signal.

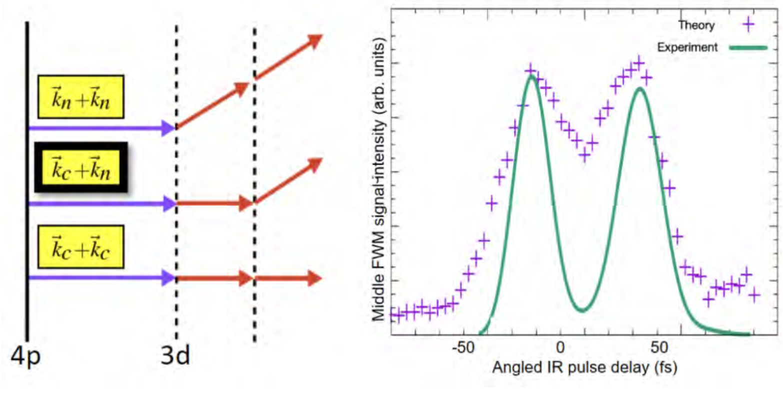

Fig. 2 In a non-collinear four-wave mixing scheme with autoionizing states of argon, middle pathway corresponds to the absorption of one collinear and one angled IR photon from XUV excited 3s^{-1}4p state. This emission shows a double peak structure as a function of the delay between the two IR pulses.

Electron-core interaction and photoemission anisotropy:

We published a study of the quantum beats in two-color photoionization of argon where we used attosecond extreme ultraviolet pulse train to prepare an electronic 3d/5s wave packet (PRA 108, 033107 (2023)). Two-photon ionization with a tunable infrared probe pulse then makes the constituent states interfere in 1/2 and 3/2 continuum channels. 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. We analyzed photoelectron spectrograms and identified phase differences between the beat signals in the spin-orbit split continua. Comparison of our experimental results with the theoretical simulations conducted by Chris Green's group allowed us to interpret the amplitudes and phases of ionization signals in terms of the off-diagonal elements of the short-range scattering matrix and the dipole matrix elements to the continuum eigenchannels. This work also highlighted the impact of light field parameters on the phases of interfering ionization pathways. We are currently analyzing the relative amplitudes and delay dependence of the angular anisotropy parameters in the ionization channels to obtain additional insights into the electron-core interaction dynamics.

Control of electron hole wavepackets and non-adiabatic dynamics:

Our recent focus has been on the tracking and steering of coherent charge dynamics. We conducted experiments where we prepare a hole in atomic or molecular system using strong-field ionization. This hole evolves and we probe its motion using XUV transient absorption. However, in contrast to prior efforts in the community, we introduce another control IR pulse with an aim to modify the hole motion. Our first proof-of-the-concept experiment was in Argon where we prepared hole in the superposition of two lowest states of ion, and then we monitor the hole beating at 0.177 eV (Figure 3). The absorption lines positions are strongly modified by the control pulse which arrives at 250 fs due to light induced couplings. We simulated our experimental results in a collaboration with the group of Nikolay Golubev. We are writing a joint experiment-theory paper on this topic.

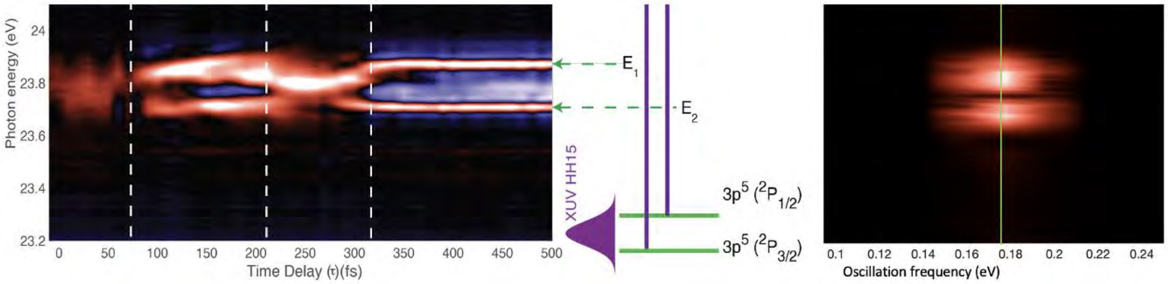

Fig. 3 XUV transient absorption spectra in Argon corresponding to transitions from the spin-orbit wavepacket created in the ground ionic state. The control pulse arrives at 250 fs and alters the absorption features.

In a previous experiment, we had demonstrated that the motion of the electron hole near the conical intersection is modified by the presence of laser dressing. In this experiment, XUV created a hole in CO_2, which oscillates between sigma and pi orbitals due to the interactions between two vibronic states. The frequency of the oscillation is dramatically changed when we apply the dressing pulse during the hole creation step. Uwe Thumm's group has recently developed the methods required to simulate this situation. We are working with them to model of our pump-control-probe experiment. Through on this collaboration, we hope to interpret the mechanisms of strong-field modification.

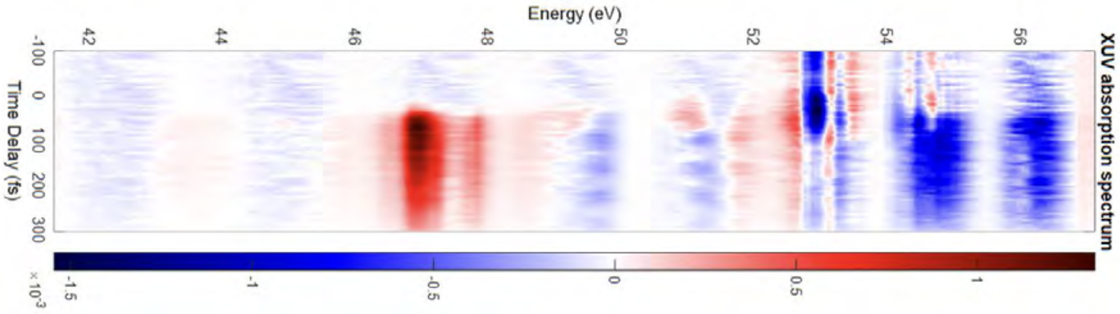

Fig. 4 Attosecond transient absorption spectra in CH_3I, representing I-edge transitions from the 4d to the valence orbitals in the neutral and ionic molecule. The blue oscillatory signal is attributed to the laser induced vibrational motion in the ground state. The peaks near 47 eV and 48 eV correspond to transitions in the ion.

Our next set of studies are on the hole dynamics in polyatomic systems starting with CH_3I and then extending to other larger molecular systems. Here, we use the Iodine absorption edge to track the hole dynamics in the molecular ions. Figure 4 shows our preliminary results on the transient absorption in CH_3I. Here we monitor Iodine 4d to HOMO/LUMO transitions. The blue oscillatory signals near 49.5 eV and 51.5 eV correspond to the transitions from the vibrational wavepacket in neutral molecule. The red signals near 47-48 eV correspond to the Iodine absorptions in the ionic CH_3I, capturing the spin-orbital splitting in the molecular states. The ongoing experiments are incorporating the third IR pulse for control of the hole dynamics in this ionic system.

Future Plans:

We are working extending our transient absorption and four-wave-mixing studies to molecular systems, to obtain light-induced control multielectron interactions and electron-nuclear couplings. We are also targeting the coherent evolution of holes in the ionic states of atoms and molecules, which includes the observation and control of charge migration.

Peer-Reviewed Publications Resulting from this Project (2022-2024)

1) 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).
2) 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).
3) 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).
4) 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).
5) S. Yanez-Pagans, C. Cariker, N. Harkema, M. Shaikh, L. Argenti, and A. Sandhu, “Optical Control of Autoionizing States in Argon”, Book Chapter in “Proceedings of the 8th International Conference on Attosecond Science and Technology”, Eds. Luca Argenti, Michael Chini, Li Fang (Springer Proceedings in Physics Vol 300) Chapter 6, pp. 61-68 (2024).

Coherent Probes of Molecular Charge Migration

Science Using Ultrafast Probes: DE-SC0012462

Kenneth Schafer[1,*], Mette Gaarde[1], Kenneth Lopata[2], Louis DiMauro[3], Robert Jones[4]
1) Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA
2) Department of Chemistry, Louisiana State University, Baton Rouge, LA
3) Department of Physics, The Ohio State University, Columbus, OH
4) Department of Physics, University of Virginia, Charlottesville, VA

*kschafer@lsu.edu

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.

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.

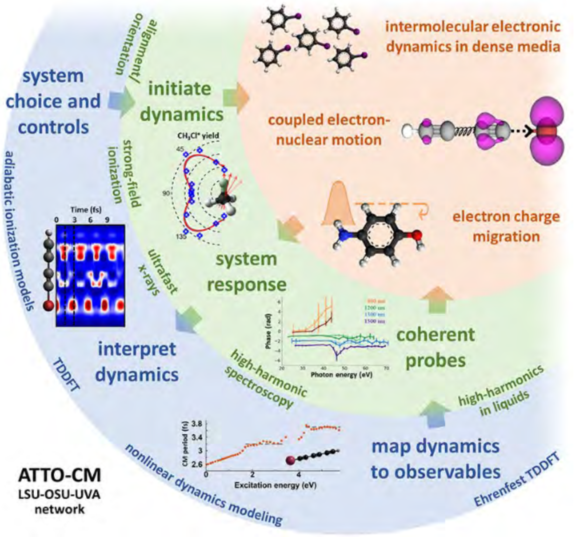

Figure 1: Theory and experiment interact in the ATTO-CM network to address fundamental aspects of charge migration (center). Blue band: theoretical tools; Green band: coherent probes and measurements.

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* – Building on our success in previous years with identifying attochemistry rules for CM, we have investigated the role of lone pairs (LPs) in CM. Our results suggest that the presence and orientation of LPs with respect to the initial hole dictate if and where the subsequent CM evolves in the molecule. In parallel, we have investigated the initiation of CM with realistic pump pulses. We found that over a wide range of mid-infrared wavelengths, strong-field tunnel ionization with a few-cycle pulse robustly leads to long-lasting field-free CM. A manuscript detailing these results is currently under review [Hamer 2024 b]. Finally, we published high-order symplectic schemes for grid-based TDDFT simulations with local (LDA- and GGA-type) exchange-correlation functionals and made our in-house TDDFT code, “QMol-grid,” for CM simulations of molecular models in one spatial dimension publicly available (with an open-source BSD 2-Clause License). A manuscript detailing the QMol-grid package functionalities is currently under review [Mauger 2024 b].
2. *Thrust 2: Time resolving charge migration dynamics* – We are exploring multiple avenues for probing CM dynamics. We are developing an experimental approach to attosecond spectroscopy using tunable visible-XUV interferometry. We continue our analysis of results from multiple LCLS-based campaigns to measure CM in para- and meta-aminophenol [Guo 2024], and we have submitted an LCLS proposal to explore the difference between CM in gas-phase versus solvated bromoaniline. At the theory level, we continue to explore high-harmonic spectroscopy (HHS) as a probe of electron dynamics. We have shown that HHS in a pump-probe scenario is sensitive to the time-dependent location of the CM hole in a halogenated carbon chain [Hamer 2024]. We have begun efforts to calculate HHG yields in solvated molecules, starting by doing quantitative comparisons of HHG yields in different ring-shaped molecules, detailed in a manuscript currently under review [Armond 2024].
3. *Thrust 3: Expanding the charge migration toolbox* – The ATTO-CM team continues to explore strong-field interactions that can serve to pump and probe CM. On the experimental side, equipment upgrades have enabled the creation of few-cycle (6 fs) laser pulses at UVA. These will enable experiments utilizing strong-field ionization (SFI) and/or strong field dissociative ionization (SFDI) to both initiate and probe CM. On the theory side, we have investigated to what extent SFI can probe CM with a delay-dependent ionizing probe pulse following the initiation of the CM. We also completed a study of SFI rates for arbitrary molecules using weak-field asymptotic theory (WFAT). These latest results include using a rigorous definition of the dipole moment and Dyson orbitals in the WFAT formulation. A manuscript detailing those results is currently under review [Wahyutama 2024].

Thrust 1: Mechanisms of charge migration

Thrust 1 of the ATTO-CM network uses first-principles simulations to discover how CM occurs in molecules, how it can be initiated with realistic laser pulses, and what properties regulate it. Through these, we aim 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 attochemistry principles? Progress in Thrust 1 continues to be instrumental in shaping recent and future research directions in the other two thrusts of the network.

Lone-pair (LP) control of CM: We previously reported that, in bromoaniline, CM occurs via hopping along the π system to the LPs on the terminal nitrogen. Building on this, an ongoing effort in our team is to determine a chemical interpretation of charge migration based on LPs and bonding, *e.g.*, a valence-bond picture. To determine the importance of LPs more generally, in the past year we performed TDDFT simulations of CM in the para-functionalized bromobenzene (Br-C_6H_4-R) family, with R groups containing different numbers and orientations of LPs.

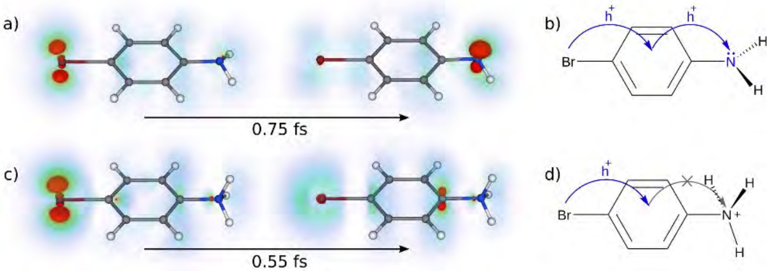

Figure 2: Charge migration in bromoaniline (a) involves hole motion from Br ↔ ring ↔ NH_2, and mechanistically (b) involves the N lone pair electrons. In contrast, in bromoanilinium (c) the hole oscillates between Br and the ring and does not move to the NH_3^+ group. This is a consequence of the lack of LP electrons on -NH_3^+ for the hole to hop to (d).

Figure 2 shows representative examples of the importance of LPs. Panel (a) shows snapshots of the hole density in bromoaniline (R=NH_2) following ionization from the Br. The dynamics occur via hopping from Br ↔ ring ↔ LPs on N, as shown schematically in (b). Panel (c) shows the dynamics for bromoanilinium (R=NH_3^+), which consists of faster oscillations of the hole between the Br and ring, without traveling to the NH_3^+ group (d). Since the N has no LPs in this molecule, it cannot easily give up electrons to the π system, and thus does not accept a hole. Additionally, we simulated how the orientation of LPs affects CM in bromonitrobenzene and bromothiophenol (not shown). We observe that, by changing the shape of the initial hole, or by bond rotation, CM only occurs when the initial hole is aligned with the LPs, and it is turned off when they are not aligned (remains localized to Br ↔ ring). Our results suggest new chemical rules for CM: In addition to our previous findings (importance of conjugation and electron donating groups), our recent simulations suggest that (i) if LPs are present, the hole will generally move to the location of the LPs, and (ii) the initial hole must be oriented parallel to LPs for CM to occur. These principles can be used to identify targets where holes can be guided to particular regions of the molecule.

Initiating localized CM-modes with tunnel ionization: We have completed a numerical study on how to initialize the type of localized hole that leads to high-contrast particle-like CM as discussed above, using a realistic pump pulse [Hamer 2024 b]. Using TDDFT, we studied the CM initiated by many different types of pump pulses, ranging from attosecond XUV to intense, MIR pulses with different central wavelengths and polarizations. We investigated two different halogenated organic molecules that we have studied extensively before [Folorunso 2021, Folorunso 2023, Hamer 2022, Hamer 2024]: the linear bromobutadyene (BrC_4H) and the extended bromoaniline (BrC_6NH_2). We found that tunnel ionization by a few-cycle MIR pulse is efficient at creating a localized hole, and subsequently high-contrast particle-like CM, and that both the periodicity and the hole contrast is robust across a wide range of laser wavelengths, spanning from 1000-2500 nm.

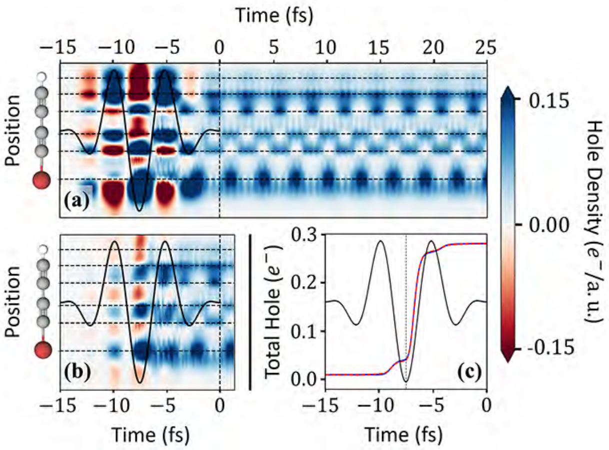

Figure 3: (a) Time-dependent hole density in BrC_4H during and after a 3-cycle, 1500 nm, 50 TW/cm^2 laser pulse polarized parallel to the molecule, integrated over the directions perpendicular to the molecular axis. (b) Same as (a), after removal of the linear polarization response. (c) Time-dependent ionization yield (blue and red) during the laser pulse (sketched in black) for the dynamics in panels (a) and (b).

The hole formation process and the ensuing CM dynamics created using a few-cycle MIR laser pulse in our TDDFT simulations is illustrated in Figure 3. During the laser pulse, we see a strong, linear response proportional to the driving field (panel (a)), which can be numerically filtered away (b) to reveal that the hole is formed on the Br atom at each maximum of the laser electric field, with most of the hole formed at the peak of the pulse, when the laser field (force on the electron) points from the center of the molecule toward (away from) Br. This interpretation is supported by the spatially integrated time-dependent hole density shown in panel (c). We note that the CM period after the end of the pulse is different from that of the laser period and stays the same even as we vary the laser wavelength between 1000 and 2500 nm. From these calculations we surmise that our approach to creating a localized hole up until now [Folorunso 2021, Folorunso 2021], using constrained density functional theory (cDFT) [Eshuis 2009], is a reasonable approximation to a tunnel-ionization-initiated hole. More broadly, this strengthens the argument that intense, few-cycle MIR pulses can be used in the lab to create initially localized holes in halogenated molecules.

Finally, we also considered the effect of nuclear motion on the hole dynamics, incorporated at the Ehrenfest-level of theory for the ground-state (equilibrium) geometry of the molecule, both during and after the laser pulse. We found that the hole dynamics in the two molecules we considered was essentially unchanged, with the slower nuclear vibration showing up as a low-frequency sideband in a Fourier analysis of the CM dynamics. This indicates that the inclusion of nuclear dynamics for rigid molecules like BrC_4H does not change the initiation of the CM mode. Calculations of more initial configurations will address the issue of the propagation of the CM hole.

TDDFT simulation of CM: TDDFT is the workhorse for our direct numerical simulation of CM in a range of organic molecules. Those simulations are computationally expensive and put limits on our ability to perform detailed parameter scans or molecular geometry/configuration averaging analyses. In a numerical-development aspect of Thrust 1, we have investigated two avenues for reducing TDDFT simulation times: (i) efficient high-order propagation schemes and (ii) dimensionally reduced TDDFT model simulations.

In [Mauger 2024] we showed that efficient high-order symplectic schemes for grid-based TDDFT simulations with local (LDA- and GGA-type) exchange-correlation functionals can easily be implemented using standard split-operator techniques. We continue our investigations to develop similar high-order symplectic schemes that are compatible with arbitrary exchange-correlation functionals and basis-set discretizations.

In the context of our previous nonlinear analysis of CM [Mauger 2022], we developed an in-house TDDFT code for CM simulations of molecular models in one spatial dimension, in MATLAB. Since then, we have extended the code's capabilities to cover DFT, Hartree Fock, and Schrödinger-equation ground/excited-state calculations as well as TDDFT and TDSE time propagation. We have documented this code, including a suite of tutorials to initiate new users for how to interact with it, and released the code as the “QMol-grid” package (with an open-source BSD 2-Clause License). QMol-grid can easily be downloaded and installed from a GitHub repository (https://github.com/fmauger1/QMol-grid) or directly as an Add-On to MATLAB via its MathWorks file exchange (https://www.mathworks.com/matlabcentral/fileexchange/171414-qmolgrid). A manuscript detailing the package functionalities is currently under review [Mauger 2024 b].

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. Given the attosecond time scale of CM, these probes must provide attosecond resolution capabilities. We describe here how we engage with (i) tunable visible-XUV interferometry, where the attosecond time resolution is given by attosecond stability of the visible-XUV time delay; (ii) LCLS-based attosecond pump-and-probe experiments, with a time resolution determined by the pump and probe durations and relative delay; and (iii) HHS, in which the time resolution is provided by the intrinsic attosecond time scale of the HHG process.

XUV attosecond spectroscopy of molecular electronic dynamics: The OSU node utilizes attosecond spectroscopy to study CM on the attosecond time scale, using well characterized XUV attosecond pulse trains to photoionize a target molecule in the presences of a phased-locked fundamental field. For molecules, a limiting factor is the spectral congestion of photoelectron spectra, due to the existence of multiple ionization channels with energy levels close to each other. To reduce this spectral congestion, in our experiment we create attosecond pulse trains using visible fundamental wavelengths instead of 800 nm, thus spacing out the direct and side-band photoionization lines in RABBITT-scan measurements. Using a 400-nm fundamental wavelength, we have investigated photoionization delays in the C-channel shape resonance of CO_2. It has been proposed that one may see an enhancement in the yield due to inter-channel coupling [Siggel 1993]. We have confirmed the inter-channel coupling and observed significant phase excursion in the A and B channels, which are predicted to have strong inter-channel coupling with the C channel [Lucchese 1990].

When using a fixed 400-nm fundamental light for RABBITT measurements, the large 6 eV energy separation between sidebands leads to lower than ideal resolution. To increase the energy resolution while maintaining low spectral congestion, we now use a tunable fundamental wavelength source in the RABBITT scans: We perform RABBITT measurements at different wavelengths, each giving the channel-resolved photoionization phase at the energies of the side bands. Then, by combining multiple wavelength results together, we obtain the phase profile for each channel with a finer resolution than what is possible when using a single fundamental wavelength [Gorman 2019].

To realize our tunable visible RABBITT scheme, we have developed a sum-frequency generation (SFG) setup using our laser's 800 nm pulse together with the output of an optical parametric amplifier (OPA) to produce tunable wavelengths ranging from 490 to 600 nm. Due to the limitation of low SFG output power, we have made various modifications to extend the HHG cutoff and increase the total count rate in these experiments. Our measurements show that we now have enough harmonics to cover the aforementioned shape resonance in CO_2. With the adequate count rate and good stability, we can see clear oscillation in the RABBITT scan, and thus extract the photoionization delay for each sideband. These runs prove the capability of the OSU node to perform attosecond spectroscopy at tunable wavelengths.

Attosecond campaign at LCLS: The OSU node continues analyses for the three previous beam times of 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). These experiments used isolated attosecond pulse pairs to measure CM in two aminophenol isomers. The efficacy of using LCLS to conduct two-color attosecond pump-probe measurements with atomic specificity was demonstrated by the collaboration in [Guo 2024]. The first pulse is tuned lower than any K-edges and ionizes the molecule to initiate dynamics. The second pulse probes the molecule either at the oxygen K-edge for X-ray absorption spectroscopy (XAS) or above it for X-ray photoionization spectroscopy (XPS), and the net absorption or emission, respectively, is measured. The pulse pair delay can be tuned over 10 fs with attosecond-scale precision to fully characterize the CM.

Results from the XAS experiments in the para-aminophenol isomer previously revealed a resonant pump-probe absorption signal near the initial time of ionization. This is followed by a rapid signal decay within 2 fs, a subsequent revival near 5 fs, and an overall reduction of the signal after 5 fs. Two independent theoretical investigations, performed by campaign members, that fully simulated the pump-probe interaction, elucidate what causes the experimental signal: The initial broadband ionization populates states above and below the double ionization potential (DIP), and the rapid initial decay is hence due to autoionization of the states above the DIP threshold. The revival is due to the coherent motion of the below-threshold DIP-states. The long timescale reduction is finally from the onset of nuclear rearrangement. All three of these physical processes are not unique to aminophenol, and hence these results will provide new insights on CM in small molecules. A manuscript on these results is currently in progress.

To understand the portions of the signal specific to para-aminophenol, the OSU node continues analysis of the repeated XAS experiment using meta-aminophenol. Here, we have revealed a similar pump probe absorption signal wherein we see a fast decay on a similar timescale to the para isomer, subsequent oscillatory revival, and finally an overall signal decay. Interestingly, the oscillatory signal seems to occur later, possibly providing evidence for the effect of isomerization in the coherent evolution of the below-threshold DIP-states. Work on this signal analysis is ongoing to remove experimental systemic effects.

High harmonic spectroscopy as a probe of CM and other ultrafast electron dynamics: The LSU node continues to explore HHS as a probe of CM, and more generally to develop a framework for calculating HHG spectra in molecular samples using grid-based TDDFT. Over the past year, we have completed and published a study of frequency-matched strobo-spectroscopy (FMSS) of CM [Hamer 2024]. In this work we showed that it is possible to track the time-dependent location of particle-like CM motion by recording the delay- and frequency-dependent harmonic yield in a pump-probe scenario. In this scenario, the pump laser creates a localized hole on the halogen end of a molecule (similar to the types of localized holes we described under Thrust 1, generated via tunnel ionization), and a second probe pulse arrives after some delay and generates harmonics from the molecule in which the hole dynamics is taking place. We found that the HHG yield is highest when the hole is far away from the halogen atom, and that this manifests as a variation of the yield with both pump-probe delay and harmonic frequency.

We have also continued our efforts to accurately calculate HHG yields from organic molecules, with the goal of being able to calculate both gas-phase and liquid-phase HHG spectra. One motivation for these studies is that liquids allow the range of molecules that can be experimentally studied to expand to those which do not have sufficient vapor pressure for HHS experiments. We have performed quantitative comparisons between the angularly averaged yields of three ring-shaped organic molecules and compared these relative yields to those from experiments [Alharbi 2015]. After implementation of an orbital-dependent tunnel-ionization-contribution correction factor, we have achieved good agreement with experimental results and have submitted a manuscript for review [Armond 2024].

Our next goal is to calculate the HHG response for molecules solvated in a liquid environment. The experimental node at OSU is interested in the HHG yield from halobenzenes solvated in alcohols, and have found that the halobenzene HHG yields, in general, strongly dominate those of the alcohol HHG yields, in both the gas and the liquid phases. Following the approach laid out in [Armond 2024] we find that, in the gas-phase, the angularly averaged HHG yield in fluorobenzene (FC_6H_5) strongly dominates that of methanol (CH_3OH) for most of the spectrum, as illustrated in Figure 4.

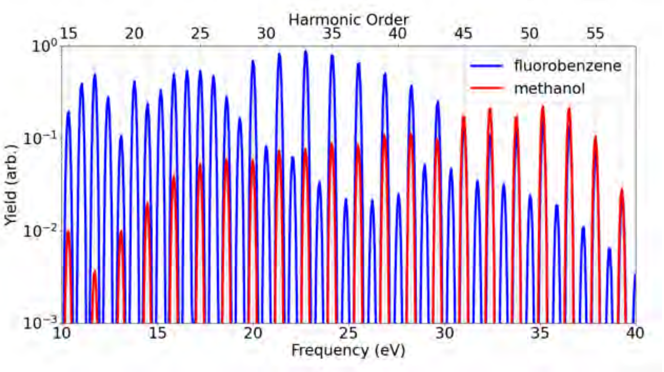

Figure 4: HHG spectra for gas-phase fluorobenzene and methanol, driven by a linearly polarized, 1825-nm laser pulse. The spectra have been averaged over the relative orientation between the molecular axis and the laser polarization, using a Lebedev grid of order 7.

X-ray absorption probing of CM in bromoaniline: The LSU node has started exploring CM in bromoaniline (BrC_6H_4-NH_2) when initiated by removing an electron from the inner-valence 3p sub-shell (localized on Br), bound by approximately 180 eV. We are interested in the influence of solvation on the CM dynamics, and we have simulated CM in bromoaniline both in its gas phase and when solvated in liquid methanol (see also the Future Plans sub-section). We find that, in both cases, the CM dynamics is fundamentally similar and dominated by a rapid oscillation of charge between the phenyl ring and the NH_2 group in bromoaniline, with a periodicity of 750 - 800 attoseconds. However, we also find that the interaction with the solvent molecules causes the CM dynamics in solvated bromoaniline to be slightly slower and to exhibit lower contrast, as in, there is less hole density at the nitrogen atom of the amine group in the liquid phase compared to the gas phase. Together with experimental colleagues from SLAC and from Imperial College, we have submitted a proposal for an experiment at the LCLS that would directly compare the CM dynamics in the two phases. The proposed experiment would use attosecond X-ray pulse pairs to first ionize the 3p electron from Br, and then probe the charge at the N edge via transient X-ray absorption.

Thrust 3: Expanding the charge migration toolbox

Strong-field ionization (SFI) has played a central role in the study of CM. The first experiments to observe correlation-driven CM in molecules utilized SFI by approximately single-cycle near-infrared pulses as a time-resolved probe of the hole dynamics created in phenylalanine cations by attosecond XUV photoionization [Calegari 2014]. Subsequent experiments using high harmonic spectroscopy to detect CM in iodoacetylene implicitly employed SFI to initiate the coherent hole motion [Kraus 2015]. Through Thrust 3, we seek to understand more generally the manifold of strong-field phenomena, including electronic excitation, ionization, and/or dissociative ionization, that can both initiate CM motion (serving as a "pump") and be influenced by those dynamics (serving as a "probe"). As part of this effort, much of our recent theoretical work has been devoted to confirming that SFI can induce particle-like CM in molecular cations (see Thrust 1) and, moreover, that subsequent SFI of the cation can be sensitive to those dynamics. Typically, both require temporal localization of an ionization event to a time interval (much) shorter than the CM period (*e.g.*, near the peak of a single half-cycle of an infrared driving field) as well as a pronounced dependence of the SFI yield on the spatial distribution of the evolving electron density within the cation.

On the experimental side, our work over the past year has focused on developing optical tools and techniques for creating and manipulating the polarization, spectral content, and sub-cycle structure in individual few-femtosecond laser pulses and pulse combinations. These will enable us to explore two different approaches for initiating and probing CM with strong optical fields. The first, frequency-matched ionization (FMI) spectroscopy, aims to induce and probe particle-like CM through SFI and SFDI initiated during consecutive field-maxima in a single, intense laser pulse. The yield and momenta of different charged molecular fragments are recorded as the wavelength of the ionizing laser is tuned. If 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 pronounced wavelength dependence in the spectrum of ion fragments produced by sequential double ionization. The second scheme is similar, but utilizes separate, time-delayed pump and probe pulses. Each of these approaches has its own strengths and technical challenges, and their implementation with specific molecular targets will be informed by calculations at the LSU node.

FMI spectroscopy: Previous experiments performed jointly by the UVA and OSU nodes explored the use of near and mid-infrared pulses with durations of 50-100 fs in an attempt to utilize FMI spectroscopy to detect CM in singly-ionized halogenated hydrocarbon rings, for which TDDFT calculations performed at LSU predict should exhibit particle-like CM with periods of ~2 fs. We are continuing to upgrade the laser apparatus and experimental techniques at UVA in preparation for next generation experiments that will involve several 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. To this end, we have installed a stretched hollow-core fiber compressor at UVA that currently enables the creation of ~6 fs pulses, and we are working to increase the coherent bandwidth further to allow for the fabrication 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 will superimpose a few-cycle visible/infrared pulse with its second harmonic, to create an asymmetric optical field with maxima occurring once, rather than twice, during the optical period of the fundamental. Second, we will utilize momentum imaging detection to identify molecular fragments, which are produced via double ionization, from molecules that are aligned perpendicular to the ionizing field. As with the HHS methods explored by the LSU node in Thrust 2 [Hamer 2022, Hamer 2024], this will allow us to focus on molecules for which the CM motion along the primary molecular axis is not significantly altered 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 already limits 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 molecular cations that were in the process of dissociating and, therefore had no well-defined CM. Calculations performed at LSU will continue to guide our choice of target. The optimal molecule should exhibit particle-like CM with a period of ~2 fs, and have significant, temporally and spatially localized, single and double ionization probabilities at the field maxima in a two-color UV-visible-infrared laser pulse that is polarized perpendicular to the CM axis.

Strong-field pump-probe spectroscopy of CM: As an alternative to FMI, we are also developing the capability to perform experiments using distinct CM pump and probe pulses. As with the FMI spectroscopy experiments described above, we intend to employ two color pulses and focus on ion fragments resulting from dissociation following strong-field double ionization. Here we will seek to use the shortest two-color pulses that we can produce, which should restrict the pump and probe ionization windows to a fraction of a single optical cycle, allowing us to detect CM over a wider range of periods. Using orthogonally polarized pump and probe pulses, we will avoid optical interference for delays less than the pulse durations. Moreover, we can make use of molecules that exhibit more robust CM when the pump laser is polarized along, rather than perpendicular to, the CM axis while still minimizing the impact of the stronger perpendicular probe field on the electron dynamics.

SFI probing of CM: In the previous year, we completed development of a method for computing SFI rates and yields for a molecule undergoing CM, as a function of the time delay between a sudden ionization and a subsequent SFI probe. In bromoacetylene, we observed that using constrained DFT (cDFT) [Eshuis 2009] to trigger CM resulted in unphysical high frequency excitations. Although these cDFT holes do not affect the CM dynamics, they do result in a significant "leakage" problem when using complex absorbing potentials (CAPs) in SFI simulations. Recently, we developed a density matrix filter, where we project the cDFT initial (t=0) density matrix onto the cation (or neutral) ground state basis, to remove those excitations. The unphysical high frequencies are removed by zeroing the coherences (off-diagonal elements) involving high energy virtual states. Figure 5 (a) shows a comparison of the field-free (a)

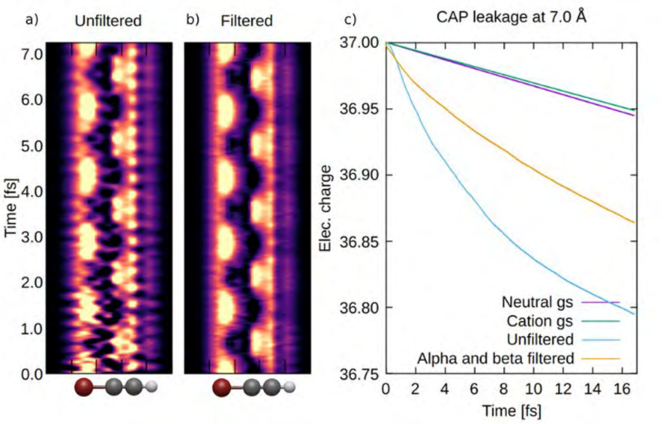

Figure 5: a) Unfiltered and b) filtered time-dependent integrated hole densities in bromoacetylene. c) The spurious leakage due to the complex absorbing potential is reduced for the filtered initial density matrix (yellow curve) versus unfiltered one (blue), allowing for calculations of delay-dependent ionization yields (not shown).

unfiltered and (b) filtered CM dynamics for bromoacetyelene. The filtered case exhibits the correct CM dynamics but without the spurious high frequencies. Panel (c) shows a comparison of the leakage yields when a CAP is applied. With a filter applied to the initial density matrix (yellow), there is substantially less leakage than without (blue; for reference, the purple and green curves show the leakage from the neutral and cation ground states, *i.e.*, without CM). We then applied this technique to compute delay-dependent SFI yields with CM and observe a modulation of ~8% in the yield, with the highest yield when the probe field is a maximum during the time when the hole is localized on the C≡C (extra electrons on Br).

SFI rate calculation with weak-field asymptotic theory (WFAT): Fast yet accurate calculations of ionization rates are a useful tool in multiple experimental and theoretical contexts for the ATTO-CM network. Previously, we published a version of the integral-representation of many-electron WFAT (IR-ME-WFAT) [Tolstikhin 2014] that uses DFT orbitals [Wahyutama 2022]. We showed excellent agreement between benchmark simulations of SFI between our DFT-based IR ME-WFAT and direct TDDFT simulations, at greatly reduced computational cost [Wahyutama 2022]. Recently we have completed work on a general IR-ME-WFAT code that is implemented in a developer version of the NWChem quantum chemistry program. We have used this new code to compare one-electron WFAT calculations, which consider ionization from the HOMO alone, to full ME WFAT calculations in selected atoms and small to medium sized molecules. We have shown that ME-WFAT improves angle-dependent ionization rates through the use of a rigorous definition of the dipole and the use of Dyson orbitals as the ionizing orbitals. In particular, we showed that angle-dependent ionization rates that are in good agreement with results from experiments and expensive time-dependent methods in CO and N_2 can be recovered by using ME-WFAT (see Figure 6). A manuscript detailing the derivation and first results of our IR-ME-WFAT code has been submitted for review [Wahyutama 2024].

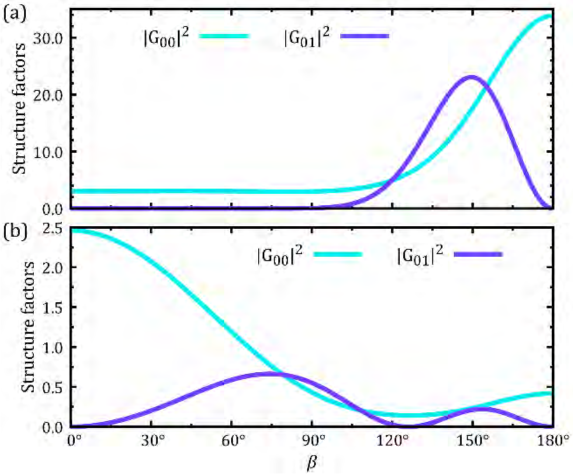

Figure 6: Structure factors that show the angle dependence of the ionization rate in the first two parabolic channels of CO simulated using (a) OE-WFAT and (b) ME-WFAT. In (a), the HOMO from Hartree-Fock calculation of CO is used. When $\beta = 0°$, the field points from C to O. OE-WFAT predicts that the ionization should be maximum at $\beta = 180°$, that is, when the field points from O to C, while ME-WFAT accurately predicts the opposite [Abu-samha 2020].

Cross-training and interactions between the network partners

We have maintained continuous communication between all the nodes of the network, including:

- Frequent (zoom) meetings, email, phone, *etc.* communications between ATTO-CM partners.
- 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.). In what follows, we briefly explain the main avenues we intend to pursue to advance our efforts to coherently probe CM in molecules.

Initiating CM: We plan to test the validity of and improve on cDFT initial states. This will involve direct TDDFT simulations of SFI on non-symmetric gas-phase molecules, and eventually solvated ones. The goal will be to determine the shape of the holes formed by SFI, the direction they point toward, and how these are affected by laser polarization. These results will be used to improve cDFT, by forcing the cDFT initial hole shape and orientation to be roughly consistent with that of direct SFI calculations.

Role of bonding in CM: We will continue the bonding-based mechanisms studies discussed in Thrust 1 above. A few of the questions we aim to answer include: How universal are LPs as a predictor of CM? Does changing the orientation of a hole with respect to LPs affect CM? Can resonance structures be used to predict CM? We will use the answers to these questions to build a more complete valence-bond inspirited picture of CM and to guide future simulations and experiments, including both CM in solvated molecules and SFI probing of CM.

Frequency-matched strong-field ionization (FMI) spectroscopy of CM: We will build on our mechanistic studies of CM to guide new simulations of FMI spectroscopy for probing CM. We will conduct these in conjunction with planned experiments at UVA, with the goal of identifying molecules that support localized holes (probably via lone-pair sites) and exhibit a strong modulation in the SFI yield with the hole "location". We will also perform studies that use explicit ionizing fields, or improved cDFT initial states, to remedy leakage problems. Finally, we will use metrics such as the time-dependent electron localization function to qualitatively describe instantaneous changes in bond strength, as a first step towards simulating fragmentation.

At the UVA node, we will continue to work on broadening the coherent spectrum and reducing the available pulse duration from the hollow-core fiber compressor, as well as developing approaches for producing phase-locked, two color asymmetric few-cycle fields with selectable central wavelengths in a single pulse, or as orthogonally polarized pulse pairs. Those pulses will then be employed in FMI and pump-probe 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.

Electron dynamics in liquid-phase molecules: The LSU node is implementing a framework for simulating electron dynamics in solvated molecules. We first simulate the solvated environment using Molecular Dynamics (MD) simulations [Thompson 2022]: We start by immersing the molecule of interest in liquid-phase solvent molecules and, after equilibration of the system in ambient conditions, we conduct MD simulations over several ns to ensure the stability and accurate modeling of the solvation environment. Figure 7 illustrates a snapshot from the MD simulation, showing one bromoaniline molecule surrounded by several methanol molecules. We then pick several different snapshots from the MD simulation as the starting configuration for a TDDFT simulation, in which we include the molecule of interest and the solvent molecules that are within the first solvation shell. So far, we have used MD to initiate TDDFT simulation of CM, as discussed in Thrust 2 above (LCLS proposal). In the future we are also planning TDDFT simulations of HHG in solvated molecules using this same two-step approach, and we have started doing simulations of HHG in multi-molecule systems.

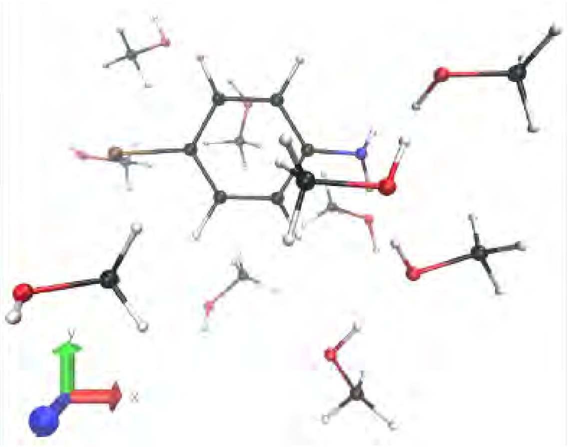

Figure 7: One example configuration for a Br-aniline molecule solvated in methanol, taken as a snapshot from an MD simulation.

TDDFT simulation of CM: The LSU node will continue its work on efficient TDDFT simulations schemes for CM. We have identified a promising mathematical framework for general-purpose high-order symplectic schemes (*i.e.*, without any restrictions on the type of exchange-correlation functional or discretization). Next, we will benchmark their efficacy against existing schemes. We will also investigate inclusion of nuclear dynamics, at the level of Ehrenfest TDDFT, in those symplectic schemes. Two foreseeable challenges in doing so are: (i) managing different time steps for the nuclear and electronic degrees of freedom, taking advantage of the fact that the former have much more inertia. (ii) In basis-set simulations, nuclear motion induces a time-dependence in the atom-centered basis set from which the Kohn-Sham orbitals are built. Such a time-dependent basis set is not immediately compatible with the Hamiltonian formalism upon which our symplectic propagation schemes are defined [Mauger 2024].

XUV attosecond spectroscopy of molecular electronic dynamics proposal: We will apply the tunable wavelengths technique develop over the past year to CO_2 and extract the ionization phase using a method similar to the 400 nm experiments (see Thrust 2 above), aiming to look at the inter-channel coupling of CO_2 with finer resolution. To connect this technique to CM probing, once we prove our capability of resolving shape resonance features in small molecules like CO_2, we will turn to larger molecules. Specifically, we plan to investigate the halogenated benzene series where LSU-node simulations have demonstrated strong CM [Bruner 2017, Folorunso 2023], and to resolve the effect of CM under shape resonance.

X-ray photoionization spectroscopy at LCLS: The OSU node will continue the analysis on the para-aminophenol XPS experiments to resolve binding energy changes in K-shell due to CM. We have measured carbon K-shell binding energies as a function of delay. We have improved the method of electron spectrum reconstruction and are refining our results via a new background-signal subtraction method.

Our team is also part of an attosecond campaign submission for LCLS Run 24 led by J. Cryan and T. Driver. The objective is to measure the neutral excited state dynamics through Raman scattering, we plan to use the new high repetition rate capabilities of the LCLS-II to perform state selective measurements in para-aminophenol by post-selecting on the pump photoelectron energy.

A separate proposal, led by T. Driver, has been submitted for beamtime at the FERMI XFEL in Trieste. The proposal title is “Probing Electron Correlation in Molecular Photoionization on the Attosecond Timescale”. This effort will complement our tabletop attosecond experiments on CO_2.

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Ultrafast Non-adiabatic Dynamics in VUV Excited Molecules with Electric-Field-Resolved Nonlinear Spectroscopy

Award number: DE-SC0024234

Principal Investigator: Niranjan Shivaram
Department of Physics and Astronomy, Purdue University
525 Northwestern Ave, West Lafayette, IN 47907
niranjan@purdue.edu

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 measurements in 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 tested and optimized our high-harmonic generation (HHG) beamline to generate VUV pulses (5th harmonic of 800 nm at 7.7 eV). As a first step, we have implemented VUV transient absorption spectroscopy with VUV and near infrared (NIR) femtosecond pulses in molecules such as carbon dioxide. **Figure 1 (a)** shows our VUV transient absorption data in CO_2 as a function of time delay between VUV/NIR pulses and VUV photon energy. This plot shows that there are likely two states (as indicated by the dashed black lines) that may be excited by the VUV pulse. These two states are not seen in the static absorption spectrum of the VUV pulse (not shown). **Figure 1 (b)** shows VUV absorption at a rotational half revival of CO_2. Absorption from two distinct states is clearly seen in this measurement which also shows that the 7.73 eV feature is a parallel transition, and the 7.6 eV absorption feature is a perpendicular transition. This also explains why the two distinct states are not visible in the static absorption spectrum. Due to their different symmetries, the two distinct absorption features are not visible in an isotropic distribution of the molecular axis as in the case of a static VUV absorption measurement.

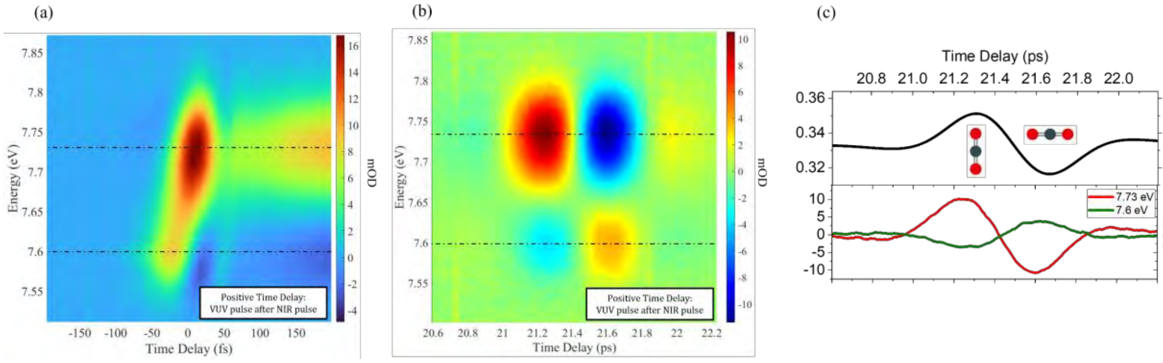

Figure 1: (a) VUV transient absorption data as a function of time delay between VUV and NIR pulses and photon energy of the VUV pulse, in carbon dioxide molecules. The dashed lines indicate two distinct absorption features from two distinct states. (b) VUV absorption at a rotational half-revival of carbon dioxide showing that the higher energy feature is a parallel transition, and the lower energy feature is a perpendicular transition. (c) Alignment parameter for carbon dioxide (top panel) and lineouts of the data in (b) at the dashed lines (bottom panel).

We are currently collaborating with Prof. Loren Greenman at Kansas State University to assign the two states giving rise to the absorptions features and to interpret the transient absorption results in this VUV regime. Furthermore, we are working on performing VUV transient absorption spectroscopy in aligned molecules to extract transient coherences in the molecular frame. We are collaborating with Prof. Varun Makhija from University of Mary Washington to build on previous tomography related work [1,2] and adapting it to four-wave mixing observables.

In parallel with VUV transient absorption, we are working on measuring the electric field of four-wave mixing observables to learn how to connect the observables to ultrafast electron dynamics. Towards this end, we are performing benchmarking experiments in solids such as MgO where we measure the complete electric field (temporal amplitude and phase) of nonlinear degenerate four-wave mixing (DFWM) signals. **Figure 2 (a)** shows the amplitude and temporal chirp (second-order temporal phase parameter) of the DFWM signal measured as a function of time delay

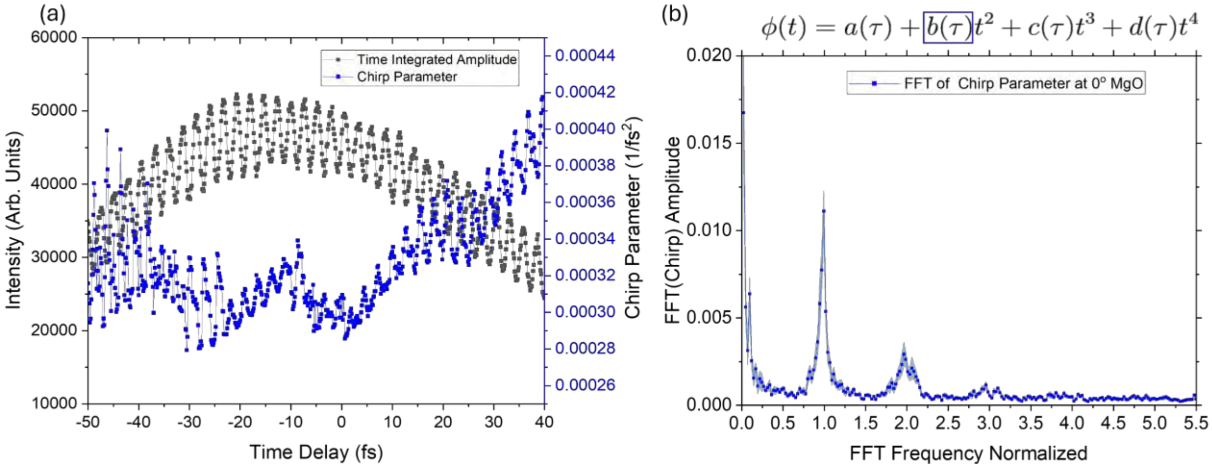

Figure 2: (a) Measured temporal amplitude (time integrated) and temporal chirp of the nonlinear signal electric field for a degenerate four-wave mixing benchmarking experiment in MgO. (b) Fourier transform of the chirp oscillations as a function of time delay in (a). The Fourier transform shows frequencies higher than the fundamental frequency.

between the DFWM pulses. As the delay is varied on sub-femtosecond time scales, we observe oscillations in both amplitude and temporal chirp. However, the temporal chirp is seen to show higher frequencies in these oscillations unlike the amplitude. As seen in our previous work [3,4], the temporal chirp in the case of MgO is likely more sensitive to electron dynamics compared to the amplitude of the nonlinear signal. We are currently working in collaboration with Dr. Liang Tan at the Molecular Foundry, LBNL, to develop a theoretical model involving strong-field modification of the band structure which results in a modulation of the nonlinear response, to explain these temporal chirp oscillations.

3 FUTURE PLANS

We will perform VUV transient absorption spectroscopy experiments in impulsively aligned carbon dioxide molecules to extract electron dynamics in the molecular frame. We are currently developing the theoretical framework with our collaborator Prof. Varun Makhija, to perform fitting of our experimental data. We will extend our measurements to other molecules such as oxygen and ethylene, which exhibit strong VUV absorption, to compare our results and gain insight into molecular frame electron dynamics. Towards our goal of using electric field observables in nonlinear spectroscopy to study ultrafast electron dynamics, we will perform VUV/NIR wave mixing experiments to measure the signal at NIR wavelengths. We will first make such measurements in a solid such as MgO for benchmarking and optimization. Upon successful demonstration, we will apply it to molecules such as carbon dioxide used in the VUV transient absorption studies. In parallel with this effort, we will develop a VUV wavefront splitting approach to perform spectral interferometry of VUV transient absorption signals such as those shown in figure 1 to sensitively measure and gain insight into non-adiabatic dynamics in VUV excited molecules.

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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

Carlos A. Trallero
Department of Physics, University of Connecticut, Storrs, CT 06268
`carlos.trallero@uconn.edu`

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 use 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 high resolution 3D velocity map imaging device that can measure photoelectron distributions in full momentum space at a high repetition rate and 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 up to 200kHz.

Once both techniques have been established, we will continue towards the quantum tomographic. This will involve the measurement of the full density matrix of a molecule in an excited state.

Interferometric transient absorption spectroscopy

iTAS is achieved by creating two spatially separated XUV beams through high harmonic generation (HHG). One beam serves as the local oscillator respect to which phase evolution is measured. In practice, 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 demonstrated phase noise between two non-local XUV beams ($\lambda = 89$nm) of ≈ 0.1mrad, corresponding to a temporal jitter of ≈ 3zs. 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 beams. 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 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 $\mathbf{S_D}(\mathbf{r_d})$. Phase information is encoded in the interference terms, $I_{\rm int}(\mathbf{r}_d, \omega)$ given by,

$$I_{\rm int}^{(1,2)}(\mathbf{r}_d, \omega) \propto \left|d_z^{(1)}(\omega)\right| \left|d_z^{(2)}(\omega)\right| \cos\left[\phi_{dip}^{(1)}(\omega) - \phi_{dip}^{(2)}(\omega) + \Delta\theta_{\rm opt}(\mathbf{r}_d, \omega)\right], \tag{2}$$

with $\phi_{dip}^{(\alpha)}(\omega) \equiv \arg\left[\tilde{\ddot{d}}_z^{(\alpha)}(t)\right]$ the spectral phase of the dipole and $\Delta\theta_{\rm opt}$ a difference in optical phase. Thus, the argument of the cos in Eq. 2 is the difference in complex phase between the two fields $E^{(\alpha)}$. An experimental measurement of $I_{\rm int}^{(1,2)}(\mathbf{r}_d, \omega)$ will provide a direct observation of the argument of the dipole $\phi_{dip}^{(\alpha)}(\omega)$.

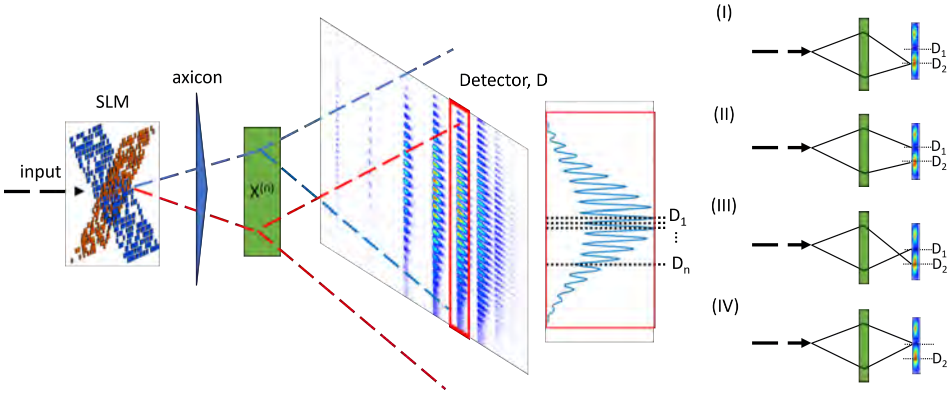

Figure 1: Two tilted Bessel beams are focused into a thin gas jet to produce harmonics of order n. These beams propagate in the absence of the intense IR beam and interfere in the far field. For largely diverging beams, this is equivalent to a mirror less Hong-Ou-Mandel interferometer, and the four different pathways are depicted on the right. For spectroscopy, the target is placed in one of the arms of the interferometer.

Generation of squeezed XUV light through higher-order harmonic generation

The resulting iTAS scheme is similar to a Hong-Ou-Mandel interferometer and the four different photon paths are achieved as shown in the right of Fig. 1, and is basically a type of interferometric homodyne detection scheme. In homodyne detection, a signal is mixed with a local oscillator (LO) before it is been detected. The interference of the two signals provides a phase-sensitive measurements of light and radio waves also called measurement in quadrature. 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 is far from the fundamental and its phase shifted from the reference, due to target excitation after interaction with the fundamental (see Eq. 2). On the other hand, our measurements are spectrally resolved and interference occurs only at each harmonic frequency as in the case for homodyning techniques.

This comparison could explain low phase error in our experimental measurements. To test this, we are analyzing the level of squeezing in the interferometer. For states of light where the uncertainty of the real and imaginary part of the field is much smaller than the intensity, the small area or angle approximation holds and thus we can arrive at an uncertainty relationship,

$$\sigma_n \sigma_\phi \geq \frac{1}{2}, \tag{3}$$

with σ_n and σ_ϕ the uncertainty or experimental error in the number of photons and the phase respectively. Our interferometer gives direct access to the phase and it's uncertainty. For the number of photons, we have done several experiments that include single photon counting and realize the entire interferometric HHG spectrum one, two, or three photons at a time for a given intensity. We have also done experiments where there are several XUV photons arriving at the detector. Both experiments seem to give the same result, that there is a slight amount of squeezing in the harmonic signal. The amount of squeezing for freely propagating harmonics is always higher for the near-threshold harmonics but it is only of about 3%. However, what is surprising is that the observable that seems to have the samllest uncertainty is the field amplitude and not the phase. This is a result we are still investigating.

Interferometric transient absorption spectroscopy in Ar

Our first iTAS measurements were done in Ar excited with an IR beam. For the HHG generation we used ethylene (C_2H_4), to guarantee low order harmonics. In this manner, we have three XUV energies corresponding to harmonics 7,9 and 11 of the 800 fundamental that interact with bound states of Ar.

The control parameter in the experiment is the intensity, that determines the amount of excitation in the atom. We measure the absorption and the phase evolution of the interferometer for each harmonic. We observe that the phase of harmonic 11 has the strongest change in phase, with three distinctive peaks. Changes in absorption for all observed harmonics were below 1%, even though absolute absorption was kept between 20 and 40%.

XUV multiphoton correlation

Theory done by Prof. A-T. Le can now reproduce the results of our iTAS in excited Ar. Simulations were done by solving the time dependent Schrödinger equation in the presence of different combination of fields. One of the surprising finds is that the phase of all XUV beams is correlated, meaning that the theory can not reproduce the experiment if we change the phase of each harmonic independently, but instead, we need to take into account the phase of all XUV fields

Angular dispersion relations in ATI revealed through 3D photoelectrons spectroscopy

For this thrust we employ 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, precursor to the formation of vortexes (see Fig. 2). These features appear when ionizing inert gases with elliptically polarized light.

The rotation of the center of mass in the first ATI ring is quite surprising, since it has not been observed before. We have measured and calculated the change in rotation as a function of momentum in the first ring for several intensities and ellipticity and the rate of change, or angular dispersion, is the same for all the conditions.

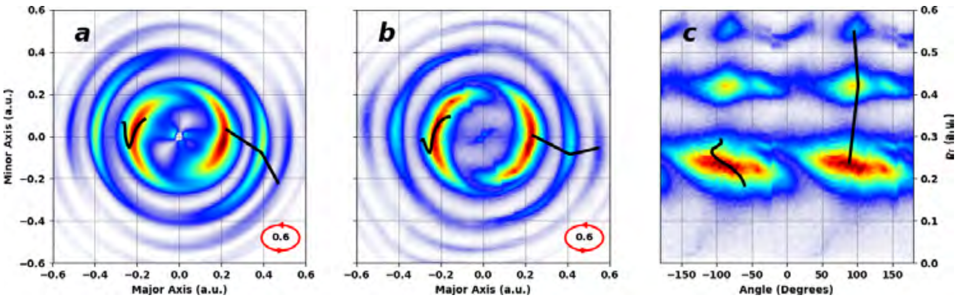

Figure 2: a) and b) Cut at pz=0 of the 3D photoelectron distribution a) theoretical and b) experimental. d) same as a) but using a different projection. Black lines show the rotatio withing the first ATI ring or from ring to ring.

Calculations are 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.

In collaboration with Prof. Le, we now understand that the conditions for forming interlocking lie in the initial conditions of the photoelectrons and it needs a balance between the laser and Coulomb Fields.

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 50kHz-100kHz. At this rate we have 4-2mJ 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.

Future plans

In the near future we will complete the following tasks:

- iTAS in aligned N_2, O_2 and CO_2
- Finish the theory development for complete experiments in iTAS for aligned molecules and compare to the theory
- Establish the amount of entanglement or correlation between the harmonics 7,9, and 11, as a function of intensity in Ar
- Demonstrate 3D photoelectron spectroscopy at high repetition rate
- 3D photoelectron spectroscopy of chiral molecules

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

No publications to report, four submissions.

Structural Molecular Dynamics Using Ultrafast Gas X-Ray Scattering

Award # DE-SC0017995

Peter M. Weber
Department of Chemistry
Brown University, Providence, Rhode Island 02912
Peter_Weber@brown.edu

I. Project Scope

Understanding the structures and chemical dynamics of molecules in 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, 1,3,5-trimethyl-1,3,5-triazacyclohexane, 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:

- We have expanded our list of molecules for which we studied the ultrafast molecular dynamics by adding 1,3,5-trimethyl-1,3,5-triazacyclohexane to the previous roster that included 1,3-cyclohexadiene, trimethyl amine, N-methyl morpholine, dimethyl piperazine, cyclopentadiene and quadricyclane.

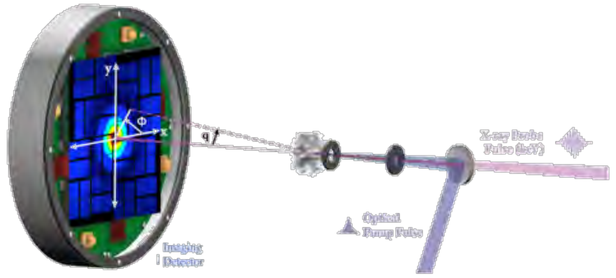

Figure 1: Experimental scheme: The molecules in the interaction region are intercepted by a linearly polarized UV laser (blue) and, at some time delay, by the X-ray pulse (red). Absorption of the UV pump pulse launches the structural molecular response. The X-ray probe is variably delayed with respect to the UV pump pulse to image the time-dependent dynamics. Scattering signals are captured by the detector.

- We have 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 are further exploring 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.
- We have learned how to measure x-ray scattering patterns quantitatively at LCLS (CXI), which enables direct comparison to theoretical calculations.

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.

The ring-closing reaction of cyclopentadiene

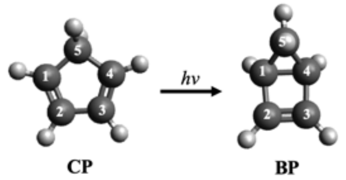

Figure 2: The photochemical reaction of cyclopentadiene (CP) has been proposed to lead to bicyclo[2.1.0]pentene (BP).

Photochemical reactions involving conjugated organic molecules include ultrafast processes such as electrocyclic reactions, isomerization, and sigmatropic rearrangements. Despite their inherent energetic disadvantages, the formation of highly strained ring structures through photoinduced reactions garners significant attention, with applications in biology, solar energy technologies and pharmaceuticals. Understanding the complete mechanisms behind these reactions could pave the way for innovative synthetic methodologies, making them a central focus of numerous experiments.

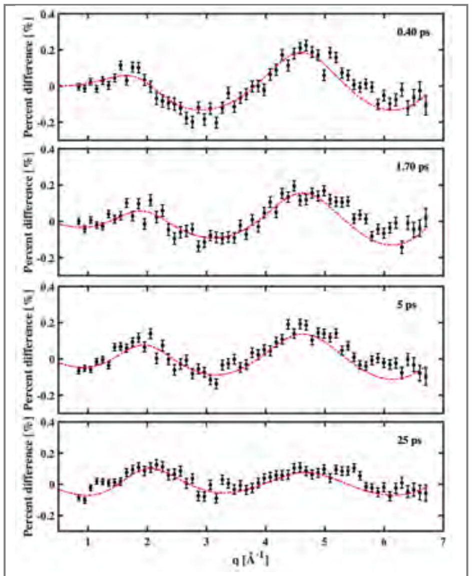

Figure 3: Experimental isotropic percent difference scattering signals at given time delays (0.40 ps, 1.70 ps, 5 ps, and 25 ps) where the black dots are the experimental data and the red dashed lines are the fit results.

Cyclopentadiene (CP) is considered an exemplary model system for electrocyclic ring conversion reactions, since it has the potential to produce bicyclo[2.1.0]pentene (BP) despite its considerable ring strain, Figure 2. The photochemical reaction follows a disrotatory pathway, in accordance with Woodward-Hoffmann rules. Computational studies indicate that optical excitation near 240 nm initiates a reaction in which the S_2/S_1 conical intersection (CI) is bypassed, leading to the formation of BP via a S_1/S_0 CI.

We studied the CP → BP reaction by x-ray scattering using the CXI endstation of LCLS, in the scheme shown in Figure 1. Irradiation at 243 nm initiates a time-dependent scattering pattern, Figure 3, which can be analyzed to directly yield scattering patterns of individual, time-dependent components (Reference 8). Comparison with computational models show unambiguously that BP is formed in the ultrafast electronic dynamics on a sub-picosecond time scale, Figure 4. The energetic BP thermally reacts back to the ground state of CP with a 21 ± 3 ps time constant, in excellent agreement with simulations.

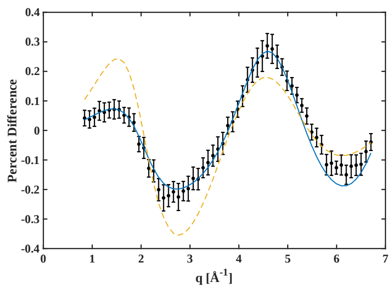

Figure 4: Comparison of the experimental pattern extracted from the fit for species BP with 1σ error bars, black circles) with the simulated theoretical percent difference pattern of vibrationally hot BP (blue line) and hot TP (orange dashed line).

The x-ray scattering experiments at CXI yield the first direct structural and quantitative evidence for the formation of BP on ultrafast timescales. No evidence for the creation of an even more energetic tricyclic isomer was observed. Future experiments, with higher optical pump photon energy, will search for that higher energy isomer. Additional experiments studying the photochemical back reaction BP → CP are also planned.

Fast Dynamics and reaction kinetics in dithiane

Dithiane, $C_4H_8S_2$, is a challenging model system containing two sulfur atoms. X-ray scattering experiments performed at LCLS show intriguing structural dynamics covering a large range of timescales, from sub-picosecond to a nanosecond. Analysis of the data points to a reaction network with several pathways, ultimately leading to the dissociation of both sulfur atoms either individually or as an S_2 molecule. Because x-ray scattering provides a quantitative measure of the relative abundance of molecular species, we were able to determine the rates of the reactions and the relative importance of the different reaction paths.

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 late 2024 and early 2025 are:

- L-10340 “Creating Strained Rings by Tuned Transitions through Conical Intersections”, PI P.M. Weber, December 2024 at LCLS – CXI.
- L-10350 “Measuring an Electronic Wave Packet by Ultrafast X-Ray Scattering” PI R. Forbes, January 2025 at LCLS – CXI.
- L-10376 “Ultrafast X-Ray Pump, X-Ray Probe Imaging of Nuclear Dynamics” PI M. Minitti, February 2024 at LCLS – CXI.
- “Probing electron dynamics in NO_2 with ultrafast x-ray scattering” PI R. Forbes, 2024B8026, to be scheduled, at SACLA, Japan.

Additional beam time proposals have been submitted for run 24 at LCLS. In particular, we hope to build on our investigation of the ultrafast dynamics of cyclopentadiene by studying its back-reaction. On the technical side, we will continue to explore extending the energy range of hard x-rays to achieve a larger coverage of scattering vectors in x-ray scattering.

IV. Peer-Reviewed Publications Resulting from this Project (2022-2024)

1. “Conformational diversity of 1-phenylpiperidin-4-one in the gas phase,” A. V. Eroshin, T. D. Phien, P. M. Weber & S. A. Shlykov, *Chem. Phys. Lett.*, 803, 139851 (**2022**). DOI 10.1016/j.cplett.2022.139851
2. “Spectroscopic identification of 2,3-dimethylbut-2-ene transients in 2,3-dimethylbut-2-ane flames,” X. Xu, F. Rudakov, P.M. Weber, *Appl. Phys. B*, 128:84 (**2022**). DOI 10.1007/s00340-022-07803-0.
3. “Transient vibration and product formation of photoexcited CS2 measured by time-resolved X-ray scattering,” I. Gabalski, M.A. Sere, K. Acheson, F. Allum, S. Boutet, G. Dixit, R. Forbes, J. M. Glownia, N. Goff, K. Hegazy, A.J. Howard, M. Liang, M. Minitti, R.S. Minns, A. Natan, N. Peard, W.O. Razmus, R.J. Sension, M.R. Ware, P.M. Weber, N. Werby, T.J.A. Wolf, A. Kirrander, P. Bucksbaum J. Chem. Phys. 157, 164305 (**2022**). DOI 10.1063/5.0113079
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Combining High Level *Ab Initio* Calculations with Laser Control of Molecular Dynamics (DE-FG02-08ER15983 & DE-FG02-08ER15984)

Thomas Weinacht
Department of Physics and Astronomy
Stony Brook University
Stony Brook, NY
thomas.weinacht@stonybrook.edu

and

Spiridoula Matsika
Department of Chemistry
Temple University
Philadelphia, PA
smatsika@temple.edu

1 Project Scope

We use intense, shaped, ultrafast laser pulses to follow and control molecular dynamics and high level *ab initio* calculations to interpret the dynamics and guide the control.

2 Recent Progress

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. A recent review in WIREs summarizes our approach.

During the last period we collaborated with the group of Martin Centurion to investigate the femtosecond time-resolved photoinduced excited-state structural dynamics of cis,cis-1,3-cyclooctadiene, a large-flexible cyclic conjugated diene molecule, using mega-electron-volt ultrafast electron diffraction and trajectory surface hopping dynamics simulations. We tracked the photoinduced structural changes from the Franck-Condon region through the conical intersection seam to the ground state. Comparison between the UED signal and TSH calculations revealed a novel primary reaction coordinate involving ring distortion, where the ring stretches along one axis and compresses along the perpendicular axis. The nuclear wavepacket remains compact until it reaches the conical intersection seam, and it rapidly spreads as it approaches the ground state, where multiple products are formed. We see 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. Figure 1 shows the important findings of this study.

2.2 Strong Field Double Ionization

Recent work we have carried out on strong field double ionization of cyclohexadiene follows up on earlier work on double ionization and dissociation of formaldehyde. Our new measurements highlight the formation of $CH_3^+/C_5H_5^+$ in coincidence, demonstrating proton migration driven dissociation of the dication. We are comparing the measurements with trajectory surface hopping of the dynamics in the dication, and with our previous measurements on formaldehyde, which could be directly compared with the calculation results by measuring and calculating the same observable.

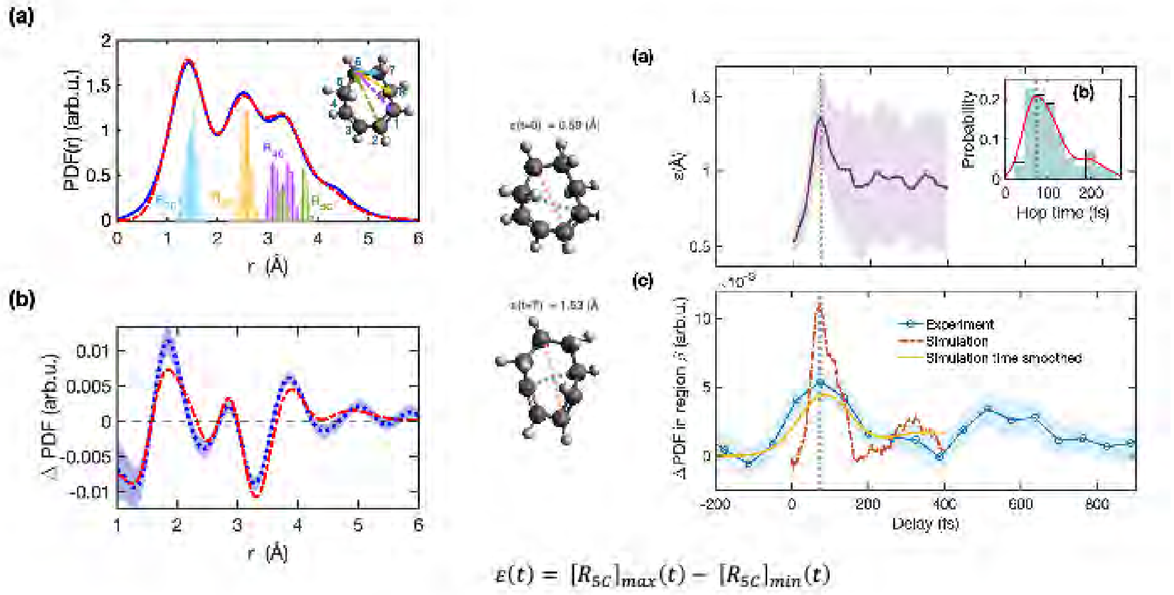

Figure 1: Left: Comparison of experimental and simulated diffraction signals in real space. Middle: Definition of ϵ as the difference between two distances shown in blue and orange. Right: Panel (a) shows the amount of ring stretching averaged over the simulated trajectories as a function of time delay (ϵ_{avg} (t)) along with the standard deviation from the mean. The inset (b) shows the probability distribution of hop times from S_1 to S_0 (excited-state to ground-state) for all trajectories. Panel (c) shows the sum of δPDF intensity in the region β ($2.6 < r(\mathring{A}) < 3$) for the experiment (blue) along with the one-standard-deviation error (shaded region), the corresponding signal from the simulation without (red) and with (yellow) 150 fs gaussian time smoothing applied. The vertical grey dotted line in Panels (a), (b), and (c) marks the most likely time (74 fs) for the wavepacket to reach the CI seam.

The comparison between the two molecules, with both experiment and theory, may highlight the transition from non-ergodic (directed) to ergodic dynamics.

2.3 Technical Developments

One important technical project that we made progress on is the development of a new data acquisition package for the Timepix camera based on the pymepix package. This allows for carrying out measurements with the camera, visualizing 3D momentum distributions, and and performing analysis on the fly. It is a significant upgrade from our previous software, which was a mix of codes that we couldn't really modify easily and that did not allow for any visualization or analysis while performing measurements. This is highlighted in Figure 2 below.

A second technical development was development of ultrafast pump pulses at a central wavelength of 195 nm. This will allow for 195 nm pump, 160 nm probe measurements of the excited state dynamics of cyclooctadiene, which can be directly compared with the UED measurements described above.

In computational developments, we have interfaced the trajectory surface hopping package Newton-X with the electronic structure package Terachem, which is running on GPUs, allowing for speedup of the calculations. This interface has allowed us to run dynamics for 10-100 ps, enabling the study of processes at these longer times.

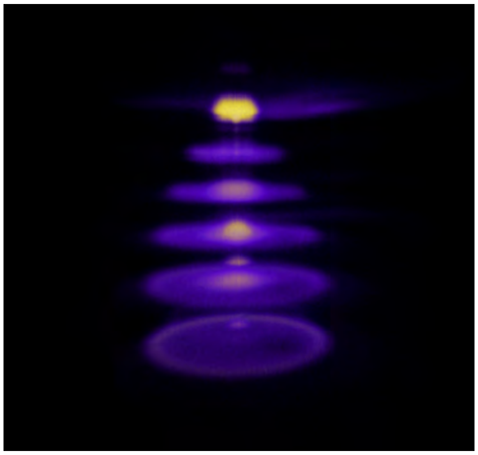

Figure 2: Screenshot illustrating new Timepix camera software which allows for real time signal monitoring, data acquisition and analysis of the 3D momentum information available with our coincidence velocity map imaging apparatus. Measurements shown are for the strong field ionization of cyclohexadiene discussed below.

3 Future Plans

We plan to complete our multimodal study of the excited state dynamics of cyclooctadiene by comparing time resolved photoelectron spectroscopy measurements using a 195 nm pump pulse with the UED measurements described above and the trajectory surface hopping calculations we have already carried out. We will also extend our strong field ionization measurements, comparing the 3D VMI measurements of fragments measured in covariance with trajectory surface hopping calculations. Finally, we will pursue our measurements and calculations of electronic coherence for highly excited molecules.

4 Peer-Reviewed Publications Resulting from this Project (2022-2024)

- "3D velocity map imaging of electrons with TPX3CAM" Chuan Cheng, Gönenç Moğol, Andrei Nomerotshi, Carlos Trallero-Herrero and Thomas Weinacht. *Review of Scientific Instruments*, **93**, 013003 (2022)

- "Stable excited dication: trapping on the S_1 state of formaldehyde dication after strong field ionization" Vaibhav Singh, Chuan Cheng, Thomas Weinacht and Spiridoula Matsika. *Phys. Chem. Chem. Phys.*, **24**, 2071-20708 (2022)

- "Nonadiabatic Excited State Dynamics of Organic Chromophores: Take-Home Messages" Pratip Chakraborty, Yusong Liu, Samuel McClung, Thomas Weinacht and Spiridoula Matsika. *J. Phys. Chem. A*, **126**, 6021-6031, (2022)

- "Conformer-Specific Dissociation Dynamics in Dimethyl Methylphosphonate Radical Cation", Vaibhav Singh, Hugo A. López Pena, Jacob M. Shusterman, Patricia Vindel-Zandbergen, Katharine Moore Tibbetts, Spiridoula Matsika, *M*olecules, **27**, 2269, (2022)

- "A simple approach for characterizing the spatially varying sensitivity of microchannel plate detectors,"D. Aglagul, B. Kaufman, C. Cheng, T. Weinacht, T. Saule, C. A. Trallero-Herrero, and A. Nomerotski. *Rev. Sci. Instrum.*, **93**, no. 7, (2022)

- "Strong Field Double Ionization of Formaldehyde Investigated using Momentum Resolved Covariance Imaging and Trajectory Surface Hopping" Chuan Cheng, Vaibhav Singh, Spiridoula Matsika, Thomas Weinacht, *J. Phys. Chem. A*, **126**, 7399-7406, (2022)

- "Multichannel photodissociation dynamics in CS_2 studied by ultrafast electron diffraction" Weronika O Razmus, Kyle Acheson, Philip Bucksbaum, Martin Centurion, Elio Champenois, Ian Gabalski, Matthias C Hoffman, Andrew Howard, Ming-Fu Lin, Yusong Liu, Pedro Nunes, Sajib Saha, Xiaozhe Shen, Matthew Ware, Emily M Warne, Thomas Weinacht, Kyle Wilkin, Jie Yang, Thomas JA Wolf, Adam Kirrander, Russell S Minns and Ruaridh Forbes *Phys. Chem. Chem. Phys.*, **124**, 15416-15427, (2022)

- "Filming enhanced ionization in an ultrafast triatomic slingshot" Andrew J Howard, Matthew Britton, Zachary L Streeter, Chuan Cheng, Ruaridh Forbes, Joshua L Reynols, Felix Allum, Gregory A McCracken, Ian Gabalski, Robert R Lucchese, William C McCurdy, Thomas Weinacht and Philipp H Bucksbaum, *Communications Chemistry*, **6**, 81 (2023)

- "Multiparticle Cumulant Mapping for Coulomb Explosion Imaging" Chuan Cheng, Leszek J Frasinski, Gönenç Moğol, Felix Allum, Andrew J Howard, Daniel Rolles, Philip H Bucksbaum, Mark Brouard, Ruaridh Forbes and Thomas Weinacht *Phys. Rev. Lett.*, **130**, 093001, (2023)

- "A plano–convex thick-lens velocity map imaging apparatus for direct, high resolution 3D momentum measurements of photoelectrons with ion time-of-flight coincidence" Michael Davino, Edward McManus, Nora G Helming, Chuan Cheng, Gönenç Moğol, Zhanna Rodnova, Geoffrey Harrison, Kevin Watson, Thomas Weinacht, George N Gibson, Tobias Saule and Carlos A Trallero-Herrero *Rev. Sci. Inst.*, **94**, 013303, (2023)

- "Ultrafast structural dynamics of UV photoexcited cis,cis-1,3- cyclooctadiene observed with femtosecond electron diffraction", Sri Bhavya Muvva1, Yusong Liu, Pratip Chakraborty, Joao Pedro Figueira Nunes, Andrew R. Attar, Surjendu Bhattacharyya, Kurtis Borne, Elio Champenois, Nathan Goff, Kareem Hegazy, Matthias C Hoffmann, Fuhao Ji, Ming-Fu Lin, Duan Luo, Lingyu Ma, Asami Odate, Shashank Pathak, Daniel Rolles, Artem Rudenko, Sajib Kumar Saha, Xiaozhe Shen, Xijie Wang, Matthew R Ware, Stephen Weathersby, Peter Weber, Kyle J Wilkin, Thomas J. A. Wolf, Yanwei Xiong, Xuan Xu, Jie Yang, Spiridoula Matsika, Thomas Weinacht, Martin Centurion, *P*hys. Chem. Chem. Phys.., submitted 2024

- "Quantum contributions to Coulomb-explosion imaging revealed by trajectory-surface-hopping molecular dynamics", Singh,Vaibhav, Cheng,Chuan, Weinacht,Thomas, Matsika, Spiridoula, *P*hys. Rev. A, **1**09, 052813 , (2024)

- "Multiparticle Cumulant Mapping for Coulomb Explosion Imaging: Calculations and Algorithm" Chuan Cheng, Leszek J. Frasinski, Gönenc Mogol, Felix Allum, Andrew J. Howard, Philip H. Bucksbaum, Ruaridh Forbes, and Thomas Weinacht, *P*hys. Rev. A, **1**09, 042802 , (2024)

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