2022
Atomic, Molecular, and Optical Sciences Research PI Meeting

Virtual Meeting
October 24-26, 2022

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Program and Abstracts

2022
Atomic, Molecular, and Optical Sciences
Research PI Meeting

Virtual Meeting
October 24–26, 2022

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

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2022 Atomic, Molecular and Optical Sciences Research PI Meeting

Office of Basic Energy Sciences
U.S. Department of Energy
October 24 – 26, 2021 (Times are EDT)

MONDAY, OCTOBER 24

11:45 AM	Zoom Sign On
11:55 AM	Meeting Logistics (Kim Olson, ORISE)

OPENING REMARKS

12:00 PM	*Welcome and Introductory Remarks* Thomas B. Settersten, AMOS Program Manager

NEW RESEARCHERS AND PROJECTS
3-minute, 1-slide summary

12:15 PM	**Ryan G. Hadt**	California Institute of Technology
12:18 PM	**Anh-Thu Le**	University of Connecticut
12:21 PM	**Uwe Bergmann**	University of Wisconsin, Madison
12:24 PM	**Jin Qian**	Lawrence Berkeley National Laboratory
12:27 PM	**Matthias F. Kling**	SLAC National Accelerator Laboratory

LAB PROGRAMS
10-minute program summary, 5-minute Q&A

12:30 PM	*Atomic, Molecular, and Optical Physics* **Linda Young** Argonne National Laboratory
12:45 PM	*Atomic, Molecular, and Optical Sciences* **Oliver Gessner** Lawrence Berkeley National Laboratory
1:00 PM	*Ultrafast Chemical Sciences* **Philip H. Bucksbaum** SLAC National Accelerator Laboratory
1:15 PM	*Structure and Dynamics of Atoms, Ions, Molecules and Surfaces* **Artem Rudenko** J.R. Macdonald Laboratory, Kansas State University
1:30 PM	*BREAK, 15 MINUTES*

SESSION 1
Uwe Bergmann (Chair) Univ. Wisconsin, Madison   *20-minute presentation, 10-minute Q&A*

1:45 PM	*Molecular dynamics imaging from within at the femto- and atto-second timescale using FELs* **Nora Berrah** University of Connecticut
2:15 PM	*Ultrafast meets real space – a femtosecond and sub-Angstrom view of molecular dynamics* **Adi Natan** SLAC National Accelerator Laboratory
2:45 PM	*Attosecond imaging of electronic wave packets: theory and experiment* **Wen Li** and **H. Bernhard Schlegel** Wayne State University
3:15 PM	*BREAK, 15 MINUTES*

SESSION 2
Jin Qian (Chair) Lawrence Berkeley National Laboratory   *20-minute presentation, 10-minute Q&A*

3:30PM	*X-ray and inner-shell interactions and applications* **Stephen H. Southworth** Argonne National Laboratory
4:00 PM	*Transient X-ray absorption as an attosecond probe of electron density* **Kenneth Lopata** Louisiana State University

POSTER SESSION 1
Leave Zoom session and join Gather.Town

4:30 PM	*See Poster Session Directory: Last names starting with A–G*
6:00 PM	*ADJOURN*

TUESDAY, OCTOBER 25	
11:45 AM	Zoom Sign On
SESSION 3	**Matthias F. Kling** (Chair) SLAC National Accelerator Laboratory *20-minute presentation, 10-minute Q&A*
12:00 PM	*Structural dynamics of charge delocalization* **Peter M. Weber** Brown University
12:30 PM	*Dynamics of molecules in excited electronic states measured by photoelectron and fragment imaging* **Daniel S. Slaughter** Lawrence Berkeley National Laboratory
1:00 PM	*Covariance & cumulants: multiparticle imaging of strong field molecular ionization* **Thomas C. Weinacht** Stony Brook University
1:30 PM	*BREAK, 15 MINUTES*
SESSION 4	**Li Fang** (Chair) University of Central Florida *20-minute presentation, 10-minute Q&A*
1:45 PM	*Imaging ultrafast photochemical processes with X-ray and near-infrared lasers* **Artem Rudenko** Kansas State University
2:15 PM	*X-ray induced ultrafast electron and nuclear dynamics in molecules* **Phay Ho** Argonne National Laboratory
2:45 PM	*Atomic and molecular dynamics by attosecond four wave mixing* **Stephen R. Leone** Lawrence Berkeley National Laboratory
3:15 PM	*BREAK, 15 MINUTES*
SESSION 5	**Anne Marie March** (Chair) Argonne National Laboratory *20-minute presentation, 10-minute Q&A*
3:30 PM	*Influencing relaxation dynamics in light-driven first row metal complexes* **Kelly J. Gaffney** SLAC National Accelerator Laboratory
4:00 PM	*Low-energy electron interactions with complex targets* **Thomas M. Orlando** Georgia Institute of Technology
POSTER SESSION 2	*Leave Zoom session and join Gather.Town*
4:30 PM	*See Poster Session Directory: Last names starting with H–M*
6:00 PM	*ADJOURN*

WEDNESDAY, OCTOBER 26	
11:45 AM	Zoom Sign On
SESSION 6	**Ryan G. Hadt** (Chair) California Institute of Technology *20-minute presentation, 10-minute Q&A*
12:00 PM	*Optical control of electronic interactions* **Arvinder Sandhu** University of Arizona
12:30 PM	*Selectivity in excitation and ionization by intense laser pulses* **Andreas Becker** University of Colorado, Boulder
1:00 PM	*Understanding complexity and correlated motion of electrons in atomic and molecular systems* **Steven T. Manson** Georgia State University
1:30 PM	*BREAK, 15 MINUTES*
SESSION 7	**Alexandra Landsman** (Chair) Ohio State University *20-minute presentation, 10-minute Q&A*
1:45 PM	*Developing an optical pump-probe instrument for resolving ultrafast wave-packet dynamics in the vicinity of a non-adiabatic transition* **Jeffrey Moses** Cornell University
2:15 PM	*Continuum electron dynamics in ultrafast spectroscopies* **C. William McCurdy** Lawrence Berkeley National Laboratory
2:45 PM	*Deciphering ultrafast electron and nuclear dynamics with strong fields* **Chii-Dong Lin** Kansas State University
3:15 PM	*BREAK, 15 MINUTES*
SESSION 8	**Anh-Thu Le** (Chair) University of Connecticut *20-minute presentation, 10-minute Q&A*
3:30 PM	*Atomic-scale imaging of (nonlinear) optically induced currents* **David A. Reis** SLAC National Accelerator Laboratory
4:00 PM	*Structured high harmonic beams for enhanced spectra-microscopies of materials* **Henry C. Kapteyn** University of Colorado, Boulder
CLOSING REMARKS	*Conclusion of technical sessions*
4:30 PM	Thomas B. Settersten, AMOS Program Manager
POSTER SESSION 3	*Leave Zoom session and join Gather.Town*
4:35 PM	*See Poster Session Directory: Last names starting with N–Z*
6:00 PM	*ADJOURN*

Direct time- and momentum-resolved imaging of exciton dynamics in monolayer WS_2
Thomas K. Allison   Stony Brook University

High harmonic generation from graphene quantum dots
Vadym M. Apalkov   Georgia State University

New correlated numerical methods for attosecond molecular single and double ionization
Luca Argenti   University of Central Florida

Elliptically polarized HHG from biorthogonal pulses
Andreas Becker   University of Colorado, Boulder

Breaking two chemical bonds in water, one at a time, with one photon
Itzik Ben-Itzhak   Kansas State University

Nonlinear X-ray optics for transition metal chemistry and coherent X-ray spectroscopy
Uwe Bergmann   University of Wisconsin, Madison

Ultrafast roaming mechanisms in ethanol probed by XUV FEL: electron transfer versus proton transfer
Nora Berrah   University of Connecticut

Universal multiphoton resonances: effects in the elastic, inelastic (DI) and recombination (HHG) channels
Cosmin Blaga   Kansas State University

2-path quantum interferences in strong-field ionization measured with a time correlation filter
Philip H. Bucksbaum   SLAC National Accelerator Laboratory

Structural dynamics of photoexcited cycloocta-1,3-diene (COD) probed by ultrafast electron diffraction
Martin Centurion   University of Nebraska

Accurate calculations of core-ionization energies for third-row elements
Lan Cheng   Johns Hopkins University

Sampling near-IR waveforms in a single shot
Michael Chini   University of Central Florida

Atomic view of molecular photocatalysis using X-ray lasers
Amy A. Cordones-Hahn   SLAC National Accelerator Laboratory

Observation of attosecond coherent electron motion in core-excited states
James Cryan   SLAC National Accelerator Laboratory

Probing electronic and vibrational excitations, and their interactions, using coherent multidimensional techniques
Steven Cundiff   University of Michigan

Femtosecond intramolecular rearrangement of the CH_3NCS radical cation
Marcos Dantus   Michigan State University

Quantum trajectory simulator
Louis F. DiMauro   Ohio State University

Resonant excitations with intense X-ray pulses
Gilles Doumy   Argonne National Laboratory

Feynman path summing after virtual detection
Joseph Eberly   University of Rochester

Interpreting multiphoton dynamics one photon at a time
Brett D. Esry   Kansas State University

Progress in construction of an attosecond XUV beamline and REMI/VMI spectrometer
Li Fang   University of Central Florida

High-harmonic sideband spectroscopy of charge migration
Mette Gaarde   Louisiana State University

Design principles for the covalent control of electronic excited state reactivity in first row metal complexes
Kelly J. Gaffney   SLAC National Accelerator Laboratory

Nonlinear molecular electronic spectroscopy via MCTDH dynamics: from Vis/UV to X-ray
Marco Garavelli   University of Bologna

Decoding the lifecycle of photogenerated charges
Oliver Gessner   Lawrence Berkeley National Laboratory

Strong-field response of topological surface states
Shambhu Ghimire   SLAC National Accelerator Laboratory

Structural dynamics of solute and solvent reorganization due to ultrafast electron transfer in the bimetallic $Fe^{II}Pt^{IV}$ complex in water
Niranjan Govind   Pacific Northwest National Laboratory

Phase lag in coherent control of barium
Chris H. Greene   Purdue University

Coordinating theory and experiment for Coulomb explosion imaging
Loren Greenman   Kansas State University

POSTER SESSION 2

Connecting molecular electronic structure and electron spin decoherence mechanisms for quantum information science
Ryan G. Hadt   California Institute of Technology

Simulating XAS and TR-XAS spectra via new DFT methods
Martin Head-Gordon   Lawrence Berkeley National Laboratory

Probing interlayer excitons and their dynamics in 2D semiconductors
Tony F. Heinz   SLAC National Accelerator Laboratory

X-ray photochemistry of protoplanetary dust
Phay Ho   Argonne National Laboratory

Orientation-dependent strong-field ionization
Robert R. Jones   University of Virginia

Structured VUV, EUV and soft X-ray light for probing quantum systems
Henry C. Kapteyn   University of Colorado, Boulder

X-ray spectroscopy of catalytic reactions at nanoscale surfaces for clean energy production
Matthias F. Kling   SLAC National Accelerator Laboratory

Rotational wavepackets and LICI dynamics in D_2^+
Vinod Kumarappan   Kansas State University

Tracking the ionization site in a neutral molecule
Alexandra Landsman   Ohio State University

Effect of autoionizing resonances on wave-packet dynamics studied by time-resolved photoelectron spectroscopy in N_2
Anh-Thu Le   University of Connecticut

Measuring bright and dark state autoionization decay lifetimes in neon with attosecond four wave mixing spectroscopy
Stephen R. Leone   Lawrence Berkeley National Laboratory

Attosecond imaging of electronic wave packets
Wen Li   Wayne State University

Deciphering ultrafast electron dynamics with femtosecond intense lasers
Chii-Dong Lin   Kansas State University

Charge migration is regulated by chemistry
Kenneth Lopata   Louisiana State University

Influence of shape resonances on the angular dependence of molecular photoionization time delays
Robert R. Lucchese   Lawrence Berkeley National Laboratory

Nondipole effects in attosecond time delay
Steven T. Manson   Georgia State University

Tracking chemical reactivity across multiple timescales
Anne-Marie March   Argonne National Laboratory

Capturing the elusive "phantom state" in stilbene
Todd J. Martinez $\qquad$ SLAC National Accelerator Laboratory

Stable excited dication: Trapping on the S_1 state of H_2CO^{2+} after strong field ionization
Spiridoula Matsika $\qquad$ Temple University

Attosecond time delays in molecular photodetachment
C. William McCurdy $\qquad$ Lawrence Berkeley National Laboratory

Single-cycle pulse converter for spectroscopy
Jeffrey Moses $\qquad$ Cornell University

Direct imaging of conical intersection passage via electronic coherences in twisted X-Ray diffraction
Shaul Mukamel $\qquad$ University of California, Irvine

Structured short wavelength light for applications in photoelectron spectroscopies and imaging
Margaret Murnane $\qquad$ University of Colorado, Boulder

State-selective probing of CO_2 autoionizing inner-valence Rydberg states with attosecond extreme ultraviolet four-wave mixing spectroscopy
Daniel M. Neumark $\qquad$ Lawrence Berkeley National Laboratory

POSTER SESSION 3 WEDNESDAY, OCTOBER 26
4:35 – 6:00 PM ET

Ultrafast meets Real-Space – a femtosecond & sub-Ångstrom view of molecular dynamics
Adi Natan $\qquad$ SLAC National Accelerator Laboratory

Unexpected new class of electron spirals revealed
Jean Marcel Ngoko Djiokap $\qquad$ University of Nebraska

Low-energy electron interactions with complex targets
Thomas M. Orlando $\qquad$ Georgia Tech

More from Less
Abbas Ourmazd $\qquad$ University of Wisconsin, Milwaukee

Towards exascale core-level spectroscopy predictions
Jin Qian $\qquad$ Lawrence Berkeley National Laboratory

Artificial neural network (ANN) assisted many-body quantum optimal control
Herschel A. Rabitz $\qquad$ Princeton University

Atomic-scale imaging of optically induced charge motion
David A. Reis $\qquad$ SLAC National Accelerator Laboratory

Simulations for x-ray imaging of wave packet dynamics
Francis Robicheaux $\qquad$ Purdue University

Recent progress with Coulomb explosion imaging
Daniel Rolles $\qquad$ Kansas State University

Direct imaging of rotational motion in molecular photodissociation
Artem Rudenko $\qquad$ Kansas State University

Optical stabilization of autoionizing polaritons
Arvinder Sandhu $\qquad$ University of Arizona

New tool for fast calculation of strong field ionization
Kenneth J. Schafer $\qquad$ Louisiana State University

Strong field ionization to produce and monitor coherent electron dynamics in HCCI - time-dependent configuration interaction simulations
H. Bernhard Schlegel $\qquad$ Wayne State University

2-color dissociative photoionization of H_2
Daniel S. Slaughter $\qquad$ Lawrence Berkeley National Laboratory

Photoelectron - Auger electron postcollision interaction in K-shell photoionization of krypton
Stephen H. Southworth $\qquad$ Argonne National Laboratory

Strong-field-driven dynamics in CO_2^+

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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, Stephen Southworth,
Linda Young

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southworth@anl.gov, young@anl.gov

1 Overview

The Argonne AMO physics program explores the frontiers of x-ray physics as enabled by accelerator-based light sources and, in so doing, lays the foundation for ultrafast x-ray applications in other scientific domains. We utilize the novel properties of accelerator-based coherent x-ray sources, primarily the Advanced Photon Source (APS) synchrotron at Argonne and the Linac Coherent Light Source (LCLS) x-ray free-electron laser (XFEL) at SLAC in concert with ultrafast lasers, to create exotic and/or non-equilibrium states and to probe their rapidly evolving properties with atomic-scale spatial and temporal resolution. The experimental work is supported and complemented by theoretical developments, often taking advantage of massively parallel codes developed for the evolving supercomputer suite at the Argonne Leadership Computing Facility (ALCF). Our expertise in fundamental interactions has generated collaborations across the DOE complex from the Isotope Program to the EFRC on Interfacial Dynamics in Radioactive Environments and Materials, IDREAM.

The program is structured in three complementary subtasks. The first subtask aims at a quantitative and predictive understanding of x-ray interactions with matter in the high-intensity limit. Here we computationally explore new atomistic imaging approaches enabled by the most intense femtosecond and attosecond x-ray pulses using massively parallel code developments built upon a knowledge base of the response of atoms and molecules. We have uncovered the importance of transient resonant excitation, and, have shown the applicability of fluorescence correlation imaging to catalytic nanoparticles. We have extended our studies beyond non-linear x-ray interactions with isolated atomic and molecular samples to include propagation in optically thick samples where substantial energy exchange between the sample and field exists.

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

The third subtask focuses on understanding photo- or x-ray-initiated dynamics in condensed phases at the atomic, molecular and electronic level. The APS is used for timescales picoseconds

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

This past year was particularly active in terms of experimental campaigns at light sources and tool development in anticipation of the new supercomputer and upgraded light source at Argonne. Our group acted as principal investigators for seven distinct experimental beamtimes at x-ray free-electron lasers, as well as three at the Advanced Photon Source prior to its shutdown for upgrade in April 2023. Theoretically, we extended our highly parallelized x-ray dynamic codes to include GPU-acceleration in preparation for the arrival of Aurora, an exascale supercomputer at ALCF, and explored AI-based methods for complex x-ray spectroscopic calculations.

2 X-ray Physics at the Intensity Frontier

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

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

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

Recent Progress: Understanding fundamental x-ray/matter interactions at high intensity is a vibrant frontier enabled by the continued development of x-ray free-electron lasers. Many experiments have now provided an understanding of x-ray–atom/molecule interactions in the single particle regime [10, 11, 39–47]. However, nonlinear propagation through resonant absorbing media where the back-action of the media alters the propagating field, basic for studies in the solid state, solution and gas phases via transmission-based x-ray transient absorption, has been much less studied. XFELs now deliver nearly transform-limited pulses with sub-femtosecond duration with the potential for MHz repetition rates [48] over a wide range of x-ray energies thus universally enabling transient absorption studies near organic (C,N,O) and inorganic (transition metal and actinide) edges. The achievable power density produces effects such as stimulated Raman scattering [49,50], amplified spontaneous emission, pulse compression [51] which are relevant to proposed nonlinear x-ray spectroscopies [52,53].

Last year we published a theoretical study of temporal, spectral, and spatial reshaping of intense, ultrafast x-ray pulses propagating through a resonant medium [7]. Our calculations used a 3D time-dependent Schrödinger equation-Maxwell wave equation approach. The code is fully generalizable with arbitrary input XFEL pulses and provides output mapping the spectral, temporal and spatial reshaping. The evolution of the combined incident and medium-generated field, including the effects of stimulated emission, absorption, ionization and Auger decay, can be evaluated as a function of the input pulse properties: energy, shape, photon energy and duration.

This year we performed two XFEL experiments on propagation through dense gases. The first was conducted at the European XFEL where propagation effects were observed in the spectral and spatial domains using SASE pulses of approximately 40-60 fs duration. Three targets were addressed in this rich and rewarding beamtime with almost 1000 data runs. While a complete data analysis is ongoing, one noteworthy initial finding is our demonstration of high-resolution stimulated x-ray Raman spectroscopy with stochastic x-ray pulses using covariance techniques [54, 55] - obtaining x-ray Raman linewidths of ~ 0.3 eV whilst using SASE pulses of $\Sigma 7$ eV bandwidth. Through simulation of many SASE pulses using the Argonne Leadership Computing Facility, it was found that while standard covariance on the transmitted beam could reveal the stimulated x-ray Raman features (anomalous dispersion, resonance enhancement and linewidth narrowing), superior background could be obtained by using covariance of the transmitted Raman scattered beam with the input SASE spectrum.

Toward the goal of having a measure of the input SASE spectrum, this year we published [13] our demonstration that the existing photoelectron spectrometer (PES) array at the EuXFEL [56]

could be used to characterize non-invasively the incoming SASE spectrum with a resolution of $\sim 1/2000$. This method involves the use of a ghost-imaging inspired algorithm [57,58] to deduce a response matrix for the PES array. The reconstructed resolution was limited by the flight time of the photoelectrons - and the longer flight path PES array at the LCLS [59] can give substantially higher resolution reconstructions.

Our second XFEL experiment was the result of our successful proposal with SLAC staff (S. Li, J. Cryan, A. Marinelli) to study propagation-induced reshaping of attosecond pulses in the temporal domain [7] using angular streaking techniques [48,60] at LCLS. The mounting of this experiment required significant rearrangement of the beamline at the TMO hutch and incorporation of a new differentially pumped gas cell (designed by Argonne) capable of sustaining atmospheric pressures and also located within ~ 15cm of the streaking interaction region. Combined with a new zone-plate spectrometer and streaking with a 2.0 μm laser, the experiment was able to obtain data on reshaping of the attosecond pulses in both the temporal and spectral domains. There was also the opportunity to observe the polarization of the atomic neon x-ray laser on a shot-to-shot basis as a function of pump-laser photon energy. Data analysis is currently underway. Beyond informing applications such as transient absorption and wave-mixing the pulse structures contain multiple peaks and intricate interference fringes, which can be used to test the limitations of the angular streaking as a pulse diagnostic tool. It also provides valuable data for more sophisticated pulse reconstruction algorithm development that can be used to improve resolution and speed of current pulse diagnostics.
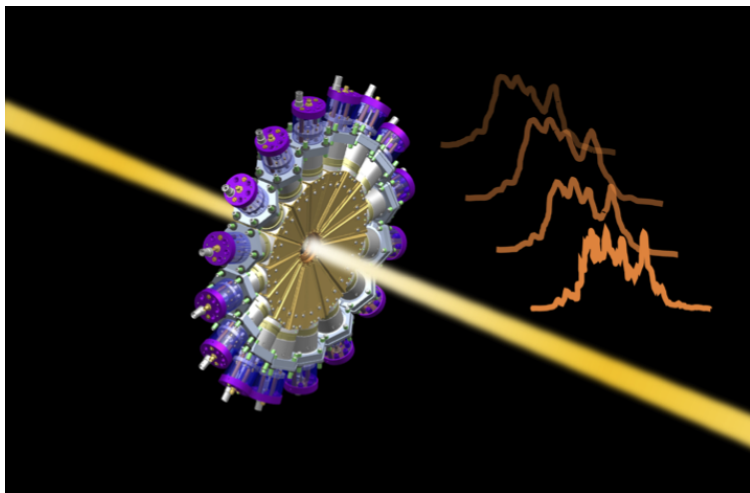
Figure 1: High-resolution single-shot SASE pulse spectral characterization using an existing photoelectron spectrometer (PES) array at the European XFEL. SASE pulses interact with dilute Ne gas in the PES array where the kinetic energy of 1s photoelectrons are measured simultaneously with the high-resolution photon spectrum on a shot-by-shot basis. A response matrix for the PES array is developed with ghost imaging techniques and the incoming photon spectrum can be recovered with a resolution of $\sim 1/2000$.

Future Plans: With beamtime at the EuXFEL, we characterized the weak- to strong-field behavior for propagation of SASE pulses through dense resonant media in the spectral and spatial domains on three separate targets. Completion of the data analysis and publication is the next step. Complementary to this, the beamtime at LCLS yielded information on propagation-based temporal and spectral reshaping of attosecond pulses. We anticipate potential theoretical extensions to the 3D code include propagation of arbitrarily polarized pulses.

2.2 X-ray Imaging Applications with Femtosecond and Attosecond Pulses

P. J. Ho, L. Young, S. H. Southworth, C. Knight[9], T. Gorkhover[10], S. Kuchel[10], C. Bostedt[11], D. Rupp[12], A. Niozu[13,14], Y. Kumagai[15], K. Ueda[14,16] and other collaborators

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

Recent Progress:

Since the early vision for single-shot imaging experiments with XFELs [61], radiation induced damage has been an important topic [5]. This year, in collaboration with the group of Tais Gorkhover and the group of Christoph Bostedt, we submitted a paper on a combined theoretical and experimental study to reexamine the role of radiation damage in single-particle iamging with coherent x-ray diffractive approach. The targets are nanosized xenon clusters and they were exposed to intense, few-fs and sub-fs XFEL pulses at LCLS. In addition to the scattering and ion time-of-flight data, fluorescence spectra were used to pinpoint the particle size and exposed x-ray fluence. We compared snapshots from individual $100\,$nm Xe nanoparticles as a function of the X-ray pulse duration and incoming X-ray intensity in the vicinity of the Xe M-shell resonance. Surprisingly, images recorded with few femtosecond and sub-femtosecond pulses are up to 10 times brighter than the static linear model predicts. Our Monte-Carlo simulation [5, 62] and statistical analysis of the entire data set confirms these findings and attributes the effect to transient resonances [5, 41, 44]. Our simulation suggests that ultrafast form factor changes during the exposure can increase the brightness of X-ray images by several orders of magnitude. Our study guides the way towards imaging with unprecedented combination of spatial and temporal resolution at the nanoscale.

In addition to the soft x-ray regime, this year we started resonant scattering investigations in the hard x-ray regime, which is important for achieving atomic spatial resolution. Guided by our theory calculations, which predict an overall increased scattering signal at a transient Fe ion resonance around 6.3 keV, we have received a beamtime to perform a resonance scattering experiment with Fe nanosized samples in hard x-ray regime at CXI endstatation in January 2023.

In February 2022, we performed an experiment to exploit x-ray induced Rabi cycling for damage reduction in single-particle, coherent diffraction approach. The experiment was performed at TMO endstation at LCLS-II using neon droplets as target. We have recorded coincident time-of-flight ion data and scattering images with XLEAP and 20-fs pulses across the Ne K-edge. The data is being analyzed.

We continue to develop theoretical tools to explore high-resolution imaging applications with few-fs and sub-fs XFEL pulses. In collaboration with Chris Knight, we have ported our Monte-Carlo/Molecular-Dynamics (MC/MD) codes [62, 63] to the new GPU-based supercomputers at ALCF, THETAGPU and POLARIS. In the first version of GPU-accerelated code, the computational intensive MD calculation is offload to the GPUs. We have received a Director Discretionary allocation to improve the efficiency of the code.

Future Plans: We plan to perform a set of resonant scattering calculations for iron oxide NPs on THETA to map out the effect of transient resonances on scattering in a complex environment under realistic experimental conditions. In addition, we plan to explore the effects of coherent electron dynamics, including Rabi oscillations, in resonant scattering to guide the interpretation of the measured data from the Ne droplet experiment.

2.3 X-ray imaging using higher-order correlations

P. J. Ho, L. Young, A. E. A. Fouda, C. Knight[9], B. Bigalke[10], and other collaborators

Project Scope: Coherent diffractive imaging (CDI) with XFEL pulses holds the promise to probe structure and follow the dynamics of non-periodic entities with atomic resolution. However, this approach remains challenging due to sample damage during the pulse [5, 63]. We aim to explore the potential of x-ray correlation methods as a high-resolution structural and dynamical probe by investigating the higher-order correlations associated with the fluorescence spectrum and speckle patterns from illuminated samples.

Recent Progress: Last year, we examined the effectiveness of the fluorescence intensity correlation (FIC) approach [64] for imaging elemental contrast in iron-oxide nanoparticles (NPs) using the $L\alpha$ emission of Mo dopants resulting from ionizing a 2p electron of Mo with a 5-keV pulse. $L\alpha$ is the fluorescence transition from 3d to 2p shell [9]. A rather high fluence was used to saturate the fluorescence yield, leading to a high background from Fe fluorescence. This year, we theoretically explore a resonant excitation scheme, in which we resonantly pump Mo atoms to excite a 2p electron to an unoccupied 4d orbital and study the $L\alpha$ emission in neutral Mo. The resulting $L\alpha$ fluorescence energy is shifted by 10 eV compared to that from the 2p-ionization scheme. Our calculations show that a pulse with the resonant photon energy, a fluence of 2.1×10^{10} photon/μm^2 and 1% bandwidth is optimal for elemental contrast imaging with the FCI approach. In comparison to the previous 2p-ionization scheme, the required fluence is a factor of 6 smaller and the ratio of the $L\alpha$ fluorescence from Mo to the background fluorescence from Fe and O atoms is increased by about a factor of 10 in the resonant excitation scheme.

We have recruited a student intern to develop a GPU code to harness the computational power of THETAGPU and POLARIS at ALCF for computing the fluorescence intensity correlation maps. The GPU-accerelated code extends our previous code on two fronts: enabling a large ensemble single-shot spectra calculations and computation of a full volumetric 2-point correlation functions.

Future Plans: To determine the feasibility of an experimental effort with FIC, we plan to perform FIC calculations that account for the effect of finite detector spectral energy resolution on the visibility FICs.

2.4 X-ray induced photochemistry in protoplanetary dust

Phay J. Ho , Lisseth Gavilan[17,18], Uma Gorti[19], Hirohito Ogasawara[20], Cornelia Jager[21], and Farid Salama[17]

Project Scope: We studied structural and chemical modification of cosmic dusts induced by stellar X-rays using a multiscale approach that combines the laboratory investigation of cosmic dust analogs, atomistic model of X-ray induced mass loss and an astrophysical model of protoplanetary disk.

Recent Progress:
This year, we published a paper to present the results of an integrated laboratory and modeling investigation into the impact of stellar X-rays on cosmic dust (see Fig. 2) [12]. Carbonaceous grains were prepared in a cooled ($<$200 K) supersonic expansion from aromatic molecular precursors, and later irradiated with 970 eV X-rays. Silicate (enstatite) grains were prepared via laser ablation, thermally annealed, and later irradiated with 500 eV X-rays. Infrared spectra of the 3.4 μm band of the carbon sample prepared with benzene revealed 84$\pm$5% band area loss, for an X-ray dose of 5.2×10^{23} eV/cm^2.

We simulate the peak radiation energies of the soft X-ray spectrum, 0.2-2keV, of low-mass

stars by performing controlled experiments using synchrotron radiation in the soft X-ray range (0.3-1 keV). Synchrotron X-rays enable us to perform highly focused monochromatic studies with remarkable reproducibility. With the high photon flux of synchrotron beams ($\sim 10^{11}$ photons s^{-1}), we can reach astronomical fluences in a few hours, comparable to lifetime-integrated (a few million years) X-ray exposures on cosmic dust grains in disks. Our carbonaceous dust analogs represent carbon-rich dust of mixed aliphatic/aromatic content in the interstellar medium. These span different chemical compositions and comprise a high concentration of aromatic structures, enabling us to study how the varied chemical and structural properties of cosmic carbon could impact its photochemical evolution under X-rays. Infrared spectra of the 8-12 μm Si-O band of the silicate sample revealed band area loss up to $63\pm5\%$ for doses of 2.35×10^{23} eV/cm^2.
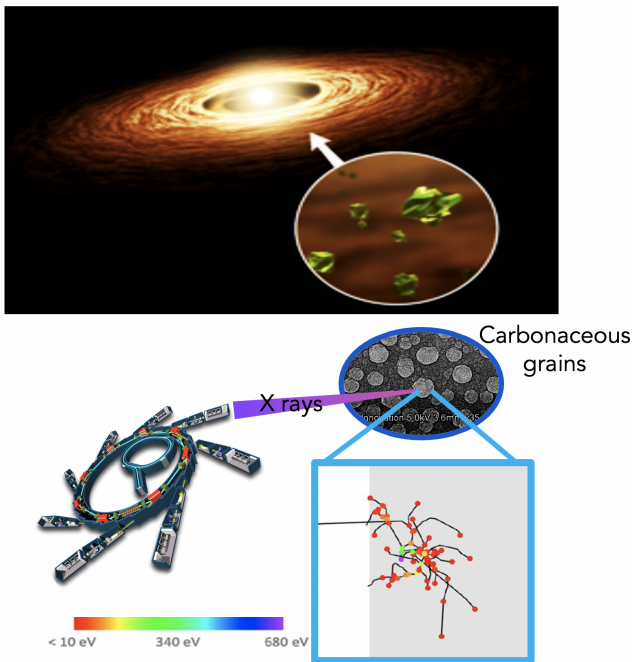
Figure 2: Simulating the effect of stellar x-rays on cosmic dusts (top) using laboratory cosmic dust analogs irradiated with synchrotron x-rays and an atomistic model for x-ray damage (colored dots show the positions and energies of electrons).

A hybrid Monte Carlo particle trajectory approach was used to model the impact of X-rays and ensuing photoelectrons, Auger and collisionally ionized electrons through the bulk. As a result of X-ray ionization and ensuing Coulomb explosions on surface molecules, the calculated mass loss is 60% for the carbonaceous sample and 46% for the silicate sample, within a factor of 2 of the infrared band loss, supporting an X-ray induced mass loss mechanism. We apply the laboratory X-ray destruction rates to estimate the lifetimes of dust grains in protoplanetary disks G and M stars. In both cases, X-ray destruction timescales are short (a few Myr, where Myr is million year) at the disk surface, but are found to be much longer than typical disk lifetimes (>10 Myr) over the disk bulk.

Future Plans:

We plan to extend our model to include atomic/molecular structure and the impact of two types of X-ray induced relaxation processes. The first type of process is the impact of inner-shell relaxation processes on the chemical bonds of the X-ray excited molecules and its near neighbors. The second type of processes is the whole sample structure transformation (e.g., to model aromatic to aliphatic structure changes) as a result of X-ray excitation.

3 Ultrafast X-ray Induced Phenomena

3.1 Time-resolved chemical shifts

G. Doumy, S. H. Southworth, D. Koulentianos, P. J. Ho, A. E. A. Fouda, K. Li, L. Young, L. Cheng[22], A. Al Haddad[11] , C. Bostedt[11], A Picon[23], S. Oberli[11], J. Marangos[24], T. Driver[8], J. Cryan[8], and other collaborators

Project Scope: The interaction of x-ray photons with inner shell electrons in molecules creates localized excitations that evolve rapidly, leading to charge redistribution, decay cascades involving emission of electrons and photons, nuclear motion and eventually bond breaking. Using two-pulse, two-color modes at XFELs [65], we aim use site-sensitivity to follow both the first steps of electron dynamics in the core-excited states and the evolution of the molecule after the first decay processes take place. This knowledge is crucial in understanding the photochemical behavior of these molecules upon x-ray absorption.

Recent Progress: Our group has pioneered x-ray pump/x-ray probe experiments at LCLS, first looking at the final products of the interaction [66]. To identify the transient species created during the interaction and the ensuing evolution of the molecule, we brought to LCLS our hemispherical electron analyzer in the old AMO beamline. An x-ray absorption spectroscopy (XAS) experiment, led by colleagues from Imperial College, studied the dynamics of inner-valence hole states created by sudden photoionization in the isopropanol molecule through resonant interactions. This measurement paves the way to observe charge migration and charge transfer phenomena with space and time resolution inside a molecule [25], which is a focus of the attosecond science campaign at LCLS 3.4.

Using x-ray photoemission spectroscopy (XPS), we followed the molecule CO after resonant x-ray excitation of the Oxygen $1s \rightarrow \pi^*$ transition performed by a first x-ray pulse, while a second x-ray pulse ionizes $1s$ electrons from the Carbon site in the ground state molecule as well as all the subsequent products (core-excited molecule, cataionic molecule following Auger decay, ionic fragments following dissociation...) through their different, evolving chemical shifts. Experimentally quite challenging due to the necessarily large bandwidth of the XFEL pulses and the variability in the machine conditions, these measurements also require advanced modeling involving a large number of decay pathways in order to account for the behavior observed in the data [67]. Signatures of the core-excited molecules, and of both metastable and dissociative ionic states are observed an reproduced by the model. In addition, modeling indicates that in the core-excited molecule, an XPS signature of a new equilibirum bond distance could be observed provided sufficient time and energy resolution.

Both of these experiments had been performed before the upgrade to LCLS-II and the new TMO endstation with the new soft x-ray undulators allowing for much larger photon energy difference between the two x-ray pulses. Our Nov 2020 experiment aimed at following the electronic and nuclear dynamics in small fluoroalkane molecules following an initial photoionization event at a carbon site. Running the beam in an $\omega/2\omega$ mode, with the first pulse centered at 370 eV (above the carbon K-edge, but below the fluorine K-edge) and the second pulse centered at 740 eV (above the F K-edge), we were able to measure pump/probe x-ray photoemission spectra using the VMI instrument in TMO. Immediately after removal of a C 1s electron, the second pulse probes core-excited molecules, inducing the formation of double core-hole states that were calculated by our collaborator Lan Cheng's group [14]. Analysis of the data collected during the experiment is ongoing but hampered by incomplete diagnostics on the two-color pulses at the time of the experiment.

Future Plans: On the soft x-ray side, we aim to follow this theme by expanding in two directions. First, obtaining better temporal resolution through the use of attosecond pulses, with 2-pulse, 2-

color available for users after being demonstrated in the attosecond science campaign. Second, we will take advantage of the high repetition rate of LCLS-II to perform measurements in coincidence to ascertain the location of the first ionization step, with first light in early 2023.

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

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

Project Scope: Resonant interaction of x-rays with matter has been studied in depth, for the practical advantages of increased cross-section, to the ability to selectively excite atoms and molecules into specific electronic or vibrational states (e.g. in our x-ray pump /x-ray probe experiment on CO). On the other hand, intense attosecond x-ray pulses can be used to produce localized valence excitation through x-ray Raman scattering [15, 23] or are seen as necessary tools to image single particles without significant x-ray damage. We aim to study both theoretically and experimentally the unexplored regime of resonant interaction with intense x-ray pulses, identifying and quantifying the new processes that can occur.

Recent Progress: While the binding energy of core electrons increases significantly when a molecule is core ionized once, our calculations predict that following core-excitation, subsequent core-excitations from a different site occur at photon energies slightly lower than in the ground state. Qualitatively, this can be understood as the result of the stabilization of valence shells due to a higher charged core, while the core electrons binding energy remains essentially the same in the still neutral molecule. This is a very general property that will be present for any molecule with two atomic sites of the same element. Through their bandwidth, pulse energy and ultrashort duration, XFEL pulses provide unique interaction conditions expected to produce neutral, two-site excited double-core-hole states by promoting two core electrons to the same unoccupied molecular orbital, as shown in Fig.3.
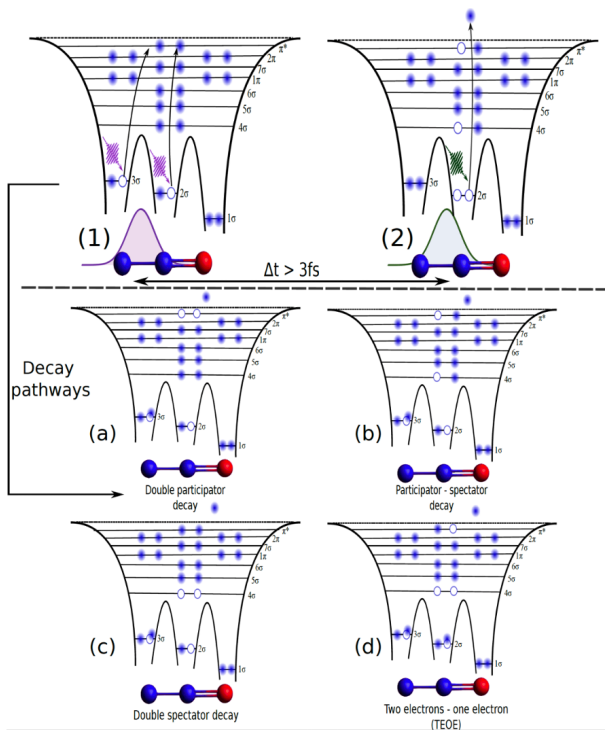
Figure 3: Double K-shell excitation from the two nitrogen sites to the π^* orbital. b) Probing the DCH decay with time resolved-x-ray photoelectron spectroscopy (TR-XPS). c) Double participator decay involving both core-excited electrons. d) Participator process involving both an inner-shell electron and the core-excited electron. e) Spectator process involving two inner-shell electrons. f) Two-eletrons-one-electron (TEOE) process involving two electrons simultaneously filling both core-holes and ejecting a single electron.

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We theoretically investigate double nitrogen K-edge excitations of nitrous oxide (N_2O) with multiconfigurational electronic structure calculations. We show that the second core-excitation energy is reduced with respect to its ground state value. A site-selective double core-excitation mechanism using intense few-femtosecond x-rays is investigated using time-dependent Schrodinger equation (TDSE) simulations. The subsequent two-step Auger-Meitner and two-electrons-one-electron decay spectra of the double core-excited states are analyzed using a Mulliken population analysis of the multiconfirational wavefunctions. The change in the electron emission lineshape between the absorption of 1 or 2 photons in the resonant core-excitation is predicted by combining this approach with the TDSE simulations. We examine the possibility of resolving the double core-excited states with x-ray pump-probe techniques by calculating the chemical shifts of the core-electron binding energy of the core-excited states and decay products. This theory paper was submitted to a Special Issue of Molecular Physics in memory of Nick Besley.

These calculations formed the basis of a successful proposal to observe the production of these neutral, doubly-core excited states in simple molecules at the EuXFEL facility. During an experiment performed in August 2022,taking advantage of the first time this facility was able to produce soft x-rays in the 250-500 eV range, we were able to measure the resonant Auger spectrum in three molecular systems: N2O, N2 and C2H4. Analysis is ongoing, but very promising results, especially in N2, were obtained.

Future Plans: A careful analysis of the results of the previous beamtime will continue, aided by additional calculations, including a more realistic way to calculate Auger spectra by directly accounting for continuum states.

3.3 X-ray and inner-shell interactions and applications

S. H. Southworth, G. Doumy, S. Li, A. E. A. Fouda, P. J. Ho, L. Young, D. A. Walko[25], M. R. Dietrich[26], P. R. Stollenwerk[26], L. Cheng[22], M. N. Piancastelli[27], M. Simon[27], S. L. Sorensen[28], R. Puttner[29], S. T. Manson[30], T. W. Gorczyca[31], and other collaborators

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

Recent Progress: A rich set of data on the ethyl trifluoroacetate molecule, having four distinct C 1s chemical shifts, was obtained by photoelectron-photoion-photoion coincidence measurements and Auger electron spectroscopy at the SOLEIL synchrotron facility. The first question explored was the degree to which C site specificity would determine ion fragmentation yields. The site specificity was found experimentally to be quite limited. This result was modeled and explained with *ab initio* electronic structure calculations [69]. That work was followed by using ion yield spectroscopy and core-valence separated equation-of-motion coupled-cluster calculations to measure the near-edge x-ray absorption spectrum and assign features to the four carbon edges [17].

In our most recent studies of ethyl trifluoroacetate, comparison of experimental and theoretical photoelectron spectra at the C 1s near-edge absorption energies and below resonance, shows selectivity in the detected spectrum with respect to the carbon site involved in the core-excitation. The theoretical analysis has determined that resonant enhancement at the CF_3 excitation is due to a higher intensity from the participator Auger-Meitner decay channels at this site than the COO core-excited states, which differed little from the below resonance spectra. The resonant Auger-Meitner decay spectra were simulated by a population analysis of multiconfigurational wavefunctions [70], the direct valence photoionization was simulated using EOM-CCSD Dyson orbitals and Coulomb waves for the continuum electron [71]. A new model was developed for simulating the valence

photoelectron spectra that uses a linear combination of EOM-CCSD Dyson orbitals to compensate for the breakdown in the molecular orbital picture in cation states of larger molecules and this significantly improves the simulated photoelectron lineshape with respect to the experiment.

Argonne's Advanced Photon Source provides hard x rays that enable experiments on heavier atoms (Br, Kr, I, Xe) and molecules (XeF_2, IBr, CF_3Br) whose K-shell vacancies have large x-ray fluorescence yields [72]. Following x-ray absorption by K-shell electrons, x-ray fluorescence transfers 1s holes to 2p, 3p, or 4p holes that then decay by emission of one or more Auger electrons. By recording ions in coincidence with fluorescent x rays, we studied the effects of pre-edge K-shell resonances in Kr, Xe, and XeF_2 [85]. Ion fragmentation of XeF_2 following Xe 1s $\rightarrow 7\sigma_u$ resonant excitation and Xe 1s ionization was also studied. X-ray/ion coincidence measurements were also used to measure charge states and energies of I^{q+} and $Br^{q'+}$ atomic ions induced by 1s ionization at the I and Br K-edges of IBr. Section 3.5 of this abstract describes a computational model that has been developed to gain insight to the ion fragmentation dynamics of IBr.

Characterization and modeling of energetic fragmentation of IBr contributes insight to "x-ray damage" of molecules containing heavy atoms. Radiation damage can be used to advantage in medical therapies by using radiopharmaceuticals to place radionuclides near cancerous tissues so that emitted Auger electrons destroy the DNA and membranes of tumorous cells [73, 74]. To fulfill the need for measurements of Auger electron multiplicities from radionuclides with which to model efficacies of radiopharmaceuticals, Argonne's Physics Division is building an instrument that will capture electrons, ions, and x-ray photons in coincidence following nuclear decays. We are contributing our expertise in theory and experimental methods of x-ray and inner-shell processes by using APS x rays to commission and characterize the electron, ion, and x-ray detectors. The electron and ion time-of-flight spectrometers and position-sensitive ion anode were commissioned in the first APS experiments.

A Scienta EW4000 hemispherical electron analyzer was used at APS beamline 7ID for inner-shell experiments on Ne and Kr. High-resolution Auger electron spectra of Ne were recorded using 6 - 8.5 keV x rays to determine KK/K, the double-to-single K-shell photoionization cross section ratio. The APS measurements extend earlier measurements over 2.3 - 6.5 keV made at the SOLEIL synchrotron facility [75]. Measurements of the energy variation of KK/K for Ne are motivated by extending measurements and theory for He [76–78]. The measured KK/K ratios are compared with calculations on He-like Ne^{8+} using the R-matrix with pseudostates (RMPS) method [79, 80]. The measured cross section ratios are estimated from ratios of hypersatellite-to-diagram Auger electron rates after appropriate scaling from double and single core holes. Other Auger electron satellites show different variations with x-ray energy, thus further demonstrating the sensitivity of high-resolution Auger electron spectra to electron correlation in single- and double-K-shell photoionization [81].

The Scienta electron analyzer was also used to measure variations in Kr $L_2 - M_{4,5}N_{2,3}$ Auger electron peaks while scanning the x-ray energy below, through, and above the K-edge. Below the K-edge, the Auger line is generated by direct L_2 photoionization. In the K-shell pre-edge and above, the yield increases by $\times 10$ due to L_2 vacancies generated by K-shell photoionization followed by KL_2 x-ray emission. Resonant Auger transitions were observed in the few-eV region below threshold due to 1s $\rightarrow$ np Rydberg states. Above the ionization threshold, the Auger electron peak was observed to increasingly shift in energy and becoming increasingly asymmetric as the photon energy approaches threshold. This effect is attributed to energy exchanges with low-energy 1s photoelectrons. These post-collision interaction (PCI) effects were modeled using a semiclassical approach modified to account for the lifetimes of K- and L_2- hole states [28].

Future Plans: Additional theoretical methods and calculations will be applied to the photoelectron and resonant Auger spectra of ethyl trifluoroacetate, leading to publications. Data analysis

and theoretical modeling of the energetic dissociation of IBr into highly charged atomic ions will be completed and a report submitted for publication. The Auger multiplicity instrument is under development and its performance will be further characterized in APS experiments. The Scienta electron analyzer will be used in new experiments at the APS to explore inner-shell resonance and threshold interactions of heavy atoms and molecules.

3.4 Attosecond science at LCLS

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

Project Scope: The unique availability at LCLS of intense, sub-femtosecond pulses in the soft x-ray regime [48] is opening new areas of investigation. The ability to study electronic processes before decay processes or nuclear motion take place, coupled with the site-selectivity afforded by x-ray interaction is opening a new window on observing electronic motion and electronic coherences.
Recent Progress: A multi-year scientific campaign to establish the basis of attosecond science at XFELs has been launched at LCLS. The effort is led by SLAC scientists, on the accelerator, beamline and photon science sides, and joined by multiple experimental and theoretical teams around the world. The effort focuses on using 2-pulse 2-color modes of operation with attosecond pulses in the soft x-ray regime. The first pulse aims at creating localized electronic coherences, while the second pulse attempts to probe processes such as charge migration.

Our group's involvement stems from years of experience as XFEL users, experience in attophysics using high harmonic sources and theoretical support. For the campaign, the main model molecule identified are the amino-phenol isomers. These rigid molecules exhibit several atomic centers (including unique O and N sites) that can be selectively excited and/or probed using soft x-ray radiation. Three experimental runs have already been performed to probe electronic coherences initiated by impulsive ionization of several inner-valence orbitals. Two observables were measured as a function of delay following the initial ionization event: transient x-ray absorption (XAS) detected through resonant Auger decay in the cations produced by the initial step, and transient x-ray photoemission spectroscopy (XPS) to detect possible chemical shifts induced by the charge migration process. The XAS measurement uses the same experimental method demonstrated with femtosecond pulses in the isopropanol molecule using our Scienta hemispherical electron analyzer [25], and has produced reliable transient signals that are being partially reproduced through a large theoretical effort inside the campaign. A critical observation is that electron coherences are very sensitive to nuclear motion and even small variations in the ground state molecule geometry, leading to a fast dampening of any oscillatory behavior. However, some features are still surviving after few femtoseconds, and vary between isomers. Several isomers have been measured in order to capture these differences.
Future Plans: Extension of the XLEAP project to the high repetition rate capabilities of LCLS-II will happen in late 2022, so the campaign will continue at 120 HZ with further studies on the para-amino-phenol molecule, including extending previous success in producing localized valence excitation using stimulated x-ray Raman scattering in the smaller NO molecule [15].

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

P. J. Ho, S. Southworth, R. Dunford, A. E. Fouda, L. Cheng[22], D. Walko[25], and others
Project scope: The goal of this project is to characterize x-ray induced relaxation processes

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

Recent Progress: Characterization of the inner-shell decay processes in molecules containing heavy elements is key to understanding x-ray damage of molecules and materials and for medical applications with Auger-electron-emitting radionuclides [82,83]. 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 [84,85]. The 1s hole states in heavy elements have large x-ray fluorescence yields that transfer the hole to outer electron shells that then decay by sequential Auger-electron transitions that increase the ion's charge state until the final state is reached. In molecules the charge is spread across the atomic sites, resulting in dissociation to energetic atomic ions [66]. We have used x-ray/ion coincidence spectroscopy to measure charge states and energies of I^{q+} and $Br^{q'+}$ atomic ions following 1s ionization at the I and Br K-edges of IBr (see Fig. 4 for the experimental setup). In addition to IBr, we have also coincidence data for Br_2, CF_3Br and CH_2IBr. As a first step, we present the charge states and kinetic energies of two or more correlated fragment ions associated with core-excited states produced during the various steps of the cascades in IBr. To understand the dynamics leading to the ion data, we develop a computational model that combines Monte-Carlo/Molecular Dynamics simulations [62] with a classical over-the-barrier model [86] to track inner-shell cascades and redistribution of electrons in valence orbitals and nuclear motion of fragments. Our calculation shows good agreement with the experimental data and reveals that inner-shell decay, charge transfer and fragmentation take place concurrently in IBr, as shown in Fig. 4. A manuscript describing the results is being prepared.
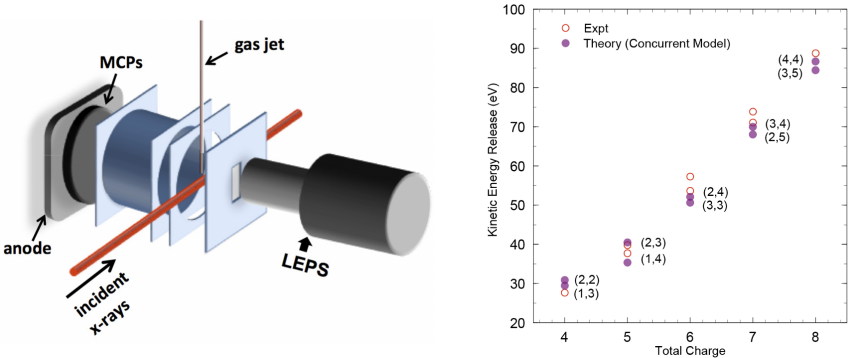
Figure 4: (Left) Schematic diagram of the x-ray/ion coincidence spectrometer consists of a ion time-of-flight spectrometer (MCPs) and a x-ray fluorescence spectrometer (LEPS). (Right) Comparison of the experimental and theoretical results of the average kinetic energy release values of various fragmentation channels IBr, where Br 1s is first ionized and followed by $K\alpha$ emission.

Future Plans: We plan to finish the analysis of the experimental data of Br_2, CF_3Br and CH_2IBr. We will explore the effect of molecular orbital during the multistep cascade processes using multi-configurational wavefunctions.

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

P. J. Ho, A. E. A. Fouda, P. Phillips[1], G. Grell[20], S. Bokarev[32] and others

Project scope: The goal of this project is to understand the fundamentals of non-linear x-ray interactions with molecules, starting from a first-principles approach. This holistic method allows investigating the effects of competing x-ray induced intramolecular processes on non-linear phenomena such as stimulated x-ray Raman excitations, and paves the way to improved understanding and execution of experiments using attosecond pulses.

Recent Progress: Motivated by a recent stimulated X-ray scattering (SXRS) experiment with broad-bandwidth, high-field nature of attosecond pulses [15], we theoretically investigated the feasibility of controlling the efficiency of SXRS in nitric oxide, at both the oxygen and nitrogen K-edges and include the effects of competing Auger-Meitner and photoionization processes [23] last year. The rates of these competing processes were obtained from a database calculated with continuum atomic wavefunctions. These atomic models are not able to account for molecular and nonlocal effects (electron-transfer-mediated decay and interatomic Coulombic decay), which can be important to predict accurate decay rates, energies of emitted electrons and photons and inner-shell cascade sequences. This year, in collaboration with Gilbert Grell and Sergey Bokarev, we implemented spherical continuum ionization [87] model that uses multiconfigurational quantum chemistry method to calculate continuum molecular wavefunctions.

Future Plans: We plan to investigate of the role of continuum and AC Stark shift on the stimulated x-ray Raman processes using SCI method. With the help of a summer intern with expertise in AI/ML, we are currently exploring AI/ML models for calculating Auger spectra of molecules.

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

4.1 Dynamics in ionized aqueous systems

L. Young, S. Li, K. Li, G. Doumy, S.H. Southworth, C. Otolski, A. M. March, P.J. Ho, Z.-H. Loh[7], J. E. Rubensson[6], Y. Kumagai[15], R. Santra[10,33], L. Inhester[33], K. Kunnus[8], G. Dakovski[8], D. DePonte[8], M.-F. Lin[8], S. Moeller[8], C. Pearce[34], E. Nienhuis[34], J. LaVerne[35], T. Orlando[36], L. Lu[37], X. Li[37] and other collaborators

Project Scope: Time-resolved x-ray spectroscopies in the water window provide a powerful and unique probe for understanding valence and inner-shell hole dynamics, electronic coherence and proton transfer in ionized aqueous systems. These elementary processes are of fundamental importance as the initiators of radiation damage in condensed phases [88, 89]. 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: Previously we reported our studies of hole dynamics in valence-ionized liquid water in two publications [29, 30]. The methodologies associated with these studies, pump-probe x-ray transient absorption (tr-XAS) [29] and resonant inelastic x-ray scattering (tr-RIXS) [30] in the water-window, enable probes of transient radicals produced during water radiolysis (H_2O^+, OH, H_3O^+, H_2O) and are readily generalizable to other situations. This has led to new collaborations aimed at understanding radiolysis on the physico-chemical timescale (a first!) and in the extreme environments associated with legacy waste management at PNNL through the Energy Frontier Research Center, IDREAM.

This year, we led three experiments at the LCLS in the area of radiolysis in aqueous systems. The first, in December 2021, was a continuation of our studies of valence ionized water. In this study using the newly commissioned ChemRIXS endstation with improved time resolution and a thinner water sheet jet, we aimed at understanding the timescale of hole localization and the identification of a signature of the hydrated electron. In preparation, we used the Argonne Center for Nanoscale Materials to characterize conditions for strong-field ionization of the sub-micron water sheet jet and developed a simple means to measure jet thickness based upon thin file interferometry. Our experimental results include an x-ray absorption spectrum near the oxygen K-edge of water that matches with excellent fidelity one measured using synchrotron radiation and a temperature controlled cell [90]; measurements of a transient absorption spectrum (520-550 eV) at 2 ps after the ionizing pulse. Theoretical calculations by Ludger Inhester and Robin Santra of small water clusters embedded in a larger system could reproduce the ground state x-ray absorption spectrum and also that for the ionized water with its extra components (OH, e(aq) and H_3O^+). With this we are confident in the identification of the x-ray signature of the solvated electron and will put effort into extracting the structural dynamics associated with the solvation process via the observed spectral shifting.

The second two experiments conducted in April 2022 are related to our successful campaign proposal set "The origin of reactive species in radiolysis" and "Radiolysis on the physico-chemical timescale in extreme environments". Our proposal pioneers x-ray pump/x-ray probe methods in liquids, building upon our experience in gases (Section 3.1), to track local vs nonlocal decay mechanisms following inner-valence ionization. Using the $\omega/2\omega$ XFEL-operation mode, delay times from $\approx 1-50$ fs were be obtained. Here, ω induces non-resonant inner-valence ionization and 2ω provides a tunable resonant probe of valence and inner-valence hole dynamics in the water window. The hole dynamics were observed directly via transmission through a thin liquid sheet jet for ionization fractions of 1%, as previously demonstrated [29]. Here the new-to-LCLS experimental scheme was to use XLEAP attosecond for the ω pump pulse and detect the 2ω probe pulse in dispersed trans-

mission. We were able to obtain robust results for the first attosecond x-ray pump/x-ray probe experiment in liquids. These transient absorption spectra at 0.6b fs delay match the photoelectron binding energies in the valence and inner-valence orbitals of liquid water [91]. Theoretical treatments of the transient absorption observations are underway. Although we planned to investigate highly concentrated alkaline aqueous solutions where the presence of other species in the first coordination shell can perturb the ultrafast dynamics, the shortened beamtime prevented this. These experiments in water provide the foundations for studies in complex systems associated with legacy waste.

Last year, we have analyzed data obtained at the Argonne Center for Nanoscale Materials (CNM)in 2019 using an infrared probe to understand the response of the hydrogen-bonding network to an ionization pulse in liquid water. Data taken on H_2O and D_2O in the OH stretching region reveal a transient red-shifted spectral feature that is consistent with Raman measurements [92]. We attribute this feature to weakening of O–H bonds adjacent to the hydrated electron. Ultrafast spectral shifting may provide information on structure near the aqueous pre-hydrated electron. We have a followup experiment to probe the bending region in H_2O and D_2O scheduled for November 2022.

Future Plans: We plan a complete theoretical analysis of our Dec 2021 experiment that identified an x-ray spectral signature of the hydrated electron and the observed spectral shift of the pre-hydrated electron. This will allow us to extract structural dynamics associated with the solvation process - analogous to our extraction of the structural dynamics associated with the proton transfer reaction [29]. We plan to complete theoretical analysis and publication of the ultrafast infrared probe experiments of ionized water in the OH stretching region and extend experimental data to the bending region. We plan to work with LCLS staff in the context of our Campaign proposal to enable radiolysis studies both in conplex liquid and interfacial environments.

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

A. M. March, C. Otolski, G. Doumy, S. H. Southworth, L. Young, X. Zhang[25], E. Kinigstein[25], S. Heald[25], S. Kelly[25] and other collaborators

Project Scope: We are preparing to take full advantage of the higher brightness x-rays and finer fill patterns that will be provided by the APS Upgrade as well as the advanced spectroscopy capabilities that will be provided at the new ASL beamline under construction at Sector 25. Our pump-probe x-ray spectroscopy setup at Sector 7 will move to Sector 25 during the upgrade dark period in 2023.

Recent Progress: The high-repetition-rate laser-pump/x-ray-probe spectroscopy endstation we have built at Sector 7 has continued to attract many collaborators. Results from collaborative projects were published this past year: a study revealing the charge carrier screening process in photoexcited nanorods [37] and a study providing supportive experimental data for an LCLS measurement exploring how mixed-valency properties in a excited state can be recovered from transient x-ray absorption measurements [38]. We are now collaborating with Xiaoyi Zhang, beamline scientist in charge of the pump-probe XAS endstation at Sector 11, to expand the pump-probe x-ray spectroscopy capabilities at APS. We will merge the strengths of our two setups to build a highly flexible, powerful endstation at Sector 25 for spectroscopy studies of liquid phase chemistry across a wide range of relevant timescales. As a result of three beamtimes to commission a newly developed data acquisition system [36] at high-repetition-rate pump-probe cycling rates, a new asynchronous pumping strategy was successfully demonstrated. Using this scheme, efficient collection of picosecond, nanosecond, and microsecond data can be achieved in single scans, with the additional
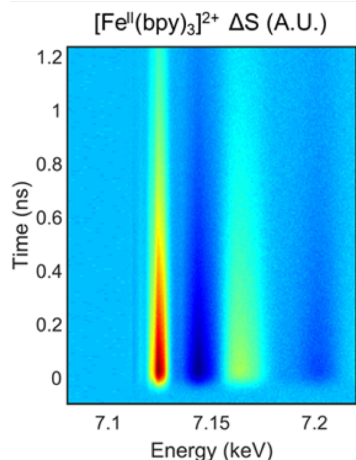
Figure 5: X-ray transient absorption data collected on the Fe K-edge of [Fe(II)(bpy)3]2+in H2O excited at 355 nm, collected with the Asynchronous X-ray MultiProbe technique. The 2D plot shows the full x-ray transient absorption data surface generated by the first bunch after the laser.

advantage of a completely passive scanning of the delay at picosecond timescales providing unprecedented stability. This stability is demonstrated in Fig .5 which captures the rise and decay of the signature of the formation of the high-spin state in photoexcited iron tris-bipyridine.

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

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

A. M. March, C. Otolski, G. Doumy, L. Young, J. E. Beetar[38], M. Chini[38]

Project Scope: Optical (UV to IR) transient absorption spectroscopy (OTA) remains an important complementary tool to x-ray spectroscopy for studies of solvated transition metal complexes. We are developing a MHz-repetition-rate OTA setup at the APS that can run concurrently with synchrotron x-ray experiments, in an optical-pump/x-ray-probe/optical-probe configuration, or as an independent OTA setup. The nominal laser pulse duration ($\sim$250 fs) limits the temporal resolution, which will be improved using a hollow-core fiber compressor to sub-30 fs while maintaining the high repetition rate [93]. Timescales <100 fs are important for enabling the investigation of structural dynamics, competitive reactive pathways, and controlled reactions of transition metal complexes.

Recent Progress: Significant developments have taken place during the last year. We have successfully generated white light in the visible and down to the UV region in conditions compatible with hundreds of kHz repetition rate. We have received, installed and commissioned a hollow-core fiber compressor system that produced 25fs pulses at 166 kHz repetition rate and better than 70% conversion efficiency. We have purchased a first detector that is allowing us to develop a robust setup at multiple kHz repetition rates before extending its capabilities with the use of a faster detector to be purchased later.

Future Plans: We will also explore the dependence of the ferrocyanide aquation reaction on different solvents (see also Section 4.4), using the clear absorption feature at 450 nm of the aquated photoproduct. This will provide valuable insight for subsequent x-ray measurements. After installation of the sub-30 fs pump pulse generation, we will explore these conditions with increased temporal resolution. We envision possibly implementing a multi-pulse excitation of ferrocyanide to interrogate the short-lived singlet species and to control the dissociation reaction mechanism by accessing higher-lying potential energy surfaces.

4.4 Tracking the photochemistry of solvated iron-based coordination complexes

A. M. March, G. Doumy, C. Otolski, S. H. Southworth, L. Young, W. Gawelda[10], G. Vanko[39], Z. Nemeth[39], D. R. Nascimento[34], A. Andersen[34], N. Govind[34], D. Hayes[40]

Project Scope: Transition metal complexes continue to be of high interest for molecular applications due to the flexible control over their reactivity that can be obtained through synthetic modification of ligands. Iron complexes are particularly interesting to replace the toxic and/or rare metals used presently in many catalysts. We are applying optical-pump/x-ray-probe absorption and emission spectroscopy to understand the complex reactivity of iron-based complexes in solution environments. We aim to understand the initial dynamics that immediately follow photoexcitation and to track the subsequent chemistry that occurs, including unwanted side reactions that may lead to irreversible damage of the molecule. Our studies focus on the wide range of timescales relevant for the photochemistry. We will utilize XFELs, such as the LCLS and the European XFEL, to probe from the picosecond to the femtosecond regime. The MHz-repetition-rate, optical-pump/x-ray-probe endstation at beamline 7ID at the Advanced Photon Source (APS), built by our group over the past several years [94–107], allows us to track reactions from about 10 ps to the microsecond regime.

Recent Progress: Our studies this past year have focused on two complexes: aqueous $[Fe^{II}(CN)_6]^{4-}$ and aqueous ferrate(VI) ion, the latter in collaboration with the group of Dugan Hayes at the University of Rhode Island. The first we use as a model system to understand ligand exchange reactions in water and the second becomes highly reactive in the presence of UV light, suggesting potential uses in water remediation. Following up on our previous "time-slicing" x-ray absorption studies of $[Fe^{II}(CN)_6]^{4-}$ where we identified a 20 ps-lived intermediate $[Fe^{II}(CN)_5]^{3-}$, that precedes aquation [99], we extended the "time-slicing" technique to x-ray emission spectroscopy to track the spin changes that occur during the reaction. We have measured the complete Fe 1s emission spectrum, including the $K\alpha$, $K\beta$, and valence-to-core regions. Our measurements confirm the triplet state of the pentacoordinated intermediate. Additionally, we have observed small spectral changes, compared to the ground state, for the aquated product $[Fe^{II}(CN)_5H_2O]^{3-}$ that demonstrate the sensitivities of the 1s emission spectrum to influences other than spin state and that provide a challenge for theoretical modelling. We have collected a series of XES spectra for several low-spin iron complexes to compare to the spectral changes we observe for $[Fe^{II}(CN)_5H_2O]^{3-}$ compared to $[Fe^{II}(CN)_6]^{4-}$. A manuscript reporting our observations is presently being prepared. In addition, we were granted one of the first general user experiments at the new ChemRIXS instrument at LCLS to use soft x-rays to probe at the Fe L-edge and N K-edge on the femtosecond timescale to try and capture the first step of the formation of the pentacoordinated intermediate. The experiment, however, was marred by a succession of technical issues inherent to a brand new instrument and will require full development of the high repetition rate capabilities at ChemRIXS to be attempted again. X-ray transient absorption results on the ferrate ion at both UV and visible laser excitations have helped disentangle the mechanism of the photophysics and photochemistry of the ion, which had surprisingly never been able to be measured. A combined optical/x-ray spectroscopy study elucidating these mechanisms is currently under review [108].

Future Plans: The next steps for our work on $[Fe^{II}(CN)_6]^{4-}$ include experimental exploration of the fastest timescales. We have started to use our high repetition rate OTA setup (4.3) to explore the aquation reaction in different solvent environments. A final experiment using our MHz pink beam setup at Sector 7 of the APS will focus on providing complementary information on the ferrate ion from XES, as well as studying the electronic decay pathways of a complex with longer

charge transfer state lifetime.

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

A.M. March, C. Otolski, G. Doumy, C. Elles[41], J. Blakemore[41], W. Henke[41], R. Sension[42], J. Penner-Hahn[42]

Project Scope: This collaborative project with groups at the University of Kansas and Michigan aims to better understand the behavior of a series of Mn-based CO_2 reduction catalysts with the form Mn(CO)3(bpy)Br, bpy = 2,2-bipyridyl. The complexes offer a promising alternative to the toxic and expensive rhenium complexes used for efficient CO2 reduction and other catalytic processes. Unfortunately, they suffer from photodegradation under even mild ambient light, which imposes serious limitations for applications. X-ray spectroscopy provides a powerful probe of the degradation mechanisms, providing insight to guide modification of the complex design.

Recent Progress: Very rich datasets were obtained during APS beamtimes in June 2018 and December 2019 where we performed transient XANES measurements at both the Mn and Br K-edges on multiple time scales (ps, ns and μs). Global kinetic modelling of the data provides insight into the structures of the 5- and 6-coordinate species produced following CO loss and solvent coordination. A structural rearrangement of the Br ligand from an axial to an equatorial position is suggested as a solvent molecule coordinates with the penta-coordinated intermediate. These results motivated the submission of a proposal at LCLS in collaboration with expert users of the facility (R. Sension and J. Penner-Hahn) to gain direct access to the very first steps of the photoreaction, from the metal-to-ligand charge transfer state to the ligand loss. This experiment took place in August 2022, and we were also able to probe both Mn and Br K-edges on three different complexes exhibiting varying photochemical behaviors.

Future Plans: These complexes demonstrate the importance of studies spanning multiple time scales. We now have a full dataset covering these different regions, and the next steps will consist in reconciling the different measurements along with published optical transient spectroscopy data to construct a consistent model for the different mechanisms at play.

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Structure and Dynamics of Atoms, Ions, and Molecules

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Overview:

The J.R. Macdonald Laboratory (JRML) focuses on studying the interaction of short and intense laser pulses with atoms and molecules for the purpose of understanding and ultimately controlling the resulting ultrafast dynamics. The timescales involved range from attoseconds, necessary for accessing electronic motion in matter, to femtoseconds and picoseconds for molecular vibration and rotation, respectively. To achieve our goals, we are advancing theoretical modeling and computational approaches as well as experimental techniques. The synergy afforded by the close interaction of theory and experiment within the Lab serves as a significant multiplier for these efforts. A significant fraction of our research is done in collaboration with others, both at JRML and elsewhere, including many within the DOE-AMOS program. Several JRML members conduct experiments at free electron lasers, such as LCLS, European XFEL and FERMI, and at other FEL and synchrotron radiation facilities. At JRML site, we run experiments with three femtosecond laser systems, several high-harmonic generation sources, and a large number of complementary charged-particle imaging instruments. Two years ago we have added our newest laser system, nicknamed FLAME, which is making a significant impact on our science program. It is a robust, 3-kHz, 5-mJ system combined with optical parametric amplifier that enables pump-probe coincidence measurements with wavelength conversion and serves all of our experimental groups. Many of our coincidence measurements will get an even bigger boost from the high-power 100-kHz, 200-W system that we recently received funding for and that will be delivered next year.

Our research projects are organized around three basic themes: "Strong-field and attosecond science", "Correlated dynamics" and "Ultrafast X-ray science". These themes serve as broad categories as the boundary between them is not always well defined. The following progress summaries provide brief updates on a select subset of our ongoing projects.

2. Strong-field and attosecond science

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

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

Project Scope:

This JRML project explores fundamental laser-matter interactions. Additionally, the project aims of developing novel ultrafast photoelectron metrologies, with a particular emphasis

on developing tools for ultrafast molecular dynamics studies. During the last decade, our research interest have been focused on advancing laser-driven electron diffraction (LIED) as a strong field imaging probe of ultrafast molecular dynamics. Leveraging the λ^2- scaling law and the rescattering mechanism of strong field physics, we pursued the development of midinfrared ultrafast lasers that allowed us to generate high energy (>100 eV) returning electron wave packets that possess the necessary resolving power to determine the location of atomic centers inside the parent molecular ion. These efforts allowed us to observe molecular transformations from bond relaxations in diatomic molecules [1] and cage deformations of fullerenes [2]. One of our primary objectives during the last year was to demonstrate that the key ingredients that facilitate high-energy LIED can also be realized in the low energy recollision regime.

Recent progress:

Target-independent Returning Electron Wave Packets in Multiphoton Ionization

Until last year, we studied multiphoton resonances measuring photoelectron spectra at various targets as a function of laser wavelength and intensity. These measurements were validated by numerical integrations of the time-dependent Schrödinger equation (TDSE) in the single active electron approximation. Although fruitful, these investigations only revealed observables after the end of the laser pulse and offered little insight at what happened at the moment of rescattering. During the last year, we began work on alleviating this limitation. Using the well-known time-frequency wavelet analysis of high-harmonic generation (HHG) spectra calculated at each point during the laser pulse we investigated the HHG emission history [3] at resonant and off-resonant laser intensities. These calculations confirmed our previous photoelectron spectra: as seen in Fig. 1, the cycle-to-cycle HHG emission at ~2.5 times the corresponding ponderomotive energy (argon @790 nm) is relatively constant off-resonance but increases markedly for the on-resonant case. This result confirms our previous photoelectron spectra results that on-resonance, an effective buildup via population trapping enhances the spectral density of the returning wave packet. Once again, this result seems general, being

Figure 1: Intensity of HHG emission at ~2.5U_P photon energies in argon during a 7 cycle, 790nm pulse. The blue curves is calculated at an intensity where large enhancements are observed in the plateau region of the photoelectron spectra (66 TW/cm^2) whereas the red curve was obtained off-resonance (80 TW/cm^2).

observed in all noble gases we investigated and at all laser wavelengths. The results shown in Fig.1 also allow us to identify the most likely return time at rescattering for a given return photoelectron momentum, the key ingredients needed for DCS extraction from the measured photoelectron spectra. We are now in the process of identifying and correlating the return times and momenta with the corresponding detected photoelectron energy. Once this is obtained, we will extract and analyze DCSs from the measured angular distributions. We have also completed a series of measurements using bichromatic 800+400nm fields in argon, molecular nitrogen, and methane. The analysis is ongoing.
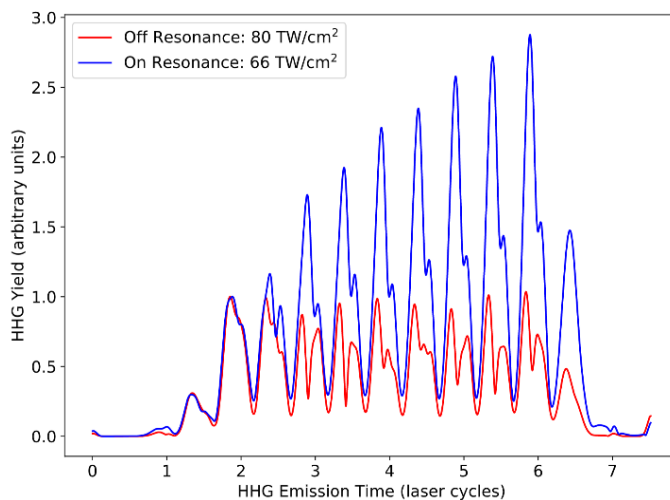
Returning Electron Wave Packets Carrying Orbital Angular Momentum

Laser beams carrying orbital angular momentum are novel light sources with significant promises for spectroscopic applications, telecommunications, optical imaging, etc. [4]. Recently, Tolstikhin and Morishita – the latter a long term JRML collaborator – have shown theoretically that vortex returning electron wave packets, i.e., returning electron wave packets carrying orbital angular momentum could be produced in atoms and molecules by a linearly polarized infrared field if the state ionized has a non-vanishing magnetic quantum number M along the laser polarization axis [5]. Furthermore, it was shown that the photoelectron angular distributions were sensitive to the chirality of the target. Although conceptually the experimental verification of this theoretical work is straightforward, preparing initial states with well-defined M is a challenge. Earlier this year, in a collaboration with DiMauro (Ohio State) and Wang (China Academy of Engineering Physics, Beijing, China) groups, we have reported the results of single and double ionization of magnesium atoms with linearly and circularly polarized 400 nm beams [105]. We demonstrated that the 3s3p (L=2) excited state plays a major role in the single and double ionization channel and that a significant amount of population remains on the 3s3d state after the 400 nm pulse has passed, as shown in Fig. 2. Although the 3s3p state is degenerate with $L=2$ and $M = 0, \pm1, \pm2$, only the $\pm L$ states are populated with

Figure 2: Population of the 3s3d state in Mg during 400 nm laser pulses at 1TW/cm2 (black curves), 0.32 TW/cm2 (red curves) and 0.1 TW/cm2 (blue curves). For each intensity, solid/dash curves are for linear/circular polarized pulses, respectively.

circular polarization and $M = 0$ with linear polarization due to dipole selection rules. This result is a significant milestone for our quest to demonstrate experimentally the existence of OAM rescattering electron wave packets since we now have identified a suitable target. Upon photoexcitation with linearly or circularly polarized 400 nm pulses, Mg*(3s3d) with or without nonvanishing M can be prepared which upon photoionization by an infrared pulse will generate OAM or "standard" plane-wave-like returning electron wave packets. This method of generating OAM returning electron wave packets is general and could prove very useful for studying chiral targets.

Ultrafast imaging of medium sized molecules with table-top LIED

During the last year, a collaborative effort spearheaded by JRML's Lin theoretical group together with Blaga's group, the DiMauro (Ohio State) and Biegert (IFCO, Barcelona, Spain) groups has demonstrated a more accurate LIED structural retrieval method based on fitting the entire measured photoelectron angular distribution [90]. The new 2D fitting method significantly improved our previously published data obtained using only 1D DCS for O_2 and N_2. Furthermore, we were able to successfully retrieve the structure of CO_2 molecules from data that was gave inconclusive results with the old 1D method. Armed with the new method, we are currently exploring the applicability limits of LIED. This project aims to retrieve the molecular structure of hydrocarbon molecules with increasing complexity from the measured photoelectron spectra at midinfrared wavelengths. For these studies, we have developed a time-of-flight apparatus for

which we designed and commissioned, multi-anode MCP detectors for high data throughput. We are in the process of filling for a US Patent for the design of the multi-anode MCP detector.

Future Plans
In the immediate future, we will continue our work on the projects highlighted in the previous section. For the multiphoton resonances project, we will record single and double ionization yields in noble gases as a function of intensity and wavelength. Just as in the elastic or recombination channel, we expect a significant increase in double ionization yields at leading intensities due to the more spectrally dense returning electron wave packet. Such investigations will allow us to better understand electron-electron correlations in (e,2e) channels. For molecules (ex. CH_4, for which we have seen a strong resonant response) it will be interesting to determine if the more efficient recollision at leading intensities correlates with higher (e,2e) driven dissociation rates. For our investigations regarding OAM-carrying returning electron wave packet, now that we have identified the suitable target (Mg*(3s3d) prepared with linearly polarized or circularly polarized 400 nm pulses), we aim to record the photoelectron spectrum and prove the existence of these vortex electron beams. Finally, for the high-energy LIED studies, we are working in collaboration with the Lin group on testing the applicability of LIED is medium sized hydrocarbon isomers. We also aim to continue our high energy LIED and ultrafast molecular imaging of field-induced cage deformations in fullerenes, focusing on mapping the dependence of the cage deformation on pulse duration and pulse chirp, both sensitive knobs to control the energy deposition into the cage via impulsive Raman scattering mechanism at play.

2.2. Filming attosecond electron dynamics with high harmonic spectroscopy (HHS) - Lin

Project scope:
Electron dynamics is the progenitor of chemical reactions that occurs at the tens to hundreds attosecond timescale. Based on elaborate experimental high-order harmonic spectra and new machine learning algorithm, we extract electron dynamics of single molecules at steps of tens of attoseconds, thus filming attosecond charge migration (or electron wave packet) movies from experimental data for the first time.

Recent Progress:
When a molecule is exposed to a light pulse, a multi-particle wave packet is created. In the first femtosecond, the nuclei are frozen such that molecular dynamics is governed by an attosecond electron wave packet (EWP). This project is to extract the EWP from the harmonic spectra.

According to the three-step model, in HHG, an electron is removed suddenly near the peak of the field cycle. Take CO_2 as the example, this would create a hole from a few orbitals (called X, A, and B) to form an EWP of the ion that would evolve in the laser field. As the freed electron returns to recombine with the ion, the emitted harmonics would carry EWP information. For 800 nm laser, the time step is about 100 as, but if probed with a small mixture of 400 nm laser, the time step is reduced to 50 as since even and odd harmonics are both generated. To extract the EWP for each single molecule from experimental spectra, one has to overcome a number of challenges. First, experimentally the data are taken from the coherent emission of harmonics of each fixed-in-space molecule, but gas-phase molecules can only be partially aligned. Thus, one has to solve the inverse problem of extracting the complex-valued single-molecule harmonic fields from the experimental spectra. This was done using machine learning algorithm. Second, the EWP of the cation is evolved in the presence of the laser field. It is interrogated only at the return time of each harmonic. For the three holes, X, A and B, each is represented by a complex amplitude. A genetic algorithm was

used to extract these complex coefficients. Once they are obtained, the whole EWP, or its modulus square which was called charge migration in the literature, can be displayed as a "movie". Fig. 3 is an example of the hole density extracted from our recent paper published in Nature Communications [100]. It shows hole density swirls in time in the laser field, instead of just moving along the laser polarization axis.

Future plans: The present method can be extended to other small molecules if the number of hole states is small. It will be also extended to NH_3 to probe sub-femtosecond nuclear dynamics.
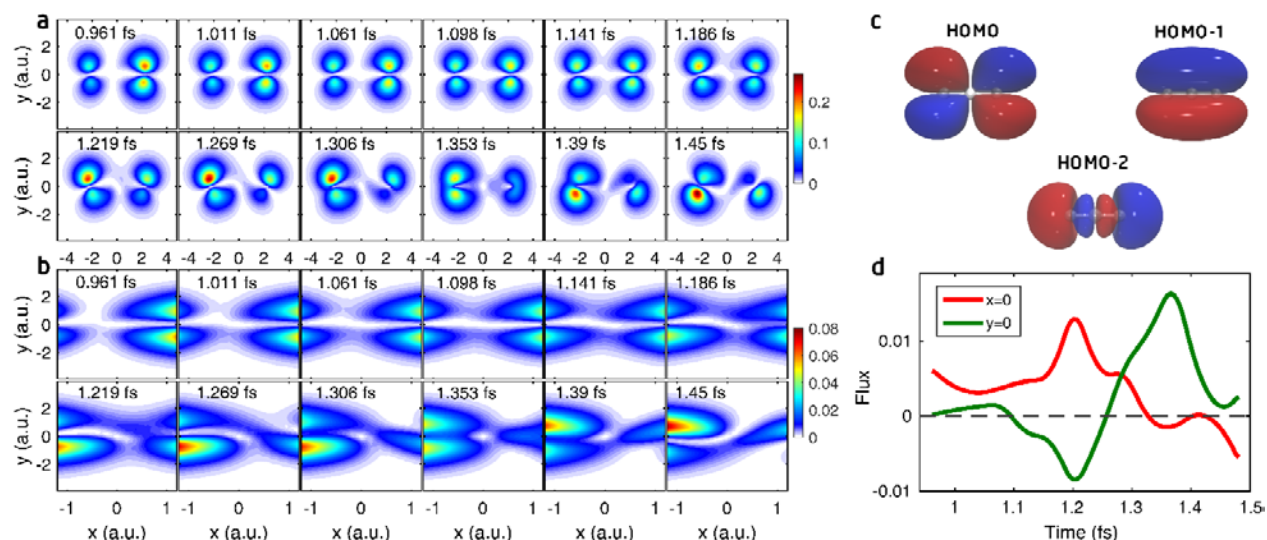
Figure 3: Charge migration of CO_2 extracted from experiments at the return times of the emitted harmonics after tunnel ionization (for H15, 16 ..., 27) in time steps of 50 as. Part (b) is the zoon-in between the two oxygen atoms. (c) shows the orbitals of the three holes. (d) shows the total flux crossing the x=0 or y=0 planes versus time. The laser polarization and molecular axis are both along the x-axis. These plots are similar but cannot be interpreted as classical migration (adapted from [100]).

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

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

Theoretically, we aim to develop conceptual, analytical, and numerical tools to (i) image and control the effects of intense light pulses of different wavelengths on the electronic and nuclear dynamics in small molecules and (ii) extend our investigations from diatomic molecules to larger

small molecules. In addition, since, for a typical ultrafast pump-probe experiment, the goal to extract the time-dependent molecular wave packet created by the pump pulse in general remains difficult, we develop a robust model for a specific probe, dissociative double ionization. In particular, we show that the information about evolving electron wave packet can be extracted from the kinetic energy release (KER) in such dissociative double ionization experiment.

Recent progress:

Fourier Spectroscopy of Post-Alignment Dynamics in Molecular Cations

The concept of light-induced conical intersection (LICI) provides an interesting perspective on nuclear dynamics in strong laser fields as well as the possibility of control through tunable non-adiabatic coupling between states. There have only been a few experimental studies that seek to directly investigate nuclear dynamics through LICIs. In this project, we seek to understand the role of coherent rotational dynamics in dissociation mediated by a LICI in molecular cations. We start with strong-field ionization and fragmentation of D_2, launching a broad and coherent rotational wave packet in several vibrational states of the cation by ionizing cold (~10 K) neutral molecule with a 30 fs, 800 nm pulse. The pulse is too long to directly observe vibrational coherences in the time domain. The rotational coherence in the cation is likely the result of a combination of factors— alignment of the neutral in the leading edge of pump pulse, angle-dependent ionization near the peak of the pulse and alignment of the cation in the trailing edge. We then dissociate the cation with a weaker pulse with the same pulse duration and wavelength, and measure the momentum distribution of the resulting D^+ ion with a velocity map imaging spectrometer. With 20-fs delay steps and 40 ps scans, Fourier transforms of the momentum distributions give us enough resolution to identify rotational lines from vibrational states from v = 5 to v = 9. These measurements not only characterize the broad rotational wave packets excited by the pump in these vibrational states, but also elucidate the role of rotational dynamics in determining the final momentum distribution of the D^+ ions.
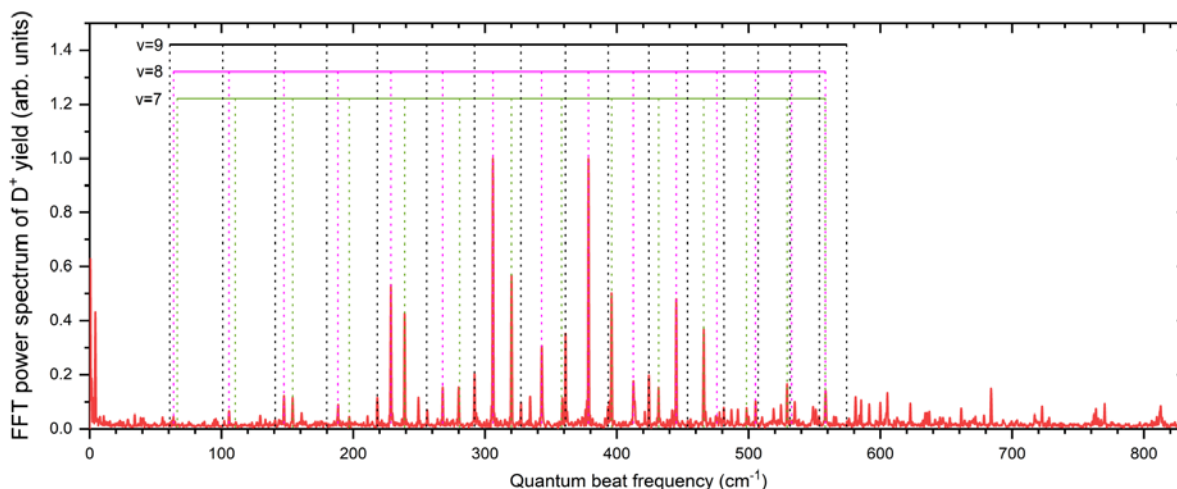
Figure 4: The FFT spectrum of the yield of D^+ from D_2 integrated over 0–1 eV KER. The pump pulse ionizes the D_2 molecule and the probe pulse dissociates it. Dashed vertical lines correspond to the expected positions of $\Delta J = 2$ quantum beat frequencies for three vibrational manifolds in the $^1\sigma_g^+$ ground state of D_2^+. Each series starts at J = 0; the first line represents a coherence between J = 0 and J = 2, the second between J = 1 and J = 3 and so on. Lines from v = 6 can be identified in the data, but the corresponding expected line positions are not shown to avoid clutter.

We analyze the delay-dependent 2D momentum distributions by first reconstructing the 3D momentum distribution using the pBasex algorithm, and then performing an FFT of all the moments of the distribution. Although the FFT signal is rather weak (the trailing edge of the pump pulse can efficiently dissociate the cation through one and three photon processes, so the measured VMI spectrum comes predominantly from the pump alone), broad rotational wavepackets can clearly be seen in several vibrational states. Fig. 4 shows a 1D FFT of the delay-dependent yield of D^+ ions integrated over a 0-1 eV KER range. The expected positions of rotational Raman lines for $v = 7$‑9 are also shown. In this energy range, dissociation proceeds through a one-photon process. In the LICI picture, the ground state potential energy curve is crossed by a one-photon-shifted dissociative curve, setting up a intersection at $v = 9$. As the pump-probe delay is varied, that wave packet that traverses the LICI is modulated by the rotational excitation that the pump leaves in the cation. These data provide experimental information on the time-dependent part of the momentum distribution from individual rotational coherences in a specific electronic/vibrational state.

Understanding dissociative ionization (DI) dynamics of CO2 molecules

Addressing open questions in the interpretation of earlier dissociative ionization (DI) experiments [6-9], we have extended our numerical modeling of the DI of O_2 [39,40,86] to H_2O and CO_2. In particular, for the latter case, this is motivated by recent ion-electron coincident XUV-NIR experiments performed at JRML [10].

We start with modelling the adiabatic potential energy surfaces for CO_2^+. Employing the multi-configurational self-consistent-field quantum-chemistry code GAMESS [11,12], we calculated *ab initio* CO_2^+ adiabatic potential energy surfaces and dipole couplings in full dimensionality. For the $A^2\Pi_u, B^2\Sigma_u^+, C^2\Sigma_g^+$ states of CO_2^+, we validated the accuracy of our GAMESS application (15 active electrons in 12 active orbitals, cc-PVTZ basis) against measured [13,14] vibrational excitation (symmetric/antisymmetric stretch & bending) energies relative to the CO_2 ground state. As a next step, we address the CO_2^+ nuclear dynamics in full dimensionality. Modeling CO_2 ionization to an initial CO_2^+ ($B^2\Sigma_u^+$) wave-packet (WP) in Franck-Condon approximation, we performed WP propagation calculations for the ensuing bound and dissociative nuclear motion, subject to dipole, (model) fine structure, and (model) dynamical couplings between the CO_2^+ states $A^2\Pi_u, B^2\Sigma_u^+, C^2\Sigma_g^+$, and $b^4\Pi_u$. Within this four-state calculation, dissociation occurs through strong fine-structure coupling and dipole coupling from the $C^2\Sigma_g^+$ to the $b^4\Pi_u$ [$O(^3P_g) + CO^+(X^2\Sigma^+)$] fragmentation channel. This is illustrated in Fig. 5.
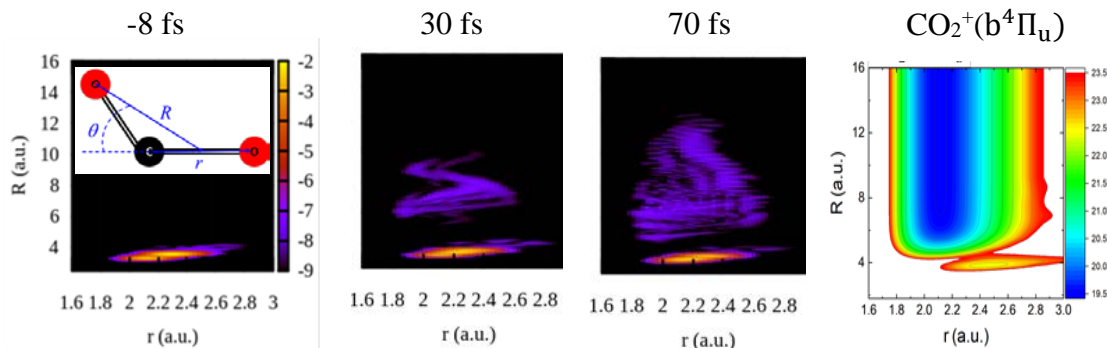
Figure 5: Nuclear WP evolution in the unbent CO_2^+ ($b^4\Pi_u$) state along Jacobi coordinates r and R.

In addition to scrutinizing the dissociation dynamics, our four-state calculation predicts the repetitive transfer of population at the conical intersection (CI) between the $A^2\Pi_u (1\pi_u)^{-1}$ and $B^2\Sigma_u^+ (3\sigma_u)^{-1}$ states with an oscillation period of 117 fs in the binding potential well of the A state of CO_2^+ (see Fig. 6), in

Figure 6: (a) Population in the $C^2\Sigma_g^+$ state as a function of time delay. (b) Fourier transform of the signal shown in (a)

good agreement with a recent XUV pump – IR probe experimental value of 110 fs [10,15]. This agreement persists for simplified calculations disregarding bending, indicating that coupling to the bending degree of freedom is irrelevant for the σ_u - π_u electron hole transfer.
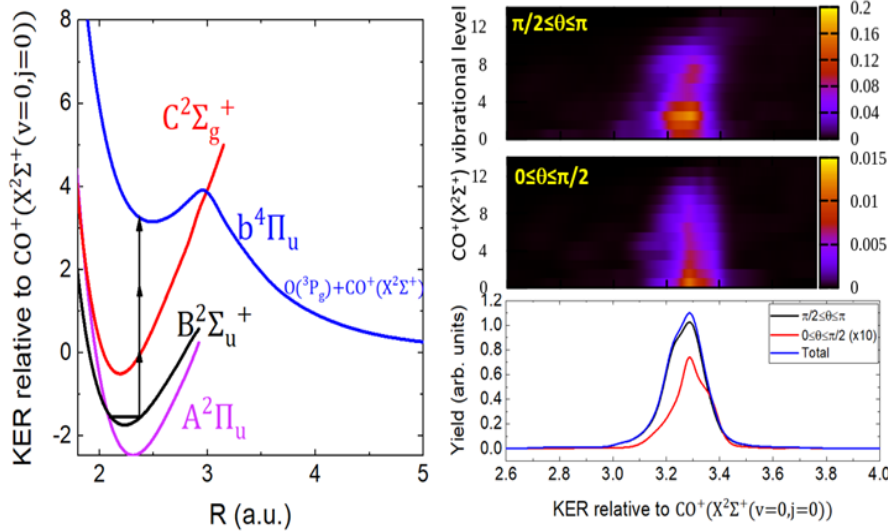
Figure 7: Left*:* $\theta=0$ cut of CO_2^+ potential energy surfaces, indicating the 3ω coupling from the $B^2\Sigma_u^+$ vibrational ground to vibrationally excited $C^2\Sigma_g^+$ states. Right*:* $CO^+(X^2\Sigma^+)$ vibrational level occupancies (top) and KER spectrum (bottom) for CO_2^+ dissociation into the $O(^3P_g)$ + $CO^+(X^2\Sigma^+)$ asymptotic $CO_2^+ (b^4\Pi_u)$ channel.

Finally, as illustrated in Fig. 7, we model the KER for the dissociative ionization CO_2. The initial $B^2\Sigma_u^+ (3\sigma_u)^{-1}$ nuclear wave packet in CO_2^+ yields a distinct peak in the KER spectrum, which we assign to dissociation via three-photon coupling from the $B^2\Sigma_u^+$ vibrational ground state to vibrationally excited $C^2\Sigma_g^+$ states, followed by fine-structure coupling between the $C^2\Sigma_g^+$ and $b^4\Pi_u$ states of CO_2^+.

Retrieval of electron wave packet from measuring kinetic energy release in dissociative double ionization of molecules by strong laser fields

To retrieve the information on molecular wave packets from a pump-probe experiment, it is desirable to have a strong probe pulse, to achieve better signals. But the typical interaction of molecules with a strong pulse is nonlinear. Since the retrieval is usually performed via an iterative process, the scattering theory should be simple. For infrared lasers, tunnel ionization is relatively simple. At higher intensities, double ionization to higher excited dication states would result in Coulomb explosion of the molecule, where the kinetic energies of the fragments can be easily measured. To demonstrate that this idea is promising for extracting the information on electronic WP, we have calculated sequential double ionization (SDI) of N_2 [103] and O_2. We have been able

to show that our SDI model can reproduce earlier experimental data [16]. We used short IR pulses for pump and probe, such that molecules can be considered fixed in space. We are investigating a pump-probe scheme where N_2^+ or O_2^+ is created by a pump pulse. The resulting free propagating wave packet will be probed by another pulse to obtain the measurable KER spectra vs pump-probe time delay. The resulting KER spectra are expected to oscillate with time, from which the electron wave packet can be retrieved. The predictions of the model can be directly compared to the final-state-specific results obtained in coincident experiments

Future Plans:
One of the major experimental goals of this project is to reconstruct the time-dependent part of the momentum distribution from individual rotational coherences in a specific electronic and vibrational state. This will enable us to focus on exclusively on the dynamics driven by the probe pulse without having to fully characterize the wave packet launched by the pump pulse in the excited/ionic state of the molecule. For instance, we will be able to explore the influence of initial rotational velocity on the passage of the molecule through the LICI by Fourier-filtering different quantum beat frequencies that can be seen in the data shown in Fig. 4 from the full VMI data set. Our data at present is not of sufficient quality for reliable reconstruction of such momentum distributions. We are working on improving the stability of our molecular beam and on characterizing the error in the reconstructed momentum distribution.

For the DI of triatomics, our future plans are to (i) investigate field-induced molecular orientation, stabilization, CI effects in the DI of CO_2, (ii) distinguish dissociation paths and calculated branching ratios for DI into $CO^+ + O^+$ and $CO^+ + O$ in XUV-pump – IR probe KER spectra, (iii) distinguish the imprint of dipole, *ab initio* fine-structure and *ab initio* dynamical couplings in KER spectra, (iv) perform a detailed comparison with our recent state-selective experimental data on CO_2, and (iv) investigate DI of H_2O, both experimentally and theoretically. Finally, we will work on improving the retrieval methods for SDI data, and extend this approach to other diatomic and then triatomic molecules. Further extension can also include the vibrational degree of freedom and dynamic systems. Specific molecules that are of interest to JRML will be prioritized.

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

3.1. Coulomb explosion imaging of polyatomic molecules – Rolles, Rudenko, Ben-Itzhak

Project Scope
This project aims at establishing the Coulomb explosion imaging (CEI) method to determine the geometric structure of 5- to 15-atomic molecules – first their static equilibrium geometry and then

the dynamically changing structure as a function of time in a pump-probe experiment. For this purpose, we are using both XFELs and our NIR lasers at JRML to trigger the Coulomb explosion process in a variety of molecules and, in parallel, are developing Coulomb explosion simulations to help with the interpretation of the experimental data.

Recent progress

In a recent XFEL experiment, we demonstrated that intense, few-femtosecond X-ray pulses can provide snapshots of the molecular structure of polyatomic molecules with up to a dozen atomic constituents, even if not all of the created ions are measured in coincidence [95]. This is illustrated in Fig. 8, where the positions of all atoms in a ring molecule can be clearly identified in momentum-space images. We have since performed further XFEL experiments on toluene and two of its isomers that showed that CEI can clearly distinguish between ring-shaped molecules and their chain isomers. Time-resolved experiments designed to image the transition between these isomers are currently under analysis.
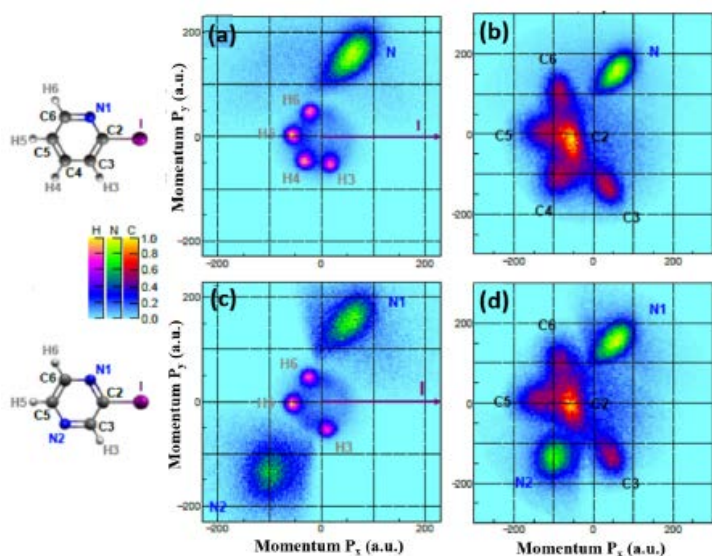
Figure 8: CEI of iodopyridine (C_5H_4IN, top row) and iodopyrazine ($C_4H_3IN_2$, bottom row) resulting from multiphoton ionization by 2-keV XFEL pulses. The Newton diagrams of (a)&(c) N^+ and H^+ (b)&(d) N^+ and C^+ are built from all shots in which I^+, N^+, and at least one H^+ or C^+ ion were detected. The image plane is defined by the momentum vectors of I^+ (which is along the positive x-axis) and N^+ ions, and the momenta of all other detected ions are projected on this plane. The sketches on the left show the corresponding structures. (Adapted from [95].)

In parallel, we were able to obtain similar images for CEI driven by femtosecond NIR laser pulses at JRML for several ring molecules such as furan and benzene as well as for bromoform ($CHBr_3$), the latter shown in Fig. 9. In order to demonstrate that CEI is able to distinguish between bromoform in its ground-state equilibrium geometry and a possible bromine-migrated isomer (*iso-CHBr_3*) predicted to occur, e.g. after UV excitation, we also performed classical Coulomb explosion simulations that are in good agreement with the experimentally observed momentum correlation but show a distinctly different momentum correlation pattern for the isomer geometry, as shown in Fig. 9(b,c). Similar CEI results have been obtained for CH_3I using an XFEL, accompanied by Coulomb explosion simulations suggesting that CEI should be able to resolve the structural changes during a coherent vibrational motion of the molecule [93]. The corresponding time-resolved experiments were performed at the European XFEL in fall 2021 and are currently under analysis.
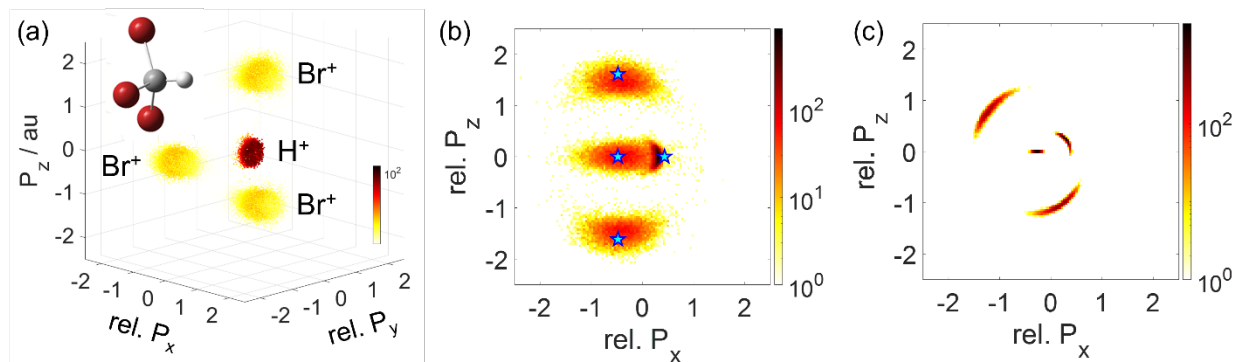
Figure 9: (a) Three-dimensional momentum correlation plot of the complete Coulomb explosion of CHBr$_3$ into H$^+$ + C$^+$ + Br$^+$ + Br$^+$ + Br$^+$. The momentum vectors of each fragment in a five-fold coincidence event are rotated such that the momentum of the reference ion, C$^+$, points along the x-axis, and the sum of the momentum vectors of the last two detected Br$^+$ ions lies in the xy-plane with positive P$_y$ values. (b) Projections of the experimentally obtained momentum correlation of H$^+$ and three ^{81}Br$^+$ ions in the five-body channel shown in (a) on the xz plane. The blue stars indicate the normalized momenta obtained from the Coulomb explosion simulations for the initial equilibrium geometry of the CHBr$_3$ ground state. (c) The same projection as in (b) obtained from the Coulomb explosion simulations of ten thousand *iso*-CHBr$_3$ geometries sampling the Wigner distribution of the ground-state molecules at 60 K. (Adapted from [110].)

Future Plans:
Pump-probe experiments to extend the CEI results shown above towards imaging time-resolved, transient geometries are currently underway both at JRML and with XFELs and will be the focus of our experiments in the near future. A dedicated beamtime to image a UV-induced ring-opening reaction via CEI has been scheduled at the European XFEL for October 2022. The multi-coincidence ion imaging technique presented here is also one of the key applications of the new DREAM end-station that is currently under construction for LCLS-II, and KSU personnel will be instrumental in the commissioning of DREAM and the early-science experiments that are planned with it.

3.2. Wavelength-dependent photochemistry of halomethanes – Esry, Greenman, Rolles, Rudenko, Blaga

Project Scope
The goal of this project is to investigate how the dynamics of photoexcited molecules depends on the excitation wavelength. We focus on halomethanes, where conical intersections lead to interesting dynamics in both neutral and ionic species. A large body of work in gas-phase photochemistry of halomethanes is dedicated to studying the wavelength dependence. While much of this work was performed with picosecond and nanosecond lasers and, thus, focuses primarily on the branching ratios and kinetic and internal energies of the photoproducts, a rapidly increasing number of studies is performed with femtosecond lasers in order to investigate the ultrafast dynamics. For technical reasons, these femtosecond laser experiments are often performed with only a few, very specific excitation wavelengths corresponding to integer harmonics of the drive laser and/or with rather long pulses with pulse durations (especially in the UV) well above 100 fs. This results in very incomplete knowledge of the wavelength-dependent reaction dynamics. Using our short-pulse and variable-wavelength UV sources at JRML, we therefore investigate if and how the ultrafast dynamics in a series of halomethane molecules depend on the excitation wavelength. We combine experimental efforts with theoretical calculations of PESs and nuclear dynamics,

which we use to address the challenge of assigning delay-dependent features to state-specific processes.

Recent progress

Experimentally, we have concentrated so far on CH_3I, CH_2I_2, CH_2ICl, and $CHBr_3$ targets [17-20, 43]. The first of these molecules is known to exhibit strongly wavelength-dependent dissociation dynamics between 200 and 270 nm, while interesting roaming and/or isomerization reactions are being discussed for the latter three molecules.

To help understand our experiments on the di-halomethanes, we have started to develop the theoretical tools to model their dynamics. Our strategy is to refine the models of the dynamics using an inexpensive but appropriate method for large portions of the potential energy surface (PES), named EOM-CCSD. Following this, we will refine the PES using the CASPT2 method, which can get the details of the conical intersections on the surface correct. This approach facilitates exploration and visualization of the surfaces themselves, providing global insight into the possible dynamics.

We have completed 400,000 PES points for CH_2I_2 using EOM-CCSD methods. EOM-CCSD has the advantage of numerical stability compared to multireference methods and the ability to get a qualitative picture of the excited state structure at parts of the PES where conical intersections are not prevalent. With multireference methods at reasonable active space sizes, we will only be able to calculate a handful of the most important states we have used EOM-CCSD to identify. We have determined that it performs well even for some bond-breaking curves, where the method would be assumed to fail. However, we have also determined that it is not sufficiently accurate for our purposes in the area of the conical intersections. This is a known issue with the method, but we have identified some surprisingly large quantitative failures.

Despite its failure, we were able to use the EOM-CCSD results to determine the methodology for the dynamics calculations and the approximate coverage of the configuration space we need for CH_2I_2, and we expect this to extend to other halomethanes. We are interested in the elimination of I and I_2 which suggests, as a first step, treating CH_2 as a rigid body, leaving the C-I bond lengths r_1 and r_2 and the I-C-I bond angle θ as the dynamical degrees of freedom. We constrained the CH_2 to lie in a plane perpendicular to CI_2 and require that plane to bisect θ.

We used MOLPRO to calculate the lowest few energies at ~400,000 unique points out to r_i ~5.5 Å at the EOM-CCSD level. These surfaces are used to calculate the force in the equations of motion for the classical trajectories, which require interpolating between the calculated potential points. Obtaining a faithful, physically sensible force that did not oscillate or show other numerical artifacts led, through trial and error, to the large number of points calculated. We estimate that a PES in the full range we wish to describe will require density of ~0.01 Å within the Franck-Condon region, and ~0.1 Å elsewhere, with a density of ~1° in θ. While 400,000 points is, on average, only about 75 points in each dimension, we have learned how to be more efficient for the next system we treat.

With the potentials and fits in hand, we can calculate the classical trajectories. To determine their initial conditions, we used a classical Boltzmann distribution in the normal coordinates of the ground state near equilibrium. Since the corresponding normal-coordinate approximation to the Hamiltonian is simple harmonic, the Boltzmann distribution reduces to Gaussians in both momenta and coordinates and is thus very simple to sample randomly. This choice also provides a convenient free parameter in the temperature which can be adjusted to suit the experimental

conditions. We additionally impose energy conservation consistent with the absorption of the pump photon – i.e., we only accept those randomly sampled initial conditions that give a total energy on the target state with the energy (within the bandwidth) of the absorbed photon. Any excess kinetic energy on the target state is thus automatically and consistently included in these initial conditions just as it would be within, for instance, a first-order perturbation theory treatment. Moreover, this strategy facilitates exploration of the pump-photon wavelength dependence.

We neglect surface hopping for the trajectories, but monitor whether any trajectories go near a conical intersection. So far, on our EOM-CCSD surfaces, they have not. However, this is the region that will be most affected by a multireference method. We have found that about 50% of the trajectories on the first EOM-CCSD excited state and 3% of the trajectories on the second excited state pass through the "isomer region" and thus have geometries upon Coulomb explosion that look like an isomer. Importantly, though, we define the isomer region as the volume of space that is enclosed by the ground-state-energy isosurface at the lowest saddle point leading out of the ground-state isomer well. Our trajectories, however, still lie on one of the excited states. Therefore, they do not represent isomers when in the "isomer region" they only have a geometry that matches it and are not a bound state in any way as they would be on the ground state.
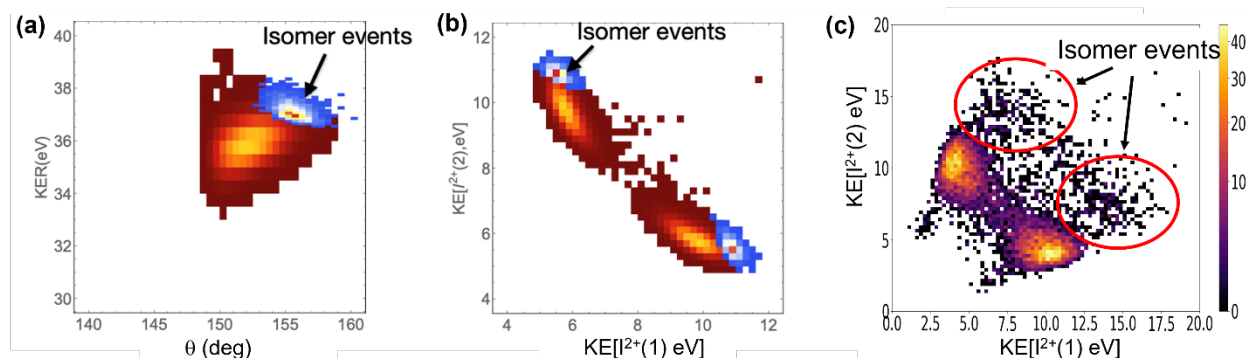
Figure 10: (a) Calculated KER vs θ (angle between iodine final momenta) at 78 fs pump-probe delay. (b) Kinetic energy sharing between two I atoms at 78 fs. The total distributions and isomer distributions (defined via a ground-state iso-surface) are separated. (c) Experimental kinetic energy sharing plot.

The machinery to match the experimental observables is also in place, as demonstrated in Fig. 10. We have implemented a Coulomb explosion simulator that uses the trajectories to guide its initial conditions. Information about the fragments' initial momenta is therefore taken into account. The results may also be constrained to those trajectories that pass through the isomer region as discussed above. Comparisons with the experimental Coulomb explosion images (Fig. 10(c)) thought to traverse this region are then possible.

Future Plans:
Most of our investigations to date have focused on the wavelength dependence of (two-body) dissociation and isomerization reactions. However, our multi-ion coincidence momentum imaging experiments also show clear signatures of (neutral) three-body dissociation reactions, which also show a pronounced wavelength dependence but have been little explored so far since they are difficult to study with other methods. We plan to address these three-body dissociation reactions in more detail in the future along with continuing our studies of two-body dissociation and isomerization reactions. Furthermore, we plan to complement our studies on CH_2I_2 by performing a UV-pump, MIR-probe high-energy LIED experiment to investigate I_2 elimination. This will

allow us to compare the LIED and CEI results for the same reaction. On the theory side, we will continue to refine our potential surfaces using multireference CASPT2 and MRCI methods. Before regenerating the PES at multireference levels of theory, we are using one-dimensional curves to understand the effects of the active space and the difference (if any) between multireference post-CASSCF methods. We have identified these curves using the EOM-CCSD surface and dynamics as those of special interest. We are comparing our results to previous multireference calculations, which have used active spaces of SA(3)-CASSCF(12,9) [21], SA(9)-CASSCF(12,8) [22], and CASSCF(16, 12) [23]. Various differences between the methods exist, for instance inclusion of spin-orbit effects, size of the one-particle basis, and use of core potentials.

3.3. Site-specific probabilities for hydrogen-bond rearrangement in ethanol and formation of tri-hydrogen, methane, hydronium, and water ions - Ben-Itzhak, Rolles, Rudenko, *in collaboration with E. Wells (Augustana)*

Project Scope
The formation of tri-hydrogen ions from organic molecules has been the subject of many studies. In previous work, Ekanayake *et al*. [24] suggested that roaming of an H_2 followed by proton abstraction from another molecular site might be an important mechanism for tri-hydrogen formation. Soon thereafter, Kling *et al*. [25] demonstrated that double hydrogen migration in ethanol ions plays a significant role. Moreover, they established that in this process the migration of the two hydrogen atoms is not correlated. These earlier studies motivated us to explore the origin site of the hydrogen atoms that compose tri-hydrogen ion formed from ethanol dications. The same question can be raised concerning the formation of other multi-hydrogen fragments of ethanol, specifically, methane, hydronium, and water ions. The importance of determining these site-specific probabilities for hydrogen migration stems from the need to provide strict quantitative constraints to guide the advancement of molecular dynamics calculations.

Recent progress
To accomplish the aboved-stated goal, we have measured the fragmentation of seven isotopologues of ethanol doubly ionized by ultrashort intense laser pulses. These isotopologues were deuterium-tagged such that each site, namely β-carbon, α-carbon, and hydroxyl, consists solely of H or D isotopes, for example CD_3CH_2OH or CD_3CD_2OH. Extreme care was needed to maintain laser pulse conditions during the whole sequence of measurements and to assure that each isotopologue is not contaminated by residual molecules from the previously measured isotopologue. These, tour de force COLTRIMS measurements of ethanol dication fragmentation were then analyzed to provide the needed branching ratios of the two-body breakup channels of interest, like $H_3^+ + H_3C_2O^+$ and $H_3O^+ + H_3C_2^+$.

Recall that our goal is to determine the site-specific probabilities for the six site combinations of hydrogen atoms in, for example, the product hydronium, which are βββ, ββα, ββO, βαα, βαO and ααO, where "O" denotes the hydroxyl-group hydrogen. To determine these probabilities, we write the sum of the contributions to a specific branching ratio of each isotopologue. For example, the branching ratio for HD_2O^+ formation from CD_3CD_2OH is proportional to $P(\beta\beta O) + P(\alpha\alpha O) + P(\beta\alpha O)$, while $D_3O^+ \propto P(\beta\beta\beta) + P(\beta\beta\alpha) + P(\beta\alpha\alpha)$. The resulting set of ten equations, excluding those containing

Figure 11: Measured site-specific probabilities of hydronium formation from ethanol dications (adapted from Ref. [26]).

other contributions that cannot be subtracted, is over complete. Therefore, we use a least-squares fit of all the equations to find the best values for these six probabilities. It is important to note that in this approach we neglect any isotopic difference due to deuterium substitution, which is common practice when using deuterium tagging. To verify that this approximation is reasonable in this case, we compared the two-body branching ratios of CH_3CH_2OH and CD_3CD_2OD and found that the differences are typically small (~1–2% for most channels, and less than 10% in the worst case). To estimate the uncertainty of these site-specific probabilities we repeatedly fit (in a Monte-Carlo fashion) a set of branching ratios randomly picked from the normal distribution associated with the measured values and their estimated error.

This method yields robust solutions for the site-specific probabilities of hydronium formation shown in Fig. 11. The dominant three combinations include the hydroxyl group hydrogen, as one may expect. It is surprising, however, that hydronium can be formed by the three hydrogens from the methyl group (i.e., β site). Similar results were obtained for tri-hydrogen, methane, and water ions [26]. Hopefully, these measured site-specific probabilities will lead to advancement of molecular dynamics theory.

Future Plans:
The protocol that we have developed for this project is readily applicable to other molecular systems and to hydrogen migration and bond rearrangement induced by processes other than strong-field ionization. In particular, we plan to apply it to XUV-NIR ion-electron coincidence experiments on alcohol molecules described in Ref. [10]. We are currently exploring other target molecules and pump-probe configurations to which we will extend these studies.

3.4. Native frames: Disentangling sequential and concerted multi-body fragmentation
- Ben-itzhak, Rolles, Rudenko, Esry

Project scope:
We continue to develop the native-frames analysis method [27] and to implement it in studies of multi-body photoinduced fragmentation of polyatomic molecules in order to improve the understanding of concerted and sequential fragmentation dynamics. In particular, we adapt it in
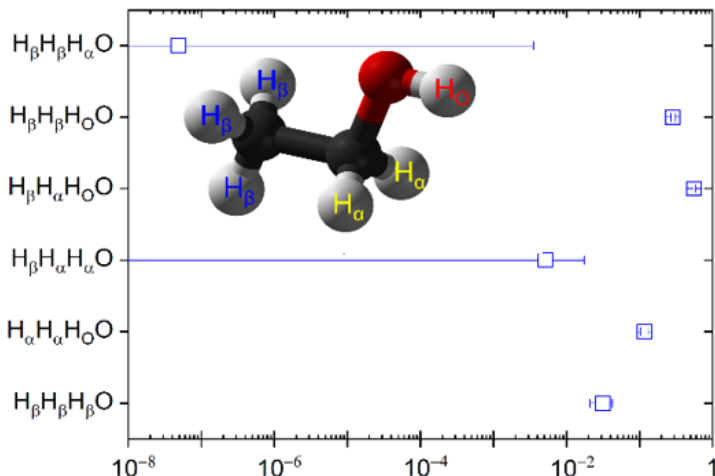
order to facilitate the interpretation of the pump- probe experiments employing multi-body molecular fragmentation as a probe scheme.

Recent progress:

First, we have implemented the native frames method [27,28] to analyze single photon double ionization data of D_2O acquired through our ALS collaboration (collaboration with R. Dörner, T. Jahnke A.L. Landers, D. Slaughter, Th. Weber, J.B. Williams, R.R. Lucchese, C.W. McCurdy, A. Orel, T.N. Rescigno, and others). Specifically, we separated sequential fragmentation of the heavy water dication leading to $D^+ + D^+ + O$ via $OD^+ + D^+$, identified two dissociation pathways involving the $b^1\Sigma^+$ and $a^1\Delta$ states of the intermediate OD^+, and followed their breakup step by step (see Pub. [111]). In a follow up project, we identified the same intermediate OD^+ states in the sequential fragmentation of D_2O^{2+} leading to $D^+ + O^+ + D$ final products. The second fragmentation step in both cases, i.e., the predissociation of the OD^+ intermediate, starts by a $b^1\Sigma^+ \rightarrow A^3\Pi$ (or $a^1\Delta \rightarrow A^3\Pi$) transition driven by spin-orbit coupling. Note that the $A^3\Pi$ state correlates with the $D^+ + O$ dissociation limit, therefore, to reach the $O^+ + D$ products additional transitions are needed. We identified the most likely path in this case to be $A^3\Pi \rightarrow X^3\Sigma^- \rightarrow B^3\Sigma^-$, where the final $B^3\Sigma^-$ state correlates with the $O^+ + D$ dissociation limit. Consequently, the ratio of the number of sequential fragmentation events (for either the $a^1\Delta$ or $b^1\Sigma^+$ intermediate state, $N_{a,b}$) associated with D^+–D^+ or D^+–O^+ coincidence events provides a measure of the $A^3\Pi \rightarrow X^3\Sigma^- \rightarrow B^3\Sigma^-$ transition probability,

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

Second, in our studies of multi-body fragmentation of $CHBr_3$ driven by intense 28-fs laser pulses (see Pub [110] and Ref. [29]), we identified sequential fragmentation of the trication proceeding via $Br^+ + CHBr_2^{2+}$ and followed by $CHBr_2^{2+} \rightarrow Br^+ + CHBr^+$, using native frames analysis [27,28]. In addition to the detailed information revealed for each fragmentation step, we determined that the concerted breakup is predominantly synchronous with a minor contribution of asynchronous-concerted breakup (see Ref. [29]).

Third, in a UV-pump–IR-probe study of CH_2BrI fragmentation we focused on the behavior of the CH_2Br fragment following the C–I bond stretching initiated by the weak UV-pump. The dynamics were probed by a delayed intense IR pulse, which multiply ionized the neutral fragments, while causing additional fragmentation of the CH_2Br (see Ref. [20] for details). Here, we focus on the $I^+ + Br^+ + CH_2^+$ channel and employ native frames analysis [27,28], frame by frame, assuming sequential fragmentation via a CH_2Br intermediate, i.e., treating the pump and probe pulses as the two steps of sequential fragmentation. The yield of these events as a function of pump-probe delay and the angle between the directions of the two "two-body" fragmentation steps, $\theta_{CH2Br,I}$, shown in Fig. 12, exhibits a clear rotation of the intermediate CH_2Br as a function of delay. The suppression near $0°$ ($180°$) is attributed to scattering of the Br^+ (CH_2^+) off the I^+ fragment, respectively.
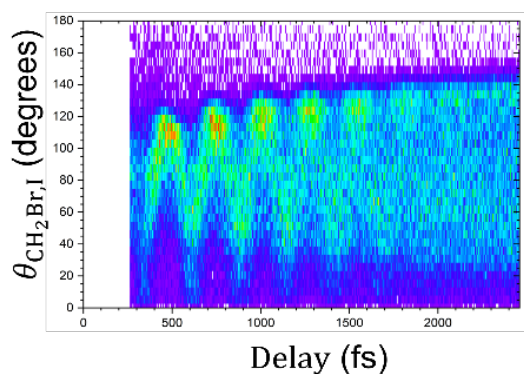
Figure 12: The yield of $I^+ + Br^+ + CHBr^+$ as a function of pump-probe delay and the angle, $\theta_{CH2Br,I}$, between the conjugate momenta (of the Jacobi coordinates) associated with CH_2BrI breakup via a CH_2Br intermediate.

Future plans:

We plan to continue examining the limitations of native frames analysis, for example, deviations from a uniform $N(\theta_{AB,C})$ angular distribution, and exploring other possible signatures of sequential or concerted breakup. In addition, we will extend native frames analysis to four-body breakup following initial studies of formic acid. We will also continue to probe molecular-ion beams, like CD_n^+ (n=2-4) and OD^+, in a strong laser field. In parallel, we will apply this type of analysis to interpret the results obtained with other pump-probe configurations.

4. Ultrafast X-ray science

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

4.1. Resonant effects in multiphoton X-ray ionization and fragmentation of molecules – Rolles, Rudenko

Project Scope

When atoms and molecules are irradiated by intense x-ray pulses, extremely high charge states can be created. At certain x-ray photon energies, electron ejection from atoms can be drastically enhanced by transient resonances created during the sequential ionization process. This project aims to study such resonant effects in ionization of molecules, in particular, focusing on the interplay between transient X-ray resonances and ultrafast intramolecular charge rearrangement.

Recent Progress

X-ray ionization observed in gas-phase high-intensity XFEL experiments is typically dominated by sequential multiphoton absorption and subsequent relaxation processes [30–32]. With sufficiently high photon flux, the highest ion charge state created is usually the last ionic charge state that can be reached before its ionization potential rises above the photon energy. However, if inner-shell electrons can be resonantly excited to high-lying orbitals, even higher charge states can be reached via subsequent autoionization of multiply excited states or by the absorption of an additional x-ray photon [31,33,34,60]. In
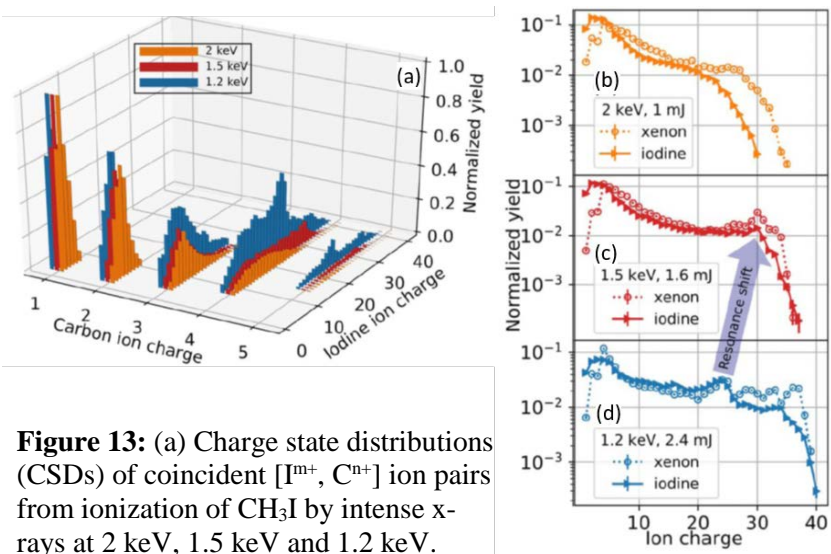
Figure 13: (a) Charge state distributions (CSDs) of coincident $[I^{m+}, C^{n+}]$ ion pairs from ionization of CH_3I by intense x-rays at 2 keV, 1.5 keV and 1.2 keV. (b-d) The CSDs of iodine atoms from CH_3I in comparison with the xenon CSDs at the same three photon energies (from [94]).

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molecules, x-ray ionization is often strongly localized at the atomic sites with the largest photoabsorption cross sections, and is accompanied by subsequent charge redistribution and molecular fragmentation. At ultrahigh intensities, the latter effect can lead to the production of much higher total molecular charge states than expected from the independent-atom model [32]. This is illustrated in Fig. 13 for the ionization of CH_3I molecules in
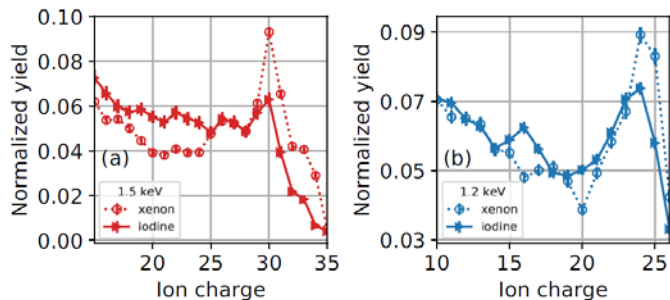
Figure 14: Enlarged view of ion CSDs near the resonant-enhancement regions for (a) 1.5 keV and (b) 1.2 keV (from [94]).

comparison with the isolated Xe atom. At all three photon energies, higher carbon ion charge states are more likely to be detected in coincidence with higher iodine ion (Fig. 13(a)). This correlation is caused by the methyl group being in close vicinity of iodine while the latter is charged up by the ultrashort x-ray pulse, which allows efficient charge redistribution from iodine to the methyl group. Comparing the iodine ion CSDs with the Xe distributions, it is noticeable that the xenon CSD resembles the iodine ion CSDs at 1.5 and 1.2 keV (Fig. 13(c,d)), meaning that the total charge of the CH_3I molecule is much higher than in Xe despite similar absorption cross section. Interestingly, the Xe CSd at 2 keV (Fig. 13(b) extends to higher charge states than for iodine, suggesting that charge-rearrangement-driven molecular enhancement is less efficient at 2 keV than at smaller photon energies, mainly because of the smaller photoabsorption cross section and lower pulse energies used. Despite the general resemblance between iodine ion CSDs from CH_3I molecules and those of xenon in Fig. 13(c,d), molecule-specific features can be discerned at some particular charge states, which are highlighted in Fig. 14. These molecule-specific enhancement regions can be attributed to ultrafast charge rearrangement during the x-ray ionization of molecules.

Future plans:
As a next step, we plan to perform a more quantitative analysis of the interplay between the resonant and charge-rearrangement-driven effects in X-ray ionization of molecules, by comparing our experimental data to the results of the simulations performed by R. Santra's group using the XMOLECULE package [35], which is currently being adapted to include resonance excitations. In parallel, we performed similar experiments on laser-dissociated CH_3I molecules, where we can extract the experimental CSD as a function of the iodine separation from the methyl group and, thus, study a transition between the resonant ionization of molecules and isolated atoms.

4.2. Tracing ultrafast valence and core-hole dynamics by inner-shell ionization – Greenman, Rolles, Rudenko

Project Scope
We study ultrafast charge dynamics migration triggered by valence and inner-shell photoabsorption using both synchrotron radiation and intense ultrashort X-ray pulses produced by XFELs. Here, we combine pump-probe experiment and few-particle coincident experiments performed with just single X-ray photon absorption. To guide and help interpret the experiments, we perform detailed theoretical calculations for some model systems, e,g, for valence ionization of thiophenone. Additionally, we develop the theoretical tools required for an adequate description of the molecular bound and continuum states involved in such processes.

Recent Progress

Nuclear-dynamics-driven charge transfer triggered by UV photoabsorption in PENNA cations

In May 2001, we have performed a UV pump / X-ray probe experiment at LCLS on PENNA molecule, which is often considered as a prototype system for studying intramolecular charge transfer in complex systems. Here, as illustrated in Fig. 15, the two-photon UV ionization at 266 nm populates two lowest excited cationic states, which are strongly localized on one site of the molecule (the benzene ring) because of the intermediate single-photon resonance [36]. This is followed by a significant nuclear rearrangement, which is expected to result in downhill charge transfer towards the amine group on ~60-80 fs time scale [37]. We probe the charge distribution in the created molecular cation by the X-ray driven photoelectron emission from nitrogen 1s shell, detected using a magnetic bottle electron spectrometer. In our preliminary analysis, we observe a delay-dependent few-eV shift of a

Figure 15: Sketch of the UV ionization, charge transfer (CT) dynamics and UV pump – X-ray probe experiment in PENNA.

nitrogen 1s photoline on ~100 fs time scale. While this coarsely agrees with the initial predictions for the change of the photoelecron kinetic energy, further data analysis, including more precise determination of the effect timing, is needed to perform a more detailed comparison with theory.

Modelling valence ionization of thiophenone.

We have been performing calculations on the thiophenone molecule (C_4H_4SO) to attempt to explain the results of recent experiments performed by the Rolles group at the Advanced Light Source. In this experiment, photoelectrons were detected in coincidence with dissociating ionic fragments (see Fig. 16), allowing the electronic states to be determined in combination with theoretical descriptions of the post-ionization breakup.

As a first approximation, we are attempting to identify one- or two-dimensional potential energy curves that can be used to describe these processes. Fragments were selected both by prevalence in the experiment and by position in the photoelectron spectra for further analysis. Then, the simplest path to fragmentation was chosen as the initial path. For instance, to produce the H_2CS^+ fragment, the C-C and C-S bonds

Figure 16: Fragment-ion-resolved photoelectron spectrum of thiophenone after ionization at 23 eV photon energy.

were increased together. The remaining degrees of freedom are optimized. The calculated potential energy curves for the formation of this fragment are shown in Fig. 17.

In some cases, finding an appropriate low-dimensional curve is not straightforward. For instance, in the C_3H_3 and C_3H_4 fragments, multiple questions arise. One issue is that on the fragmentation

path considered, some minima corresponded to ring structures that were clearly not part of the fragmentation path. We currently deal with this by taking the parts of the path that match fragmentation and extrapolating them towards the regions that are ambiguous. This may be done by linear interpolation or by freezing additional coordinates. Other questions such as the nature of additional H dissociations remain to be investigated.

Once a suitable reaction coordinate is found, we proceed to calculate the energies of multiple excited states of

Figure 17: Potential energy curves for the formation of the H_2CS fragment from thiophenone. The breaking bonds are stretched uniformly and all other degrees of freedom are optimized.

the ion using, for example, a SA(6)-CASSCF(10,10) calculation. We will refine these methods in the future. We then compare the binding energies near the Franck-Condon region with the photoelectron spectra. In this manner, we obtain an idea which states likely contribute to a given fragment. The $C_3H_n^+$ fragment, for instance, peaks near 15 eV. This corresponds to two possible states that we calculate that have binding energies near 15 eV and are open to dissociation.

In addition to the above studies on thiophenone, we have continued our work on the attosecond dynamics after double photoionization of N_2. Most recently, we have worked to produce a computer algebra code that determines the necessary matrix elements automatically. We found that this was required because while the fundamental equation is simple and requires matrix elements between doubly-ionized states and singly-ionized states in reality we approximate these with a series of methods. The original method we used replaced all integrals with versions from N atom, so replacing the corresponding integrals in each expression was straightforward. However, we have since developed numerous approximations including using neutral molecular matrix elements in all expressions, and neutral and ionic singly-ionized matrix elements in various parts of the expression depending on which doubly-to-singly ionized matrix element we are replacing. The proliferation of possibilities introduced significant room for error, and so we proceeded to develop the computer algebra code. This development is complete, and we are currently implementing the results back in our calculations of N_2 x-ray–x-ray double photoionization as a function of time delay.

Future plans:
We will continue our participation in the LCLS attosecond campaign, which aims at studying X-ray induced charge migration in real time. In parallel, we will proceed with the detailed analysis of our recent charge transfer experiment on PENNA, including shot-by-shot correlation between the photoelectron spectra and the measured photon spectrum of the LCLS pulse. From the theory side, with the machinery in place to describe the double photoionization of N_2, and the computer algebra program for calculating matrix elements, we will move to other molecules like OCS. We will also explore the use of other observables in both of these molecules for identifying attosecond charge dynamics. Motivated by recent experiments [38], we will consider Auger-Meitner observables. We will also examine ion-electron coincidence observables that may illustrate charge migration.
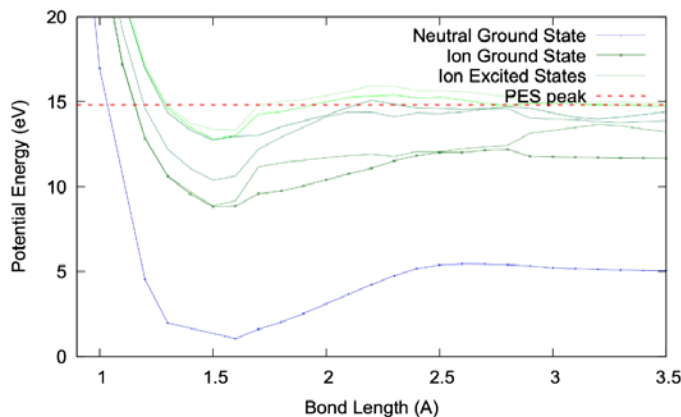
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Atomic, Molecular and Optical Sciences (AMOS) at the Lawrence Berkeley National Laboratory

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Project Scope: The AMOS Program at LBNL seeks to answer fundamental questions in atomic, molecular, and chemical sciences that are central to the mission of the Department of Energy's Office of Science. The Program consists of a variety of closely coupled experimental-theory efforts, united by the overarching goal to provide deep insight into the physics and chemistry of the fundamental interactions that drive key chemical processes in simple molecules, complex molecular systems, and molecules in complex environments. Major areas of emphasis include 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 combinations of laboratory- and facility-scale pulsed XUV and X-ray light sources and electron beams with state-of-the-art experimental techniques. Table-top femtosecond and attosecond XUV and X-ray light sources, X-ray free electron lasers, synchrotron radiation, 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, 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, and Th. Weber

Attosecond Dynamics *(Lucchese, McCurdy, Leone, Neumark)*

The attosecond dynamics subgroup develops new nonlinear spectroscopies that utilize attosecond extreme ultraviolet (as-XUV) pulses, produced by high harmonic generation (HHG) with two non-collinear near-infrared (NIR) pulses, to generate four-wave mixing (FWM) signals. The FWM technique exploits the phase-matching condition to generate spatially isolated emission signals with a noncollinear beam geometry. The transient emission signals encode the evolution of excited states and therefore represent background-free measurements of XUV-induced chemical dynamics. Our as-XUV FWM spectroscopy method disentangles the complex spectral effects of traditional transient absorption spectroscopy and has so far proven its power in several applications such as monitoring the vibronic coherence in H_2 (Cao et al. **2018**, *Phys. Rev. A* 97, 023401), characterizing a previously inaccessible dark state in N_2 (Warrick et al. **2018**, *Faraday Discuss.* 212, 157), and detecting light-induced states in He (Fidler et al. **2020**, *J. Phys. Photonics* 2, 034003). This technique has also enabled direct measurements of ultrafast decay dynamics in the time-domain. The lifetimes of the $^2P_{1/2}$ *ns/d* autoionizing states in Kr (Fidler et al. **2019**, *J. Chem. Phys.* 151, 114305) as well as the few-fs decay lifetimes of the 3s Rydberg states in the ionic c $^4\Sigma_u^-$ state series in O_2 have been measured (Lin et al. **2021**, *Faraday Discuss.* 228, 537). A refined understanding of the signal generation, achieved in collaboration with theorists Mette Gaarde and Kenneth Schafer at Louisiana State University, identifies a time-dependent accumulation of an AC Stark phase grating at play (Fidler et al. **2019**, *Nat. Comm.* 10, 1384). These developments have also inspired the implementation of a variant of as-XUV multidimensional spectroscopy (Marroux, et al. **2018**, *Sci. Adv.* 4, eaau3783).

Recent Progress: Recent work makes use of the enhanced signal specificity of FWM to understand short-lived dynamics in more complicated systems. FWM spectroscopy was applied to study few-fs complex electronic dynamics of atom-like excitations in solids (Gaynor et al. **2021**, *Phys. Rev. B* 103, 245140). Here, the Na^+ $L_{2,3}$ edge (Na $2p\rightarrow3s$) is studied in NaCl crystalline thin films. The core-excitons are bound electron core-hole pairs, which, in this case, are highly localized on the Na^+ ion of NaCl. Employing FWM, we measure many more core-excitons than previously observed, which yield 6-8 fs coherence decays, driven by many-electron correlations. FWM experiments and simulations have also investigated excited electronic wave packets in autoionizing Rydberg states of Ar from $3s\rightarrow np$ excitation (Gaynor et al. **2022**, *in preparation*). Strong coherences with nontrivial dynamics are apparent in the transient FWM signals. Modelling the emissions as an electronic wave packet fits the data well, and we find that the FWM signals emitted from each np state are significantly influenced by the dynamics of the $(n+1)p$ state. Simulating the experimental spectrum by solving the time dependent Schrödinger equation with the calculated transition dipole moments and appropriate NIR pulses confirms this interpretation.

Currently, FWM experiments on isolated polyatomic CO_2 molecules target the lifetimes of autoionizing inner valence excited Rydberg states (Fidler et al. **2022**, *in preparation*). We observe FWM signals from the $n = 5 - 8$ states of the $nd\sigma_g$ character Henning "sharp" Rydberg series, which converges to the ionic B $^2\Sigma_u^+$ threshold. We measure decay times of 38 ± 2 fs, 55 ± 1 fs, 93 ± 3 fs, and 124 ± 4 fs, respectively. Calculations by C. William McCurdy and Robert R. Lucchese in the Berkeley AMOS program (see also Subtask 3) suggest that those values are close to the

lifetimes of the short-lived n = 6 – 9 members of the $ns\sigma_g$ character Henning "diffuse" Rydberg series. The calculated oscillator strengths verify the dominant FWM pathway, and they confirm our experimental observation of probing the lifetimes of the Henning "diffuse" Rydberg series via the emission from the Henning "sharp" Rydberg series. The results represent the first meaningful measurements of ultrafast dynamics in polyatomic systems with the FWM technique.

Recently, we have renovated the laboratory and installed a new high-power laser system, which increased the flux of the XUV pulse, enabling us to push our FWM technique to deeper bound states. We have performed an experiment to measure the dynamics of inner valence electronic excitations in Ne atoms around 45 eV, as shown in Fig. 1-1 (Puskar et al. **2022**, *in preparation*). The XUV pulse excites Ne into its $2s2p^63p$ Rydberg series, and then two broadband NIR pulses couple through the neighboring $2s2p^63s$ or $2s2p^63d$ XUV-dark states to produce FWM signals. By
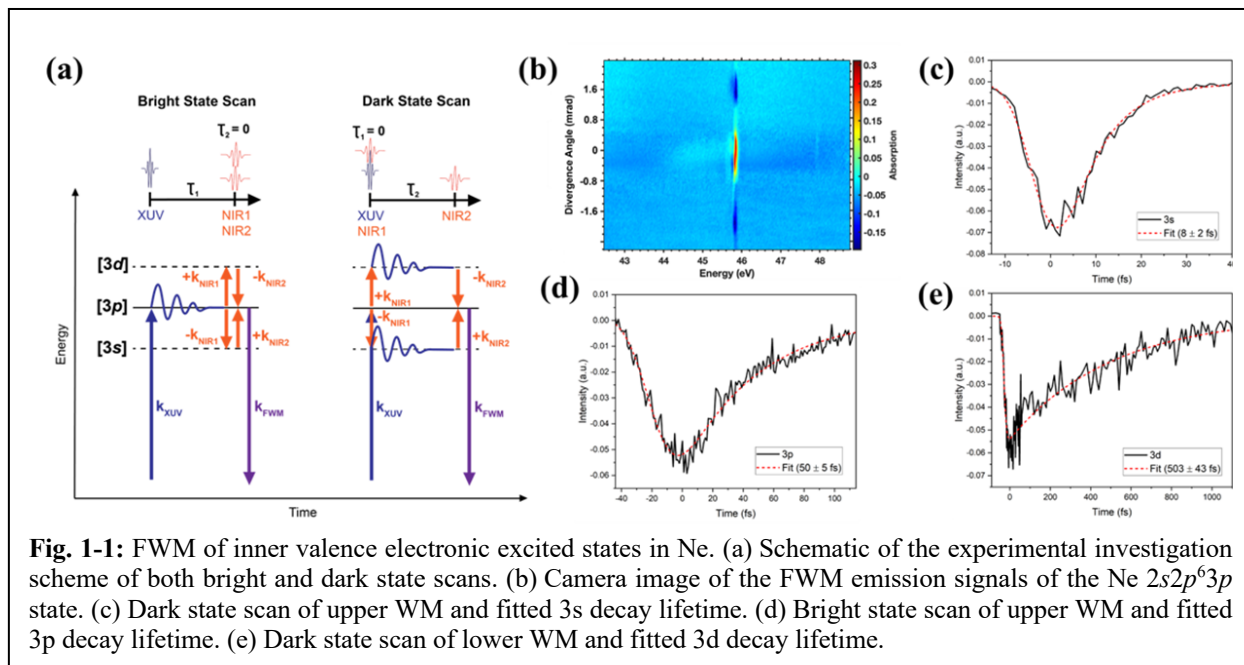
Fig. 1-1: FWM of inner valence electronic excited states in Ne. (a) Schematic of the experimental investigation scheme of both bright and dark state scans. (b) Camera image of the FWM emission signals of the Ne $2s2p^63p$ state. (c) Dark state scan of upper WM and fitted 3s decay lifetime. (d) Bright state scan of upper WM and fitted 3p decay lifetime. (e) Dark state scan of lower WM and fitted 3d decay lifetime.

controlling the pulse sequence of the NIR pulses and their delays, we probe the temporal evolution of both, the dark and bright states, as shown in Fig. 1-1(a). A FWM camera image is shown in Fig. 1-1(b), and the transient behavior of different scan methods are presented in panels (c), (d), and (e). The lifetimes for the 3s, 3p, and 3d states are measured to be 7 ± 3 fs, 48 ± 12 fs, and 427 ± 60 fs, respectively. The experimental results align well with the calculated values of 5 fs, 61 fs, and 571 fs from our collaborator Luca Argenti at the University of Central Florida and support the prediction that the autoionization decay lifetime is directly related to the Coulomb interaction of the hole state, which in this case is a 2s orbital, with the 3s, 3p, and 3d Rydberg states.

Future Plans: We are currently working towards generating XUV pulses with even greater flux above 50 eV to enable FWM measurements of core-excited states. The FWM signals of Xe $4d^{-1}np$ core-excited states around 65 eV have just been observed, and detailed experiments are ongoing. Meanwhile, the production of 400 nm and 266 nm pulses through second and third harmonic generation of the Ti:sapphire 800 nm fundamental laser beam is in preparation. These developments will enable FWM experiments on the $4d^{-1}6p$ core-excited states of iodine-containing molecules, such as ICl. An experiment to probe the non-local Auger decay with I-Cl bond distance dependence can be achieved with an UV-XUV-Vis-Vis pulse sequence and will serve as a benchmark for

future theoretical models. Future incorporation of a broadened 1.3 μm laser pulse output from a high-power optical parametric amplifier will enable attosecond pulses at the carbon K-edge (~300 eV). These developments will provide an incisive picture of the otherwise inaccessible electronic and nuclear motions governing chemical reaction dynamics.

Ultrafast Excited State Dynamics Probed by Multidimensional Momentum Imaging

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

Role of Spin Orbit Coupling and Super Excited States in the Dissociation Dynamics of D_2O^{2+} Fragmenting into $D^+ + O^+ + D$ *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: Triatomic molecules like water exhibit rich dissociation dynamics leading to several reaction channels upon photo double ionization (PDI) with a single photon. In the recent past we successfully investigated the state selective photodissociation of water dications into $D^+ + D^+ + O$ fragments via direct 3-body (Reedy et al. **2018**, *Phys. Rev. A* 98, 053430) and sequential 2-body breakup (Severt et al. **2022**, *Nat. Comm.*, 13, 5146), governed by asymmetric stretch and a range of DOD emission angles at the Advanced Light Source (ALS). Now, we and our collaborator Itzik Ben-Itzhak from KSU turned our attention to the scarce $D^+ + O^+ + D$ production, which plays an important role in multi-photon ionization but contributes with only 0.5% to the PDI yield with a single photon of 61 eV. The heavy water dication is produced either via (a) direct PDI (56% of the $D^+ + O^+ + D$ channel) or (b) via autoionization (44%):

For case (a) the measured particle momenta, angular, and energy distributions of our COLTRIMS experiment at the ALS revealed distinct electronic dication states and their fast sequential dissociation steps via spin-orbit couplings (SOC) for the events that are produced with high kinetic energy release (KER) (66%). The experiment showed how specific geometries and orientations of the deuterated water molecule with respect to the polarization vector enables charge redistribution and electron transfer at intermediate internuclear distances (Iskandar et al. **2022**, *in preparation*). Aided by multi-reference configuration-interaction calculations by Robert Lucchese, William McCurdy, and Thomas Rescigno (see also Subtask 3), the ultrafast time scales for the dissociation dynamics on the potential energy surfaces (PESs) and their conical intersection seams could be deduced. The

events producing low KER (34%) originate either from direct 3-body breakup following symmetric stretch, or a (dominating) slow 2-body breakup requiring SOC and an additional charge transfer (Iskandar et al. **2022**, *separate draft in preparation*). It turns out that for the slow sequential 2-body breakup the $a^1\Delta$ and $b^1\Sigma^+$ states of the transient OD^+ ion play an important role for producing both, the $D^+ + O^+ + D$ as well as the $D^+ + D^+ + O$ reaction products. Via our state-selective measurements and the native frame analysis of the dissociation, we could deduce the branching ratio

for the wave packet on this specific part of the potential energy landscape to produce the different reaction channels from the transient OD^+ fragment (see Fig. 1-2).

For case (b) we identified a super-excited cationic state located above the PDI threshold of D_2O with the autoionizing electron pos-

Fig. 1-2: The measured $D^+ + O^+ + D$ to $D^+ + D^+ + O$ branching ratios for the $OD^+(a^1\Delta)$ state (blue triangles) and the $OD^+(b^1\Sigma^+)$ state (red squares) in the sequential breakup of D_2O^{2+} for the same max $KER(OD^+) \leq 0.25$ eV. The theory values (blue diamonds) for the $OD^+(a^1\Delta)$ state are currently ~ 6 times lower than the experiment (analysis is ongoing).

sessing a fixed energy of about 0.5 eV, which is a signature of atomic oxygen autoionization. Our analysis, guided by simple Coulomb explosion modeling combined with Potential Energy Curves (PECs), extracted from multi-reference configuration interaction calculations of Ann Orel from the University of California Davis and Thomas Rescigno (see also Subtask 3), identified the direct fragmentation process, undergoing symmetric OD stretch with fixed DOD angle (105°), to contribute with 28% to the $D^+ + O^+ + D$ channel and the sequential dissociation to dominate with 72% (Iskandar et al. **2022**, *separate draft in preparation*). From our molecular frame autoionization electron angular distribution and electron scattering calculations we found that the creation of the super-excited radical D_2O^{*+} cation results in a long-lived $O^*(^3P)$ fragment (5 to 25 ps) that can act as a destructive probe, traveling long distances unperturbed before it releases its low energy electron that can initiate secondary dissociation processes.

Future Plans: After we were able to distinguish and compare the formation, rotational excitation, and KER of dissociating transient OD^+ fragments via two pathways in the 3-body breakup of water (Severt et al. **2022**, *Nat. Comm.* 13, 5146), we want to extend our investigations of state selective ionization mechanisms and dissociation dynamics to (I) more complex molecules and (II) van der Waals bound systems. For aspect (I) we choose deuterated methanol CH_3OD as a simple hydrocarbon molecule containing the methyl group; this system is known for ultrafast dynamics such as, e.g., rapid hydrogen migration/elimination (Champenois et al. **2019**, *J. Chem. Phys.* 150, 114301) and CH_3 umbrella excitation. Our first test experiments on the PDI with single 63 eV photons show six 2-body and four 3-body fragmentation channels, which we can distinguish in the electron-ion 3D momentum coincidence measurements. While the latter reaction channels are dominated by direct PDI, we observe remarkable contributions from autoionization for the 2-body channels producing H^+, D^+, HD^+, and H_2D^+. These channels are excellent candidates to track Rutherford scattering in the body-fixed angular distribution of the autoionization electron. Such diffraction patterns enabled us in the past to estimate the internuclear distance at which autoionization took place and, hence, deduce the decay time (Sann et al. **2011**, *Phys. Rev. Lett.* 106, 133001). Further data taking is necessary to yield MFPADs with statistical significance.
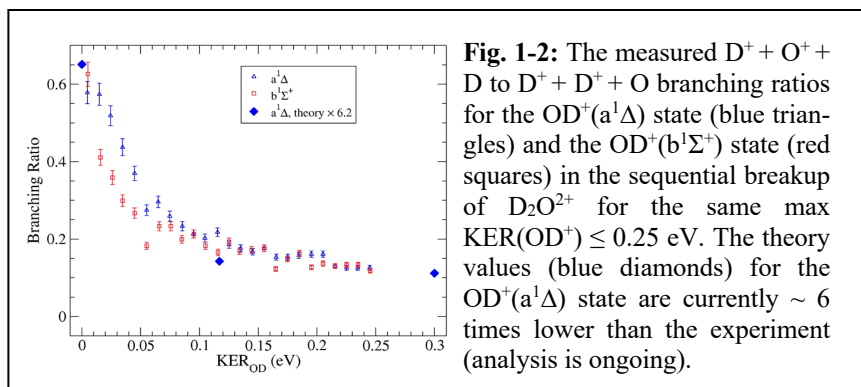
For aspect (II) the competition of ionization mechanisms will be investigated in water dimers. While ICD has proven to be a prominent ionization mechanism, direct PDI and autoionization cannot be neglected. This became apparent in first test measurements with single photons at 60 eV in which we isolated two new 3-body breakup channels, i.e. $D_2O^+ + D^+ + OD^*$ and $D_2O^+ + D^* + OD^+$ that are not discussed in the literature. These two channels may originate from single ionization via a Zundel type intermediate ($D_2O—D^+—OD^*$), and investigating the fragmentation channel $D_2O^+ + D^+ + OD$ might provide direct access to the geometry of the dimer. Further analysis and data taking in collaboration with the workgroup of Thomas Orlando from Georgia Tech. will be necessary to shine more light on these new reaction channels and their dissociation pathways.

Inner-Shell-Ionization-Induced Femtosecond Structural Dynamics of Water Molecules Imaged at an X-ray Free-Electron Laser *(Weber)*

Recent Progress: Recently we successfully investigated the charge-up dynamics of oxygen molecules upon two X-ray absorption within a single intense light pulse from the European XFEL (EuXFEL). Detecting electron and ions in coincidence, we did set up an internal clock, which was based on a simple Coulomb explosion model using Newtonian equations of motion. This approach enabled us to trace the evolution of the Molecular Frame 2nd Photoelectron Angular Distributions (MF2ndPADs) as a function of KER in the quadruple ionization of O_2 (Kastirke et al. **2020**, *Phys. Rev. Lett.* 125, 163201) and follow the Coulomb explosion of the molecular ion in the quintuply ionized molecule as a function of internuclear distance and real-time (Kastirke et al. **2022**, *Phys. Chem. Chem. Phys.*, accepted). In collaboration with the Frankfurt group (T. Jahnke & R. Dörner) DOE BES-AMOS PIs from KSU and LBNL (D. Rolles, A. Rudenko, Th. Weber) and others, we now extended the studies to the more complex water molecule. Focusing solely on the nuclear dynamics, we demonstrated that, on a timescale of a few femtoseconds after core ionization and subsequent Auger decay, water undergoes structural deformation such as asymmetric O-H bond stretching and/or opening of the bond angle all the way up to 180 degrees, eventually leading to rapid 2-body or 3-body fragmentation in asymmetric and/or unbent geometries (Jahnke et al. **2021**, *Phys. Rev. X* 11, 041044). The evolution in time of the unbending and asymmetry parameters is reported in Fig. 1-3. Based on our simulation (red and blue dots), panel (a) shows the relation of

Fig. 1-3: (a) KER as a function of time between the 1st and 2nd photoionization (measurements: yellow stars). (PAPA: blue) and (PPAA: red) sequences, are marked in different colors (simulation). (b) and (c) show the fraction of coincidence events with large angle (b) and large relative asymmetry (c) in the proton momenta as a function of KER for the data from both experiment and simulation with good agreement.

the KER as a function of time between the photoabsorption steps (yellow stars). While most of the events correspond to a photoionization-Auger photoionization-Auger sequence (PAPA simulation: blue), a small fraction can be related to the alternative photoionization-photoionization-Auger-Auger succession (PPAA simulation: red); the latter corresponds to a particularly short time delay between the two photoabsorption events. Combining panels (a) – (c), lower asymmetry and lower angles, related to higher KER, can, in turn, be connected to shorter times between the X-ray ab-

sorption events. In this way, the increase of bond asymmetry and bond angle is imaged as a function of delay, and snapshots of the dissociating molecular dication are obtained in real-time.

Future Plans: Building on our recent success investigating the charge up dynamics of H_2O at the EuXFEL, we aim to *study and control the role of coupled electron-ion motion* in the multiple ionization of water by exciting several vibrational modes with a NIR pulse. This will link the quantum mechanical Wigner distribution of the molecule to a probability distribution in phase space that is represented by a new observable, i.e., the molecular frame electron-emission ratio map, which we have established in our experiments on O_2 (Kastirke et al. **2022**, *Phys. Chem. Chem. Phys.*, accepted). There, the backward-forward emission-ratios of the electrons with respect to the produced O^{3+} and O^{2+} ions in the PA-MF(2nd)PADs clearly illustrated the influence of the molecular stretch mode, because the electron emission pattern strongly depended on the multiple scattering process of the outgoing electron waves for each internuclear distance R; they showed an oscillatory trend with respect to the measured KER of O_2^{5+}. In a triatomic system like water, the required new observable will be represented by the oscillating photoelectron-flux ratio plotted as yield in a nuclear conformation map. This structure map is spanned by the measured HOH breakup angle $\alpha(H,O,H)$, representing the bent, and the kinetic energy difference between the protons $\Delta E(H,H)$, constituting the (a)symmetric stretch mode. The $O^+ + H^+ + H^+$ and $O^{2+} + H^+ + H$ breakup channels will be compared to distinguish between vibrations of the neutral water molecule and the dissociating transient dication.

Near-Resonant One-Color Two-Photon Single Valence Ionization of O_2 *(Lucchese, McCurdy, Rescigno, Slaughter, Weber)*

Recent Progress: Conical intersections for triatomic and larger molecules as well as avoided crossings (ACs) in diatomics are the locus on the PESs where the Born-Oppenheimer approximation fails and coupling between electronic and nuclear motion becomes important, allowing non-adia-batic processes, which are common in photochemistry, to take place. Studying transitions through such molecular funnels via de-excitation or excitation is thus important for understanding reaction mechanisms and dynamics. In our experiment, which is similar to our previous investigation on N_2 (Larsen et al. **2020**, *Phys. Rev. A* 102, 063118), we studied the transition through an AC by investigating energy- and angle-resolved near-Resonant One-color Two-Photon Single Ionization (near-ROTPSI) of molecular oxygen using 3-D momentum imaging. Using a 400 nm driving field, we produced femtosecond VUV pulses with an energy of 9.3 eV via High Harmonic Generation (HHG) and spectral filtering. These high-intensity VUV pulses are used to excite molecular oxygen in the first step and singly ionize it in the second step. The experiment is sensitive to the
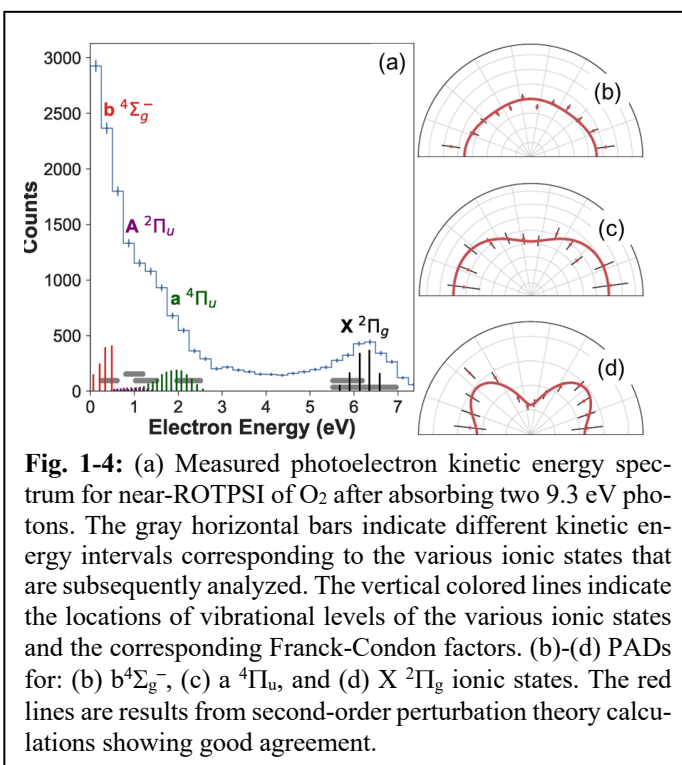
Fig. 1-4: (a) Measured photoelectron kinetic energy spectrum for near-ROTPSI of O_2 after absorbing two 9.3 eV photons. The gray horizontal bars indicate different kinetic energy intervals corresponding to the various ionic states that are subsequently analyzed. The vertical colored lines indicate the locations of vibrational levels of the various ionic states and the corresponding Franck-Condon factors. (b)-(d) PADs for: (b) $b^4\Sigma_g^-$, (c) a $^4\Pi_u$, and (d) X $^2\Pi_g$ ionic states. The red lines are results from second-order perturbation theory calculations showing good agreement.

strong dependence of the electronic transition amplitudes on the internuclear distance at an AC. We found that a superposition of the $B^3\Sigma_u^-$ and $E^3\Sigma_u^-$ electronic states was generated in the first photoabsorption step. The contribution from each component of this superposition varied with the internuclear separation in a way that creates always a valence-character wavepacket. The photoelectron kinetic energy spectrum for electrons measured in coincidence with the O_2^+ cation is shown in Fig. 1-4(a). The measured (solid circles with error bars) and calculated (red lines) photoelectron angular emission patterns (PADs) for select ionic states are presented in panels (b), (c), and (d). They are in very good agreement, which is surprising as the 2nd-order time-independent perturbation theory calculations of Robert Lucchese and William McCurdy solely employ the fixed equilibrium internuclear distance of R = 2.3 Bohr. This could be a result of the short duration of the pulse where there is sufficient intensity to drive two-photon ionization and/or the details of the AC formed by the superposition of the $B^3\Sigma_u^-$ and $E^3\Sigma_u^-$ states. The investigation is ongoing.

Future Plans: We are in the process of installing a new Yb-fiber based laser system capable of producing 100 W, 600 fs, 1030 nm light pulses at 55 kHz repetition rate that will be compressed by a combination of a hollow core fiber and a chirped mirror array to around 30 fs. A sum-frequency-generation setup is under construction to produce high harmonics in a gas cell. We aim to generate enough intensity to absorb two VUV photons (2×12 eV or $7.2 + 12$ eV) in molecular gas jet targets (O_2, CO, N_2O, and NO_2) and study state selective ROTPSI and near-ROTPSI dissociation processes with our electron-ion coincidence 3D momentum imaging setup. Time resolved MFPADs will be used to investigate dissociation dynamics after excitation of Rydberg and (dark) valence states.

Investigations of Dynamics in Transient Anions Formed by Electron Attachment

Transient anions formed by electron attachment to polyatomic molecules can exhibit highly-coupled electronic and nuclear motion, which is often rooted in conical intersections between metastable electronic states. Dissociative Electron Attachment (DEA) is an electron-molecule reaction in which free electron energy is efficiently converted into nuclear degrees of freedom such as dissociation and vibrational excitation. The flow of energy and charge within the molecular anion provides rich information on fundamental chemistry beyond the Born-Oppenheimer approximation and has relevance to applications involving reactive anionic and radical species that are often produced by dissociation. We recently investigated the possible role of Feshbach and shape resonances in the breaking of a model peptide bond (Panelli et al., **2021**, *Phys. Rev. R*, 3, 013082) and the simplest organic acid (Griffin et al. **2020**, *J. of Phys.: Conf. Series*, 1412; Slaughter et al. **2020**, *Phys. Chem. Chem. Phys.*, 22, 13893-13902) by electrons with low energy near, and even below, the lowest electronic transitions in formamide and formic acid, respectively.

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

Recent Progress: We are investigating the effect of chemical substitutions on the DEA dynamics in these model systems. The goal is to understand the fundamental mechanisms that allow substitutions to enhance or suppress DEA. Our anion fragment momentum imaging experiments and *ab initio* electron scattering theory allow access to the body-fixed frame of the molecule, providing detailed information on the resonance symmetries, electronic structure, and dissociation dynamics. This is initially achieved within the axial recoil approximation, where we assume the dissociation axis does not rotate. In acetic acid (CH_3COOH), we focus on the sharp electron attachment resonance peaked at 6.7 eV, which breaks only the O-H bond to produce a hydride anion H^- and an acetoxyl radical CH_3COO^*. In Fig. 1-5 we compare the measured angular distribution for this
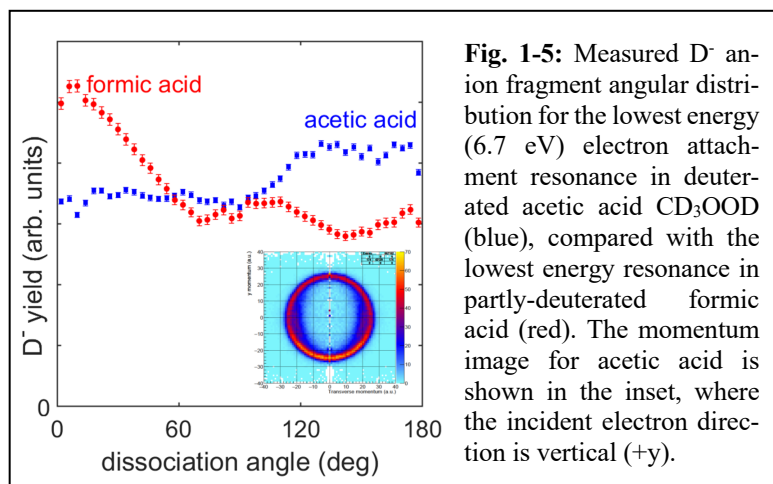
Fig. 1-5: Measured D⁻ anion fragment angular distribution for the lowest energy (6.7 eV) electron attachment resonance in deuterated acetic acid CD₃OOD (blue), compared with the lowest energy resonance in partly-deuterated formic acid (red). The momentum image for acetic acid is shown in the inset, where the incident electron direction is vertical (+y).

resonance in fully-deuterated acetic acid (CD₃OOD) with the corresponding resonance in partly-deuterated formic acid (HCOOD). The latter has been deuterated at the hydroxyl site only, which enables us to isolate the relevant O-D dissociation for the comparison. In fully-deuterated acetic acid (CD₃COOD) we observe the dissociation of D⁻ to mainly occur in directions > 90°, opposing the incident electron momentum. This contrasts with partly-deuterated formic acid, which dissociates mainly in the same direction as the electron beam, consistent with the calculated maximum probability for electrons attaching to the molecules oriented with the O-H direction parallel to the incident electron (Panelli et al. **2021**, *Phys. Rev. R*, 3, 013082). This work is performed in collaboration with Martin Centurion from the University of Nebraska, Lincoln.

Future Plans: The analysis of the 6.7 eV resonance in acetic acid, as well as two nearby resonances at higher electron attachment energy, is ongoing. The measured D⁻ fragment angular distribution (Fig. 1-5) indicates that the probability for electron attachment is highest when the incident electron direction is parallel to the O-D bond. As this is also in the plane of the molecule, the experiments strongly suggest that the lowest resonance has A′ symmetry. Thus, the experiments will guide electronic structure investigations and electron scattering calculations to be performed in Subtask 3 by Robert Lucchese and William McCurdy in the future. Additional experiments are in progress to gain a more complete picture of the enhancement or suppression of DEA by methyl substitutions. For example, N-methylformamide has CH₃ in place of one of the two hydrogens bound to the nitrogen atom in formamide, and this replacement is reported to suppress the cross section for C-N bond fission, while decreasing the energetic thresholds for some other dissociation channels. We will investigate the DEA dynamics of this model system experimentally and theoretically with the high detail offered by momentum imaging and electron scattering calculations. Since formamide is one of the simplest organic molecules containing a C-N bond, this could reveal the fundamental mechanisms of protection and sensitization to ionizing radiation in more complex systems.

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

O. Gessner, M. Head-Gordon, S. R. Leone, D. M. Neumark, J. Qian (contributor), D. S. Slaughter, Th. Weber

Ultrafast Core-to-Valence Transient Absorption Spectroscopy

Femtosecond time-resolved transient XUV absorption (TXA) spectroscopy and X-ray transient absorption spectroscopy (XTAS) are employed to study excited-state molecular dynamics from

local, atomic perspectives, provided by inner-shell transitions. A combination of high-order harmonic generation (HHG) based experiments with high-level *ab initio* electronic structure and molecular dynamics (MD) calculations provides novel insight into photoinduced molecular transformations.

Monitoring Dissociation of CCl_4^+ by Transient X-ray Spectroscopy *(Head-Gordon, Leone, Neumark)*

Recent Progress: Theoretical calculations (Head-Gordon, under AMOS support), and XTAS experiments (Leone, Neumark, under separate GPCP support) have been used to study CCl_4^+ prepared by 800 nm strong-field ionization (Ross et al. **2022**, *Chem. Sci.* 13, 9310). The XTAS experiments and calculations simultaneously probe atoms at the carbon K-edge (280–300 eV) and chlorine L-edge (195–220 eV). Comparison of experiment to X-ray spectra computed by orbital-optimized density functional theory (OO-DFT) (Hait et al. **2021**, *J. Phys. Chem. Lett.* 12, 4517), indicates that after ionization, CCl_4^+ undergoes symmetry breaking driven by Jahn–Teller distortion away from the initial tetrahedral structure (T_d) within ~6 fs (see Fig. 2-1) to an ensemble of symmetry-broken covalently bonded structures, where all four Cl atoms remain covalently bonded to C. All these bonded forms can be viewed as vibrationally excited C_{2v} CCl_4^+, as this geometry is predicted by theory to be the only stationary point on the cation potential energy surface with four C–Cl covalent bonds. The resultant symmetry-broken covalently bonded form subsequently separates to a noncovalently bound complex between CCl_3^+ and Cl over ~90 fs, as predicted by our calculations, and consistent with experimental observations. As an illustration of how well the OO-DFT calculations (see Subtask 3 for discussion of the method) can associate different intermediates along the photodissociation pathway with XTAS spectra at different times, Fig. 2-2 illustrates calculated and

Fig. 2-1: The sequence of intermediates and appearance times involved in the photodissociation of CCl_4^+ identified by comparing OO-DFT calculations (on individual species) with experimental XTAS observations (as a function of time). See Fig. 2-2 for example comparisons.

Fig. 2-2: Examples of comparisons between computations on intermediates and experimental measurements (green and blue traces), as well as the neutral parent (black trace) showing the basis for assigning the time-resolved features.

observed carbon K-edge spectra associated with the parent CCl_4^+ ion, the symmetry-broken form of CCl_4^+, and the non-covalently bound complex. The results for Jahn–Teller distortion to the symmetry-broken form of CCl_4^+ and formation of the Cl–CCl_3^+ complex characterize previously
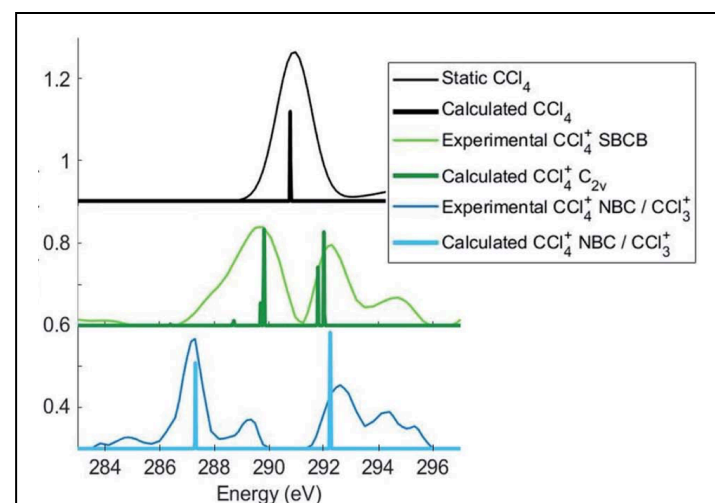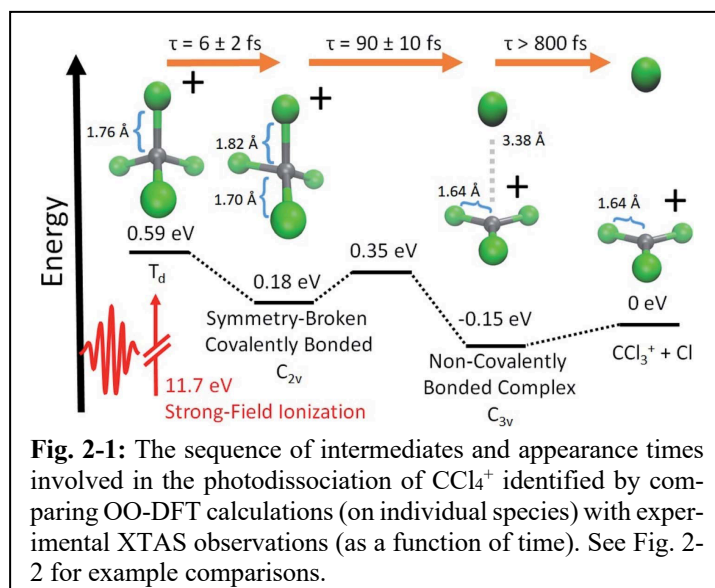
unobserved new species along the route to dissociation.

Future Plans: The excellent agreement between simulations and experiments suggests that a range of other experiments where assignments are potentially ambiguous based on experiments alone can benefit from computations using the OO-DFT approach (see Subtask 3 for further discussion of the theoretical developments and plans). Several more such collaborations are underway between Head-Gordon and Gessner (2-iodothiophene, see below), and Head-Gordon and Leone and Neumark (pentamethyl cyclopentadiene, hexafluoroacetyl acetone, CO_2, and butadiene).

UV-Induced Excitations and Relaxation Dynamics in 2-iodothiophene *(Gessner, Head-Gordon, Leone, Neumark)*

Recent Progress: UV-excited aryl-halides are prominent model systems for fundamental studies of isomerization, ring-opening, and dissociation dynamics in moderately complex molecules. We perform a combined experiment-theory study of 268 nm induced dynamics in 2-iodothiophene (C_4H_3IS). Femtosecond TXA measurements are complemented by density functional theory, time-dependent density functional theory, and restricted open-shell Kohn-Sham (ROKS) calculations, as well as quasiclassical trajectory simulations (also see Subtask 3). In particular, UV-induced excitation and relaxation pathways toward possible ring-opening and/or dissociation to form atomic iodine fragments are probed in detail. The combination of transient inner-shell absorption spectra recorded at the iodine $N_{4,5}$ (4d) edge (~50 eV), calculated oscillator strengths and transition energies of valence and inner-shell excitations, and MD simulations provides a comprehensive picture of the competition between $\pi\pi^*$, $n\sigma^*$ and $\pi\sigma^*$ excitations, as well as ensuing coupled electronic-nuclear relaxation dynamics on multiple electronic surfaces. A manuscript describing the findings is in an advanced stage of preparation.

Future Plans: An advanced HHG setup is currently assembled, consisting of a combination of a high-power optical parametric amplifier (OPA) and a high-pressure HHG cell. The new light source will extend the range of laboratory based TXA studies to the sulfur $L_{2,3}$ (2p) and, ultimately, carbon K (1s) edges, enabling significantly more detailed studies of ultrafast dynamics in thioaromatic molecules.

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

The photochemistry of halogen-containing molecules has significant implications for polar ozone depletion, with bromoform being a major contributor. Complementing a previous TXA study on the UV-induced photodissociation dynamics of bromoform (Toulson et al. **2019**, Struct. Dyn. 6, 054304), a mega-electron-volt ultrafast electron diffraction (MeV-UED) study is performed to probe chemical dynamics in bromoform following 268 nm excitation on femtosecond to picosecond timescales. The main reaction channel is dissociation into a bromine atom and a $CHBr_2$ fragment, for which 2 different mechanisms have been proposed. One is the direct dissociation through an approximately C_s symmetric trajectory and the other is a roaming-like dissociation where $CHBr_3$ isomerizes into an intermediate BrHCBr–Br species.

Recent Progress: Significant progress has been made in the analysis of the UED data. In particular, imperfections of the experiment were analyzed in great detail and corrected, partly on a shot-to-shot basis. These include time-dependent drifts of the pump-probe overlap and an improved diffraction center finding algorithm to correct for variations in electron beam pointing. Additionally, analysis and correction of detector anisotropies and suppression of noise from a variety of sources reveals chemical dynamics at an excitation ratio of only 0.3%, more than an order of magnitude below characteristic values of previous UED studies. Crucially, the improved data analysis enables

Fig. 2-3: False color plot of the time-dependent difference pair distribution function during the UV induced photodissociation of bromoform. The two blue features centered at 1.9 Å and 3.2 Å are due to the depletion of the ground state C-Br and Br-Br distance pairs, respectively. The emerging feature centered at 4.5 Å gives insight into the trajectory of the fragment bromine atom as it departs from the molecule.

a faithful transformation from momentum space to real space, as illustrated in Fig. 2-3. It shows the photoinduced difference pair distribution function (ΔPDF) as a function of the time delay between the UV pump pulse and the UED probe pulse from -0.6 ps to +1.1 ps. Blue and red features indicate loss and gain of signal, respectively, relative to ground state bromoform. The plot shows a depletion of the two distinct major atomic pair distances in bromoform, the C-Br bond at 1.9 Å and the Br-Br distance at 3.2 Å. Signal loss at these distances indicates the C–Br bond cleavage associated with UV excitation. The emergence of new signals around 4.5 Å is tentatively ascribed to predominant Br–Br distances associated with the trajectories of the departing bromine atom. The longevity of this feature and the extended bond distances could support a roaming-like dissociation pathway. Interestingly, such a pathway was not detected in the previous TXA study but suggested by earlier calculations.

Future Plans: We will resolve possible bromoform dissociation mechanisms in more detail by applying a structural fit to the experimental data and by complementing the experimental findings with further *ab initio* theory calculations. The complementary findings of the TXA and UED studies on the same molecular relaxation pathway strongly indicate that the combination of both techniques enables a much deeper insight into the involved chemical dynamics. Going forward, we will continue to pursue this route of complementary ultrafast XUV spectroscopy and electron imaging studies to gain more comprehensive understanding of photochemical transformations.

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

In this effort, synchrotron and XFEL based time-resolved X-ray photoelectron spectroscopy (TRXPS) and time-correlation X-ray photoelectron spectroscopy (TCXPS) techniques are developed and employed to interrogate interfacial electronic and chemical dynamics. A particular focus is to identify critical, short-lived intermediate configurations that affect photon-to-current or photon-to-fuel conversion efficiencies in heterogeneous solar light harvesting systems.

Multi-Step Charge Transfer and Spatial Confinement of Injected Electrons at Molecule-Semiconductor Interfaces *(Gessner, Qian)*

Recent Progress: Hybrid interfaces have emerged as ubiquitous model systems for their potential in addressing activity and selectivity challenges in solar light harvesting systems. However, exploiting the full potential of these hybrid interfaces, and identifying their performance bottlenecks require a molecular-scale understanding of the complex lifecycle of photo-generated charge carriers. A picosecond TRXPS study performed at the Advanced Light Source (ALS) provides such a molecular-level perspective of the transient electronic configurations during photo-induced charge

Fig. 2-4: Picosecond time-resolved X-ray photoemission spectroscopy provides real-time electron distributions of donors and acceptors in a prototypical bipyridyl-ZnO hybrid light harvesting system (Neppl, Mahl et al. **2021**, *J. Phys. Chem. Lett.* 12, 11951).
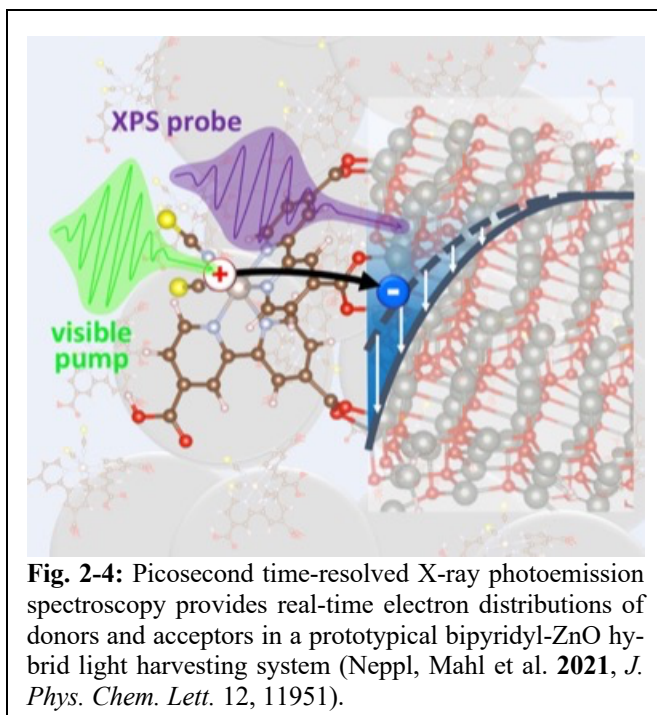
injection in a hybrid model system consisting of a nanostructured ZnO substrate sensitized with N3 polypyridine chromophores. A multi-step, optical photo-injection process involving a short-lived intermediate interfacial charge-transfer (ICT) configuration is revealed, followed by confinement of the injected electrons within a distance of less than 6 nm from the molecule-semiconductor interface (Fig. 2-4, Neppl, Mahl et al. **2021**, *J. Phys. Chem. Lett.* 12, 11951). The strong confinement is the result of a previously overlooked, pronounced downward band-bending inside the semiconductor toward the interface (Mahl et al. **2021**, *ACS Appl. Nano Mater.* 4, 12213), which is further enhanced by the electron injection. This self-trapping-like mechanism forces injected electrons to remain localized in the defect-rich surface region, reducing the chances for successful charge extraction, which likely contributes to well-known challenges of using ZnO as electrode material in solar light harvesting applications.

Photoinduced Interfacial Electron Dynamics in Pure and Oxidized Silicon *(Gessner)*

Recent Progress: Crystalline silicon is the by far dominant material for photovoltaic energy conversion and a key ingredient for optoelectronic devices. Correspondingly, it is one of the most intensely studied model systems for the interaction of matter with light, sometimes leading to the conclusion that "everything is known" about the photoresponse of this material. We have performed a comprehensive picosecond TRXPS study of photoinduced electronic dynamics in the surface regions of pure and oxidized Si(100) as a function of doping concentration, illumination fluence, and character of the majority carriers. A surprising inversion of the ultrafast surface photovoltage (SPV) response is observed for some p-doping concentrations at high fluences that cannot be explained by conventional SPV models and that may point to a previously neglected competition between surface and bulk excitations. A manuscript describing the findings has recently been submitted (Roth et al. **2022**, *submitted*).

Future Plans: A major focus is the extension of TRXPS efforts at the ALS into the near-ambient pressure regime, with the long-term goal to transition toward real-time probing of interfacial chemistry. Preliminary test experiments with nanoplasmonic light harvesting systems consisting of gold nanoparticles deposited on nanoporous TiO_2 substrates indicate a significant impact of a water atmosphere on the interfacial electronic dynamics. A multi-pronged experiment-theory approach is applied in collaboration with the groups of Jin Qian (LBNL) and Tod Pascal (UCSD) to elucidate the underlying fundamental mechanisms (also see Subtask 3). Together with our international collaborators, we compete for beamtime at the FLASH Free Electron Laser in Hamburg with a number of proposed experiments that will complement the ALS based studies on model light harvesting systems with TRXPS enabled insight into photoinduced charge generation mechanisms on femtosecond timescales.

Dynamics in Helium Nanodroplets

In this effort, ground and excited state dynamics in helium nanodroplets are studied by ultrafast spectroscopy and imaging techniques. XFEL based coherent X-ray scattering and diffractive imaging techniques, as well as laboratory/HHG-based spectroscopy techniques are used to explore dynamic phenomena emerging from the collective response of up to ~10^{10} helium atoms. Topics of interest range from fundamental quantum mechanical dynamics in isolated, neutral bosonic and fermionic helium droplets, to coupled electronic-nuclear dynamics in XUV-excited and highly ionized systems including optically and X-ray induced nanoplasmas.

Time-Resolved Studies of ICD in Dense Media *(Gessner, Neumark)*

Recent Progress: Ultrafast resonant interatomic Coulombic decay (ICD) in He nanodroplets is studied via ultrafast photoelectron spectroscopy, using a custom HHG light source. In conventional ICD, the energy released during relaxation of an excited atom or ion is transferred to a neighboring atom that is ionized. In helium droplets, another collective ionization mechanism has previously been observed at XFELs, whereby multiple photons with energies below the droplet ionization potential are absorbed by multiple atoms, followed by ionization via ICD-enabled energy transfer between excited atoms. A dedicated HHG source was developed to target the droplet 2p band, enabling femtosecond time-resolved studies of ICD near the intensity threshold for multiphoton absorption. Fig. 2-5 shows photoelectron spectra in different kinetic energy regions as a function of the time delay between the 21.6 eV (57.4 nm) pump pulse and a 3.1 eV (402 nm) probe pulse. At negative time delays, only the fast ICD signal (top panel) is present. However, near zero delay and at small positive delays, the ICD signal is notably suppressed. Depletion and recovery of the ICD channel are complemented by the emergence and decay of a slow photo-emission signal below ~0.2 eV kinetic energy (bottom panel). Complementary ion

Fig. 2-5: He droplet photoelectron spectra as a function of XUV-pump/UV-probe time delay. The top panel is centered around the ICD feature and the bottom panel is zoomed in on the low kinetic energy signal produced by the probe pulse.

yield measurements have been performed for a variety of XUV fluences and droplet sizes. Model calculations are underway to interpret the experimental results in terms of the efficiency of ICD in the previously unexplored threshold region for multiphoton absorption and to explore the relationship between the density of excited atoms and the efficiency of ICD.

Anisotropic Nanoplasma Dynamics Revealed in Real-Time *(Gessner, Neumark)*

Recent Progress: A femtosecond time-resolved X-ray coherent diffractive imaging study of strong-field NIR laser induced nanoplasma dynamics in ~600 nm diameter He droplets was conducted at the LCLS XFEL. Single-pulse X-ray scattering patterns and coincident ion time-of-flight (TOF) spectra confirm a theoretically predicted anisotropic surface expansion, and reveal an unexpected, anisotropic plasma depletion process that continues across timescales up to ~3 orders of magnitude beyond the laser-droplet interaction time (Bacellar et al. **2022**, *Phys. Rev. Lett.* 129, 073201).

An Experimental Model System for the Thomson Problem *(Gessner)*

Recent Progress: The challenge to find the configuration of *N* unit charges on a sphere that minimizes the overall Coulombic energy was formulated by J.J. Thomson in 1904 but has so far only been studied via numerical simulations. We conducted an ultrafast X-ray coherent diffractive imaging (CDI) study of neutral and highly charged, superfluid He nanodroplets, using the Small Quantum Systems (SQS) instrument of the European XFEL (EuXFEL). The results demonstrate that droplets up to a few hundred nanometers in diameter can be used as experimental realizations of Thomson's problem with up to ~1000 charges. They also confirm that atomic dopants may be used as contrast agents to trace charge locations within extended, nanoscale droplets by femtosecond X-ray CDI (Feinberg et al. **2022**, *Phys. Rev. Res.* 4, L022063).

Aggregation of Solutes in Bosonic Versus Fermionic Quantum Fluids *(Gessner)*

Recent Progress: In this project, comparative ultrafast X-ray CDI studies on Xe-doped ^{3}He and ^{4}He droplets are performed at the LCLS. The results provide unequivocal proof that the unavoidable rotational excitation of both ^{3}He and ^{4}He nanodroplets in vacuum beam experiments leads to highly non-uniform dopant distributions. The findings are in stark contrast to the well-established paradigm that, in particular, ^{4}He droplets provide a perfectly homogeneous, cryogenic matrix for the study of dopant atoms and molecules, which were believed to move throughout the host droplet unhindered and stochastically. Moreover, the study demonstrates that the mere change of spin statistics, which has no impact on any property of ordinary solvents at higher temperatures, leads to entirely different dopant distributions in ^{3}He and ^{4}He host matrices. In contrast to the quantum vortex patterns observed in ^{4}He droplets, dopants in ^{3}He droplets form ring-shaped patterns that would be expected for impurities in classical rotating droplets subject to centrifugal forces (Feinberg et al. **2021**, *Sci. Adv.* 7, eabk2247).

Future Plans: A EuXFEL proposal for an ultrafast X-ray CDI study of extreme control of plasma seeding by single charge doping of He nanodroplets has received very favorable reviews but was not awarded beamtime due to operational constraints. A second attempt has been made toward an experimental campaign in 2023. The laboratory-based ultrafast spectroscopy efforts on He nanodroplets will be discontinued after finalizing the ICD study due to budgetary constraints.

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

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

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

Recent Progress: X-UTPS is an XUV extension of UTPS, which we recently demonstrated using near infrared (NIR) pulses (Thurston et al. **2020**, *J Phys Chem A*, 124, 2573). A new experimental setup has been designed, and the installation is progressing with a new vacuum chamber acquired and undergoing alignment, to enable 3 pulses to be spatially separated and independently controlled after high harmonics generation (HHG). We already produce XUV by HHG using a long 6 m focus of intense (15 mJ) ultrashort (40 fs) NIR (780 nm) pulses at a repetition rate of 1 kHz. A new grazing-incidence XUV-reflective NIR-transparent beamsplitter has been procured and installed, enabling the separation of the initially colinear NIR and XUV pulses in vacuum. After this separation, a waveplate and polarizer control the NIR intensity and polarization. The XUV and NIR beams are focused using curved split mirrors on an existing optical delay stage into a continuous-flow windowless gas cell. A new reflective XUV polarizer (calculated extinction ratio 750:1 and transmission 5%, at 88 nm), and a new XUV spectrometer, employing a variable line spaced grating in reflection geometry, have been designed, procured, and their installation is in progress. To effectively read out X-UTPS signals from the XUV spectrometer, we have developed a data acquisition technique to process amplitude-modulated data arrays for lock-in amplified XUV polarization-sensitive FWM spectra (Nadgir et al. **2021**, *Meas. Sci. Technol.*, 32).

On the theory side, detailed interpretation of UTPS and X-UTPS experiments demands the development of new methods to model and predict the 3rd-order polarization response of molecules in excited electronic states. In collaboration with Liang Tan (Molecular Foundry, LBNL), we have developed two complementary theoretical methods to simulate the time evolution of a molecular system in Liouville space. In the first method, we compute the derivatives of the time-dependent polarization response of the model molecule to the optical pulses using finite differences. This provides the tools to model a time-resolved 2-color FWM experiment using a simple system of 3 or more levels to understand the evolution of the molecule in terms of electronic decay and dephasing rates. While nuclear dynamics are not yet included in this model, the low computational cost favors future applications to a series of geometries. We will next compare the results from the time-dependent finite difference method with those of a second type of simulation we recently developed, where we compute the time-dependent polarization using 3rd-order perturbation theory.

Future Plans: The installation of the X-UTPS HHG beamline is ongoing. When the new NIR + XUV split-and-delay beamline is complete, we will have independent delay and polarization control. We will achieve space and time overlap between the XUV and NIR pulses using an existing velocity map imaging (VMI) photoelectron spectrometer (Shivaram et al. **2016**, *Appl. Phys. Lett.*, 109, 254101), which will be inserted and removed from the X-UTPS endstation without changing any upstream optics. We will then replace the VMI instrument with the X-UTPS sample cell and investigate the ultrafast transient 2-color OKE response in N_2, in a femtosecond FWM experiment. This will allow us to develop and test the essential instrumentation on dynamics of excited bright ungerade and dark gerade electronic states in N_2, by 2-color NIR + XUV FWM, while working towards future X-UTPS experiments. A resonant 14 eV XUV pulse (~20 fs duration) and a NIR pulse (~40 fs duration) will be focused in a noncolinear geometry in a windowless gas cell containing ~10 Torr of the target gas. With the linear polarization of the NIR pulse tilted 45° relative

to the linear XUV polarization, the NIR pulse delay will be scanned a few femtoseconds before and after the XUV pulse to measure OKE signals that are emitted in the same direction as the XUV pulse, carrying information on the dynamical resonant coupling between the ground electronic state, the XUV-excited electronic states, and the a″ $^1\Sigma_g^+$ dark state, in 2-NIR-photon down-up transitions. Time-resolved dynamics involving higher lying Rydberg states may also be observed due to up-down 2-NIR-photon transitions from the XUV excited state. These first experiments will establish the 2-color OKE FWM probe technique, leveraging the knowledge and experience developed in the Attosecond Dynamics project of Subtask 1, where the evolution of the same electronic states in N_2 was studied by FWM with NIR and isolated attosecond XUV pulses (Warrick et al. **2018**, *Faraday Discuss*, 212, 157-174). The XUV + NIR FWM signal, arising from the OKE, will be emitted *in the XUV propagation direction* with the polarization orthogonal to the XUV probe pulse. The signal spectrum will be analyzed as a function of time delay τ between the XUV and NIR pulses using a reflective XUV polarizer and an XUV spectrometer. Following this proof of concept, we plan to apply the XUV + NIR FWM signal in X-UTPS experiments to probe dissociation dynamics in O_2 (see Fig. 2-6). There, one 8 eV XUV pump pulse will excite O_2 to the dissociative B $^3\Sigma_u^-$ state. The dissociation dynamics will be probed by the OKE polarization signal produced by a second XUV pulse and a NIR pulse, with variable time delays, effectively measuring the variation of the 2-color OKE signal for different O=O interatomic distances as the B $^3\Sigma_u^-$ state dissociates.

Fig. 2-6: Proposed X-UTPS experiments to investigate the dissociating B $^3\Sigma_u^-$ excited electronic state in O_2 using a 2-color NIR-XUV OKE probe. The XUV pump initiates a dissociating wavepacket on the B $^3\Sigma_u^-$ excited electronic state. The delayed XUV probe *A* and NIR probe *B* pulses (see timing scheme, inset), produce a four-wave mixing signal in the probe *A* direction due to the OKE. The signal will be sensitive to the electronic structure of the dissociating wavepacket, and to resonant coupling to higher-lying Rydberg and valence electronic states.

Our computational efforts are now directed at making direct comparisons between the simulations and our recent experiments on nitrobenzene with NIR pulses (Thurston et al. **2020**, *J Phys Chem A*, 124, 2573-2579), 2-color FWM experiments, and X-UTPS experiments. Depending on the success of the numerical model to describe purely electronic dynamics on the low-lying electronic states of nitrobenzene, the model will be extended to include nuclear motion along one or a few relevant degrees of freedom.

Ultrafast Energy Exchange and Charge Transfer in Solvated Biomolecules *(Slaughter, Weber)*

Future Plans: Two of the important decay pathways that create ion fragments after the ionization of small, hydrated biomolecular complexes like tetrahydrofuran-water or glycolaldehyde-water dimers are intermolecular coulombic decay (ICD) and electron transfer mediated decay (ETMD). Using a momentum imaging approach similar to our previous studies on $(N_2)_2$ and $(O_2)_2$ (Trinter et al. **2014**, *Nature* 505, 664)), we propose to study the competition between ICD and ETMD in complex dimers after X-ray excitation by reaction microscopy at (a) a synchrotron, targeting the energy/momentum domain, and (b) an XFEL, in order to gain time-domain access to the dissociation dynamics via an ultrafast pump/probe technique. In the XFEL studies, a time delayed optical pulse will close ICD/ETMD decay channels by direct ionization before decay. The goals for project (a) are to identify and isolate the charge transfer, the ionization mechanisms, and the dissociation pathways of the dimers at PETRA-III. In the next step, the cluster size and photon energies

shall be varied. For project (b) we aim to record and investigate time-resolved snapshots of the dissociation dynamics, demonstrating that the core hole was filled by valence electrons through different decay pathways via X-ray pump/optical probe spectroscopy, once the reaction microscope of the DREAM endstation at LCLS-II is operational at high repetition rates (>10 kHz). These snapshots can form the basis of a "molecular movie" for the charge transfer event. Both projects will be carried out in collaboration with the group of Prof. Thomas Orlando at Georgia Tech.

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

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

Time Delay in Molecular Photoionization and Photodetachment (*Lucchese, McCurdy, Rescigno*)

Recent Progress: Measurement of attosecond time delays in photoionization has become a well-established probe of the interaction of the emitted electron with the residual ion. Observations of the delay, $\tau = \hbar \frac{\partial}{\partial E} \arg \left\langle \Phi_k^{(-)} \middle| \sum_i \epsilon \cdot r_i \middle| \Phi_0 \right\rangle$, measure the energy derivative of the relative phase of the photoionization amplitude and can reveal signatures of resonances and their interference with background scattering in the body frame. However the divergent Coulomb phase, $\eta_l = \arg \Gamma(l + 1 - iZ/k)$, dominates photoionization time delays below a few eV and commonly obscures intrinsically molecular aspects of the delay at low energies. In preliminary calculations using the complex Kohn method we predict that photodetachment of electrons from polyatomic anions will display time delays revealing low energy resonances and details of the interaction of the photoelectron with the residual molecule unobscured by Coulomb scattering. In the body frame these time delays offer a probe of the dynamics of the outgoing electron that is sensitive to the detailed asymmetry

of the electron-molecule interaction and to long range dipole effects. Moreover, X-ray photodetachment of the core electrons creates a neutral molecule with a core vacancy that will Auger decay and can lead to dissociation (e.g. $OH^- + h\nu \rightarrow O(1s^{-1})H + e^- \rightarrow O + H^+ + 2e^-$) opening the possibility of observing photodetachment time delays
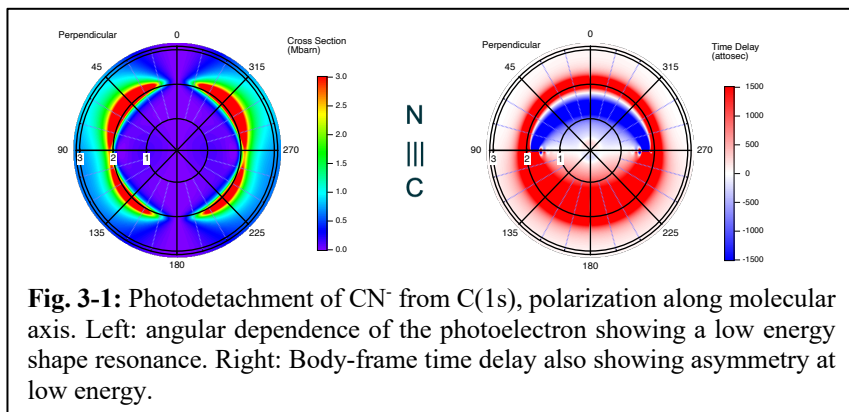
Fig. 3-1: Photodetachment of CN^- from $C(1s)$, polarization along molecular axis. Left: angular dependence of the photoelectron showing a low energy shape resonance. Right: Body-frame time delay also showing asymmetry at low energy.

in the body frame in a coincidence measurement. We have performed time-delay calculations for core and valence photodetachment of CN^-, BN^-, C_2^- and O_3^- anions. Preliminary results indicate that in addition to the time delay features associated with low-energy resonances, low-energy non-symmetric delays also appear, as shown in Fig. 3-1, that may originate from long range dipole or medium range asymmetries in the scattering potentials. This work is being done in collaboration with C. Trevisan (Cal State Maritime Academy, LBNL BLUFF).

We have published a study of the photoionization time delays for a series of small water clusters in collaboration with the experimental group of H.-J. Wörner (ETH Zürich) (Gong, X., et al. **2022**, *Nature* 609, 507, DOI: 10.1038/s41586-022-05039-8). In this study, clusters with one to six monomers were ionized from the HOMO of the monomer. For a photon energy of 18.6 eV, for small

clusters the time delay increased with increasing cluster size from 100 as up to a value of 250 as in $(H_2O)_4$ where it reached its maximum value. The value of the time delay did not change significantly as larger clusters were considered. In general, the more delocalized the hole state, the larger the time delay. For small clusters $(H_2O)_n$ with n from 1 to 4, as n increases the extent of delocalization increases up to the exceptionally symmetric $n = 4$ cluster which has symmetry belonging to the S_4 point group. Beyond that size, the structure of the clusters does not have such high symmetry, leading to more localized hole states. A second effect that limits the time delay due to delocalization is that when there are nearly degenerate ionization channels, coupling between such channels can be strong, leading to photoionization amplitudes that are significantly changed from the results obtained when channel coupling is ignored. In the photoionization of $(H_2O)_4$, time delays computed in the single-channel approximation, using hole states described by the four different delocalized canonical Hartree-Fock orbitals composed of the HOMOs of the H_2O monomer, were 310 as compared to 230 as in the fully coupled calculation. This significant reduction of the time delay implies that the channel coupling yielded an effective reduction in the size of the delocalized holes.

Also in collaboration with the group of H. J. Wörner (ETH Zürch) we have continued studies of photoemission time delays in a series of azabenzenes in support of the analysis of an experiment that was performed at the LCLS. We found that both the cross sections and the time delays for $N(1s)^{-1}$ ionization in the azabenzenes studied, pyridine, pyrimidine, and S-triazine,

Fig. 3-2: Computed photoionization cross section and corresponding photoionization time delay for S-triazine.

can be modeled using localized hole states within a single-channel approximation. Cross sections and orientation averaged time delays for S-triazine are shown in Fig. 3-2. We can see that there is a narrow resonance at about 4 eV above the threshold of 404.9 eV in both the theory and an earlier photoabsorption experiment. The computed cross section is more sharply peaked and is slightly narrower than in the experiment. The calculation also predicts a very narrow peak in the time delay. This work is being done in collaboration with Prof. C. Trevisan (Cal State Maritime Academy, LBNL BLUFF)

Future Plans: The wavelengths of low-energy electrons are larger than molecular dimensions and undermine the interpretation of attosecond time delays using classical particle and compact wave-packet ideas. We therefore are actively developing numerical models to isolate the effects of molecular dipole potentials and the role of the initial state wave function to interpret predicted delays in photodetachment.

In the study of photoionization time delays, we will extend the study of time delays in $(H_2O)_2$ and $(H_2O)_3$ clusters, which depend strongly on the hydrogen-bonding environment around the O atom that is being ionized from its HOMO. We will consider the dependence of the photoionization time delays on the O-O bond distance and the orientation of the H_2O monomers. The goal is to determine the extent to which the time delay in a larger cluster can be decomposed into an average of the time delays from its constituent interaction motifs and the extent to which the time delays are determined by scattering from more distant parts of a cluster.
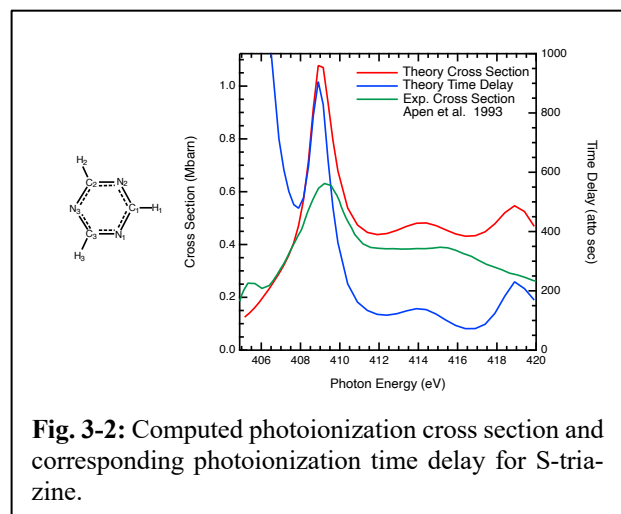
Intense Field Double Ionization in Molecules *(Lucchese, McCurdy)*

Recent Progress: Continuing our collaboration with the Bucksbaum group (Stanford) and the Weinacht group (Stony Brook) our classical trajectory calculations and *ab initio* potential surfaces for H_2O^{2+} were modified to model a two-pulse experiment, led by A. Howard (Stanford), that probed the dynamics of dissociating D_2O^{2+} in real time. A first intense 6 fs optical pulse produces D_2O^{2+}, which is further ionized during dissociation by a second pulse to produce a water trication, D_2O^{3+} that immediately Coulomb explodes to O^+ + $2D^+$. Those trajectory calculations match the experimental momentum images of the ions emerging from the complete dissociation of H_2O^{3+} strikingly well, as shown in Fig. 3-3, and the theoretical dynamics allowed the discovery of a region of enhanced multiphoton ionization occurring while the dication is near linear geometry. The "slingshot mechanism" that we found in earlier studies of dissociation of the three water dication states for which the axial recoil approximation breaks down, causes H_2O^{2+} dissociating on those states to pass through a linear geometry, where tunneling and overbarrier ionization are enhanced. A manuscript is in preparation.
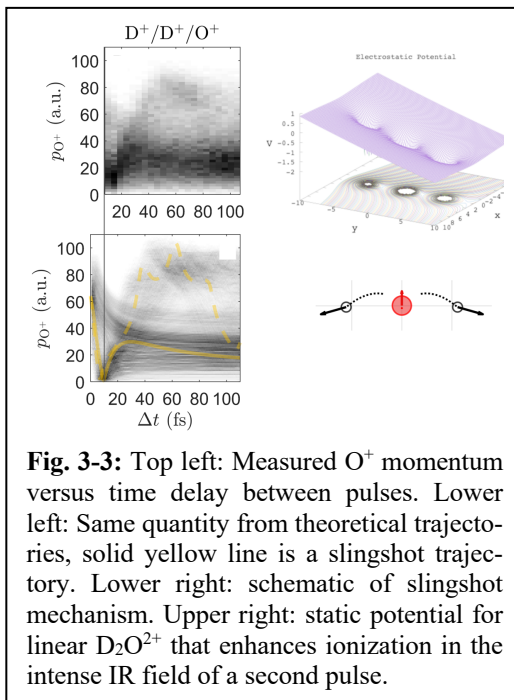
Fig. 3-3: Top left: Measured O^+ momentum versus time delay between pulses. Lower left: Same quantity from theoretical trajectories, solid yellow line is a slingshot trajectory. Lower right: schematic of slingshot mechanism. Upper right: static potential for linear D_2O^{2+} that enhances ionization in the intense IR field of a second pulse.

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

Future Plans: After a pause in code development, we will continue enhancing the general electron scattering and photoionization code based on the Overset Grid method that has been the subject of two published papers so far. In collaboration with L. Greenman (Kansas State), we have found a promising alternative to our previously published method of switching the representations of the wave function and operators from local subgrids, centered on the nuclei, to the master grid that covers all of space but is a complete representation only at large distances. The new approach uses grid switching based on the Hilbert spaces of discrete variable representation functions in each subgrid, instead of operating in coordinate space, and promises both increased efficiency and accuracy, as we extend the existing code to multichannel capabilities.

Core Hole Localization in Photoionization *(Lucchese, McCurdy, Rescigno)*

Recent Progress: We have continued our study of the degree of core-hole localization, which can be detected in the ionization of systems with chemically equivalent atoms using coincident detection of the photoelectron and of the fragments of the molecule formed after Auger decay. We have begun a study of the photoelectron angular distributions (PADs) produced in the Cl $(2p)^{-1}$ ionization of $C_2H_2Cl_2$ in collaboration with J. Williams (Univ. of Nevada, Reno), who led the experiments performed at the ALS. In such systems, there are two conditions that are required for an experiment to observe the PADs from a localized hole state. First, the energy separation of the delocalized hole states must be less than the lifetime broadened linewidth of the core levels. In this case, an experiment can be equivalently described using hole states in terms of delocalized or localized holes. The second requirement is that there is a high probability that the atom where the

localized hole is created becomes a fragment in an asymmetric dissociation. If both of these requirements are satisfied, then there is a possibility for the experimental detection of a PAD from a localized hole state. This was the situation in the F $(1s)^{-1}$ ionization of CF_4 where there was clear evidence in the measured recoil-frame PADs of the localized holes (McCurdy et al. **2017**, *Phys. Rev. A* 95, 011401(R)). However, this pure localization was not observed in a later study of Cl $(2p)^{-1}$ photoionization of CCl_4 (Gaire et al. **2022**, draft in preparation). In the experiment on $C_2H_2Cl_2$, the core ionized molecule dissociates into three fragments, thus allowing the molecular-frame PAD to be determined. In Fig. 3-4, computed localized and delocalized polarization-averaged molecular-frame PADs are given. In this system there is a striking difference between these two possibilities, indicating that if the fragmentation

Fig. 3-4: Computed polarization-averaged molecular-frame PADs for Cl $(2p)^{-1}$ ionization of $C_2H_2Cl_2$ for a photoelectron kinetic energy of 3.2 eV. The green lines indicate the position of the Cl atoms that are being ionized.

process is rapid, then it should be possible to see localization. However, preliminary results indicate that, similar to what was seen in the case of CCl_4 Cl $(2p)^{-1}$ photoionization, the experimental molecular-frame PADs are dominated by the molecular-frame PADs from the delocalized Cl $(2p)^{-1}$ hole states. This work is being done in collaboration with Prof. C. Trevisan (Cal State Maritime Academy, LBNL BLUFF).

Dynamics of Rydberg States in CO_2 (*Lucchese, McCurdy*)

Recent Progress: In collaboration with the group of Leone and Neumark on four-wave mixing (FWM) experiments (see also Subtask 1) probing the dynamics of autoionizing states of CO_2, we computed autoionization lifetimes for a series of Rydberg states below the threshold for the ionization to the B $^2\Sigma_u^+$ state of CO_2. In particular, there is a series of ns σ_g and nd σ_g states, which have very different widths relative to autoionization. The computed widths of the ns σ_g Rydberg states were in very good agreement with the decay of the signal as a function of delay in the FWM experiments. However, the emission seen in the experiments were at the energies corresponding to the transition from the nd σ_g Rydberg states. This suggested that the initial excitation is to the ns σ_g Rydberg levels, then through a dark state accessed in the FWM process, the nd σ_g Rydberg states are populated leading to the final observed emission. We computed the oscillator strengths between the ground state, the $n\sigma_g$ B $^2\Sigma_u^+$ autoionizing Rydberg states, and the dark state which is believed to be the $3p\sigma_u$ B $^2\Sigma_u^+$ state. The computed values of these oscillator strengths were consistent with the observed emission from the $nd\sigma_g$ B $^2\Sigma_u^+$ after the initial excitation of the $ns\sigma_g$ B $^2\Sigma_u^+$. A manuscript is in preparation.

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

Recent Progress: As part of our ongoing study of single-photon double ionization of water, we have directed some effort to examining $O^+ + H + H^+$ production, which appears as a rare (0.6% of total DPI signal), but nonetheless measurable, channel in the ALS experiment led by Th. Weber. The O^+ fragment can be produced by either direct or indirect (i.e., autoionization) processes (see

also Subtask 1).

Since there are no dissociative states of the water dication below ~61 eV leading to $O^+ + H + H^+$, the direct pathway to this channel must necessarily be sequential and must involve a spin-orbit induced charge transfer. A "native frames" analysis of the experimental data by the Kansas State group, led by I. Ben-Itzhak, revealed a sequential process in which O^+ emerges from OH^+ ions at large OH^+ --- H^+ distances. We found that the most likely mechanism involves an initial production of $H^+ + OH^+$ ($a^1\Delta$ and $b^1\Sigma^+$) ions; the latter then undergo a spin-orbit transition to $OH^+(A^3\Pi)$. An atomic spin-orbit interaction strongly mixes the $A^3\Pi$ and $X^3\Sigma^-$ states, while an asymptotic electronic coupling between the $X^3\Sigma^-$ and $B^3\Sigma^-$ states triggers the charge-exchange that leads to the final channel of interest with low KER (see Fig. 3-5 (left)). The veracity of this mechanism was tested by solving a three-channel time-dependent Schrödinger equation, coupling the $A^3\Pi$, $X^3\Sigma^-$, and $B^3\Sigma^-$ states with appropriate off-diagonal spin-orbit or non-adiabatic terms.

Fig. 3-5: (left panel) Selected OH^+ states relevant to sequential O^+ production. Only $X^3\Sigma^-$, $B^3\Sigma^-$, and $1^5\Sigma^-$ dissociate to $O^+ + H$; (center) H_2O^+ and H_2O^{++} states in C_{2v} symmetry relevant to direct O^* autoionization; (right) Selected potential energy curves of OH^+ and OH^* relevant to indirect 0^* autoionization.
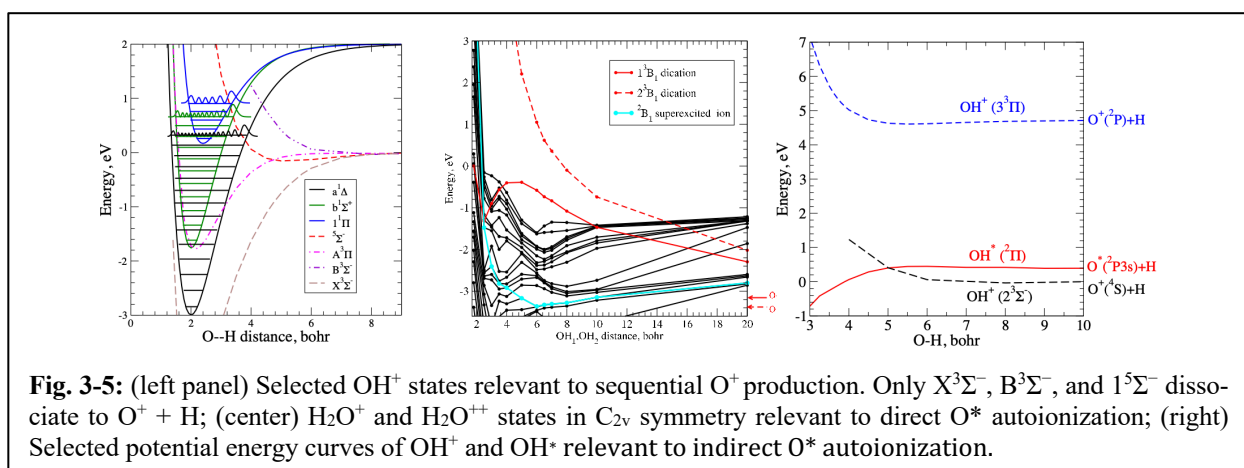
For the production of O^+ by autoionization, two mechanisms were examined, one direct and one sequential. The initial step in both cases is the creation of a super-excited H_2O^+ ion by a one-photon inner-valence excitation-ionization process that removes a $2a_1$ electron and simultaneously promotes a $1b_1$ electron to $4a_1$. For the direct process, we carried out a series of MRCI calculations (approx. half a million configurations) on H_2O^+ and H_2O^{++} ions for a series of geometries in which the two OH bonds were symmetrically stretched, keeping the HOH angle fixed at the equilibrium angle of the neutral molecule. By examining the dominant CI coefficients of the roots at each geometry, we could construct a diabatic curve (see Fig. 3-5 (center)) that represents the super-excited monocation. As it moves away from the Franck-Condon region, the super-excited ion takes on increasing Rydberg character and ultimately dissociates into $O^*(2p3(^2P)3s) + H + H^+$. O^* auto-ionization produces an $O^+(^4S)$ ion, which, according to our calculations, can occur at O–H distances greater than ~ 35 Bohr. We also examined a sequential process initiated by fast ejection of H^+ followed by a subsequent autoionization of OH^* into $O^+(^2P) + H + e^-$. The only parent ion triplet states of OH^+ that dissociate to $O^+(^2P) + H$ are the repulsive $3^3\Pi$ and $1^3\Sigma^+$ states, which have similar potential curves. From MRCI calculations in $^2B_1$ symmetry and examination of a number of discretized OH^* states, we were able to extract a diabatic $^2\Pi$ resonance curve (see Fig. 3-5 (right)). The autoionizing $^2\Pi$ state is flat for O-H distances greater than 6 Bohr and parallels the $OH^+(2^3\Sigma^-)$ state to which it can autoionize. The theoretical analysis of O^+ production by both direct and indirect ionization was done in collaboration with Prof. Ann Orel (UC Davis). Two separate manuscripts describing this work are in preparation.

We are continuing our major project to calculate full body-frame triple differential cross sections (TDCS) for double ionization of H_2O to compare with and interpret the experimental results obtained at the ALS by Th. Weber and W. Iskander. We have developed a new approach in which a numerical continuum orbital basis is constructed from the finite-element discrete variable representation used in our earlier calculations that dramatically reduces the size of the problem, thus enabling the first polyatomic double ionization calculations. In addition, this method makes time propagation feasible, and that approach, together with projection on Coulomb final states is how our first calculations are being done. Additionally, in collaboration with F. Yip (Cal State Maritime Academy, LBNL BLUFF) we have finished calculations on Li_2 and LiH and discovered how bond length can determine the role of initial state correlation in double photoionization. Two manuscripts describing these developments are in preparation. A paper in collaboration with Itzik Ben-Itzhak at Kansas State, in which our classical trajectory studies of the dissociation of D_2O^{++} form the basis of interpretation of sequential breakup seen in an experiment with the LBNL group at the ALS has been published, Severt et al. **2022**, *Nat. Comm.* 13, 5146.

Future Plans: In collaboration with Roger Bello, a postdoc in our group until last May and now at the Autonomous University of Madrid, we will complete the TDCS calculations for double ionization of water to produce the three states in which two electrons are removed from one valence orbital.

Real Space Pseudopotential Methods for Core-Excited States (*Qian*)

Recent Progress: X-ray photoelectron spectroscopy is a powerful characterization technique widely adopted in the context of physics, chemistry, and materials science. The result of XPS chemical analysis relies on the measurement of core-level electron binding energies, often referred to as the binding energy shifts, which are used for distinguishing the local structures around a given atom. With rapid growth in the application of XPS to *in situ*/operando measurements for chemical identification, particularly in energy storage and catalysis applications, the interpretation of XPS signals increasingly relies on theoretical estimates of absolute or relative core-electron binding energies that go beyond simple molecular systems. XPS can also be used as a subsequent probing tool in pump-probe photoexcited experiments to differentiate charge states (Gessner). As an important complimentary effort to the current theoretical portfolio of the program (Head-Gordon, McCurdy, Lucchese), we recently derived the binding energies expression and their shifts from the definition of cohesive energy, thereby clarifying a long-standing mis-

Fig. 3-6: Example binding energy shifts for carbon 1s excitation. With the Dirichlet boundary condition, the pseudopotentials-based calculations can provide accurate core-level binding energies and their shifts for molecular systems, when compared with the results from all-electron method and experiments.

conception from the quantum chemistry communities that pseudopotentials cannot be used to predict the XPS binding energy. We then implemented our derivation and systematically studied the real-space pseudopotential method for the calculation of the $1s$ core-level binding energies of the second-row elements B, C, N, and O within the theoretical scheme of the real-space Kohn-Sham
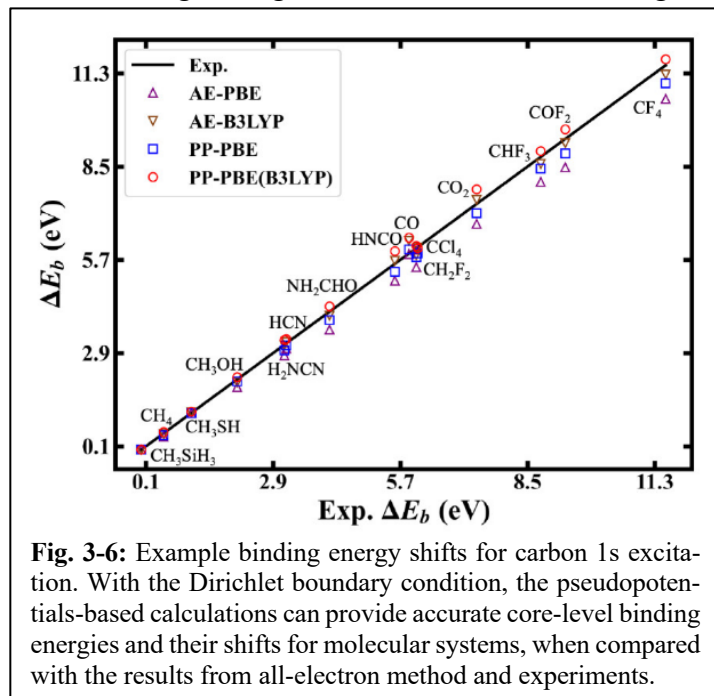
density functional theory (real-space KS-DFT). With the Dirichlet boundary condition, the pseudopotentials-based calculations can provide accurate core-level binding energies and their shifts for molecular systems, when compared with the results from the all-electron method and experiments (see Fig. 3-6). Furthermore, we report that with one simple additional non-self-consistent calculation as the refined step using the hybrid exchange-correlation functional, one can generally improve the accuracy of binding energy shifts (improving MAE from ~0.3 eV to ~0.1 eV). This represents a promising a strategy for improving the accuracy at a lower computational cost. The specializations in the present approach, together with our efficient real-space KS-DFT backbones, provide key advantages for calculating accurate binding energies of large-scale systems (Xu et al. **2022**, *J. Chem. Theory Comput.* 18, 5471).

Future Plans: With the foundational derivation, implementation, and validation in place, we are aiming to expand the application scenarios of this method to investigate the excitation of intermediate and large systems (> 10,000 atoms). Such systems include core excitation of nanodroplets (collaboration with T. Pascal, UC San Diego) and interfacial charge-transfer dynamics studied by pump-probe experiments (collaboration with Gessner, see also Subtask 2). These systems have profound real world renewable energy implications and are well beyond the traditional capabilities of KS-DFT (~ hundreds of atoms).

State-Targeted DFT for Core Excitations *(Head-Gordon)*

Recent Progress: It is a fact that surprisingly many *excited* states of molecules can be quite well described using *ground* state DFT with the usual closed shell determinant replaced by a 2 configuration restricted open-shell Kohn-Sham (ROKS) wavefunction. This reference wavefunction models an optically allowed single excitation, and the orbitals are optimized specifically for each individual excited state, such that the resulting orbital-optimized DFT (OO-DFT) energy is a minimum only for the lowest excited state; higher excited states are saddle points. This OO-DFT approach is remarkably successful for core excited states. For instance, we demonstrated that RMS errors for the K-edge of light elements can be as low as 0.25 eV for the standard SCAN meta-GGA (Hait et al. **2021**, *J. Phys. Chem. Lett.* 12, 4517−4529), representing more than a 20-fold reduction relative to standard TDDFT. This code is now released as part of the latest version of the Q-Chem program (Epifanovsky et al. **2021**, *J. Chem. Phys.* 155, 084801).

One main limitation of the initial research was neglect of relativistic effects, which are known to be important in the description of changes in electronic structure associated with the creation of the core hole in an XAS excitation (as well as in an XPS photoionization). To address this challenge in a tractable and formally justified way, we have now reported an extension of the OO-DFT/ROKS approach that uses the exact 2-component scalar one-electron Hamiltonian (Cunha et al. **2022**, *J. Phys. Chem. Lett.* 13, 3438–3449). As shown in Fig. 3-7, the RMS errors obtained for K edges of heavier elements (Na-Ar) are now comparable to the values previously limited to the lighter elements. In turn, this translates to simulated spectra that have sufficient
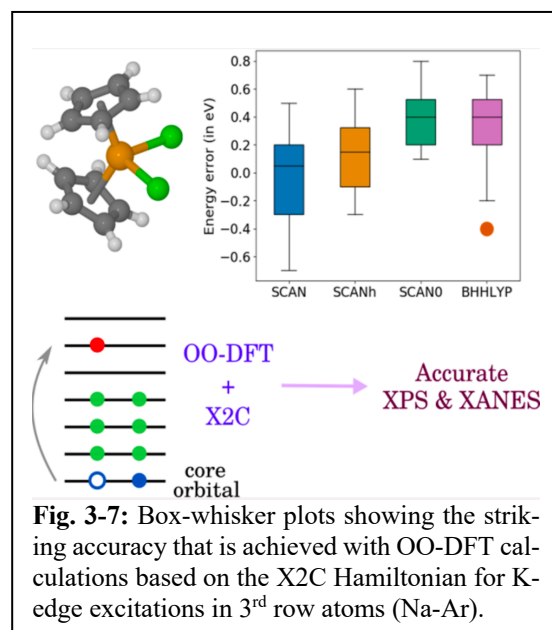

Fig. 3-7: Box-whisker plots showing the striking accuracy that is achieved with OO-DFT calculations based on the X2C Hamiltonian for K-edge excitations in 3rd row atoms (Na-Ar).

accuracy to assign not only the K-edge but also features that lie between the K-edge and the ionization threshold, as illustrated in Fig. 3-8 for the S-edge of the OCS molecule.

Future Plans: There are also some remaining limitations in our implementation, and the associated theory. Specifically we have only considered scalar relativistic effects to date. We are investigating approaches that will enable us to include spin-orbit coupling within the OO-DFT/ROKS framework at tractable compute cost. The X2C approach can also be extended to permit geometry optimizations which is of practical interest. New chemical applications of the OO-DFT/ROKS approach are underway in collaboration with the Leone and Neumark groups.

Fig 3-8: Calculated S K-edge XAS spectrum (>2470 eV) and S K emission (<2470 eV) for the OCS molecule using OO-DFT with the SCAN functional, against the corresponding experimental data. Excellent agreement is obtained for all main features without any empirical shifting of the computed spectra.

Full DFT-Based XAS Spectral Calculations without Linear Response. *(Head-Gordon)*

Recent Progress: Early research on calculating XAS spectra using Hartree-Fock as ground state and specialized, non-orthogonal versions of configuration interaction with single substitutions (CIS) led to useful results with the static exchange approximation (STEX) and further improvements with our non-orthogonal CIS method (NOCIS) (Oosterbaan et al. **2020**, *Phys. Chem. Chem. Phys.* 22, 8182-8192). The essence of these methods was to optimize orbitals for the core ion, and then perform NOCIS using those cation orbitals to uncover the final state of the electron. With the tremendous success of OO-DFT, STEX/NOCIS appear to be superseded as methods of choice for tractable XAS calculations on medium to large molecules. However, STEX/NOCIS have the advantage of yielding a full spectrum in a single shot rather than requiring state-by-state specific optimization as in OO-DFT.

Is there a way to get the best of both worlds? In pursuit of this goal, we developed an approach (Hait et al. **2022**, *J. Chem. Phys.* 156, 201104) to generate an approximate core-excited state density for use with the OO-DFT/ROKS energy ansatz, which is capable of giving reasonable accuracy without requiring state-specific optimization. This is achieved by fully optimizing the core-hole through the core-ionized state, followed by the use of electron-addition configuration interaction singles to obtain the particle level. This hybrid approach can be viewed as a DFT generalization of the static-exchange (STEX) method and can attain ~0.6 eV rms error for the K-edges of C–F through the use of local functionals, such as PBE and OLYP. This ROKS(STEX) approach can also be used to identify important transitions for full OO-ROKS treatment and can thus help reduce the computational cost of obtaining OO-DFT quality spectra. ROKS(STEX), therefore, appears to be a useful technique for the efficient prediction of X-ray absorption spectra.

Future Plans: Inspired by our success with the ROKS(STEX) approach, we are investigating whether or not it is possible to recast the NOCIS/STEX approach itself within density functional theory. What we seek is an approach that reduces to NOCIS/STEX when the density functional is chosen to be Hartree-Fock, but which then provides a suitable, hopefully superior, generalization when modern density functionals are employed instead.
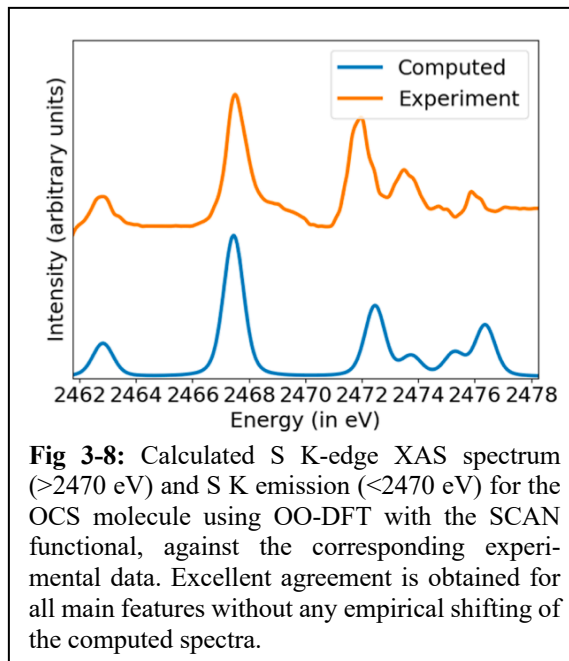
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PULSE: Ultrafast Chemical Science at SLAC

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

Major themes: Ultrafast science has emerged as a primary arena for scientific progress across all areas of BES, and it has also been established as a primary mission focus for SLAC.[1] PULSE has been advancing this area for more than a decade, starting with this AMOS program, and so we are in leadership positions now in selected broad areas of the field. We have a growing list of research accomplishments in sub-femtosecond or femtosecond-resolved investigations that capture the motion of electrons within molecules, using methods that require the improved characteristic of the LCLS-II linac and x-ray laser.   We also have developed methods with Angstrom resolution to record chemistry at the level of the intramolecular bonds. And we also have investigated a range of multiphoton x-ray interactions using x-ray nonlinear spectroscopy.

Research themes: The AMO research that is especially pushed forward by the capabilities of LCLS-II and at UED can be grouped into three main research themes:
• Imaging on the nanoscale in space and the femtoscale in time.
• The architecture of light conversion chemistry.
• Harnessing coherence on the eV scale in time, space, and field strength.

Science frontiers: Linked to these themes are three science frontiers, which encompass the activities of our FWP:
• The frontier of attosecond electronic motion
• The frontier atomic field strengths
• The frontier of collective electron dynamics

The scientific case for these advances was highlighted in a recent BES workshop on LCLS-II science opportunities, "*Virtual Workshop: Non-Linear Multidimensional Methodologies for Studying Chemical Sciences,*" that was organized by a collaboration including LCLS, Nora Berrah, and five of the PIs from this FWP (Reis, Cryan, Cordone-Hahn, Wolf, and Bucksbaum) in December 2020. In addition, these science areas are themes of the BESAC 2017 report *Opportunities for Basic Research at the Frontiers of XFEL Ultrafast Science* (a.k.a. *Ultrafast Roundtable Report*),[2] and also the BESAC 2015 report, *Challenges at the Frontiers of Matter and Energy: Transformative Opportunities for Discovery Science,*[3] especially the section on *Imaging Matter across Scales*, and *Harnessing Coherence in Light and Matter.*   The tasks are also in line with the 2004 report

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[1] https://www6.slac.stanford.edu/blog-tags/ultrafast-science
[2] https://science.energy.gov/~/media/bes/pdf/reports/2018/Ultrafast_x-ray_science_rpt.pdf
[3] https://science.energy.gov/bes/efrc/research/transformative-opportunities/

Directing Matter and Energy: Five Challenges for Science and the Imagination (a.k.a. *Grand Challenges Report*)[4] where our work is particularly relevant for the *Energy and Information on the Nanoscale* and *Control at the Level of Electrons* challenges.

Key Personnel:

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

Recent personnel changes: In addition to the PIs listed above, this year Professor Matthias Kling has received funding through this FWP to begin a research program in ultrafast photochemistry at nanoscale surfaces.

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 Prof. Kelly Gaffney, which in turn is part of the SLAC Energy Sciences Directorate, directed by Associate Lab Director Prof. Tony Heinz. The intellectual vitality of the program is assisted greatly by its organization within a parallel Stanford University organizational unit, the Stanford PULSE Institute, which directed by Prof. David Reis.

Recent organization changes: The UCS FWP was formerly organized with one subtask for each of its principal investigators. This year we reorganized our subtask structure by reducing the total number of subtasks to encourage synergy among the programs of our PIs. The FWP is now organized into four subtasks, with two or three primary investigators responsible for the scientific program within the subtask:

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)

Program highlights: Here are recent examples of research progress:

Direct observation of attosecond coherent electron motion: We mapped the time-dependent electron current during the Auger-Meitner emission by means of angular streaking. This work demonstrates the ability to use x-ray free-electron lasers for exploring electronic coherences in the charge transfer processes on the attosecond time scale. [S. Li, T. Driver et al. Science 375, 285-290 (2022)]

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

Non-linear optical method probes topological phase transitions: High harmonics generation detected an abrupt transition in efficiency when a Bi_2Se_3 crystal is known to lose topological protection. This confirmed that high-harmonic generation probes topological phase transitions, in ambient conditions and in a contact-free manner. [Heide, et al., Nature Photonics 16, 620–624 (2022)]

Symmetry Conservation Rules for Photochemistry Confirmed by Imaging Reaction Dynamics in Space and Time: We directly observed the reaction product of the electrocyclic chemical transformation of α-phellandrene to be dictated by the reactant conformer. The experiment confirms the predictions by the Woodward-Hoffmann rules (Chemistry Nobel Prize 1981) about the conformer-specificity and concertedness of pericyclic reactions. [Champenois et al., Science, 374(6564):178–182 (2022)].

Molecular Movie of a Prototypical Photochemical Reaction: Electrocyclic ring-opening of 1,3-cyclohexadiene was observed in real space and real time by ultrafast electron diffraction. This is the first imaging of a photochemical reaction in an isolated molecule exclusively comprised of light elements with sub-Å spatial and femtosecond temporal resolution. [Nature Chemistry 11, 504–509 (2019)]

These are just a few of the advances this year. More summaries of our work are in the four individual task abstracts that follow this overview.

Awards Prizes, and other Honors this year:

- **Tony Heinz:** AAAS Fellow; Optica Shawlow Prize
- **Todd Martinez:** Borden Lecturer, University of Washington; Remsen Award of the Maryland Section of the American Chemical Society; Plenary Lecturer, 19th Annual Cardiff Chemistry Conference, Cardiff University; Abbvie CADD Council Speaker, Abbvie
- **Philip Bucksbaum:** AAAS Fellow

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 instrument development teams at LCLS for the development of the next-generation LCLS-II instruments.

- We have assisted in the development of laser and timing tools currently at LCLS.

- Several PULSE scientists 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. This year's Chair was Dr. James Cryan. The 2022 UXSS in June had nearly 150 participants from around the world who came to SLAC for a week of training sessions. A highlight was a new set of special workshops during the week, which were devoted to collecting and analyzing data from LCLS instruments using test data sets from recent experimental runs. Next year the UXSS will be held in Europe, but it is scheduled to return to PULSE and SLAC in 2024.

Attosecond and Femtosecond Atomic and Molecular Physics (AFAM)

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Participants: Phil Bucksbaum (PI), James Cryan (co-PI), Taran Driver, Siqi Li,, Jordan O'Neal, Anna Wang, Jun Wang, Nick Werby, Ian Gabalski, Erik Isele, David Reis, Todd Martinez, Thomas Wolf

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

Project Scope: We study motion of electrons and atoms in molecules on their natural time scales to understand and control the earliest stages of chemical change; and to study fundamental ultrafast and strong-field interactions that reveal their internal dynamics. The natural timescale for electron motion is the attosecond-to-few-femtosecond scale associated with the period of motion 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 to fields of atomic structure, chemical bonds, inner-shell atomic dynamics, and even in atomic nuclei. The field strengths that we employ are typically in the range of $3 - 10\ V/Å$, but they can range as high as focused X rays at $3kV/Å$ (several hundred atomic units). We use a variety of techniques to produce a coherent superposition of electronic states which evolve on the attosecond scale. These techniques include laboratory, high harmonic generation (HHG) based attosecond pulse production, and new opportunities which are becoming available at the LCLS and are expected to be standard operations at LCLS-II. We also apply strong ultrafast coherent fields with frequencies 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:

Sub-cycle sub-femtosecond time-correlation analysis of field-ionized electrons maps the attosecond quantum tunneling dynamics during Strong-field Ionization: The photoelectron momentum distribution (PMD) produced in strong-field ionization (SFI) contain intricate holographic features from interference between distinct quantum tunneling trajectories. These are uniquely defined by their ionization times and subsequent evolution. In FY21 we introduced a time filter technique to highlight features in the PMD that originate from trajectory pairs that ionize less than one field cycle apart. This year we have determined the ionization time separation between these interfering pairs. These results are critical tests of the Coulomb quantum orbit strong-field approximation (CQSFA), or of any similar theory of strong-field ionization in atoms and molecules (Figure 1).
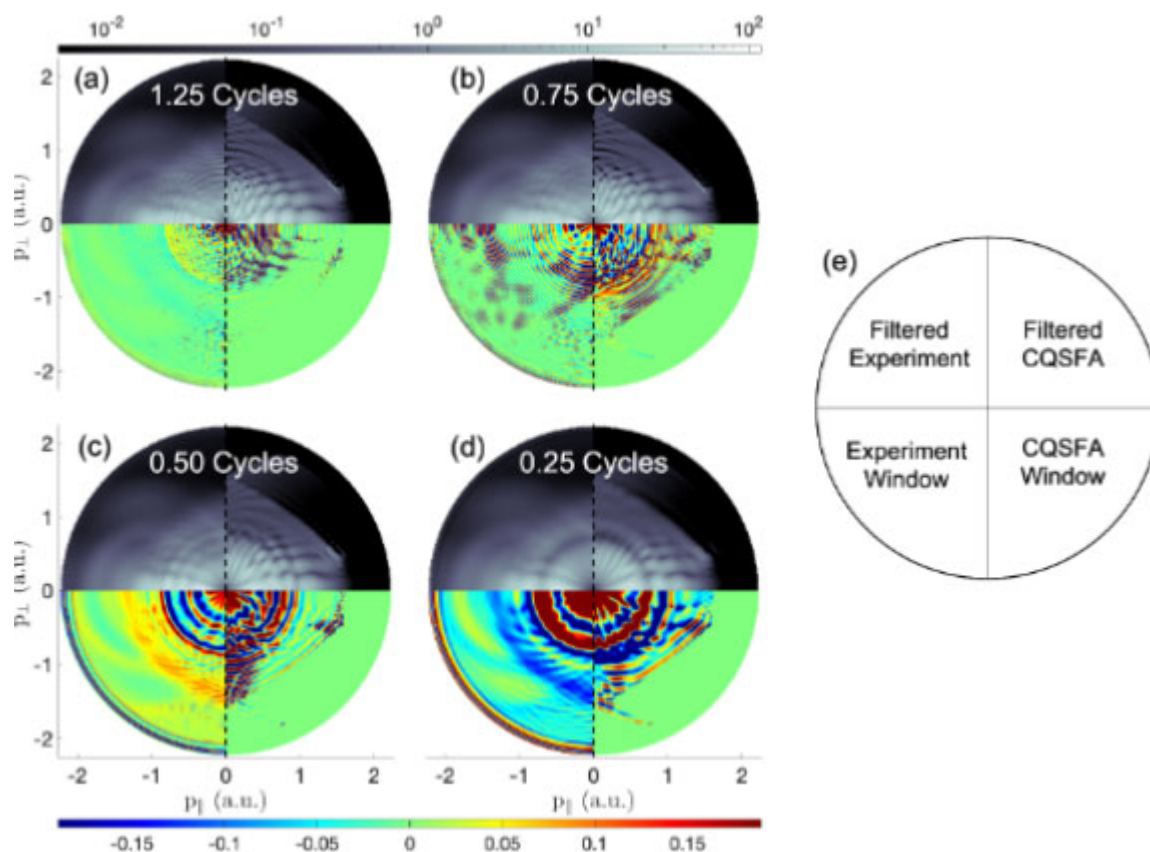
Figure 1 - Each four-quadrant panel shows strong-field ionized electron momenta for Ar ionized by a horizontally polarized 50 fs pulse with ~3 v/A peak field. The NW quadrant of each panel (a) through (d) has the correlation time filter as labeled. For example, in (a) the data show only features that survive a time filter roll-off at 1.25 cycles. The NE quadrant shows CQSFA simulations with the same time filter. The SW and SE quadrants show the electron residual difference between the filtered data at two successive rolloff positions. This residual signal represents pairs of electron trajectories that are between two roll-off positions. For example, in (a) the bottom two quadrants show the data and the theory for the pattern of electron trajectory pairs that are emitted more than 1.25 cycles apart. Panel (b) shows electron pairs emitted between 0.7 and 1.25 cycles apart, which of course includes all ATI electrons. Panel (c) shows electron trajectory pairs between 0.5 and 0.75 cycles apart. Panel (d) shows trajectory pairs between 0.25 and 0.5 cycles apart. Panel (e) is a guide to the source of each quadrant's data.

Femtosecond-resolved x-ray scattering reveals details of fast and slow dissociation channels in photoexcited CS₂. Photoexcited carbon disulfide is a model for intermodal coupling. 200 nm excitation leads to rapid bending in the SCS angle followed by dissociation of a sulfur atom in either the ^3P ground state or the ^1D excited state. The time evolution of these two decay channels has been controversial: Some studies conclude that both exit channels appear fairly promptly following laser excitation, and then decay with different time constants; others show that the triplet decay is delayed following the initial excitation, and this time lag contributes to the slower

appearance of triplet final states. This discrepancy is important because it indicates barriers to the intersystem crossing required for the initial singlet state to populate the triplet manifolds.

We studied this system using femtosecond time-resolved x-ray scattering of 9keV x rays from a gas of CS_2 photoexcited with 200nm 50 fs pulses. Our x-ray scattering data showed that photoexcitation launched oscillatory bending and stretching motion leading to dissociation of atomic sulfur in under a picosecond. The oscillations were on the time scale of the SCS bending mode, but were strongly anharmonic, suggesting considerable motion on the three-dimensional excited state potential energy surface prior to dispersion and decay of the coherence.

To analyze the data further we developed transform techniques to isolate dissociation features in the data. These involve transforming the pump-probe scattering signal S(Q,t) to S(Q,ω); and then implementing a Hough transform to analyze the velocity of the fragments. During the first 300 fs following excitation there is dominant dissociation of the lower-velocity singlet state sulfur. Around 1400 fs this signal has largely been replaced by a higher velocity triplet state. This result favors models where intersystem crossings limit the growth of the triplet states (Figure 2).
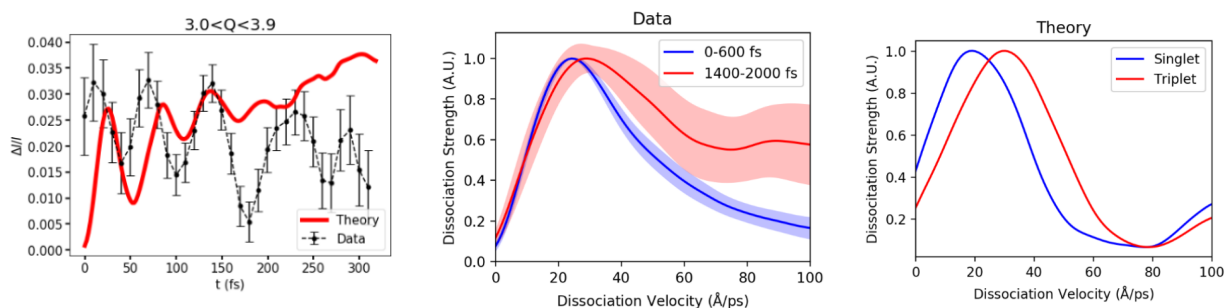
Figure 2 - Left: The x-ray scattering strength at Q=3-3.9A-1 oscillates in an anharmonic manner for the first 300 fs following excitation. Center: The measured distribution of fragment velocities, obtained by a Hough transform of the data vs. pump-probe delay. Right: The simulated Hough transform for trajectories that dissociate to ^{1}D or ^{3}P sulfer. The correspondence of singlet dissociations with early probe times, and triplet dissociations with late probe times, indicates that singlet dissociation is prompt compared to triplet dissociation.

Creating and probing electronic coherences in molecular systems: In small quantum systems superpositions of electronic states evolve on femtosecond or even sub-femtosecond timescales, resulting in an ultrafast transient in the charge density. In FY22 we published results demonstrating time-resolved measurements of coherent charge motion in core-excited molecular states initiated by the interaction with attosecond soft x-ray pulses [Li2022]. We probed this coherence using the angular streaking technique [Hartmann2018, Duris2019], where a circularly-polarized, infrared laser field is superposed with the isolated attosecond pulse. The IR field manipulates the trajectory of electrons released in the Auger-Meitner (AM) decay of the excited state, which modifies the measured electron momentum distribution depending on the relative phase of the IR field at the time when the electron is released. We observe a quantum beat in the time-dependent AM emission, indicating the coherence of the initial excitation. We are able to change the magnitude of the coherence by tuning the wavelength of the incident SXR

pulse. We show that core-excited states are an interesting testbed for probing coherent electronic phenomena.
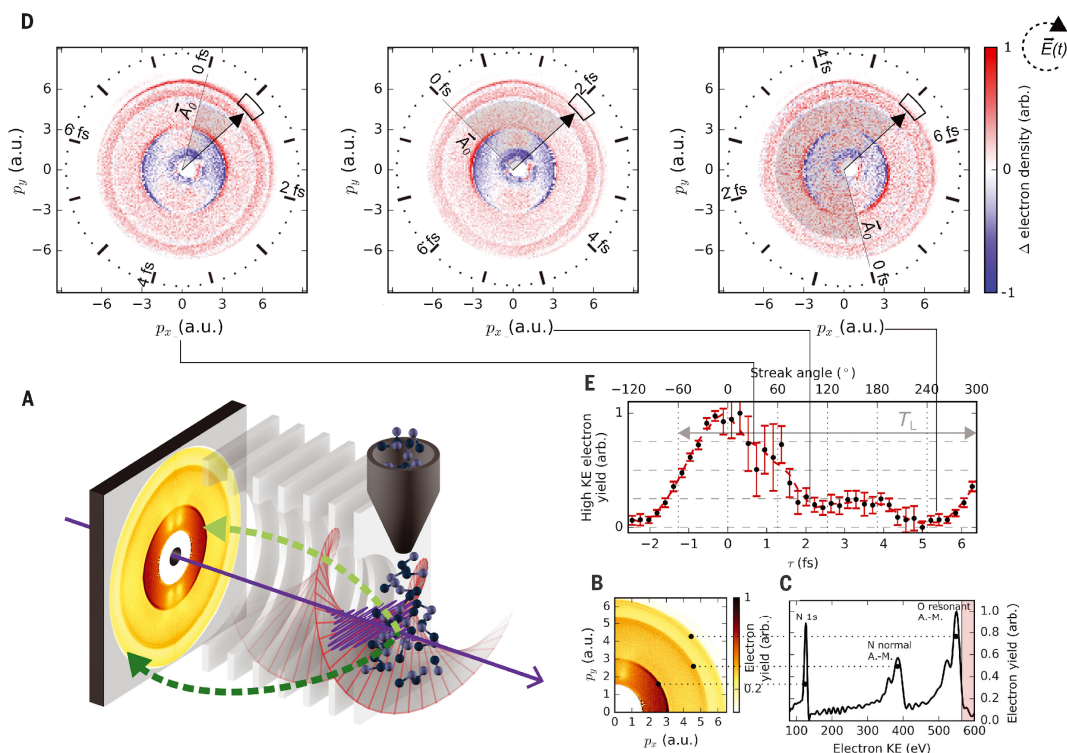
Figure 3 - Observation of the Temporal Evolution of Auger-Meitner (AM) Emission. (A) shows the experimental schematic, NO gas is ionized by attosecond XFEL pulses (~530 eV) in the presence of the 2.3 um, circularly polarized streaking field. The photoelectron momentum spectrum is measured with our coaxial velocity map imaging (cVMI) spectrometer. (B) The x-ray only projected photoelectron momentum spectrum was recorded, and (C) shows the pBasex inverted spectrum. (D) shows the differential (with streaking laser minus without streaking laser) momentum distribution for different directions of the streaking vector potential at the time when the x-ray pulse arrives at the sample (marked by A_0). (E) shows the yield of AM electrons in the black box shown in (D) as a function of angle between the observation box and the instantaneous vector potential at the time of ionization. We observe a quantum beat around 175 deg (3 fs).

Progress in the Attosecond Campaign: In FY22 we continued our efforts in the analysis of the data collected as part of the Attosecond Science campaign at LCLS ("Real-time Observation of Ultrafast Electron Motion using Attosecond XFEL Pulses" – PIs: J. Cryan, A. Marinelli, and P. Walter). In the previous year (FY21) we conducted the first two experiments in the campaign, which focused on measuring ultrafast charge motion in para-aminophenol (pAp; $NH_2C_6H_4OH$) using x-ray absorption (XAS) and x-ray photoelectron spectroscopy (XPS). The XAS dataset, measured near the oxygen K-edge, shows clear signatures of sub-femtosecond charge motion following inner valence ionization with 250 eV SXR pulses (Fig. 4). The absorption signatures match well with theory from our collaborators at Imperial College (Marco Ruberti and Vitali Averbukh).

Also in FY22 we conducted the third campaign experiment which focused on oxygen *K*-edge XAS of the meta-isomer of aminophenol, to study the effect of molecular linkages on charge migration. In FY23 we plan to continue in the analysis of the XPS dataset in pAp and compare with recent calculations from the group of Fernando Martin. We also plan to complete the analysis of the mAp dataset and compare with our previous results.
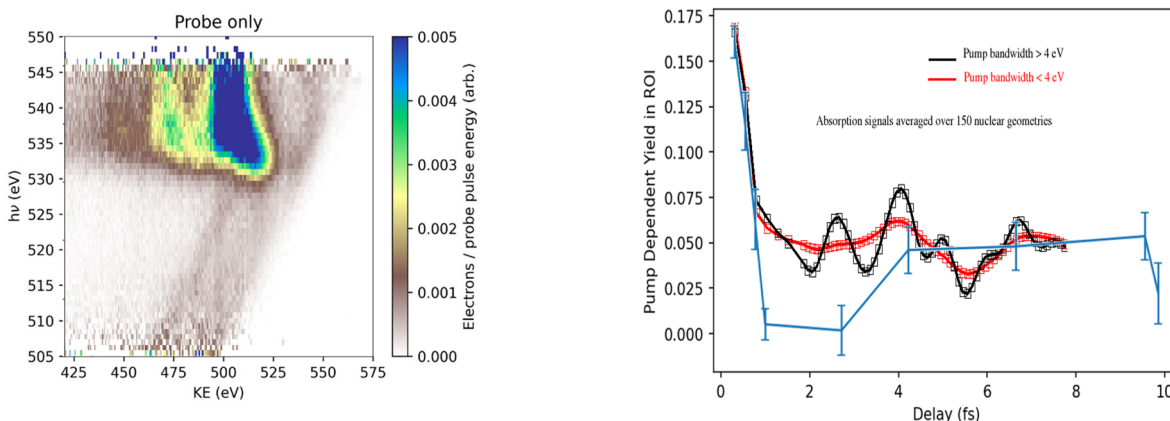
Figure 4 - Left: Single pulse resonant Auger-Meitner map record in para-aminophenol (pAp) target. An absorption spectrum is obtained by summing over the measured electron kinetic energy (KE). Right: The time-resolved absorption signal in blue, measured for the range between 522 and 527 eV. This can be compared to the simulations from Marco Ruberti shown in red and black.

Probing Photoionization in the time domain: In addition to probing coherence in core-excited states, the angular streaking technique described above, can be used to study the attosecond-scale dynamics of x-ray ionization of *K*-shell electrons. To this end, we have measured the photoionization delay between different *K*-shell continua in the nitric oxide (NO) molecule (Fig. 5). Scanning the photon energy across the oxygen *K*-shell threshold we observe many features in the photoemission delay. We can compare with calculations from the group of Agapi Emmanouilidou. We hope to finalize the comparison with the theory results and publish our measurements in FY23.

In addition to *K*-shell ionization, we have also explored the coupling of electronic and nuclear degrees of freedom in photoemission experiments. In our recent measurements of time- and vibrationally-resolved ionization of H_2, we show a distinct breakdown of the adiabatic approximation typically used in describing photoionization of small molecular systems [Wang2022].

Making better measurements thru correlation: Typically the shot-to-shot fluctuation inherent to SASE (stimulated amplification of spontaneous emission) based FELs is thought of as a nuisance, and produces an overall degradation of the measurement fidelity. However, we have been working to exploit the inherent correlation between these fluctuations and the resulting fluctuations in measured x-ray observables. We have demonstrated how this technique can be exploited in XPS measurements to recover high-resolution photoelectron spectra despite having significant fluctuations in the incident x-ray pulse and overlapping features in the photoelectron spectrum [Li2021a, Li2021b]. We have applied our previous demonstration of the correlated

analysis of XAS datasets [Driver2020] to the dataset recorded in the attosecond campaign to produce the curve shown in Figure 4.
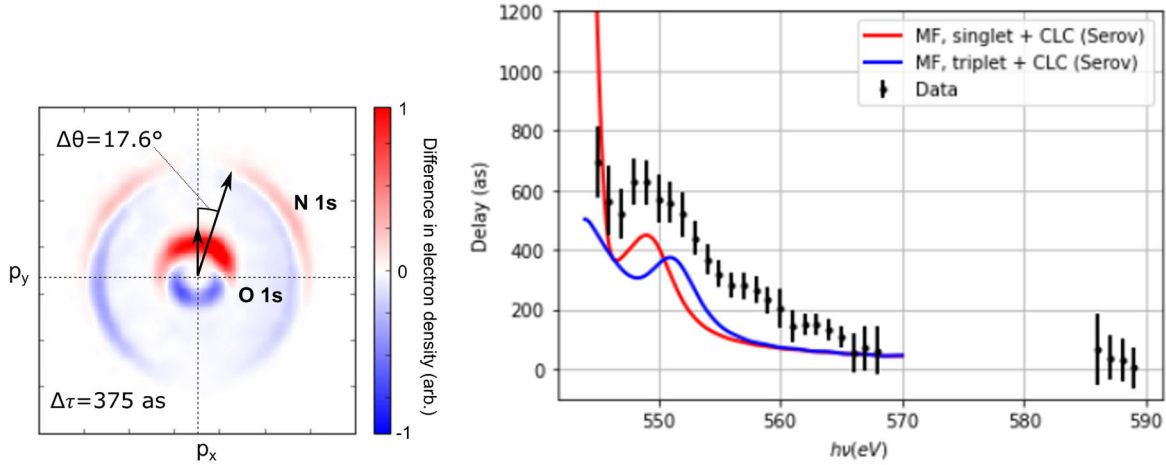
Figure 5 - Photoemission Delays of Core-Level Electrons: (Left) differential (with streaking laser - without streaking laser) electron momentum distribution measured from a nitric oxide target. (Right) The relative angle between the momentum shift in the nitrogen *1s* and oxygen *1s* electrons is related to the photoemission delay. We plot the relative momentum shift (in delay = angle shift / laser period; which is 7.35 fs) as a function of photon energy. We compared to simulated delays from our collaborator Agapi Emmanouilidou.

Future Plans:

Phase of the phase (POP) and phase of the phase of the phase (POPOP) analysis of trajectories in strong-field : Field ionization of a coulomb-bound electron is exponentially sensitive to the binding energy I_p and to the instantaneous field amplitude F: $\Gamma(F) \sim exp\left(\frac{-2\left(2I_p\right)^{\frac{3}{2}}}{|3F|}\right)$. Introducing a small 400nm (2ω) perturbation combined with a strong 800nm (ω) fundamental therefore alters the ionization probabilities according to the relative phase of the two fields, so-called "phase of the phase (POP) analysis." POP has been used to test predictions about the cycle phase value at the moment of tunneling for electrons that produce different features of the ATI spectrum, such as the tunneling phases that produce electrons that can rescatter. POP cannot, however, reveal the tunneling phases responsible for holographic features, since they are caused by interference between two different trajectories that tunnel at different phases of the optical cycle. When two different tunneling phases contribute to the same part of the spectrum, POP only finds the average of the two phases.

We've analyzed this problem and conclude that addition of a third color at the third harmonic can provide two distinct points of reference, which can unambiguously determine the phase of ionization for both trajectories in regions of the momentum spectrum where multiple trajectories contribute. We will test this idea in the coming year. POPOP results would complement our time-filtering results.

Time-resolved x-ray scattering from strong-field ionized molecules: The x-ray scattering experimental analysis methods that have been developed for molecular photochemistry in this program may also be used to study strong-field ionization. We are particularly interested in the question of cascaded multiple ionization followed by coulomb explosion. Previous work on strong-field multiply ionized water have been done in a different PULSE Institute program on coherent control, which is supported by NSF. We would like use femtosecond x-ray scattering at free-electron lasers to gain similar insights for the process involved in strong-field physics.

Probing electronic coherence in core-excited states: Core-excited states offer a fundamental test bed for studying coherent electron dynamics in highly excited and strongly correlated matter. Building on the angular streaking methodology, described above, for probing core-excited coherences, we performed subsequent experiments at the LCLS measuring the time-dependent AM emission from 1,1-difluoroethylene (CF_2CH_2). Excitation with the broad bandwidth SXR pulse creates a superposition between the non-equivalent carbon $1s$ core-hole states. These two states have an energetic separation of ~4 eV, and the superposition state creates a charge density which migrates back and forth between the carbon sites. We are currently in the process of analyzing the data and will continue these efforts in FY23.

Probing correlated electronic phenomena using photoemission: In a previous work, we demonstrated the sensitivity of attosecond photoionization delays to correlated electronic phenomena [Kamalov2020]. We are working to exploit this sensitivity to better understand shake-off ionization in neon atoms using the angular streaking technique. In FY22 we developed an approach to analyze a data set from LCLS which exploits angular streaking to measure the delay in the photoemission of single-photon double ionization (SPDI) relative to neon K-shell ionization. We plan to compare these results with theory calculations and publish the result in FY23.

Attosecond Campaign: With the upgrade of LCLS-II that can now reach high repetition rates, the attosecond campaign will begin to pursue nonlinear excitation of molecular charge densities. We plan to implement impulsive stimulate X-ray Raman scattering (SXRS), which was recently demonstrated by this task [O'Neal 2020], to produce a transient charge distribution. SXRS will produce charge densities that are initially localized around a specific atomic center which then spreads across the molecule. This relaxation will be probed with a second time-resolved x-ray pulse.

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Project Scope

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

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

- Identify how metal-ligand molecular orbital hybridization influences the electronic excited state properties of metal complexes and target desired photocatalytic properties.
- Understand the role of coherent solute motions in complex environments on solvation and energy transfer dynamics with atomic-resolution in space and time with ultrafast structural probes and simulation.

Achieving these scientific objectives also requires development of ultrafast x-ray and electron methods. Our previous research has emphasized the development of simultaneous hard x-ray solution scattering (XSS) and x-ray emission spectroscopy (XES) as probes of charge, spin, and metal-ligand bonding dynamics in electronic excited states (Gaffney 2021). Moving forward, our method development activities will focus on two developments. Firstly, we will use the extension of the 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 solvent and solvation structure. Secondly, we will use the increase in 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 (Jay 2022).

Recent Progress

***Controlling metal complex excited state properties with metal-ligand covalency* (Kunnus 2020a; Kunnus 2020b; Ledbetter 2020b; Tatsuno 2020; Vacher 2020; Gaffney 2021; Larsen 2021; Reinhard 2021; Jay 2022; Kunnus 2022)**: Our long standing goal of controlling charge transfer

excited states of 3d complexes continues to broaden the scope of ligands investigated. Mechanistic studies of excited state relaxation in Fe model photosensitizers focused on the mixed ligand complex $[Fe(pp)(CN)_4]^{-4}$, where pp is a polypyridyl ligand and the incorporation of CN ligands is known to destabilize MC states and extend the MLCT lifetime. Our most recent work has focused on ligand control of MLCT lifetimes, using polypyridyl ligand modifications as a pathway to controlling excited state relaxation processes (Kunnus 2020a). These studies have used a novel combination of ultrafast optical spectroscopy and Fe L-edge resonant inelastic x-ray scattering (RIXS) to demonstrate that the MLCT relaxation mechanism transitions from one mediated by metal-centered excited states at large chemical driving force to one driven by vibrational tunneling in the Marcus inverted region at lower chemical driving force. These findings strongly indicate that successful design of ligands for long MLCT lifetimes requires both reducing the chemical driving force and minimizing the charge transfer induced distortions of the electron accepting ligand. These finding are directing the next steps of this research project.

We have continued a project focused on understanding the impact of metal-ligand covalency on charge transfer excited state lifetimes by investigating highly covalent iron carbene and iron amido complexes (Kunnus 2020b; Tatsuno 2020; Vacher 2020; Larsen 2021; Kunnus 2022). The general concept we are targeting in this work is the extension of the spatial distribution of the Fe 3d orbitals through increased covalency to increase the ligand field interactions, decrease electron exchange interaction, and ultimately destabilize the high spin metal centered (MC) states that deactivate charge transfer excited states. This work highlights the ability of Fe 2p3d resonant inelastic x-ray scattering (RIXS) to directly characterize the energies of the MC excited states, inaccessible from traditional optical spectroscopy. Two Fe carbene complexes were investigated with steric groups that vary the Fe-carbene interaction (Kunnus 2022). Bulker ligand groups were found to decrease the σ donation by the ligand, thus tuning the 3d orbital splitting (10Dq) and MC state energy. RIXS was used to identify a ~1 eV destabilization of the 5MC excited states of the more covalent system (less bulky substituent groups). This covalency effect on electronic structure explains the large increase in MLCT lifetime (10 ps vs. 200 fs) for the more covalent system. Similarly, amido containing Fe complexes were investigated to identify the influence of strong π donation by the amido ligands and Fe electronic structure (Larsen 2021). Fe L-edge and N K-edge x-ray absorption and RIXS were used to validate the strong mixing of the amido N π and Fe t_{2g} orbitals. This covalent interaction was found to decrease the electron exchange interaction, offsetting the effects of the weaker ligand field. Overall, the stabilization of MC excited states for the Fe amido complex compared to a polypyridyl complex was significantly less than that expected by the decrease in 10Dq alone, by a factor of 2 (^{3}MC state) to 4 (^{5}MC state). Thus, tuning metal-ligand covalency was found to be a novel tool for the systematic design of Fe photosensitizers with long-lived charge transfer excited states.

Real-space methods for viewing chemical dynamics in complex chemical environments (Bucksbaum 2020; Kierspel 2020; Ledbetter 2020a ; Nunes 2020; Biasin 2021; Lin 2021; Natan 2021; Yang 2021a; Yang 2021b): The CDS sub-task has pursued three parallel developments focused on establishing direct structural probes of complex chemical dynamics in solution. We have:

- Developed and commissioned a new liquid-jet endstation for solution-phase ultrafast electron

diffraction measurements in collaboration with Thomas Wolf, Jie Yang, and Xijie Wang.

- Implemented high-energy (18 keV) XSS to effectively separate the solute and solvation response to electronic excitation in solution.
- Established a model-free approach to invert scattering signals to real space images, surpassing the diffraction limit, using scattering kernels and signal priors that naturally arise from the measurement constraints.

Using the new liquid-phase UED capabilities, we probed the photo-induced structural changes of liquid water under conditions ranging from vibrational to strong field excitation. In collaboration with Jie Yang, following vibrational excitation of water we observed a transient hydrogen bond contraction occurring on the ~80 fs timescale, followed by thermalization. This result captures the intermolecular structural response of water that precedes vibrational relaxation for the first time and demonstrates the spatial distribution of the proton in the H-bond must be treated quantum mechanically to accurately model the magnitude of the contraction (Yang 2021a). In collaboration with Ming-Fu Lin, following the strong field ionization of water we characterized the structure of the short-lived $OH^{\cdot}(H_3O^+)$ radical-cation complex formed via ultrafast proton transfer within 140 fs of water ionization for the first time (Lin 2021). Looking beyond neat water solutions, we investigated the ability of liquid-phase UED to interrogate photochemical structural dynamics of solute molecules dissolved in solution. We probed the photodissociation reaction of aqueous I_3^- to form I_2^- and I. By comparison with molecular dynamics simulations, we were able to extract an average dissociation speed for the reaction, and observe geminate recombination of the fragment molecules on the few ps timescale (Ledbetter 2020a).

UED has multiple strengths, in particular the high spatial resolution and large elastic scattering cross-section for relativistic electrons. These strengths notwithstanding, as presently implemented, space charge effects, even for MeV electrons, still require a compromised between the time resolution and signal-to-noise. This motivates our continued effort to use the increased photon energy range of LCLS-II to advance ultrafast XSS. We recently led an ultrafast XSS experiment using 18 keV (0.7 Å) x rays that has demonstrated the ability to decompose ultrafast chemical dynamics into specific changes in the solute and the solute-solvent pair distribution function with a particular focus on how electronically excited states change the interaction between the solvent and photo-catalytically active metal sites. We directly trace the spatiotemporal shape of coherent vibrational wavepacket motions and energy redistribution of different atom-pairs that take places simultaneously, without bias toward the Franck-Condon active modes or the constraints of normal mode analysis.

The success of this analysis has depended critically on the development of model-free inversion methods, capable of surpassing the diffraction limit, using scattering kernels and signal priors. We have used the approach on simulated and experimental data, recovered the simulated atomic motions at sub-Å resolution, and shown how signal fidelity determines the recovery accuracy and resolution limit. The approach offers a robust path to high-resolution real-space structural dynamics using time-resolved X-ray and electron scattering sources. This approach may help bridging the established pair-distribution function analysis that requires much higher Q-ranges ($Q > 30$ Å^{-1}) with ultrafast x-ray and electron scattering measurements that only now are achieving high signal-to-noise transient signals to $Q \approx 10$ Å^{-1}. In addition to the application of these inversion

methods to XSS measurements, we have also applied them to UED studies of ring opening in photoexcited 1,3-cyclohexadiene. Our results are in excellent agreement with the ab initio multiple spawning (AIMS) simulations conducted by Todd Martinez and co-workers, without further processing the trajectories.

Future Plans

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

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

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

Obtaining a microscopic view and control of Coherence in Solution Phase: We propose to develop and implement ultra-wide-angle (<100 degrees) high-energy ultrafast x-ray scattering, optical control methods, QM/MM simulations, and advanced imaging approaches, to study the microscopic aspects of quantum mechanical decoherence in solution. The extended Q-range and anisotropy in the x-ray scattering will enable the shape of time-dependent vibrational wavepackets to be resolved. Once we have established to ability to image the shape of vibrational wavepackets of solvated molecules, we will focus on understanding how changes in the optical excitation and solvent environment influence quantum mechanical decoherence. Our initial studies will focus on two chemical systems.

- Metal augmented M-PtPOP (PtPOP = $[Pt_2(P_2O_5H_2)_4]^{4-}$) complexes, where M = Ag^+ or Tl^+. For PtPOP, without ion complexation, the Pt_2 core is decoupled from the solvent, leading to very slow dephasing of the Pt-Pt stretch vibrational wavepacket. The situation changes significantly when PtPOP is complexed to Ag^+ or Tl^+ because these ions strongly couple to the solvent and provide a conduit for the solvent to modulate the Pt-Pt stretch vibrational dynamics.
- Coherently controlled and selective excitation of IrDimen, where IrDimen = [Ir$_2$(1,8-diisocyano-*p*-menthane)$_4$]$^{2+}$. IrDimen provides a valuable molecular system because the shape of potential that controls the Ir-Ir stretching vibration enables broadening and focusing of the vibrational wavepacket as a probe of the onset of decoherence for large anharmonic motions.

So far, the measurements have been restricted to measuring changes in mean bond lengths of only one or two structural degrees of freedom. 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.

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Gas phase Ultrafast Chemistry

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Project Scope

Our interest is the investigation of elementary chemical processes in the excited states of isolated molecules on their natural time scale of femtoseconds and picoseconds. We are especially interested in non-Born-Oppenheimer approximation (non-BOA) dynamics, because of its importance for light harvesting, atmospheric chemistry and DNA nucleobases photoprotection. For this purpose, we combine state-of-the-art experimental and theoretical approaches connected to the unique ultrafast facilities at SLAC.

Recent Progress

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

We have investigated the structural dynamics leading into the pericyclic minimum of a photochemical electrocyclic ring-opening reaction with a combination of megaelectronvolt ultrafast electron diffraction and *ab initio* multiple spawning (AIMS) simulations. We used a derivative of the prototypical molecule 1,3-cyclohexadiene (CHD), α-terpinene (aTP). It exhibits an isopropyl and a methyl substituent on opposite sides of the carbon ring, whereas both substituents are bound to sp^2-hybridized carbons. The presence of the substituents does not substantially alter the ring-opening dynamics of aTP with respect to CHD. However, the presence of the additional carbon atoms of the substituents generates additional carbon-carbon distances and, therefore, additional strong features in the static and time-dependent atomic pair distribution functions. These "reporter" distances are sensitive to details of the relaxation into the pericyclic minimum of the excited state, which could not be observed in CHD. In particular, we observe an out-of-plane bending motion of the methyl substituent prior to ring-opening. With the help of the AIMS simulations, we interpret this motion as the signature of rehybridization

dynamics of the two carbon atoms, which are directly involved in the bond dissociation during the ring-opening. The rehybridization largely happens in the excited state and prior to the structural opening of the ring. Therefore, the pericyclic minimum represents an early stage of the ring-opening and a substantially later stage of the hybridization change.

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

Future Plans

We plan to continue our studies of the interplay between electronic and nuclear degrees of freedom during ultrafast dynamics in isolated molecules. We plan a series of combined experimental and theoretical studies focused on tuning the accessibility of photochemical reaction pathways by the structural modification of the reactant.

Peer-Reviewed Publications Resulting from this Project (2020-2022):

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Ultrafast Electron Dynamics in Extended Systems (UEDES)

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Scope of the program

This sub-task focuses on fundamental light-matter interaction in extended systems such as bulk crystals, nanoscale 2d-crystals, interfaces, and surfaces. We are interested in how strong-field driven dynamics in condensed matter system compare with their atomic and molecular counterparts and what it can tell us about excited states and strongly-driven dynamics. 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. For excitation, we typically use intense near and mid-infrared laser pulses such that 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 task 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 optical media 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

HHG from stacked 2d-crystals: Strong-field interactions in stacked 2d-crystals subjected to intense mid-infrared laser fields produces non-perturbative high-order harmonics. Measured spectra consist of plateau features with harmonic orders extending to about 19th orders when the peak field strengths of mid-infrared drivers are about 1.1 V/nm (peak intensity about 3×10^{11} W/cm^2). The spectrum exhibits even and odd orders depending on how monolayers are stacked on top of each other and their crystallographic orientations.

In natural bulk crystals of transition metal dichalcogenide (TMDC), the crystallographic orientations of adjacent layers are rotated by 180 degrees, which is denoted by ABAB configurations. In this configuration, the bulk crystals exhibit inversion symmetry, therefore, they produce only odd-order harmonics in the dipole approximation. The isolated monolayers, on the other hand, are non-centrosymmetric, and they generate both even and odd-order harmonics. Interestingly, the polarization directions of even-orders are not necessarily along the same direction as the driving laser fields. They are

orthogonal to the laser fields when the laser fields are aligned perpendicular to the mirror planes of the crystal. However, odd orders strictly follow the direction of the laser field regardless of their crystal orientation. These polarization analyses helped us understand the underlying microscopic mechanism of HHG in the optical media at the nanoscale. A detail report about polarization anisotropy has been published [Kobayashi2021].

Artificial stackings of monolayers provide additional degrees of freedoms in the synthesis of novel optical media. For example, special twist angle between two graphene layers has shown to form interesting moiré patterns leading to superconductivity. In our experiments, we stacked up to 4 layers in various crystallographic configurations such as AAAA or ABAB as shown in figure 1. We find that in the AAAA configuration high-harmonic efficiency increases quadratically as a function of number of layers. AAB and AAB
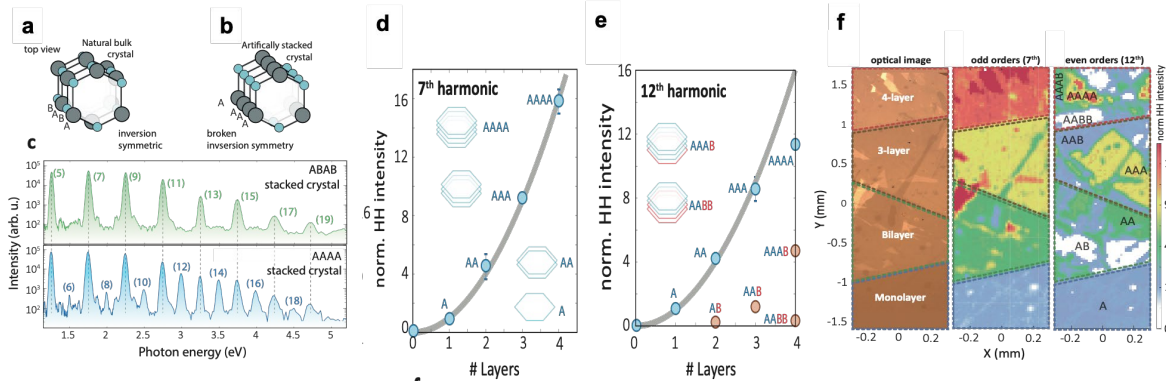
Figure 1. a) shows the ABAB configuration of natural bulk crystal b) shows one example artificial stacking in AAAA configuration. c) shows measured harmonic spectra from ABAB and AAAA configuration stacks. d) and e) show harmonic efficiency as a function of number of layers. f) shows optical, odd-harmonics, and even-harmonics microscopic images, along with their optical counter parts.

configurations provide a controll on the efficiency of even order harmonics as both AB and ABAB stacks do not produce even-orders.

Typical sample synthesis process is such that it is often difficult to distinguish between different number of stacks, based on their optical images. High-harmonics provide better contrast including the layer configurations. The potential advantage of high-harmonic microsocpy over fluorescence microscopy or second harmonic generation microscopy is the the possibility of probing high energy and momentum in the electronic bandstructure, which have relavance in the study of flat band and many body correlation dynamics. In the real space, if the excursion distances of driven electrons are on the order of Moiré lattice, high-harmonics could be an ultrafast probe of such novel optical media. High-harmonics have also shown the sensitivity to probe not only the electronic band structure but also the topology[Baykusheva 2021, Heide 2022, Bauer2022].

Probes of heterostructures of 2D materials and their dynamics: We have been investigating heterostructures formed from two different semiconducting monolayers in the transition metal dichalcogenide family that exhibit type II (staggered) band alignment. Above-gap optical excitation produces an initial state in which the electron and hole reside in the same monolayer. These intralayer excitons then quickly relax into interlayer excitations, with the electron in one layer and the hole in the other, forming interlayer excitons.

In recent research results, we have investigated the formation and properties of these prototypical charge separated interlayer states with two methods: (1) using direct absorption measurements of the interlayer excitons through an electro-modulation technique [Barré 2022] and (2) using time-resolved photoemission (tr-ARPES), in a collaboration with the group of Keshav Dani at OIST, Japan, to image these interlayer excitons in momentum space [Karni 2022].

The absorption measurements of interlayer excitons must tackle the issue of their low oscillator strength and relatively weak spectroscopic signature. This property can be understood as the counterpart of the reduced radiative rate associated with the small overlap of the spatially separated electron and hole. To overcome this obstacle, we developed an electro-modulation technique. It relies on the large linear Stark shift of the energy of the interlayer exciton under an applied perpendicular field, which follows from the large static dipole of moment of this exciton species.
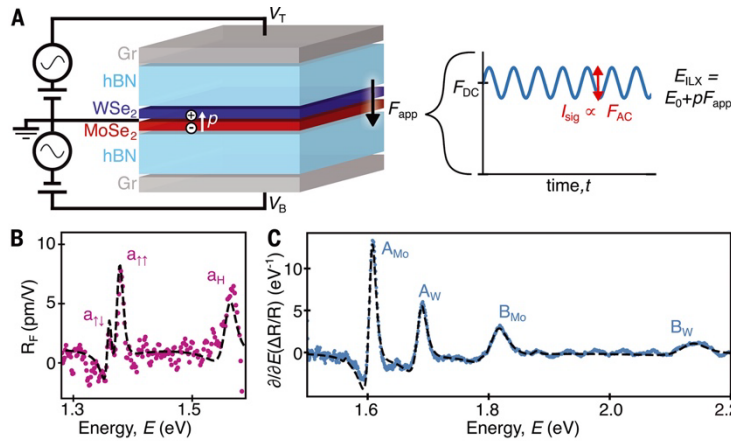
Figure 2: *Direct spectroscopic characterization of interlayer excitons in a WSe₂/MoSe₂ heterostructure obtained using an electro-modulation method depicted schematically in (A). The corresponding interlayer exciton absorption in the lower spectral region is shown in (B), with the intralayer exciton absorption in each of the separated layers shown in (C). The strength of the interlayer transitions was less than 1% of that of the intralayer excitations.*

Representative results for the absorption spectrum of the interlayer exciton (compared with the intralayer states) are shown for a WSe₂/MoSe₂ heterostructure in figure 2, with the concept of the experiment illustrated in (A). The magnitude of the susceptibility for the resonant interlayer response (B) is found to be over two orders of magnitude smaller than that of the intralayer transitions (C).

The application of this method provided a wealth of information about this heterostructure. We were able to determine the intrinsic radiative rate of the interlayer states (from analysis of the absorption), the variation of the interlayer exciton energy and oscillator strength with twist angle between the crystallographic axes of the two monolayers, and the value of the interlayer exciton static dipole moment (from the magnitude of the Stark shift for a known applied field). This latter quantity provides a means of assessing the degree of hybridization of the states of the two layers, since it reflects the average position of the electron and hole forming the interlayer exciton.

The time-resolved, angle-resolved photoemission spectroscopy (tr-ARPES) measurement of interlayer excitons gave us a highly complementary view of these interfacial excited states and their dynamics. The measurements also examined a heterostructure formed by stacking two different transition metal dichalcogenide layers on top of one another. Interlayer excitons were created by photoexcitation with a femtosecond pulse and subsequently probed through electrons emitted by the application of a second, XUV ultrafast light pulse using the capabilities in the group of Keshav Dani (OIST, Japan), as indicated schematically in figure 3. The interlayer exciton states could be imaged both by the presence of photoexcited electrons in the layer with the lower-lying conduction band and also through the signature of holes in the layer with the higher lying valence band. We

were thus able to image both the electron and hole forming the interlayer exciton and the position of each in momentum space (Figure 3).

The experiment yielded several significant findings. In addition to a direct confirmation of the valley and layer character of the electron and hole making up interlayer exciton, we were able to determine the widths of the momentum distributions for the electrons and holes. Since the excitons were cold (relaxed in energy with the sample at low temperature), these widths reflect fundamental characteristics of the interlayer excitons. As established in collaboration with theory collaborator Felipe Jornada (Stanford), the experimental momentum widths determined the electron-hole correlation and the degree of exciton localization. The latter was the result of the presence of a moiré potential formed by the slight lattice mismatch of the well-aligned MoS_2 and WSe_2 monolayers.
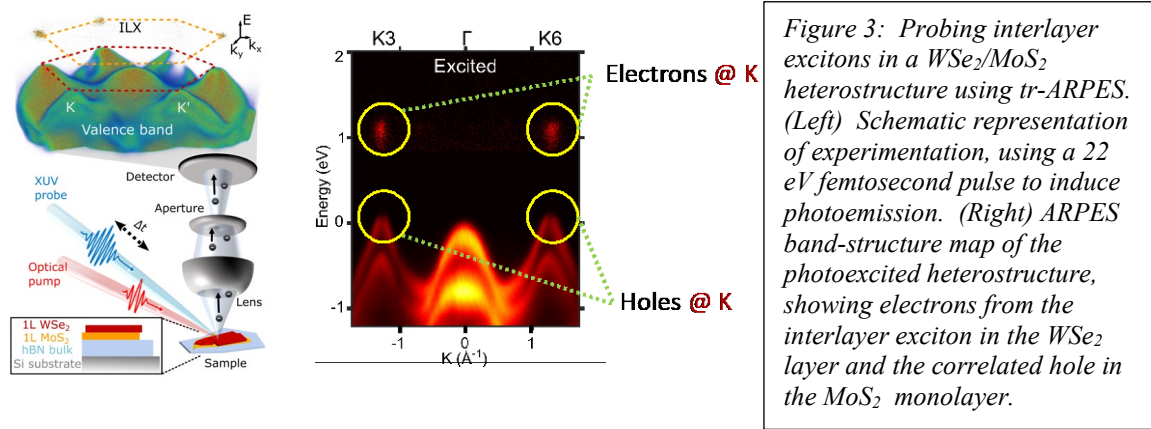
Figure 3: Probing interlayer excitons in a WSe_2/MoS_2 heterostructure using tr-ARPES. (Left) Schematic representation of experimentation, using a 22 eV femtosecond pulse to induce photoemission. (Right) ARPES band-structure map of the photoexcited heterostructure, showing electrons from the interlayer exciton in the WSe_2 layer and the correlated hole in the MoS_2 monolayer.

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

environment, while the (non-dipolar) x-ray probe further breaks symmetry in the scattering geometry (this previously allowed us for example to observe the first x-ray second harmonic generation in diamond [Shwartz2014]). At an intensity of $\sim 10^{12}\,\text{W/cm}^2$ we measure the relative efficiency between the second to first order to be 10^{-3} when the applied field is parallel to the 110 direction. As shown in Figure 4, the second order charge density shows nontrival polarization dependence compared to the first order which depends on the projection of the field perpendicular to the lattice planes.

Figure 4. *Polarization dependence of the second order XSFG signal in silicon. The maximum signal strength for the elastic diffracted beam was about ~2x10⁶ Photons/Shot (and about 2/shot for the first order side-band). The polarization was varied in the (001) plane parallel to the surface. The dashed line is based on a fit to the expected form of the second order Fourier component of the 220 charge density. The upper inset shows predictions for the spatial distribution for the relevant components of the microscopic charge density for the laser polarized in the (001) planes. The lower inset shows the 2nd order XSFG side-*
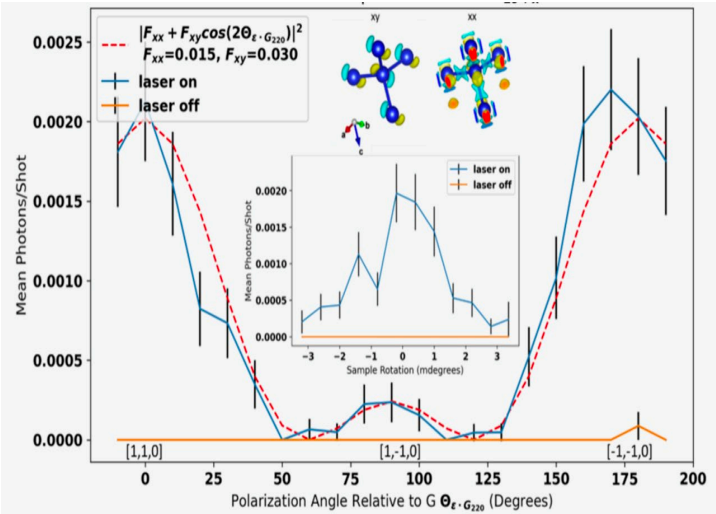
Planned Research

Element specific ultrafast probing of driven many body dynamics: Recently the LCLS had a spectacular success in generation and characterization of attosecond x-ray pulses using angular streaking method [Li2022]. Much of attosecond experiments are being conducted in dilute gas phase samples. We plan to extend those capabilities to periodically driven condensed matter systems, where nonequilibrium dynamics are expected to occur on the time scale of the periodicity present in the carrier of the driving MIR laser pulse [Dejean 2018]. These dynamics are expected to be qualitatively different to their atomic and molecular counterparts because of the extended nature of optical media (high-density and periodicity). We will compare the strongly correlated electron system NiO with other wide band-gap dielectrics, where strong correlations are not expected but contain ample amount of sub-cycle dynamics as indicated from their HHG response.

Our recent collaborative beamtime with Hermann Dürr at the LCLS in standard configuration ($\geq$50 fs x-ray pulses) shows changes in the O-k-edge [Grånäs2022] as opposed to the expected changes in the Ni-L-edge according to the theory from the Rubio group [Dejean2018]. The theory considers the expected role of many-body interactions for example in the form of Ni-d-electrons repulsion. Shorter x-ray pulses are required to resolve this discrepancy.

Charge transfer across interfaces: We will continue our investigations of model interfacial systems provided by 2D semiconductor heterostructures to elucidate the dynamics of electron motion at well-defined boundaries. In addition to the already

established experimental tools based purely on optical methods (pump-probe and time-resolved photoluminescence) and time-resolved ARPES, we will prepare for measurements using the capabilities of the new high repetition rate LCLS-II free electron laser. By exploiting core-level atomic transitions (through x-ray absorption and emission measurements), we will be able to add *element specificity* to our probe methodology, as well as having a possible route to extend the measurements down into the sub-femtosecond time regime.

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

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X-ray spectroscopy of catalytic reactions on nanoscale surfaces for clean energy production

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Staff and students: Alexandra Feinberg (Postdoc), Martin Grassl (graduate student)

Project Scope: Photochemical reactions on the surface of nanoparticles (NP), such as those with molecular adsorbates, play a fundamental role in clean energy science. Such reactions can be induced and/or enhanced by electric field localization on the NP surface. In this project, we aim to develop and implement techniques to interrogate photochemical reactions that can occur in gas-NP and liquid-NP interactions. Specifically, we will focus on reactions fundamental to clean energy science, such as those of catalytic water splitting and hydrogen production. To achieve these ambitious goals, we will leverage high-repetition rate, next generation optical and x-ray light sources with the ultimate goal of achieving atomic specificity with down to attosecond time resolution.
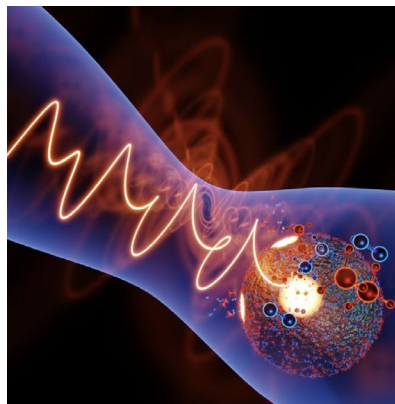
Recent Progress: Our reaction nanoscopy [1] technique, based on the three-dimensional momentum spectroscopy of charged molecular fragments, enables imaging near-field-induced reaction yield distributions from the surface of aerosolized nanoparticles [2]. The technique is derived from COLTRIMS (cold target recoil ion momentum spectroscopy), but with the important difference that the cold target is replaced by an aerosolized nanotarget. Reaction nanoscopy has recently facilitated the observation of the formation of trihydrogen cations from water molecules on silica nanoparticles [3].

Previous works on the optical control of particle emission dynamics from laser–NP interactions have concentrated on near field induced electron emission [4]. Presently, we have expanded on these works to study ion emission. Tailoring the surface near field by phase-controlled linear or bicircular two-color laser pulses enables generating well-defined, anisotropic charge distributions on the nanoparticle surface, in turn allowing manipulation of the charge-driven, directional proton emission from the surface. Using reaction nanoscopy as an ultra-sensitive technique to track the proton emission angle, we can ascribe the inhomogeneous charge distributions induced by the near field on the NP surface. This all-optical control scheme has recently facilitated the observation of site selective proton emission from the dissociative ionization of adsorbate molecules on the surface of SiO_2 NPs. Reaction nanoscopy is expected to be applicable to a wide class of more complex nanosystems, both isolated and surface-based. These results pave the way toward the all-optical control of catalytic photochemical reactions on the surface of structured NPs.

In addition to NPs, other nanosystems such as nanodroplets can expand our understanding of strong-field induced surface chemistry. Recently, using reaction nanoscopy, we have reported on the near field driven ion emission from liquid propanediol (PDO) droplets ionized by strong, few-cycle laser pulses. Our technique facilitated recording the full three-dimensional ion momenta which was used for an in-situ determination of the droplet size and charge. Comparing ion emission from two different isomers (1,2-PDO and 1,3-PDO) in both the

gas phase and in droplets permitted identifying droplet specific, as well as isomer specific effects in the ion emission. Our results prove that reaction nanoscopy is a versatile tool for studying emission from laser-ionized droplets, which is highly relevant to surface chemistry studies using electrospray ionization sources.

Future Plans: We plan to utilize the unique capabilities of next generation free electron laser light sources, such as the soon to come online LCLS-II, to provide elemental specific, pump/probe measurements of ultrafast reaction dynamics on the surface of nanosystems. Excitation and detection at different absorption edges would allow us to observe the charge and energy flows within systems, from e.g. a nanosystem to a molecular adlayer and vice versa. Along this line, we have a proposal under review for an experiment at EU-XFEL where we aim to investigate proton and H_3^+ production from various NPs using ultrafast x-ray pulses, both core-level resonant and off resonant. By comparing these results with those from laser driven experiments, we can better understand the key roles that charge build-up and local near fields play in nano-catalytic surface chemistry. We will also extend ultrafast x-ray studies to include multiple nanosystem moieties such as liquid droplets and rare-gas clusters. Reactions within and on the surface of superfluid helium nanodroplets present another frontier; in particular, helium's superfluid nature and high ionization potential make the droplets an ideal matrix to study chemical reactions in an environment where the background itself does not contribute to any substantial signal when excited by optically. The droplets can be used to interrogate solution-phase photochemical processes in ways not possible with traditional, time-resolved chemical dynamic studies. Additionally, they can be used as a physical support for coherent diffractive imaging studies of fragile nanosystems, which can open a new avenue of experiments.

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[2] - Rosenberger, P. *et al.* Near-Field Induced Reaction Yields from Nanoparticle Clusters. *ACS Photonics* **7**, 1885-1892, doi:10.1021/acsphotonics.0c00823 (2020).

[3] - Alghabra, M. S. *et al.* Anomalous formation of trihydrogen cations from water on nanoparticles. *Nature Communications* **12**, 3839, doi:10.1038/s41467-021-24175-9 (2021).

[4] - Seiffert, L. et al. Strong-field physics with nanospheres Advances in Physics: X, 7:1, DOI: 10.1080/23746149.2021.2010595 (2022)

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

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Program Scope

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

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

Recent Progress

We have recorded valley-polarization dynamics after photoexcitation of monolayer WS_2 with circularly polarized light. Circularly polarized light preferentially excites excitons at only 3 of the 6 corners of the Brillouin zone due to chiral selection rules in these materials. After extensive analysis, we have now completed a paper on these dynamics [1]. While these exciton dynamics have been previously studied using optical spectroscopy, these constitute the first momentum-resolved measurements, i.e. the first momentum-space images, of valley-selective excitation and subsequent valley depolarization in a 2D material. Figure 1 shows the photoelectron distributions from the initially pumped K^- valley and also the K^+ valley populated via valley depolarization. The nearly identical photoelectron distributions observed in K^- and K^+ valleys strongly indicate the intervalley Coulomb exchange mechanism and rule out competing mechanisms involving electron-phonon coupling or direct Coulomb interaction between the excitons [1]. We know two other groups working on this problem, so we are fortunate (this time) to get the paper done first. At the time of writing, our paper is still going through the peer review process. Since submission, we have presented this work at several conferences, including the *International Conference on Ultrafast Phenomena* in Montréal, where we presented three papers on ARPES in total [2–4].

We have also recorded time-resolved ARPES data from monolayer graphene. At time-zero (pump/probe overlap) one sees the k-dependence of the dipole matrix elements beautifully in the raw data, with nodes along the pump polarization direction as predicted by theory. We have been working to carefully model this data accounting also for both the pump and probe matrix elements via calculations based on the tight binding model for graphene. We are also working to quantify
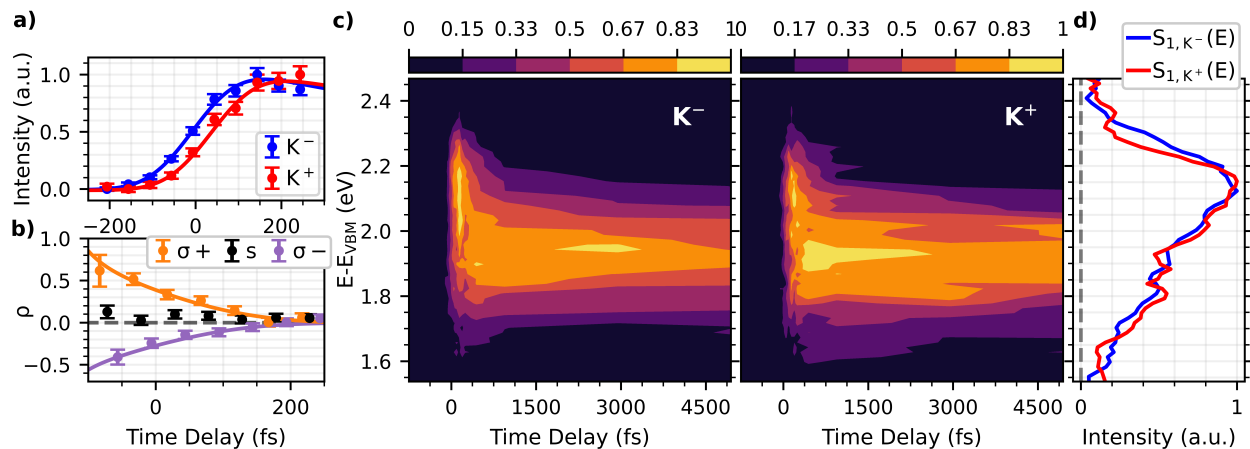
Figure 1: **Time-resolved ARPES of initially valley-polarized excitons in monolayer WS$_2$ formed by excitation with σ^--polarized light. a)** Integrated intensities for the K$^-$ and K$^+$ valleys following σ^- excitation. **b)** The valley asymmetry (ρ) for σ^+, σ^-, and *s*-polarized photoexcitation. Points are experimental data, lines are global analysis (GA) fits. The observed valley asymmetry decay time scale of $\sim$250 fs is limited by the instrument response. **c)** Comparison of the K$^-$ and K$^+$ valleys following σ^- excitation shows that the two valleys present nearly identical dynamics, the difference being a 43 ± 4 fs delay in the appearance of signal in the unpumped K$^+$ valley. **d)** The GA spectral components $S_1(E)$ for the K$^-$ and K$^+$ valley signals show that the population transfer from the pumped valleys to the unpumped valleys does not involve significant changes in the energy distribution. Complete details can be found in [1].

the competition between electron-electron and electron-phonon scattering via fluence-dependent measurements. This will form the basis for graduate student Jin Bakalis' dissertation.

In the meantime, we have also made progress towards experiments on polyacene crystals. We are pursuing both ex-situ and in-situ crystal growth. For ex-situ growth, we have obtained 300 nm thick tetracene crystals grown on silicon and recorded first photoelectron spectra. Sample charging does not appear to be a major issue, but we have not yet obtained good enough surface quality to record ARPES. We need to try different methods for cleaving the crystal in vacuum. For in-situ growth we have purchased a new small vacuum chamber to better grow the crystals before in-vacuum transfer to the main ARPES end station chamber. We have assembled this chamber now and are ready to install it on the system.

We continue to participate in the LCLS momentum microscope collaboration and will participate in a beam time for commissioning the instrument at PETRA III this fall.

Future Plans

We will apply the Stony Brook tr-ARPES instrument to crystals of tetracene, pentacene, and eventually hexacene. We will also perform experiments at the LCLS and the NSF NeXUS. The data sets produced from this work will provide important guidance to theory in this area. Indeed, there are already many theoretical predictions for the delocalization of the triplet excitons, and the resulting band dispersion, but this has not been measured. The ultimate improvement in fundamental understanding and modeling can lead to engineering of optoelectronic devices based on singlet fission, just as deep fundamental understanding of conventional semiconductor physics has enabled high-performance silicon-based electronics.

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

Papers still under review.

References

[1] Alice Kunin et al. *Momentum-Resolved Exciton Coupling and Valley Polarization Dynamics in Monolayer WS$_2$*. 2022. DOI: `10.48550/ARXIV.2203.02419`. URL: `https://arxiv.org/abs/2203.02419`.

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[3] J. Bakalis et al. "Anisotropic Carrier Dynamics in Graphene Probed with Time- and Angle-Resolved Photoemission Spectroscopy". In: *The 23rd International Conference on Ultrafast Phenomena*. 2022.

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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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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 2020-2022 and is illustrated by publications [1-16].

2.1 Ultrafast nonlinear electron dynamics of graphene quantum dots [12]

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

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

more paths can contribute to the formation of high harmonics coherently, resulting in more significant intensity.

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

2.2 Topological resonance in graphene-like materials [13]

We developed a complete theory of topological resonance in multilayer graphene-like materials. The origin of topological resonance is an accumulation of topological phase in the materials, interacting with short and strong optical pulses. Such a phase can compensate the dynamic phase, which results in strong inter-band coupling. The topological resonance is similar to the regular resonance when the dynamic phase is canceled by the phase of the time-dependent electric field. The fundamental difference between these two resonances is that while the regular resonance depends on the frequency of the pulse but not on its amplitude, the topological resonance depends only on the pulse amplitude but not on its frequency.

The unique feature of the topological resonance is that the corresponding topological phase is determined not only by the intraband Berry connection but also by the phase of the interband Berry connection, which is proportional to the interband dipole matrix element. Thus, the net topological phase can be zero even for topologically nontrivial solids, for which the intraband Berry connection is nonzero within the whole Brillouin zone. For example, for a multilayer graphene system, the two contributions to the topological phase cancel each other if the system has an inversion symmetry and correspondingly zero bandgap. For such gapless materials, the topological resonance cannot be observed. But if the inversion symmetry is broken, then the net topological phase is nonzero, and the conditions for the topological resonance in the multilayer graphene system depend on the number of layers. Namely, for graphene monolayer, the topological resonance can be observed only for an elliptically/circularly polarized pulse, but for multilayer graphene, the topological resonance can be realized not only for an elliptically polarized pulse but also for a linearly polarized optical pulse.

The topological resonance brings some extra features and extra control to the properties of solids by placing them in the field of an ultra-strong and fast optical pulse. But the topological resonance cannot be realized in any topologically nontrivial solids. There are special conditions, both on the system and the polarization of the optical pulse, under which the topological resonance can be observed. The topological resonance manifests itself in the conduction band population distribution in the reciprocal space. For a circularly polarized optical pulse, the topological resonance results in ultrafast valley polarization of the gapped graphene multilayer-like systems. For a linearly polarized optical pulse, the topological resonance results in valley polarization of the edges of the sample of multilayer graphene if the number of layers is at least two. Such properties of topological resonance can find their application in valleytronics, where the valley degree of freedom can be controlled at the femtosecond time scale.

2.3 Ultrafast nonlinear absorption of TMDC quantum dots [16]

We studied theoretically absorption properties of MoS_2 QDs placed in an ultrashort and strong optical pulse with the duration of a few femtoseconds and the amplitude up to 1.5 V/A. While the monolayer of MoS_2 has a bandgap f $\approx$ 1.8 eV, the quantum dots of MoS_2 have in-gap edge states, which open additional absorption channels, which can change the absorption properties of transition metal dichalcogenide (TMDC) materials.

The interaction of TMDC QDs with ultrashort optical pulse strongly depends on two parameters of the pulse: its frequency and amplitude. The pulse amplitude introduces an energy scale, aF_0, where a is the lattice constant and F_0 is the pulse amplitude. Such an energy scale competes with the energy scale determined by the pulse frequency, $\hbar\omega$. As a result, at small field amplitude, $F_0 < 0.5 \, V/A$, the absorbance strongly depends on the pulse frequency. Here, the absorbance varies from around 2% at a small pulse frequency, ~ 1.5 eV, to $\approx$ 25% at a large frequency, ~ 3 eV. The absorbance at low pulse frequency mainly occurs due to in-gap edge states, where the bulk bandgaps of TMDC monolayers are around 2 eV. Concerning the absorbance of the high-frequency laser pulse, which occurs between the bulk states, the localized nature of the electron wavefunctions results in the enhancement of the corresponding absorbance. While the absorbance of TMDC monolayer is around a few percent, in our case of an ultrashort pulse, the absorbance of TMDC QDs can be up to 25% at low pulse amplitude.

Also, at small field amplitude, depending on the pulse frequency, the absorbance shows different behavior as a function of the pulse intensity. Namely, at large pulse frequency, when the transitions occur between the bulk states, the TMDC QDs show saturable absorption, while, at small frequency, when the main contribution comes from the edge states, the TMDC QDs show reverse saturable absorption. Thus, at a high frequency of the pulse, the high intensity components of the pulse are mainly transmitted. In contrast, the low-intensity pulse components mainly pass through TMDC quantum dots at small frequencies.

We also found that the absorbance of QDs of different TMDC materials (WS_2, $MoSe_2$, WSe_2, $MoTe_2$, and WTe_2) shows universal behavior at large pulse amplitude, $F_0 > 0.5 \, V/A$, where the absorbance mainly depends on the parameters of the pulse but is almost independent on the materials of QD. At small values of F_0, the absorbance strongly depends on the bulk band gap of the corresponding TMDC.

3. Future Plans

We plan to develop a theory of ultrafast nonlinear optical response of nanoscale topological systems. In addition to a gapped structure of the energy spectra of such systems, they also have in-gap edge states, for which the inter-electron interactions can be significant. We will include such interactions in our model and analyze their effect on the nonlinear optical response, for example, high harmonic generation and nonlinear absorption. The systems that will be considered include multilayer and bilayer graphene and transition metal dichalcogenides.

4. Peer-Reviewed Publications Resulting from this Project (2020-2022)

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

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

[3] D. O'Brien and V. Apalkov, *"Infrared optical spectrum of topological crystalline insulator SnTe (001) surface states",* Journal of Physics: Condensed Matter **33** (6), 065703 (2020).

[4] R .Ghimire, J.S. Wu, V. Apalkov, M.I. Stockman, "*Topological nanospaser*", Nanophotonics **9** (4), 865-874 (2020).

[5] Jhih-Sheng Wu, Vadym Apalkov, and Mark I. Stockman, "*Topological Spaser*", Phys. Rev. Lett., **124**, 017701 (2020).

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

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

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

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

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

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

[12] 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).

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

[14] 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).

 [15] 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).

[16] 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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New correlated numerical methods for attosecond molecular single and double ionization

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Project Scope

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

This project concerns the merge of hybrid-basis close-coupling approaches with numerical techniques for the single- and double-ionization continuum, and for correlated ion bound states, to describe both single- and double-escape processes from poly-electronic molecules. Whereas recent interfaces of quantum-chemistry codes to hybrid Gaussian-B-spline close-coupling (CC) space give promising results, more advanced methods are required to achieve ~1keV energies for single core photoionization, and to describe the multi-photon double-ionization processes targeted by upcoming attosecond experiments. For this reason, we are developing and integrating in the new ASTRA code (AttoSecond TRAnsitions) the numerical tools for the representation of free-electron and electron pairs with electronic-structure molecular packages to lay the foundation of a new hybrid CC program for the time-dependent description of molecular single and double-ionization processes, with a quantitative account of light-driven static and dynamic electronic correlation. Most of the fundamental quantities needed to carry out this program (hybrid integrals and high-order transition density matrices) are not available yet. Computing and incorporating them in scalable programs is a major theoretical, computational and algorithmic challenge. Successfully tackling this challenge will allow us to directly image correlated motion in matter, thus opening the way to a transformative expansion of attosecond science.

Recent Progress

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

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

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

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

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

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

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

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

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

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

x) We have developed decoherence models for the strong-field N1s core ionization of the N2O molecule, to reproduce the ATAS spectrum measured by the group of Prof. Jiro Itatani **[Ref. 3]**, as a precursor to the *ab initio* calculations we will conduct with ASTRA.
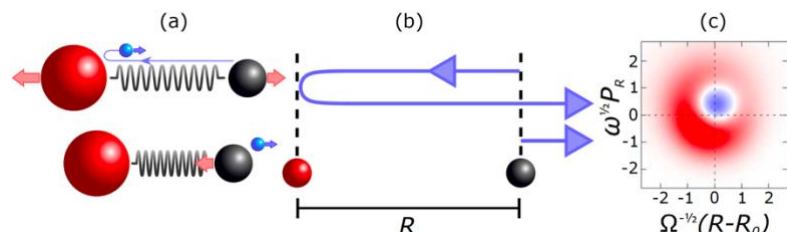

Figure 1(a) Pictorial representation of the nuclear recoil as the photoelectron from the C-1s ionization of CO is emitted towards the other nucleus, possibly reflecting many times (top), or directly out (bottom), resulting in an expansive and compressive boost, respectively. (b) Representation of two interfering pathways of the outgoing photoelectron. (c) The corresponding ionic nuclear Wigner Distribution when the molecule is ionized by an ultrashort pulse, showing that the ion emerges in a non-classical coherent state.

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

xii) We have implemented the calculation of the total photoionization cross section of molecules, based on the optical theorem, and ascertain excellent agreement with reference data for the N_2, and H_2CO (formaldehyde) molecules, and for the boron atom. We have explored the scalability of the code to larger molecule, by computing the photoionization spectrum of Mg-porphyrin ($MgH_{12}C_{20}N_4$).

xiii) We have implemented the calculation of the transient-absorption cross section and started reproducing experimental and theoretical results, in fixed-nuclei approximation, for the O_2 molecule, in collaboration with Arvinder Sandhu's group, at AU.

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

xv) We have involved an undergraduate student from the college of Optics (Dylan Perkowski) to compute the bound states, autoionizing states, photoionization spectrum, and susceptibility of the N2 molecule. We have involved two undergraduate students from physics (Felipe Kalluf Faria, and Christopher Klatt) for a similar study in the CO molecule. We are working with, Suchita Vennam, a talented female sophomore high-school student, who is using ASTRA to study the pump-probe third-harmonic generation from the ethylene molecule. We have two new graduate students (Andrew Short and Nicholas Lewis) in the group, who will work with ASTRA to compute the transient-absorption spectrum of molecule, and pump-probe photoelectron spectra, respectively.

xvi) We have implemented a two-photon double-ionization virtual-sequential model to reproduce the pump-probe double ionization of atoms and molecules. Currently, the model has been benchmarked for the helium atom. Extension to neon and to molecules are under way.

xvii) These results have been presented at conferences (DAMOP and ATTO VIII), and the associated manuscripts are either submitted or in preparation. The contribution J. M. Randazzo, C. Marante, S. Chattopadhyay, H. Gharibnejad, B. I. Schneider, J. Olsen, L. Argenti, *ASTRA, A Transition Density Matrix Approach to the Interaction of Attosecond Radiation with Atoms and Molecules*, Proceedings of the ATTO VIII Conference (under review, 2022), is due to be published open access by Springer-Nature.

Future Plans

Since we focused on the implementation of transient absorption modules, we have not ported yet to ASTRA the calculation of the multi-channel scattering states. Doing so will be a major thrust of this coming year. The two-photon double-ionization model will be extended to polyelectronic atoms and molecules. On the quantum-chemistry structure side, we will generalize the CI method to compute the ionic states, currently limited to CASCI, to RASCI, which will allow us to reproduce dynamic correlation. This will be particularly important for large systems with delocalized charge.

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2. V. J. Borràs, J. González-Vázquez, L. Argenti, F. Martín, 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, (under review at Sci. Rep., 2022).

Ultrafast Atomic and Molecular Dynamics Driven

by Ultrashort Intense Laser Pulses

(Award No. DE-SC0001771)

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Project Scope

The quest of studying the dynamics of matter at ultrashort time scales has driven the development of a variety of ultrafast laser technologies. Nowadays, laser pulses with a duration of a few tens of attoseconds (1 as = 10^{-18} s) have been generated in research laboratories. The controlled electron dynamics over a subcycle of the driving laser pulse allows for the emission of coherent light at extreme ultraviolet and soft X-ray wavelengths on a suboptical cycle time scale, i.e., on the attosecond time scale, through the process of high-harmonic generation.

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

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

Recent Progress

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

A. Ionization with short circularly and elliptically polarized laser pulses

A.1. Doorway states to ionization

In the previous year we reported about the first results of a new project in which we study the dependence of the laser induced ionization probability of atoms on the magnitude and sign of the magnetic quantum number of the initial state. The selectivity in ionization is a key element for the generation of ultrashort spin-polarized electron pulses, which are sources to probe chiral systems and magnetic properties of materials

on ultrafast timescales. Experiments have shown that in the highly nonperturbative intensity and wavelength regime spin polarization of about 30%–50% can be achieved [1,2].

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 [DOE7]. We now have further investigated this process and could explain the transition from dominant emission of electrons co-rotating with the polarization of the field in the single-photon regime to the stronger ionization probability for counter-rotating electrons in the strong-field tunnel ionization regime via a systematic study with calculations spanning over a few magnitudes of laser wavelengths [DOE8]. Currently, we work on the interpretation of photoelectron energy and angular spectra within the mechanism of doorway states. As suggested in the literature before [3], this may provide an efficient way to select spin-polarized electrons.

A.2. Asymmetries in photoelectron emission

We have extended our studies on the ionization in circularly and elliptically polarized laser pulses in view of other recent experiments on the photoelectron emission in such fields with different polarization stages. First, we are interested in the analysis of 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 [4]. First results of full 3D simulations of the time-dependent Schrodinger equation (TDSE) confirm the observed flip and will be now analyzed along with results from adiabatic and non-adiabiatic model calculations to provide a detailed interpretation. Second, in a recent experiment [5] it has been observed that the most probable emission angle increases with energy, a trend opposite to previous theoretical predictions. While our initial numerical results support this observation at high electron energies, we find deviations from the trend at low energies. The analysis and interpretation of the underlying effect using ab-initio numerical simulations as well as model calculations is ongoing.

B. Analytical calculations of ionization rates

Ab-initio numerical solutions of the time-dependent Schrodinger equation, even for the single-electron atomic case are time-consuming. A popular alternative method is based on the so-called strong-field approximation, in which calculations are often performed using the saddle point approximation [6]. While applications of this approximation method have been successful, especially in the tunnel ionization regime, less is known about the limits of the application range of the technique. In revisiting the formulation of the strong-field approximation in length gauge we developed an alternative approach by solving the resulting integrals analytically without using the saddle point approximation. Comparison of the results with those of ab-initio numerical calculations for a short-range Yukawa potential show a surprisingly good agreement over a large wavelength regime, from single-photon to tunnel ionization and for different kinds of polarizations. Potentially, this approach can therefore provide a way to obtain fast and reliable

estimates of ionization probabilities as well as it may allow us to determine the application range of the widely used saddle point approximation.

C. High harmonic generation in bichromatic laser fields

A recent experiment has shown that in bichromatic cross-polarized laser fields interacting with noble gas atoms high-order harmonics with a surprisingly large ellipticity can be generated [7]. Even though this observation is counterintuitive and in disagreement with earlier theoretical predictions, attempts of theoretical analysis of the mechanism behind the surprising experimental result are sparse [8]. The development of our numerical TDSE solver in 3D puts us in the position to perform a systematic study of high harmonic generation in such fields. Preliminary results indeed confirm that elliptically polarized light is generated in cross-polarized fields, further calculations and analysis are under way to establish systematics and dependencies.

Future Plans

The long-term goal of our studies of the laser-driven excitation and ionization with structured light of various polarization stages remains the interaction of such laser pulses with molecules. We are currently in the progress to develop single-active-electron potentials for diatomic molecules, like those published earlier by us in a different project [9], and incorporate those potentials in our various 3D TDSE solvers. As indicated above in each of the projects within the three thrusts we are currently in the process of analyzing numerical results, it is therefore expected that we will develop deeper understanding of the mechanisms behind the various experimental observations over the next time.

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[DOE3] R. Reiff, T. Joyce, A. Jaron-Becker and A. Becker, *Single-active electron calculations of high-order harmonic generation from valence shells for quantitative comparison with TDDFT calculations,* Journal of Physics Communications **4**, 065011 (2020).

[DOE4] J. Venzke, A. Becker, and A. Jaron-Becker, *Asymmetries in ionization of atomic superposition states by ultrashort laser pulses,* Scientific Reports **10**, 161164 (2020).

[DOE5] Y. Gebre, J. Venzke, A. Jaron-Becker, and A. Becker, *Transitions between Rydberg states in two-color corotating circularly polarized laser pulses,* Physical Review A **103**, 013101 (2021).

[DOE6] J. Venzke, A. Becker, and A. Jaron-Becker, *Imaging attosecond ring current dynamics in helium atom,* Physical Review A **103**, 042808 (2021).

[DOE7] S. Walker, L. Kolanz, J. Venzke, and A. Becker, *Enhanced ionization of counterrotating electrons via doorway states in ultrashort circularly polarized laser pulses*, Physical Review A **103**, L061101 (2021).

[DOE8] S. Walker, L. Kolanz, J. Venzke, and A. Becker, *Selectivity in electron emission induced by ultrashort circularly polarized laser pulses,* Physical Review Research **3**, 043051 (2021)

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

Award # DE-SC00267108

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I. Project Scope

This project focuses on developing X-ray free-electron laser (XFEL)-based nonlinear hard x-ray optics to probe the dynamics of electrons that control chemical bonding and reactivity. Our approach exploits the phenomenon of stimulated X-ray emission spectroscopy (S-XES) from $K\alpha$ and $K\beta$ 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: **1) Develop S-XES into a New Ultrafast X-ray Spectroscopy Probe of Electronic Structure and Dynamics with Enhanced Sensitivity; 2) Develop Phase-Stable Femtosecond X-ray Pulse Pairs for Application to Coherent Spectroscopies**. The research makes use of intense X-ray pulses at XFEL sources like LCLS at SLAC National Accelerator Laboratory and the SACLA XFEL in Japan.

Background

The molecular-level exploration of the electronic structure and dynamics of 3d transition metal complexes is critical for understanding their many important functions in physics, chemistry, biology, and materials science. X-ray spectroscopy methods, including X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), and resonant inelastic X-ray scattering (RIXS) are powerful, element-specific, probes of the electronic structure, and for many years synchrotron radiation (SR)-based studies have been at the center of such investigations. Over the last decade this research has been extended to X-ray free electrons lasers (XFELs), where ultrabright femtosecond (fs) X-ray pulses have opened the door to investigate ultrafast phenomena and to characterize systems under conditions beyond the reach of the SR probe. Critical for the application of XFEL-based techniques to many samples is the so-called 'probe-before-destroy' approach, where the X-ray damage is outrun by the ultrafast XFEL probe pulse and the sample is replaced after each XFEL pulse [8].

For the study of 3d metals, hard X-ray spectroscopy (K edge) has practical advantages over soft X-ray spectroscopy (L edge) related to the larger penetration power and a higher fluorescence yield. Due to its short wavelength, hard X-ray spectroscopy can also be applied simultaneously with high-resolution atomic structure probes. XES has proven very powerful for XFEL-based studies because it neither requires monochromatic excitation, nor a specific excitation energy (as long as it is above the absorption edge). This advantage is being increasingly exploited at XFELs, where XES is performed simultaneously with scattering and diffraction, using the full power of self-amplified spontaneous emission (SASE) XFEL pulses. Most experiments employ

the wavelength-dispersive von Hamos geometry, where the entire XES spectrum is collected shot-by-shot. As SASE pulse intensities can vary by almost 100% from shot to shot, this dispersive shot-by-shot method simplifies the normalization of the XES spectra. This approach, and its combination with scattering and diffraction, has been very successful and is currently the workhorse of XFEL-based hard X-ray spectroscopy applications to 3d transition metal systems. However, XES has two fundamental limitation that restrict its application, especially when the electronic structure changes are very subtle. 1) Most XFEL-based XES experiments use the strongest emission lines, K$\alpha_{1,2}$ and K$\beta_{1,3}$, which provide a much larger emission signal but less chemical sensitivity than the very weak valence-to-core (VtC) transitions. This spectral sensitivity limitation is exacerbated by the fact that XES has a large core-hole lifetime broadening (1-2 eV). 2) XES signals are emitted quasi-isotropic, and even state-of-the-art X-ray analyzers can collect at best a few percent of the total emission signal's 4π sr, with additional losses caused by the Bragg crystal optics. **Our goal for Thrust 1 is to develop a new nonlinear approach, stimulated X-ray emission spectroscopy (S-XES), to overcome these two fundamental limitations of XES.**

The principles of the inner-shell X-ray lasing phenomena that are at the heart of S-XES have also been discussed as a means for creating new coherent X-ray sources, which is our aim of Thrust 2. In such applications, the sample is not the object of the spectroscopic characterization, but rather the gain medium for creating the new X-ray source. The idea behind this approach is the fact that stimulated emission processes can be employed to generate intense fs X-ray pulses with unique properties. We will develop a new inner-shell X-ray laser source that generates phase-stable fs X-ray pulse pairs for applications in nonlinear coherent X-ray imaging and spectroscopy. In the optical domain, nonlinear coherent imaging and spectroscopy techniques have revolutionized our understanding of the structures and dynamics of molecules and materials and our work will be the extension of nonlinear optical techniques to the X-ray spectral domain to exploit the advantages of atomic spatial resolution and element sensitivity by core-level excitations. While phase-locked fs pulses have opened the powerful techniques of two-dimensional femtosecond spectroscopy in the optical regime, the experimental realization of many of the proposed nonlinear X-ray techniques has been very challenging for lack of intense, coherent, femtosecond X-ray pulses with fixed relative phases. We have just reported experimental evidence for the generation of phase-stable fs X-ray pulse pairs through observation of interference fringes in Mn Kα S-XES. **In Thrust 2 e will develop this finding into a new source of phase-stable fs X-ray pulse pairs and explore their application for coherent X-ray spectroscopies**. This work complements the X-ray laser oscillator scheme and other recently proposed approaches to create phase-stable hard X-ray pulse pairs.

Thrust 1: Develop S-XES into a New Ultrafast X-ray Spectroscopy Probe of Electronic Structure and Dynamics with Enhanced Sensitivity

The chemical sensitivity of Kα and Kβ X-ray emission is provided by the energies and intensities of multiplet (final state) lines that comprise each spectrum. In Thrust 1, we will first determine the optimal range of XFEL pump and seed pulse parameters to achieve Kα and Kβ S-XES in Mn compounds. Based on these findings, we will control the enhancement of individual multiplet lines by appropriate tuning of the seed and pump pulse parameters. We pump and seed Kα and

Kβ S-XES in chemically and spectroscopically important Mn model compounds using two-color XFEL pulses. We establish the concentration limits for seeded S-XES and investigate if this approach can be extended to metalloproteins. The last aim is to observe stimulated resonant inelastic X-ray scattering (S-RIXS), which might further enhance the spectral sensitivity of our new approach.

Thrust 2: Develop Phase-Stable Femtosecond X-ray Pulse Pairs for Application to Coherent Spectroscopies

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

II. Recent Progress

- We have obtained the first beam time submitted under this proposal at SACLA, the beam time will be carried out on November 15-18, 2022

III. Future Plans

- Apply for beam times at LCLS and SACLA to carry out the research for the two thrusts.
- Finish the analysis of existing data and start analysis of data from the November 2022 beam time
- Dissemination of results at conferences, meetings, and in peer-reviewed journals

IV. Peer-Reviewed Publications resulting from this Project (2019-2021)

N/A

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

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Project Scope

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

Our current interests include: **1)** Femtosecond and attosecond time-resolved molecular dynamics investigations using pump-probe techniques using free electron lasers (FELs), such as the LCLS-II x-ray FEL at SLAC National Laboratory but also at the XUV FERMI FEL in Italy, at the XUV FLASH-II FEL and at the XFEL in Hamburg, Germany where we were awarded beamtimes. **2)** The study of non-linear phenomena in the soft and hard x-ray regime. **3)** The investigations of electron dynamics in molecules at the attosecond timescale with the new XLEAP capability at LCLS-II via the collaborative attosecond campaign. **4)** Time-resolved molecular dynamics using the MeV-UED instrument at SLAC Nat. Lab.

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

Recent Progress

1. Resonance-Enhanced Multiphoton Ionization (REMPI) in the X-Ray Regime

Resonance-enhanced multiphoton ionization (REMPI) for long wavelengths has been well studied and has been a useful spectroscopic technique, since it provides a highly sensitive and selective means to ionize molecular compounds without strong fragmentation effects. REMPI has been used in a wide variety of physical, chemical, and biological systems such as catalytic surface chemistry [a], nuclear-spin conversion [b], and metrology [c]. REMPI relies on the laser wavelength being tuned to an electronic resonance, which leads to promotion to an excited state followed by ionization. As the absorption cross section for resonant excitation is typically stronger than the ionization cross section, REMPI provides an efficient means to ionize these systems at photon energies below the ionization threshold. Although XUV FELs have been predicted, but not observed, to allow REMPI for shorter wavelengths [d], we were motivated to extend REMPI to the x-ray regime, which requires entirely different physical processes and interpretation. Conventional REMPI relies on the excitation of a valence electron where the only relaxation pathway is radiative decay. On the other hand, a core-excited electron

after x-ray resonant excitation can additionally relax by Auger-Meitner decay, which is orders of magnitude faster than radiative decay. Thus, the complex interplay between ultrafast decay processes and REMPI renders this fundamental nonlinear process challenging to fully resolve in the X-ray regime.

We were successful in measuring the nonlinear ionization of argon atoms in the short wavelength regime using ultraintense x rays from the European XFEL. Our goal was to produce Ar^{17+} through a non-linear process. After sequential multiphoton ionization, high Ar charge states are obtained. For photon energies that are insufficient to directly ionize a 1s electron, a different mechanism is required to obtain ionization to Ar^{17+}. We found that Ar^{17+} production occurs through a two-color process where the second harmonic of the FEL pulse resonantly excites the system via a 1s ➔ 2p transition followed by ionization by the fundamental FEL pulse, which is an x-ray resonance-enhanced multiphoton ionization (X-REMPI). This resonant phenomenon occurs not only for Ar^{16+}, but also through lower charge states, where multiple ionization competes with decay lifetimes, making X-ray REMPI distinctive from conventional REMPI. With the aid of state-of-the-art theoretical calculations, we explain the effects of X-ray REMPI on the relevant ion yields and spectral profile. Our work demonstrated that the X-ray REMPI technique is general and can be used to study in detail molecules with the added benefit of site and element specificity. Additionally, we show that with short pulse duration (3fs) and narrow bandwidth we can resolve resonance structures. X-REMPI is thus a new tool to study molecular structure and dynamics (Pub 2).

2. **Relaxation dynamics in excited helium nanodroplets by FERMI XUV radiation probed with high resolution, time-resolved photoelectron spectroscopy**

Superfluid helium nanodroplets are often considered as transparent and chemically inert nanometersized cryo-matrices for high-resolution or time-resolved spectroscopy of embedded molecules and clusters. However, resonant excitation with XUV radiation from the FERMI FEL initiates various ultrafast processes, even in pure helium nanodroplets, such as ultrafast relaxation into metastable states, formation of nanoscopic bubbles or excimers, and autoionization generating low energy free electrons. We have measured the full spectrum of ultrafast relaxation processes observed at XUV photon energies ranging from the droplets' lowest excited states up to states near the ionization threshold. Owing to the high resolution of photoelectron spectra recorded in this study, afforded by the seeded FERMI FEL, we evidence the relaxation into metastable triplet and excimer states, unobserved in previous studies. This work is under review with Phys. Chem. Chem. Phys.

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Future Plans.

Our goal is to finish and start new projects and the principal areas of investigation planned for the coming year are: **1)** Analyze the time-resolved experiment we conducted at our FEL beamtime scheduled in December 2021 at FERMI. The beamtime consisted of probing, time-resolved, interatomic Coulombic (ICD) decay in helium nanodroplets. **2)** Analyze the data generated by the time-resolved experiment at the FLASH-II FEL beamtime in October 2021. The experiment consisted to investigate intermolecular interactions of molecular iodine solvated in small water clusters. The experiment used a COLTRIMS to measure ion-ion coincidences with 400 Hz rep rate. This experiment prepared us to use the future high rep rate at LCLS-II. **3)** Finish the interpretation with theorists and write the publication of the time-resolved ultrafast dynamics experiment, subsequent to the ionization of C_{60} near a giant resonance in the XUV regime using the FLASH-II FEL. This resonance consists of strongly correlated electrons. **4)** Finish the analysis and interpretation of the data from the successful time-resolved UED experiment conducted January 2021 at SLAC National lab. The work regards the study of ring opening in 2-bromothiophene (C_4H_3BrS).

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

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Program Scope or Definition

This project aims to investigate photochemical reactions at the molecular level by observing how the molecular structure changes upon light absorption. The project relies on ultrafast electron and X-ray diffraction to image photo-induced reactions in isolated molecules with atomic resolution. A sample of molecules in the gas phase is excited by a femtosecond laser pulse, and the structure is probed by a femtosecond electron or X-ray pulse. The scattering pattern contains information on the structure of the molecule, and under certain conditions an image of the molecule can be retrieved with atomic resolution.

Introduction

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

A gas-phase UED experiment comprises four major parts: i) An electron gun that delivers short pulses on a target, ii) a laser that triggers both the electron gun and the photochemical reaction, iii) a sample delivery system that creates a gas jet target in a vacuum environment, and iv) a detection system. Two different systems will be used in this project. The first is the MeV electron gun at the ASTA test facility at SLAC National Lab. This RF photoelectron gun produces femtosecond electron pulses in an energy range between 2 MeV and 5 MeV, with a repetition rate of 360 Hz. We have designed and constructed an experimental chamber for gas phase diffraction experiments, in collaboration with the group of Xijie Wang at SLAC. The main advantage of using MeV electrons is that they are relativistic, which minimizes the velocity mismatch between laser and electrons and also the pulse spreading due to Coulomb forces. The velocity mismatch has been a major limitation in the temporal resolution of UED experiments with sub-relativistic pulses. Experiments will also be performed in the PI's lab at UNL using a photoelectron gun that combines a DC accelerator with an RF compression cavity. Electrons are accelerated to an energy of 90 keV and then temporally compressed at the target position by a small RF cavity, at a repetition rate of 5 kHz. This setup includes an optical system to deliver laser pulses with a tilted intensity front on the sample. The tilted pulses will serve to compensate the velocity mismatch of laser and electrons through the sample to reach femtosecond resolution. We are now planning to also carry out X-ray diffraction experiments at the LCLS, which will be complementary to the UED measurements.

Recent Progress

Over the last year we have made progress analyzing UED existing data, carried out experiments, developed new analysis methods and improved instrumentation. We completed the data analysis of a UED experiment on a proton transfer reaction in o-nitrophenol (manuscript under review) and the isomerization of cis-stilbene which we are now interpreting with the aid of theory. We have started the data analysis of a MeV-UED experiment carried out at SLAC National lab on the photodissociation of bromocyclopropane. We developed new theoretical tools to retrieve the molecular orientation distribution from a sample of aligned molecules. The method was demonstrated experimentally using our UED setup at UNL to capture the angular distribution of the pair distribution function, from which the molecular orientation distribution is extracted. We are also currently testing a new sample delivery system to work with samples that have low vapor pressure. We were scheduled to carry out an X-ray scattering experiment at LCLS and a UED experiment at the MeV-UED at SLAC this year, however both were postponed until 2023 due to issues at the facilities.

UED data analysis of UV excited bromocyclopropane (BCP): Organobromides are important in atmospheric chemistry because they can absorb UV light to generate highly reactive fragments that contribute to the depletion of ozone. Multiple pathways have been proposed in the photodissociation of BCP, producing a bromine atom an a cyclopropyl radical or an allyl radical, where an intermediate step might produce a transient allyl-Br radical. We have carried out UED measurements at the SLAC MeV-UED instrument and we are currently carrying out the data analysis and interpretation and comparing with simulations. The experiments were led by Pedro Nunes (formerly at UNL, now at Diamond Light Source in the UK) and the simulations were carried out by Conor Rankine (University of York). A first comparison of the data with simulations shows qualitatively good agreement up to the range of the calculations of 500 fs (Figure 1). Interestingly, the data shows modulations in the intensity of the signal at early times and additional changes in the signal between 500 fs and 1 ps. We are currently working on a quantitative analysis to determine the reaction products and the relative weight of the different reaction paths.
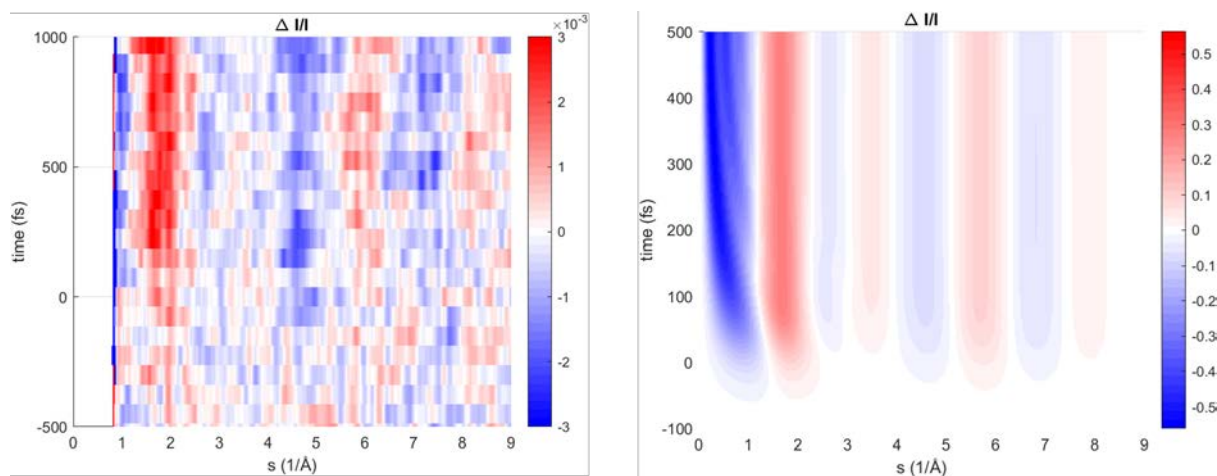

Figure 1. Difference diffraction signal for photoexcited bromocyclopropane. Experimental (left panel) and simulated (right panel). The simulation has been time-average to match the temporal resolution of the experiment.

UED data analysis of photoexcited cis-stilbene. We have investigated the ultrafast cis-trans isomerization of stilbene using the MeV-UED instrument at SLAC in the Fall of 2020. We have made significant progress in the data analysis, and are currently working with our collaborators in the group of Todd Martinez to interpret the results with the help of AIMS simulations of the dynamics. We have identified, in addition to the expected isomerization signal, a contribution from ionized cis-stilbene resulting from multiphoton absorption. Over the past year we have worked to incorporate the contribution of the ionized molecules into the analysis with the help of simulations. By including the ionization, we now have a much better agreement between theory and experiment.

Retrieval of molecular orientation distribution: Retrieving the three-dimensional molecular structure directly from diffraction measurements, without input from theory, is important for developing a non-biased method to track structural dynamics. Alignment increases the information content of the diffraction patterns and aid the retrieval of structural information. However, it remains a challenge to retrieve the molecular orientation distribution, the observable that characterizes the rotational dynamics in a molecular ensemble, directly from experimental measurements. We have developed a general theory to retrieve the molecular orientation distribution from the experimentally accessible angular distribution of the atom pairs. We demonstrated the retrieval experimentally with laser-aligned symmetric top molecules using ultrafast electron diffraction to capture the atom pair distributions. We have measured the diffraction patterns of impulsively laser aligned CF_3I molecules using our UED instrument at UNL. The molecules were aligned using femtosecond laser pulses at 800 nm and probed by scattering femtosecond electron pulses. The angularly resolved pair distribution function was constructed from the measured diffraction patterns, and from this, the molecular orientation distribution was retrieved. The advantages of this method are that it is applicable regardless of the alignment method, it does not require solution of the Schrodinger equation for the retrieval, and can in principle be applied to asymmetric top molecules.

Instrument development. A new laser was installed at UNL, which provides higher pulse energy and better stability, at the cost of a lower rep rate. The higher pulse energy was needed to excite a sufficient percentage of the sample for UED experiments, and the stability is expected to help improve the long term synchronization of laser and electron beams. The new laser provides 7 mJ, 40 fs laser pulses at 1 kHz, compared to 1.6 mJ, 50 fs pulses at 5 kHz for the previous laser system. We have constructed new optical paths to guide the IR and UV laser pulses (produced using a frequency tripler) from the laser to the experiment. We also installed and are currently testing a new sample holder with heating capability up to 300 C, which will help us carry out experiments with samples with low vapor pressure.

X-ray scattering experiments at LCLS:

We have submitted a proposal and were granted beam time for an ultrafast X-ray scattering experiment at LCLS run 20 (LX 74 "Imaging roaming mediated dynamics in halogenated alkanes by ultrafast X-ray scattering" PI: Martin Centurion) to investigate a possible roaming channel in the photodissociation of CH_2I_2. If successful, this would be the first time that a roaming reaction is spatially resolved. The experiment was originally scheduled for May 2022, but due to facility issues it was postponed, and is now scheduled for April 2023.

Future plans

A UED experiment on Thymine for which were awarded beam time at the SLAC MeV-UED instrument for the Fall of 2022 (U115: Isolated nucleobase UED studies for understanding

photoprotectionPI: Markus Guehr) has been postponed due to issues at the facility. We expect that the experiment will take place in 2023. We will continue with the development of our heated sample delivery system can carry out UED experiments at UNL with UV photoexcitation and at SLAC if possible. We plan to explore dynamics in ionized molecules.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

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

Award number DE-SC0020276

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Program Scope or Definition

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

Introduction

One of the research priorities for the Chemical Sciences, Geosciences, and Biosciences Division within the US DOE Basic Energy Sciences Program is to develop and implement novel tools to probe the dynamics of electrons and nuclei that underlie chemical bonding and reactivity, and to elucidate structural dynamics responsible for chemical transformations. After many successful proof-of-principle studies performed with a variety of ultrafast methods in recent years, the next important strategic step is a concerted effort to employ several of the new and complementary techniques on a specific class of photochemical reactions. Application of complementary methods, coupled with a coordinated computational model and data analysis, is expected to yield significant new insights into the reaction dynamics and pathways.

The interconversion between different ring structures is an important theme in organic synthesis. Ring conversion reactions change the number of atoms in organic ring structures, and are therefore essential in the creation of a large number of cyclic molecular motifs. They involve a range of chemical transformations including redistribution of charges, creation or release of ring strain, making or breaking of aromaticity or electron conjugation, and the conversion between simple and complicated multi-ring motives. Ring interconversion reactions are an important theme in organic

synthesis, industrial chemistry, chemical biology and pharmacology. Photochemically induced electrocyclic reactions in particular are widely seen in nature in the synthesis of natural products, and have tremendous commercial applications in the synthesis of pharmaceuticals. They featured prominently in the development of the Woodward-Hoffman rules that aim to rationalize pericyclic reactions, and play an important role in the photo-induced vision mechanism and the light-induced formation of previtamin D. To date, only a few select model systems have been studied using advanced time-resolved spectroscopic and scattering methods. Consequently, many aspects of the nuclear and electron dynamics of ring interconversion reactions remain unknown.

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

Recent Progress

Over the last year, we have made progress on several fronts. For the interconversion between quadricyclane and norbornadiene, we now have UED and X-ray scattering data, Time resolved photo-electron spectroscopy data and calculations following the electronic relaxation and nuclear dynamics. We have also completed the analysis of the UED experiment on cyclooctadiene and carried out time resolved X-ray scattering experiments on cyclopentadiene. We also report on Coulomb explosion imaging experiments and calculations on attosecond X-ray scattering.

I. Interconversion between quadricyclane and norbornadiene

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

I.1 QC and NBD absorption

Some of the challenge in supporting our experimental studies of the QC-NBD conversion dynamics with molecular dynamics calculations arises from the fact that QC and NBD have quite a large number of overlapping electronic states that can be excited in the deep UV region, and matching up theory and experiment directly is difficult since the calculated excitation energies are often shifted with respect to the experimental values. We therefore applied for beamtime at the

high-resolution Fourier Transform Spectrometer at SOLEIL to measure high-resolution absorption spectra of both molecules to benchmark our calculations. The preliminary spectra are shown in Fig. 1. The most striking observation at first sight is the presence of a distinct vibrational structure in NBD, which is almost completely absent in QC (most of the structures visible in QC below 5000 cm^{-1} are due to NBD contamination of the QC sample). Based on our electronic structure calculations, we attribute this lack of vibrational structure in QC to two major reasons: (i) The presence of many overlapping vibrational progressions with comparable oscillator strength that wash out any distinct peaks; and (ii) a much stronger coupling of the relevant Rydberg states to dissociative vibrational states in QC as compared to NDB that leads to significantly shorter lifetimes and thus spectral broadening. Further analysis including a definitive assignment of all spectral features is in progress.

Figure. 1: Preliminary analysis of the high-resolution absorption spectra of QC and NBD measured at SOLEIL

I.2 Ultrafast electronic relaxation

We have achieved a major breakthrough in the interpretation of our FERMI TRPES data thanks to significantly improved electronic structure calculations, which now enable much more accurate dynamics calculations. Furthermore, we are now able to calculate directly the experimental observables such as the time-resolved photoelectron spectra (see Fig. 2), which allows for a better, more quantitative comparison between theory and experiment. The calculated spectra are consistent with our experimental observations, confirming the presence of two dominant and

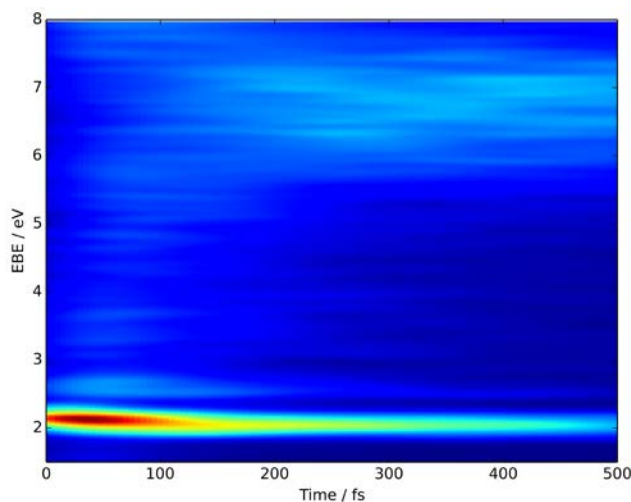**Figure. 2**: Calculated time-dependent photoelectron spectrum (in terms of electron binding energy, EBE) of QC after 200-nm excitation. To reproduce the experimental conditions, the calculations are convoluted with Gaussians with a width of 0.1 eV (FWHM) in energy and 94 fs (FWHM) in time.

competing electron relaxation channels after excitation of QC at 200 nm: (i) A "slower" relaxation via the 3p and 3s Rydberg states on a timescale of several hundred femtoseconds, visible in Fig. QC2 at 2.1 eV (3p) and 2.5 eV (3s) binding energy; and (ii) an extremely fast (< 100 fs) relaxation via strong Rydberg-valence coupling that appears as a faint, light blue and nearly vertical structure at small delays. Both relaxation pathways can lead to interconversion from QC to NBD as well as to the formation of hot ground-state QC, both of which appear at ~7 eV binding energy in Fig. QC2.

I.3 Picosecond ground-state dynamics

Once the UV-excited QC and NBD molecules have returned to the electronic ground state, the dynamics are far from over, and the molecules can continue to interconvert and, eventually, break up into smaller fragments, e.g., by emission of a hydrogen or a C_2H_2. We can see signatures of these ground-state dynamics in the data FERMI TRPES data since contrary to most other TRPES experiments, we used XUV pulses with a sufficiently high photon energy to ionize the ground-state molecules. We can also monitor any structural changes in the ground state using our UED and X-ray scattering data (see Fig. 3), all of which show significant structural changes on the few to few hundred picosecond scale, consistent with the TRPES data. We are currently working on developing a comprehensive understanding of these long-time dynamics by carefully analyzing, comparing, and combining the data sets obtained with the different methods.
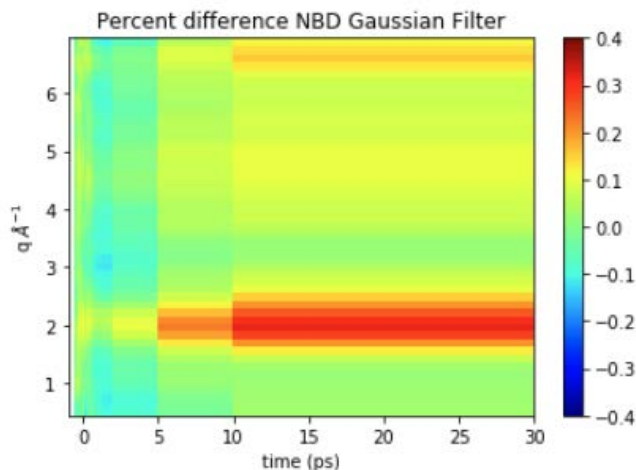

Figure 3: Preliminary results of the X-ray scattering beamtime at LCLS. The plot shows the difference scattering signal of pumped and unpumped NBD excited at 200 nm.

II. Structural dynamics of cyclooctadiene measured by UED

Photoexcitation of the eight-membered ring cycloocta-1,3-diene (COD) can lead to the formation of the four-membered ring bicyclo [4.2.0]oct-7-ene (BCO). Prior work on this reaction has determined that BCO is formed mostly after the molecule reaches the ground state, either thermally or by sequential excitation from cis COD to trans-COD and then from trans-COD to BCO. Previous studies using femtosecond high-intensity photoionization mass spectrometry by Fuss and collaborators, concluded that the main reaction products on the femtosecond scale to be trans-COD and hot COD, with BCO accounting for only 1% of the products[Fuss2006]. Mass spectrometry, however, is only indirectly sensitive to the structure. Time resolved photoelectron spectroscopy measurements (TRPES) measurement of the same molecule have found the relaxation to the ground to take place in approximately 100 fs after excitation with a photon energy of 4.75 eV [Liu2020]. Here we present UED measurements, supported by theory, on the dynamics of COD excited by 6.2 eV photon energy (Fig. 4). The experiments and data analysis were carried out in collaboration with Thomas Weinacht and Yusong Liu, and the theory was performed in the group of Spiridoula Matsika. At a 6.2 eV excitation energy, we see clear evidence for the prompt (within

150 fs) formation of BCO and hot cis-COD, with only a very small fraction of trans-COD. The ratio of hot cis-COD to BCO is approximately 4:1, with only a few percent of trans-COD found in the products. Interestingly, the simulations show significantly more trans-COD than BCO, and we are

Figure 4. Experimental and theoretical difference pair distribution function (ΔPDF) for photoexcited COD. a) Experiment. b) Theoretical signal constructed based on the trajectories leading to hot cis-COD and BCO in a ration of 4:1.

currently investigating the origin of this discrepancy. We have also observed coherent vibrations that persist up to a picosecond in the ground state. By comparison to theory, we have assigned this signal to ring puckering in the hot ground state COD. We are currently investigating whether this coherent oscillation is triggered directly by passage through the conical intersection or indirectly through coupling from other vibrational modes.

III. Cyclopentadiene: preliminary analysis of XFEL scattering experiments

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
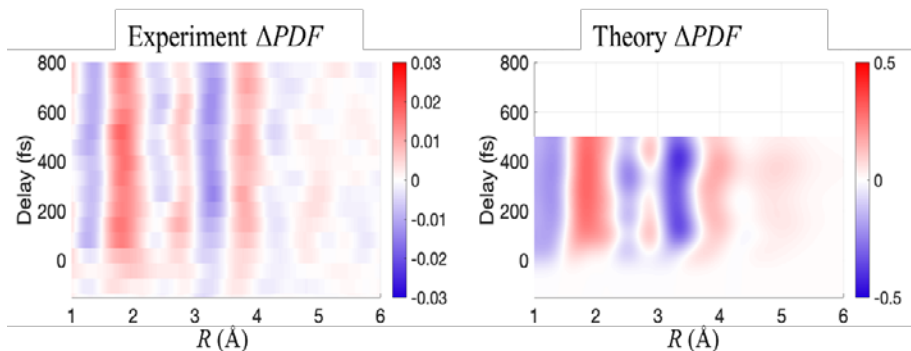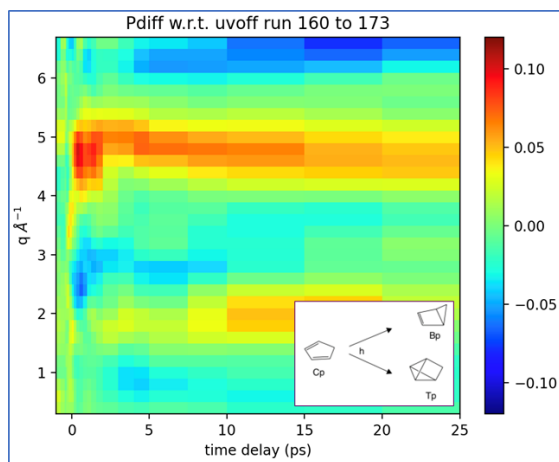

Figure 5: Raw experimental data from LX65 at LCLS, June 2022. Shown is the percent difference signal (color scale) as a function of time delay. Time stamping has not been applied yet to this data.

bicyclo[2,1,0]pentene (BP) [Brauman66, vanTamelen71]and tricyclo[2,1,0,02,5] pentane (TP)[Andrews77].

In the first experiments on the CP system, we use gas phase X-ray scattering at LCLS to determine the time-dependent molecular structures (geometrical structures, electron density distributions). In LX65, June 2022, we conducted experiments at several wavelengths to map the dependence of the reaction on the energy. Figure 5 illustrates the data we obtained. Shown is the time-dependent difference scattering signal, i.e. the percent difference between the pump-laser on and the pump-laser off. This is just the raw data, binned with the experimental time points. Data were obtained in the sub-picosecond regime, in the range up to 25 ps (shown), and for very long time delays up to 1 ns. A detailed analysis of this data is ongoing at the present time. But already it is clear that well-structured difference scattering patterns were obtained in LX65. The long-time data appears consistent with a dissociation of CP into acetylene and a three-carbon molecule that remains to be identified.

Going forward, the experimental results will be compared to detailed quantum chemical calculations that are currently being conducted. It is further our aim to explore this interesting system using other methods, including photoionization photoelectron spectroscopy via Rydberg states, time-resolved mass spectrometry at different excitation wavelengths, and directly with 21 eV photons at the FLASH beamline, scheduled for Jan 2023.

IV. EuXFEL Coulomb explosion imaging

Besides our efforts relying on ultrafast X-ray and electron diffraction described above, we have continued to develop the so-called Coulomb explosion imaging (CEI) approach as a complementary tool for studying ring-conversion reactions. Following up on a recent breakthrough experiment at the European XFEL (EuXFEL), which demonstrated that this technique can visualize the position of each individual atom in ring molecules with an iodine marker [Boll2022], we applied it to "ring" and "chain" isomers of C_7H_8 molecules without any marker atoms. Fig. 6 depicts the CEI patterns measured at the EuXFEL for highly-
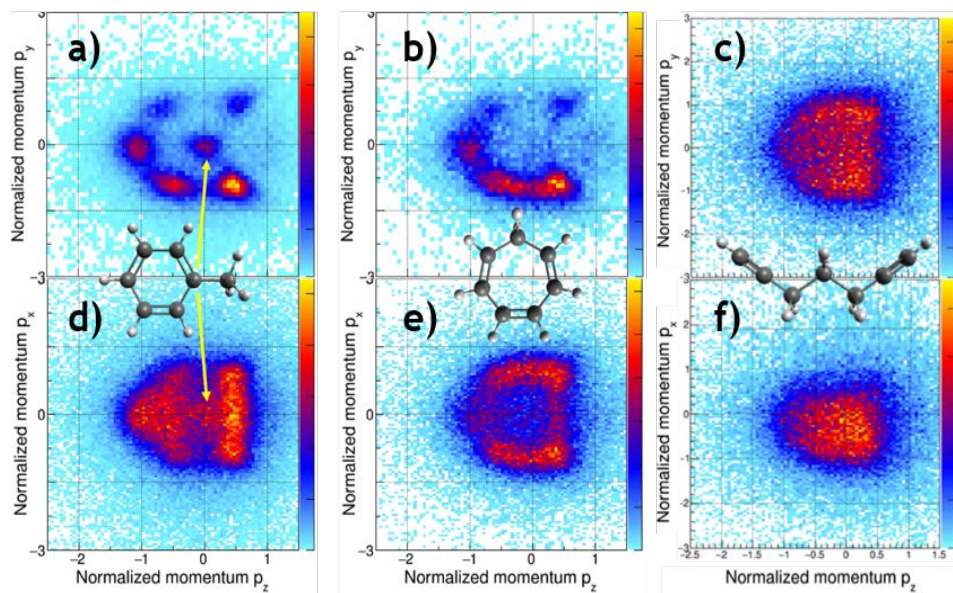
Figure 6: Molecular-frame ion momentum plots (Newton diagrams) recorded at 1.5 keV photon energy for (a,d) toluene, (b,e) cycloheptatriene, and (c,f) heptadiyne molecules for the three detected carbon ions. The plots depict the correlated momenta of the two detected C^{++} ions, with the z-axis determined by the momentum of the C^+ ion (not plotted), and the y-z plane ("the molecular plane") determined by the momenta of the C+ and .the first C++ ion. Shown are two different cuts of the 3D momentum distribution, parallel (top) and perpendicular (bottom) with respect to the molecular plane.

ionized toluene and its two isomers, cycloheptatriene (a seven-member ring) and 1,6-heptadiyne (a seven-member chain), plotted in the plane parallel (a-c) and perpendicular (d-f) to the molecular plane determined from the experimental data. As can be seen from Fig. 6(a-b), the positions of the individual carbon atoms can be traced in the ring isomers, including a clear signature due to the influence of the out-of-the-ring carbon atom in toluene (marked by the arrows). For the chain isomer, however, the CEI pattern is smeared out in this representation, filling the middle part of the corresponding Newton diagram in Fig. 6(c). The three isomers also manifest distinctly different CEI patterns in the projection perpendicular to the molecular plane, shown in Fig. 6(d-f), reflecting the "floppy" nature of the 1,6-heptadyene configuration. Very similar signatures of the more planar ring structure and a "floppier" open ring can be clearly traced in the time-dependent 3D momentum distributions of the fragments obtained in a recent follow-up KSU experiment on UV-induced ring opening reaction in furan molecules. Here, the ring opening dynamics after the initial photoexcitation was probed with the Coulomb explosion induced by intense near-infrared pulses. We are currently working on the optimized schemes of data analysis and representation for chain / open ring structures, which would allow us to discriminate between the central and terminal carbon atoms, and to highlight the dynamics occurring out of the molecular plain. Besides the ongoing KSU experiments, the next CEI beamtime at the EuXFEL is scheduled for October 2022.

V. Attosecond X-ray scattering

As a compliment to the ongoing ring-opening studies in this collaboration, the Lopata and Kirrander groups also made substantial progress towards simulating how hard X-ray scattering can be used to probe electron density currents in excited molecules at the attosecond time scale. Recent advances in attosecond X-ray pulse generation, and improvements in sensing and analyzing the scattering signals, have opened the door extending XFELs to measure X-rays scattered off time-evolving electron densities in molecules. Interestingly, X-ray scattering is not a probe of the local density, but rather the time-derivative of the density [Hermann2020, Carrascosa2021].

In the past year, we built on these results and addressed two critical questions: what is the role of the initial state, and how does the molecular geometry dictate the currents and scattering? We studied a range of linear molecules and ring-shaped molecules excited with different excitations (inner-shell ionization, outer-shell ionization, UV pumping). Two representative 1D and ring examples are carbon monoxide and aminophenol, respectively. Fig. 7 shows the scattering (a) and time-dependent dipole moment (b) in the carbon monoxide molecule for the first 500 attoseconds following UV pumping. The scattering exhibits simple behavior: at times when the dipole is low (high current), there is a large scattering signal around 1.5
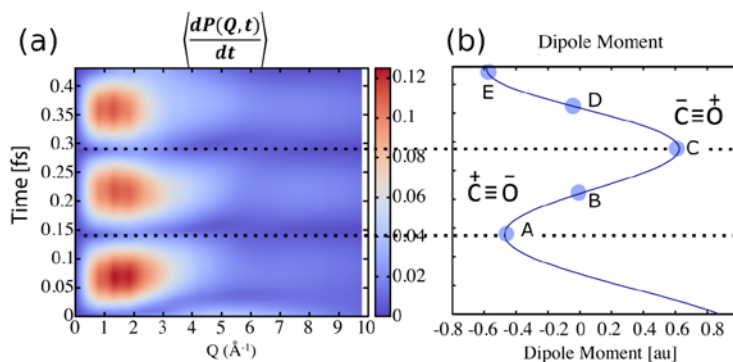

Figure 7: (a) Simulated attosecond X-ray scattering in carbon monoxide following pumping with a broadband UV pulse, and (b) the corresponding expectation value of the dipole. The simple oscillatory behavior reflects the linear shape of the molecule, i.e., large scattering at times when there is a large electron current, low scattering at the maxima of the oscillations.

A^{-1}, corresponding to electron flow between C and O or vice versa. Preliminary results on longer 1D chains (not shown) are similar. The relative simplicity and high contrast of the scattering signals make linear molecules a good candidate for initial XFEL experiments.

Results for UV-pumped aminophenol (a bi-substituted ring molecule) are shown in Fig. 8. During the ~360 as it takes for the density to flow across the molecule, the scattering (a) shows pronounced modulations and an evolution from a lower-Q to higher-Q signal. The scattering at 0.86 fs is dominated by a 0.6

Figure 8: (a) Simulated X-ray scattering signal as a function of time-delay after UV pumping of aminophenol. The modulations in the scattering can be attributed to distinct long-range (b) and shorter-range (c) attosecond ring currents.

A^{-1} signal, which corresponds to long-range homogeneous ring current (b) flowing from right to left. At 0.95 fs (c), the global ring current is broken into two localized flows, which results in the low-Q peaks shifting to 1.5 A^{-1}, and emergence of a higher Q peak at 3.5 A^{-1}. These results demonstrate how X-ray scattering can be a sensitive probe of both the shape and the magnitude of electron density flows in ring-shaped molecules. Since scattering does not require heteroatoms, and probes currents instead of densities, it is likely excellent complement to transient X-ray absorption, and opens the door to measuring the dynamics immediately preceding ring-opening, where ring-currents may play a role such as by selectively softening particular bonds.

Further work has examined the different contributions to the scattering signal, particularly examining the role of continuum states in the inelastic x-ray scattering signal. Comprehensive numerical simulations of the two-electron Shin-Metiu model Hamiltonian made it possible to

Figure 9. Scattering cross sections, without Thomson factor, for Shin-Metiu model Hamiltonian, showing total (blue dotted), elastic (red dotted), and total inelastic scattering (orange). The bound-bound inelastic contributions are shown in shaded green, with the reminder of the total inelastic made up by scattering into the one and two electron continua.

isolate the bound-bound inelastic components from those corresponding to x-ray scattering induced transitions to the one and two electron continua. Fig. 9 shows the elastic and total inelastic components, as well as their sum which is the overall total scattering. The green shaded region in the figure shows the part of the total inelastic scattering which is due to bound-bound inelastic transitions. The gap between this shaded region and the total inelastic scattering curve demonstrates the important role of inelastic transitions into the continuum states for the large-angle scattering signal.

VI. Instrument and code development

The TOPAS that was purchased for KSU in the first cycle of this grant has been fully operational for over a year and is being used extensively for pump-probe experiments with variable wavelengths in the UV to support and complement our off-site facility experiments. We have also placed an order for a dedicated XUV HHG source that is being custom-designed to run with the new 100-kHz laser system at KSU. The HHG source (and the new laser) are scheduled for delivery in spring 2023.

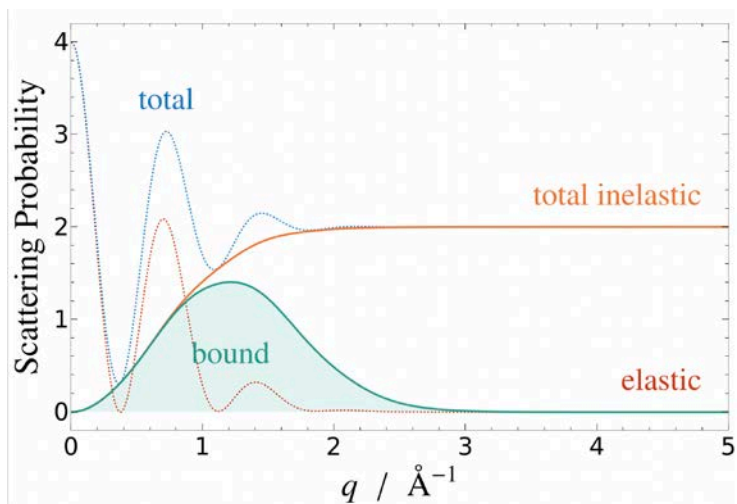The new laser at UNL was installed and provides a significant upgrade in laser pulse energy from 1.6 mJ to 7 mJ. This is essential to carry out UED experiments at tunable wavelength because it will significantly enhance the pulse energy after the frequency conversion with the TOPAS. We have built the optical lines to deliver the pulses from the new laser to the electron gun and target chamber. The new laser provides 7 mJ, 40 fs pulses at a repetition rate of 1 kHz, compared to 1.6 mJ, 50 fs pulses at 5 kHz. While the repetition rate is lower, this is more than compensated by the increased pulse energy and higher sample excitation fraction. Additionally, the new system is far more stable than the previous laser, which will allow us to more efficiently acquire data for longer times and reduce the timing drifts that often limit the temporal resolution.

Two sets of code have been developed by the Brown University team for processing of x-ray scattering data at the CXI endstation of LCLS: A fast analysis framework to monitor data during the experiment, and a more thorough set of codes to process the data after the experiment. These codes are used to create high quality detector masks, determine appropriate thresholds through statistical analysis, bin the data radially, azimuthally and in time, and calculate the error associated with the dataset. The codes are shared with the team for all x-ray experiment analyses.

A new photoelectron spectrometer will be built at Brown University, with the aim to reach a time resolution better than 10 fs. An important part of the impetus to build this spectrometer is to align the performance specification of the spectroscopy experiments to those at the CXI beam line when LCLS-II-HE becomes available. The new instrument is based on an iPEPICO (imaging photoelectron-photoion coincidence) electron spectrometer using a newly purchased coincidence imaging- time-of-flight (TOF) detector system (DLD40 – DET40, Roentdek). The laser system uses a high power 1030 nm laser (PHAROS-SP-2mJ-20W-200kHz, Light Conversion) and hollow fiber capillaries to create two tunable UV beams with pulse durations <10 fs in the UV. For the latter, we are collaborating with Prof. J. Travers, Heriot-Watt University, who is an expert on the hollow core fiber technology.

As part of the theory work at Brown, a new module in the scattering cross section code has been implemented that calculates the isotropic and first and second order isotropic components, making it possible to efficiently calculate the signal for varying degrees of system alignment, for instance following excitation by a linearly polarized pump pulse. The computations benefit from a

significant speed-up from the implementation of Slater-Condon rules using hardware bitwise operations when solving for the two-electron reduced density matrix. Furthermore, a new computer code for analyzing scattering data in a basis of trajectories has been implemented and applied to experimental data. The new code allows self-similar trajectories to be clustered according to the degree of similarity, making it easier extract characteristic motions from the experimental data.

As part of our attosecond scattering simulation efforts, the LSU group has finished development of a real-time time-dependent density functional theory (RT-TDDFT) based module for computing electron currents in the NWChem software package. This module computes and visualizes 4D currents (xyz + time) in parallel on a high-performance computing system, without needing to transfer to a local workstation. This enables rapid simulation and interpretation of attosecond electronic processes without time-consuming and inconvenient data transfers. This package is generalizable to time-evolving arbitrary scalar and vector fields, including densities, gradients, and similar, and is expected to be widely useful for RT-TDDFT simulations. In-place parallel computation of the corresponding elastic scattering is a work-in-progress.

Future Plans

In the coming year, we will be carefully analyzing the x-ray scattering data from LX65 on the cyclopentadiene system. We now have all the codes in place, and the quantum dynamics simulations are underway. The analysis will follow procedures we have developed previously, in particular the million-structure analysis method to determine time-dependent molecular structures. The same codes are also being employed for the analysis of the QC and NBD X-ray diffraction data, which is currently ongoing and which will continue for several more months. For the QC/NBD system, the molecular dynamics calculations are close to being completed, including calculation of the time-dependent scattering signal, which can be compared to the LCLS results once the experimental data analysis has caught up. We now have X-ray and UED data for the conversion from QC to NBD, which will allow us to do a detail comparison of time-dependent UED and X-ray scattering signals. We anticipate that the U100 MeV-UED beam time on cyclopentadiene and derivatives will be scheduled for February 2023.

A FLASH TRPES beamtime on methylated cyclopentadiene is scheduled for January 2023. In preparation for this beamtime and to complement the data from the LX65 X-ray diffraction experiment, we will be performing a series of time-resolved mass spectrometry experiments on CP and its methylated derivatives at KSU that include a systematic study of the pump-wavelength dependence. For the most promising wavelengths, we will also attempt to apply time-resolved CEI with intense near-infrared pulses to probe the same dynamics.

At UNL, we plan to take advantage of the new laser system to carry out UED measurements. We will first focus on experiments at a single UV excitation wavelength before moving to probing the wavelength dependence of the reactions.

At Brown, we will build a new photoelectron spectrometer and implement the associated laser system. Our target is to obtain a time resolution of <10 fs, which will be achieved using hollow core fiber technology.

The theoretical effort will continue simulations of target molecular systems, with particular focus on improving the level of electronic structure theory so that the equilibrium spectra are in good quantitative agreement for all molecules. A new methodology for the quantum molecular

simulations is being implemented that will better account for nonadiabatic transitions in the Rydberg state manifold which is involved in the dynamics in several of the molecules considered. In terms of observables, the focus is on improving the accuracy of the predicted photoelectron signals. A continued schedule of improvements in the scattering cross-sections codes will be carried out, with a focus on making the new fast computer codes usable for the wider consortium and to exploit the achieved speed gains in new inversion algorithms for experimental data. The Brown theory team will formulate the calculation of the scattering cross sections in terms of densities to link to the RT-TDDFT simulations developed at LSU to the existing scattering codes.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

1. S. Bhattacharyya, K. Borne, F. Ziaee, S. Pathak, E. Wang, A. Venkatachalam, N. Marshall, C. Fehrenbach, T. Severt, I. Ben-Itzhak, A. Rudenko, D. Rolles, *Investigating the strong-field-induced Coulomb explosion of tribromomethane using coincident ion momentum imaging*, Phys. Chem. Chem. Phys., in press (2022).

2. S. Bhattacharyya, K. Borne, F. Ziaee, S. Pathak, E. Wang, A. Venkatachalam, X. Li, N. Marshall, C. Fehrenbach, T. Severt, I. Ben-Itzhak, A. Rudenko, D. Rolles, *Strong-field-induced Coulomb explosion imaging of tribromomethane*, J. Phys. Chem. Lett. **13**, 5845 (2022). https://doi.org/10.1021/acs.jpclett.2c01007

3. T. Severt, D. R. Daugaard, T. Townsend, F. Ziaee, K. Borne, S. Bhattacharyya, K.D. Carnes, D. Rolles, A. Rudenko, E. Wells, I. Ben-Itzhak, *Two-body dissociation of formic acid following double ionization by ultrafast laser pulses*, Phys. Rev. A **105**, 053112 (2022). https://doi.org/10.1103/PhysRevA.105.053112

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7. Yanwei Xiong, Kurtis Borne, Andrés Moreno Carrascosa, Sajib Kumar Saha, Kyle J. Wilkin, Mengqi Yang, Surjendu Bhattacharyya, Keyu Chen, Wenpeng Du, Lingyu Ma, Nathan Marshall, J. Pedro F. Nunes, Shashank Pathak, Zane Phelps, Xuan Xu, Haiwang Yong, Kenneth Lopata, Peter M. Weber, Artem Rudenko, Daniel Rolles and Martin Centurion, *Strong-field induced fragmentation and isomerization of toluene probed by ultrafast femtosecond electron diffraction*

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

9. Haiwang Yong, Andrés Moreno Carrascosa, Lingyu Ma, Brian Stankus, Michael P. Minitti, Adam Kirrander, Peter M. Weber, D*etermination of Excited State Molecular Structures from Time-Resolved Gas-Phase X-Ray Scattering,* Faraday Discussions, 228, 104 (2021). DOI: 10.1039/D0FD00118J.

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[Carrascosa2021] Andrés Moreno Carrascosa, Mengqi Yang, Haiwang Yong, Lingyu Ma, Adam Kirrander, Peter M. Weber and Kenneth Lopata, "*Mapping Static Core-Holes and Ring-Currents with X-ray Scattering",* Faraday Discussions, 228, 60 (2021).

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

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Program Scope

The ability to measure and control ultrafast dynamics in excited states of atoms and molecules has opened new frontiers in the study of internal energy conversion, charge transfer, and coupling of electronic and nuclear degrees of freedom. Recently, such control has been extended to the attosecond (1 attosecond = 10^{-18} seconds) regime, owing to the development of carrier-envelope phase-stabilized few-cycle lasers and isolated attosecond extreme ultraviolet (XUV) pulses. This project aims to drive strong-field excitation of bound electronic coherences in gas-phase atoms and molecules using a novel source of single-cycle optical field transients, to reconstruct the time-dependent wave packets and probe their decoherence using attosecond interferometry, and to control the dynamic evolution of the system on attosecond to few-femtosecond (1 femtosecond = 10^{-15} seconds) timescales.

Recent Progress

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

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

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

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

Figure 1. (a) Measured and **(b)** retrieved FROG traces. **(c)** Retrieved pulse.

Using the pulses compressed by MDSS, we have demonstrated a novel technique for single-shot optical field sampling in the near-infrared. Recently, our group showed that the TIPTOE technique (tunnel ionization with a perturbation for time-domain observation of electric fields)[6] can be adapted to a solid-state target[7], which allowed us to demonstrate single-shot field sampling of mid-infrared electric fields using a silicon-based CMOS camera as *both* the nonlinear medium and the detector[8]. This year, we have extended the technique to near-infrared wavelengths and demonstrated the first single-shot measurement of electric field waveforms in this important
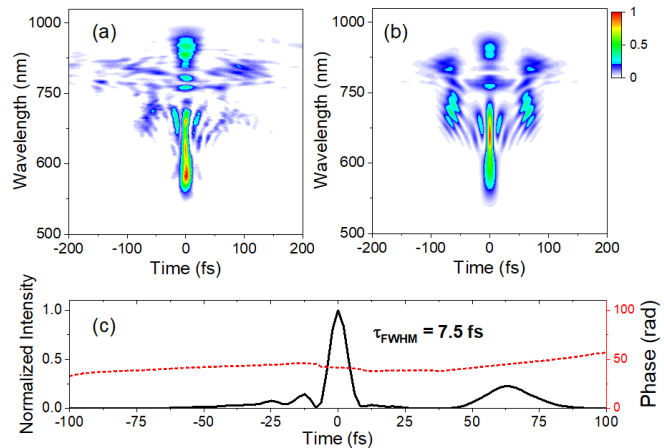
spectral region. In the experiments, we combine an intense "fundamental" pulse and a weak "perturbation" pulse on a thin ZnO crystal with a small noncollinear angle. The fundamental pulse induces nonlinear excitation in the crystal, which can be monitored by measuring the yield of band fluorescence emission, and which is modulated by the field of the perturbing pulse. The noncollinear geometry allows us to map the time-delay axis onto one of the spatial axes of the crystal plane, thus encoding the full electric field waveform of the perturbing pulse on the spatial dependence of the band fluorescence emission. The band
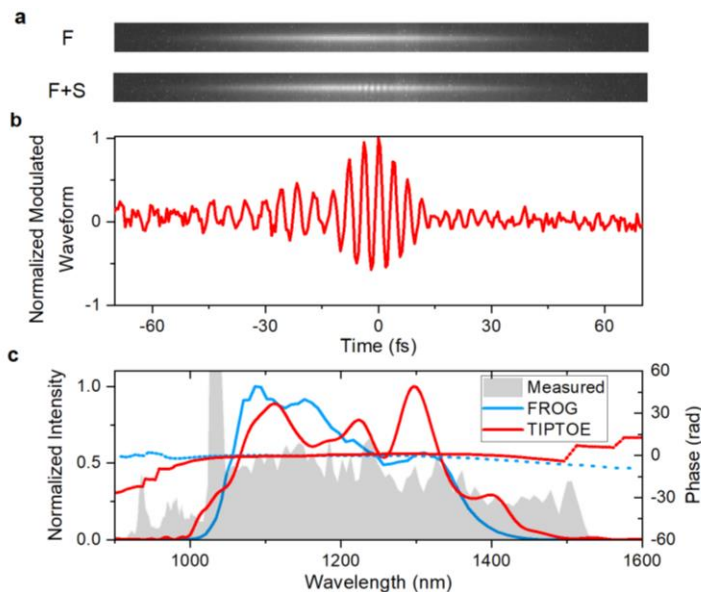

Figure 2. (a) Band fluorescence images without (top) and with (bottom) perturbing pulse. **(b)** Delay-dependent electric field waveform. **(c)** Spectrum and phase obtained from the waveform measurement (red) and from FROG (blue).

fluorescence is collected using a lens, spectrally filtered, and imaged onto a CMOS camera detector. Figure 2 shows a comparison of the measured electric field waveform with that retrieved using FROG. The two measurements show excellent agreement, indicating the high fidelity of the waveform measurement technique. The single-shot field sampling technique is a valuable addition to the proposed attosecond interferometry measurements, as the combination of the two techniques will allow us to simultaneously measure both the electronic and vibrational coherences excited in molecular gases by the strong near-infrared fields.

Finally, we have investigated the power scaling of MDSS with the goal of generating few-cycle pulses at high repetition rate. The few-cycle pulses obtained in ref. 4 and in Figures 1 and 2 above were all obtained at low repetition rates below 1 kHz, whereas our laser is capable of operating at 50 kHz repetition rate with the full pulse energy of 400 μJ. Unfortunately, we have found that the supercontinuum spectrum narrows considerably at high power, which is accompanied by a drop in the pulse energy coming out of the fiber. These effects can be attributed to rotational heating[9], which reduces the degree of molecular alignment and thus the spectral broadening, and thermal lensing, which prevents efficient coupling into the fiber. Operating the fiber in a pressure-gradient geometry can eliminate the worst effects of thermal lensing[10], but leads to turbulent gas flow and instability in the spatial profile and pulse energy of the pulses exiting the fiber. Furthermore, since the gas flow remains too low to provide a fresh gas sample for the laser to interact with, differential pumping does not mitigate the effects of thermal excitation on the spectral broadening. Recently, we have identified two promising approaches. First, by filling the fiber with a mixed gas of N_2O and helium, we find that thermal excitation effects are strongly suppressed. We attribute this behavior to collisions between N_2O molecules and helium atoms, which can efficiently carry energy away from N_2O and eventually couple it of the fiber through collisions of helium with the fiber walls. Second, by placing the in- and out-coupling windows of

the fiber very close to the fiber tip, we strongly suppress the effects of thermal lensing. Further tests are ongoing, but preliminary results suggest that these approaches will be sufficient to allow power scaling of few-cycle compression up to the maximum output of our laser.

Future Plans

In the next year, we aim to demonstrate the generation of sub-two-cycle pulses at average powers up to 20 W using molecular gases in combination with the thermal mitigation strategies described above. Even if scaling all the way to 20 W is not possible, the source is now sufficient to move forward with the proposed attosecond interferometry experiments to characterize bound electronic coherences initiated by strong-field excitation. To this end, we will first characterize the carrier-envelope phase dependence of the high-order harmonic spectrum and the XFID emission driven by single-cycle pulses. Second, we will perform the first measurements of attosecond interferometry using two isolated attosecond pulses, with the goal of measuring the recombination phases for comparison with the measurements in Ref. 1. Finally, we will perform attosecond interferometry measurements of excited state dynamics in Ar and N_2 gases.

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2. Y. Liu, et al. "All-optical sampling of few-cycle infrared pulses using tunneling in a solid," Photon. Res. 9, 929-936 (2021).
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Early Career: Atomic View of Molecular Photocatalysis using X-Ray Lasers

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Project Scope:

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

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

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

Recent Progress:

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

proposed to act as acceptor in the subsequent photo-induced electron transfer reactions. However, this proposed active species has never been isolated or characterized experimentally. Using a combination of in situ Ni K-edge and S K-edge x-ray absorption spectroscopy (XAS) we directly probed the protonation mechanism of the catalyst. The Ni K-edge spectrum reports on the coordination geometry of Ni and the first coordination sphere bond lengths, while the S K-edge spectrum reports on the protonation state and metal coordination state of the ligand S atom. Our results indicate a new mechanism for protonation, not realized in previous optical spectroscopy measurements (Ledbetter, 2022). We find that protonation of the pyS ligand N atoms results in total decoordination of the ligand, followed by solvent coordination at the open sites of the metal. This newly realized protonation mechanism results in two possible active species, a solvated Ni(II) species or a protonated pySH ligand, which can act as electron acceptor. We find that the solvated Ni complex accepts electrons in the subsequent photo-induced reduction reaction. These results highlight an important role for x-ray spectroscopy methods in identifying precise chemical reaction mechanisms, even differentiating metal versus ligand reactive sites, which is critical to understanding the role of 'non-innocent' ligands in photocatalysis.

The second goal we are addressing in this program extends this same combination of the metal and ligand atom x-ray absorption spectroscopy to the time domain to investigate the excited state relaxation processes of Ni-based hydrogen evolution photocatalysts with 'non-innocent' ligands. This work has focused on Ni bis(dithiolene) and related complexes that are characterized by their large metal-ligand covalency in their valence orbitals.[5,6] While this covalency is known to play a large role in dictating the redox reactions of the catalysts, little is known about how the ligands dictate their excited state charge distributions or excited state relaxation mechanisms, both critical to understanding how light absorption initiates the proton reduction reactions of the catalysts. We measured the transient S K-edge XAS at the SwissFEL facility and the transient Ni K-edge XAS at the LCLS facility to assess the excited state charge distribution on both metal and ligand atomic sites for a series of Ni bis(dithiolene) like complexes. Using Ni(mpo)2 (mpo = 2-pyridinethiolate-N-oxide) as an illustrative example, we observed evolution in both the Ni and S spectra indicative of two prominent excited state species, with <1 ps and ~15 ps decay times, as well as a long-lived photoproduct. For the short-lived excited state, signatures of ligand-based hole density are observed at the S K-edge and of reduced Ni oxidation state are observed at the Ni K-edge. Thus, the initial excited state is preliminarily assigned to have ligand-to-metal charge transfer character. For the longer-lived excited state signatures of a tetrahedral high spin Ni center are observed in the Ni K-edge XAS spectrum, consistent with a metal-centered excited state. The long-lived photoproduct is assigned as the photo-reduced species by comparison with the chemically reduced catalyst. While theoretical simulations are currently underway to facilitate the excited state assignments, the experimental results are already suggestive of a clear photochemical pathway for initiating proton reduction reactions by direct excitation of the catalysts.

Future Plans:

The future plans for this research program will continue to emphasize a combination of metal and

ligand atom x-ray spectroscopies to understand how strong metal-ligand covalency influences the photochemical reactions and excited state relaxation processes of Ni-based hydrogen evolving photocatalysts. Our immediate plans focus on the continued analysis of the SwissFEL and LCLS datasets already measured. As high repetition rate soft x-ray methods become available with the LCLS-II upgrade, these studies will be extended to the soft x-ray regime to focus on the Ni L-edge as a direct probe of metal-ligand covalency in the excited state. This work will focus on a series of photocatalyst ligand composition and charge states with varied metal-ligand covalency to identify the influence of this design property on excited state reactivity.

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

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

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

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

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

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

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

Once the cell was received, we developed an approach to reliably heat it to the required temperature while keeping the windows hotter than the side arm to prevent condensation of liquid iodine on the windows. We found that a rather simple approach of wrapping nichrome wire around the cell body close to each window worked best. Measurements of the absorption spectrum, as shown in Fig. 1 verify that we can achieve an optical density in the desired range near 0.3 at a cell temperature of approximately 300 C. The optical density can be tuned by cell temperature.

Changing the light source for the ultrafast pulses used for the spectroscopy, also meant that a separate CW laser was needed for the reference beam used to implement active locking of the path lengths in the Multidimensional Optical Nonlinear SpecTrometer (MONSTr). The previous ultrafast system used a 532 nm CW pump laser, from which we split off a small portion to use as a reference laser. The new system is fully integrated and directly pumps the ytterbium gain medium with diode bars. Thus we acquired a 50 mW CW frequency-doubled Nd:YAG laser to provide the reference beam.

Figure 1: Absorption spectrum of the iodine cell at a temperature of 295 C.

The new light ultrafast light source and the new reference laser have been aligned into the MONSTr. Due to the shutdown and delay in the delivery of the laser, the group members who were familiar with the apparatus had all moved on. Thus there was a lack of experience with this particular spectrometer once we were had everything realigned, in particular with the electronics that lock the path lengths. The current graduate student has had to figure out how to get all four servo loops locked and characterize their stability. This step is complete and the iodine cell has been installed in the setup. Currently we a searching for the four-wave-mixing signal. Scatter of the incident laser beams from the cell window has been identified as an issue, and is currently being addressed. The scatter is due to residual adhesive from some earlier iterations of the cell heating. We are attempting to remove it, but are also planning on order a new cell as a back-up.

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

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

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

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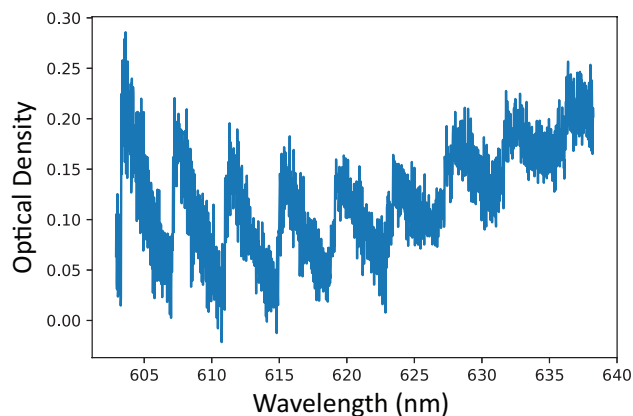
surfaces. To directly measure the position of the wave-packet will require using the diffraction pattern provided by a time-resolved hard X-ray probes, as can be done at the LCLS and discussed below.

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

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

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

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

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

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

To marry multidimensional coherent methods with x-ray probes, requires a different approach than used by our current apparatus. The current apparatus uses excitation beams with distinct directions, such that their interference results in a spatial modulation of the excited state populations, which forms the grating that is mapped into the absorption and acts as a diffraction grating to scatter the final pulse into the signal

directions. The resulting spatially inhomogeneous excited state populations would give spatially varying x-ray diffraction patterns, which would average out. To overcome this problem, fully collinear beams are needed to realize a spatially uniform excitation. The simplest implementation is to use pulse pair for the excitation in an experiment similar to that performed by Glownia et al. [2]. The challenge will be to separate the diffraction due to the pulse pair rather than the individual pulses. This can be realized by exploiting the sensitivity to the relative phase of the two pulses and cycling the phase such that the signals due to the individual pulses cancel, whereas that due to the pair adds constructively.

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

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

Peer-Reviewed Publications resulting from this project (2019-2022): None as this project started in 2020.

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

DOE Grant No. DE-SC0002325

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Project Scope

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

Recent Progress
(a) Pulse shaping in strong-field ionization: Theory and experiments
Shuai Li , Bethany Jochim , Jacob Stamm, Dian Peng , Hua-Chieh Shao, Jean Marcel Ngoko Djiokap , and Marcos Dantus, *Phys. Rev. A 105, 053105 (2022)*

Intense ultrafast pulses cause dissociative ionization and shaping the pulses may allow control of both electronic and nuclear processes that determine ion yields. We report on a combined experimental and theoretical effort to determine how shaped laser pulses affect tunnel ionization, the step that precedes many strong-field phenomena. We carried out experiments on Ar, H_2O, N_2 and O_2 using a phase step function of amplitude ¾π that is scanned across the spectrum of the pulse. Semiclassical as well as fully quantum mechanical time-dependent Schrödinger equation calculations are found to be in excellent agreement with experimental results, as shown in Figure 4. We find that precise knowledge of the field parameters in the time and frequency domains is essential to afford reproducible results and quantitative theory and experiment comparisons.
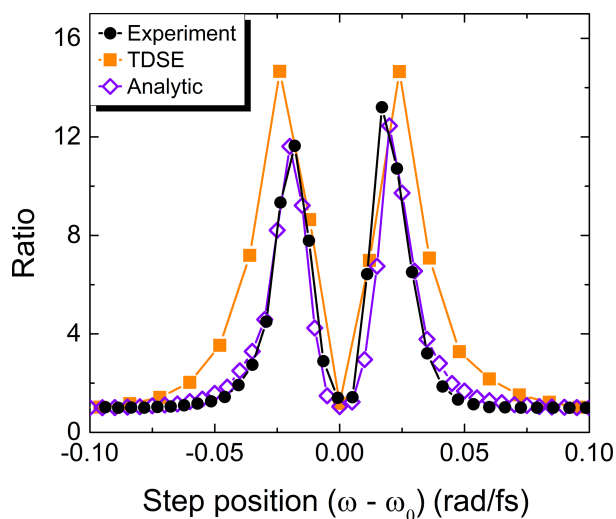

Figure1. *Results from simulations based on an analytic ADK formula and from quantum mechanical TDSE calculations for Ar atoms. The analytic results are scaled down by a factor of 5 to match the experimental figure, and the TDSE results have not been scaled, showing excellent agreement with experiment.*

(b) Ultrafast Disruptive Probing: Simultaneously Keeping Track of Tens of Reaction Pathways
Bethany Jochim, Lindsey DeJesus, and Marcos Dantus, Rev. Sci. Instrum. 93, 033003 (2022).

Ultrafast science depends on different implementations of the well-known pump-probe method. Here we provide a formal description of ultrafast disruptive probing, a method in which the probe pulse merely perturbs a transient species that may be a metastable ion or a transient state of matter. Disruptive probing has the advantage of allowing simultaneous tracking of the yield of tens of different processes. We describe the model and the expected signals based on a kinetic model. Experimental data on multiple products resulting from the strong-field ionization of two different molecules, methanol and norbornene, are then analyzed using the model. Disruptive probing in combination with ion imaging and/or coincidence momentum imaging, or as complementary to atom-specific probing or ultrafast diffraction methods, is a particularly powerful tool for the study of strong-field laser-matter interactions.
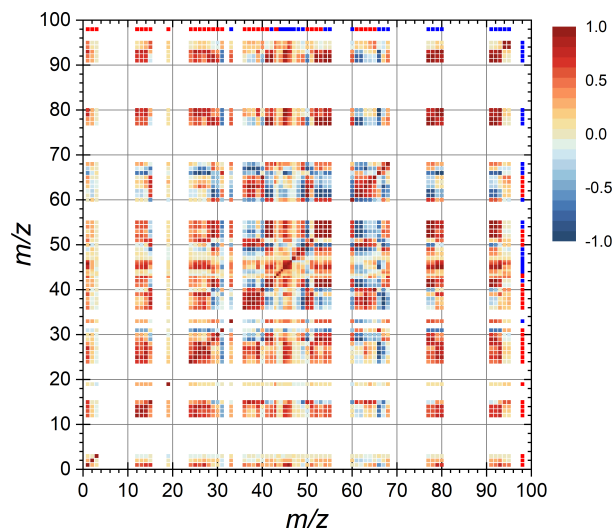

Figure 2. *Pearson correlation map of the 60 distinguishable ions detected following strong-field ionization of norbornene. Most transient signals show either a short-lived enhancement (red) or depletion (blue) as shown in row/column98.*

(c) Femtosecond intramolecular rearrangement of the CH3NCS radical cation
Jacob Stamm, Shuai Li, Stephen H. Yuwono, Swati S. Priyadarsini, Piotr Piecuch and Marcos Dantus, J. Chem. Phys. (2022), *successful peer review, being revised*.

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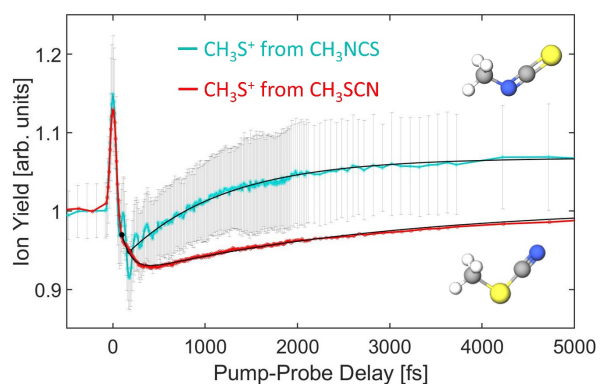

Figure 3. *The time-resolved yield of CH_3S^+ from CH_3NCS (blue) and CH_3SCN (red) following ultrafast ionization. Both ion yield traces are normalized such that the yield at long negative time delays is unity. Error bars for the CH_3S^+ yield from CH_3NCS show +/- 1 standard deviation.*

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Future Plans

i. We have carried out a series of measurements on substituted methanes (CH_3X). Photoelectron experiments on CH_3I failed to form H_3^+, those on CH_3Cl formed H_3^+, but with a formation time that is up to four times longer than in methanol. We explored compounds containing the pseudohalogens SCN, NCS, and OH, listed in order of increasing electronegativity. Past experiments on methanol, and new experiments on CH_3NCS show that H_3^+ is formed readily. No H_3^+ was formed from CH_3SCN. We surmise that electronegativity plays a key role because the reaction mechanism requires the formation of neutral H_2, and this occurs following the reduced electron density at the methyl carbon.

ii. Experiments on the double-ionization continuum of cyclopropane using synchrotron radiation at photon energies from 25 to 35 eV suggested the possibility that H_3^+ can be formed by a "closed ring" reaction mechanism in which three H atoms in one plane form three bonds in a concerted process. Alternatively, ring opening leads to H_2 formation and the appearance of $C_3H_4^{2+}$ [Phys.Chem.Chem.Phys.,2017,19,19631]. We have made preliminary measurements in which we reach the doubly ionized state via strong-field ionization. We then measured the H_3^+ formation via disruptive probing and found the formation time is 174 fs. The relatively long formation time, corresponding to multiple C-H vibrational periods, is not consistent with a concerted mechanism. We thus conclude that the mechanism involves ring opening, followed by formation of H_2 which then roams the dication to and abstracts a proton to form H_3^+.

iii. We hosted the traveling velocity map imaging (VMI) instrument from Kansas State University, and the Timepix3 camera from Augustana University obtained through a collaborative (Augustana, MSU, UVA, KSU, U of Mary Washington) NSF-MRI grant. Unfortunately, there was a problem with ion detection. The problem has been identified and we are planning a new set of experiments this Fall. We have results from a collaboration with Stephen Leone on time resolved X-ray absorption spectroscopy experiments CH_3NCS, where the L edges of sulfur shows evidence of CH_3S^+ formation. Finally, we are collaborating with Martin Centurion on ultrafast electron diffraction following the strong-field ionization of dicyclopentadiene which produces two cyclopentadiene fragments within one picosecond and shows vibrational coherence.

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

Peer-Reviewed Publications Resulting from this Project (2020-2022)

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

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

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

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

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)*

B. Jochim, L. DeJesus, M. Dantus, "Ultrafast Disruptive Probing: Simultaneously Keeping Track of Tens of Reaction Pathways," *Rev. Sci. Instrum*. 93, 033003 (2022).

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1.1 PROJECT SCOPE

The primary focus is to explore the realm of ultrafast electron and molecular dynamics using different but complementary tools. In one thrust, we explore and exploit fundamental aspects of generation and measurement of high harmonic and attosecond pulses to assess fundamental atomic and molecular processes. In recent years, our attention has turned to using attosecond pulses to extend the realm of strong field studies. A second thrust provides a natural link to our attosecond effort utilizing the same underlying strong field physics, laboratory infrastructure and technical approach. The strong field driven "self-imaging" method uses elastic scattering of the field-driven electron wave packet as an alternative route for spatial-temporal imaging in the gas phase. In 2011, the viability of this approach for achieving femtosecond timing and picometer spatial resolution was demonstrated in collaboration between OSU and KSU groups. A third 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 controlling strong field ionization, (2) initiate investigations for studying high harmonic generation from liquids and (3) investigations utilizing the attosecond capabilities of the XLEAP mode of the LCLS.

1.2 PROGRESS IN FY2022

The Quantum Trajectory Simulator concept. A recent thrust of our laboratory is to develop a new capability for selecting and controlling quantum trajectories, we dubbed this method the Quantum Trajectory Simulator (QTS). The concept is based on Feynman's principle that the outcome of a quantum process is dictated by the sum over all the quantum trajectories that contribute to it. Naturally, when analyzing experiments, we often refer to these individual trajectories even though they have not been measured individually. Over the past two years, we have demonstrated a fully functioning QTS which allows us to directly measure 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 future experiments will probe the limitations of this model.

In a typical strong field ionization experiment, a single high-intensity mid-infrared (MIR) 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 other atomic and molecular systems.

In the semi-classical view, tunnel ionization and wave packet propagation are directly coupled by the same low-frequency strong field. Furthermore, the exponential dependence of the tunneling rate confines the birth phases near the field extrema. This significantly constrains 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 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 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.

In 2019-2020 a new apparatus was constructed at OSU for conducting QTS experiments. The 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 bandwidth (~ 5 eV). In our experiments so far, the central photon energy used is either 16 eV or 26 eV which is determine by two different multilayer mirrors and metal filters. To produce the maximum number of photons at these energies, xenon gas is an ideal HHG generator. Note, the price of xenon gas has increased 20-fold, making it prohibitively expensive. Consequently, we are evaluating alternate generation methods, as

Figure 1: QTS concept applied to the argon double ion yield as a function of delay between the XUV attosecond pulse and a 23 TW/cm^2, 1.7 μm MIR dressing field. The XUV pulse has a central photon energy of 16 eV near threshold for the argon atom (15.7 eV). The dressing field has a ponderomotive energy of 6.5 eV.

described in our future work. We have also optimized the mechanical and optical design for good interferometric stability between the XUV and MIR pulses of approximately 50 *as*.

During the past year, we have begun to study 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. In all cases, a clear dependence on the delay is observed in the streaked electron energy spectrum (see Fig. 2[a]). Double ionization induced by the two-color field is also observed but for the case of helium the signal-to-noise is insufficient for a delay scan. However, the yield of argon double ion is adequate to produce an observable $2\omega_{MIR}$ oscillation in the delay spectrogram, as shown in Fig. 1. This strongly suggests that the Ar^{2+} is being produced by rescattering in our QTS measurement. Note, the MIR or XUV fields alone produce little or no double ion, respectively.

Figure 2: Spectrogram of the (a) streaked electrons and (c) integrated double ionization yield of argon using the QTS approach. (b) The phase difference between the two spectrograms. The conditions are the same as Fig. 1.

In the semi-classical model, double ionization 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. We have developed a model that incorporates both impact ionization from direct and excitation mechanisms. The theory work is a collaboration between Ken Schafer (LSU) and Abraham Camacho (OSU).

Once the experimental XUV-MIR signature for double ionization was established, the next QTS experiments addressed measuring the phase difference between the direct electrons and the (*e,2e*) process. Figure 2 is illustrative of this measurement, here the data collection for the (a) electrons and (c) double argon ion was interleaved at each delay step. Note, the double ion yield in (c) is the integrated counts from Fig. 1. The symbols are the measured Ar^{2+} yield, and the solid line is calculated using a model which includes both impact ionization and excitation. Both spectrograms oscillate at $2\omega_{MIR}$ and the extracted relative phase difference between the two is shown in (b). Examining the phase difference at the $2U_p$ electron energy, we extract a phase difference consistent with the semi-classical expectation. We are currently investigating this behavior in greater depth but the viability of the QTS approach is clearly demonstrated. We are currently preparing a manuscript for *Science*.

High Harmonic Generation (HHG) from liquid sheets. HHG 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 unknown since there is relatively little experimental 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 binary mixtures. We have also tuned the fundamental wavelength used for generation across a wide range to assess if liquid HHG has similar wavelength scaling properties that are well established for the gas phase.

The solvents that have been studied can be sorted into three classes: aromatic, polar, and aliphatic hydrocarbons. HHG from these classes were studied to see if there is any trend in yield and spectral structure based on class. Aromatic molecules such as toluene and fluorobenzene have been observed to have the highest HHG yield by at least an order of magnitude over polar solvents like isopropanol. This is an interesting observation since aromatic molecules are known to have bright HHG yield in the gas phase. The enhanced harmonic yield observed in both gas and liquid phase for the aromatics brings up an important topic in the understanding of the physical mechanism behind HHG in liquids: Does HHG in liquids behave more similarly to HHG in gas or solids? The current investigation route is to determine if the HHG

Figure 3: HHG spectra from liquid toluene at 1.6 μm and 2.4 μm wavelengths at constant intensity. The cutoff is unaffected by the wavelength. The relative yields can be compared between the wavelengths.

mechanism in liquid phase can be described by the coherent sum of individual atomic responses or if the intermolecular structure plays a dominant role.

A wavelength comparison at 1.6 μm and 2.4 μm has also been conducted to observe the effect on harmonic yield and cutoff energy as a function of wavelength. Figure 3 shows that the harmonic cutoff energy in toluene (defined as the end of the harmonic plateau) exhibits a wavelength independence from 1.6 μm to 2.4 μm at constant intensity (20 TW/cm^2). This contrasts with gas HHG where the cutoff energy is proportional to λ^2. We also observe an intensity independent cutoff which is again in contrast to gas HHG where the cutoff is linear with intensity. Further investigation is required to determine the underlying mechanism of this wavelength independence of the cutoff in liquids but suggests a mechanism limited by a correlation length. The same cutoff energy and wavelength independence is also observed in isopropanol suggesting a general property of liquid HHG.

Investigations at the LCLS. The group has collaborated in two different LCLS runs that focused on measuring the ultrafast decay of the Auger-Meitner process. These efforts are reflected in publications [3A] and [6A].

1.3 FUTURE PLANS

Quantum trajectory simulator: We have now conducted an initial survey of both energy resolved photoelectron and ion yield for argon and helium. The oscillation in the rate of argon double ionization as a function of MIR/XUV delay supports that the QTS is driving a two-color recollision process, a promising direction for future studies. Over the next year, we will (i) continue to explore the phase differences between direct electron emission and inelastic scattering. (ii) Explore alternative methods for generating bright attosecond pulses without xenon. This includes driving the HHG source at the 2nd harmonic of the MIR fundamental wavelength and bi-chromatic schemes. Preliminary evidence along these lines is encouraging. (iii) Once the HHG source brightness is increased we will pursue 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. (iv) Survey QTS control of molecular ionization as a prelude of controlled LIED. By completing (i) and (ii) we will gain the necessary knowledge and technical advance to carry out experiments (iii) and (iv) more effectively. Ken Schafer (LSU) and Abraham Camacho (OSU postdoc) will provide theory support for this program.

HHG from liquid sheets. We plan on using longer driving wavelengths (3-4 μm) to further study the cutoff energy with increasing pondermotive energy. Furthermore, this will allow us to better understand how the yield scales with increasing wavelength and how much it differs from the gas phase. We plan on also studying the effect of exciting fast vibrational modes in liquid HHG by generating harmonics using a fundamental wavelength at the OH stretch modes of liquid water and comparing to harmonics from heavy water where the fundamental is off the vibrational resonance. This excitation will perturb the intermolecular bonds in the structure in the case of H_2O. This deuterated comparison can also be performed in the alcohols where the OH group can play a decreasingly dominant role in the structure by using alcohols of increasing size. These studies could therefore be a way of addressing the role of intermolecular structure in liquid HHG. To that end we also plan on continuing studies with binary mixtures. Of particular interest are aromatic-alcohol mixtures. With increasing aromatic concentration, the alcohol's chain-like structure will be increasingly broken. A comparison of HHG versus the aromatic's concentration could therefore be another way of studying the role of intermolecular structure and local order in liquid HHG.

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

1.4 PEER-REVIEWED PUBLICATION RESULTING FROM THIS PROJECT (2020-2022)

1A. "Attosecond transient absorption spooktroscopy: a ghost imaging approach to ultrafast absorption spectroscopy", Taran Driver *et al.*, Phys. Chem. Chem. Phys. **22**, 2704 (2020). doi: 10.1039/c9cp03951a.

2A. "High-power few-cycle Cr: ZnSe mid-infrared source for attosecond soft x-ray physics", Vyacheslav Leshchenko *et al.*, Optica **7**, 981 (2020). doi: 10.1364/OPTICA.393377.

3A. "Clocking Auger electrons", D. C. Haynes *et al.*, Nat. Phys. **17**, 512 (2021). doi: 10.1038/s41567-020-01111-0.

4A. "Attosecond metrology", P. Agostini, A. Piper and L. F. DiMauro, in Handbook of Laser Technology and Applications (CRC Press) p. 307-320 (2021).

5A. "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.

6A. "Attosecond coherent electron motion in Auger-Meitner decay", Siqi Li *et al.*, Science **375**, 285 (2022). doi: 10.1126/science.abj2096.

Project Title

Electron Dynamics under Strong Field Irradiation
Grant No. DE–FG02-05ER15713

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Project Scope
Our work is targeted on high-field electron coherences revealed in the SENE approach (see [1, 2]) by incorporating it with the innovative Feuerstein-Thumm virtual detector method [3]. Connection to experimental reports, for example of longitudinal momentum distributions (see [4] for background), are given by Tian, et al., in [5]. Following recent work, we have explained recent work in response to two invitations: (a.) to present our analysis [6] of new strong-field calculations (in a special issue of J. Phys.B). and (b.) to discuss computational innovations via "Virtual Detector Theory with Path Summation for Nonsequential Double Photoionization" during the 6th International Quantum Coherence Workshop, organized at Stevens Institute of Technology for Oct. 12-14 (2022). These are concerned with high-field electron response via path-integral summation of the fully space-time-dependent Schrödinger equation (TDSE) during, and then following, virtual detection of the evolved TDSE solution. This approach will become even more important as it provides a new route to sorting the dynamics of high-field processes [7] of molecular electrons.

Recent Progress
In last year's AMOS contribution, we described an initiative to investigate the applicability of simplified, few-level quantum theory to explain or even approximately predict the strong-field rate of quantum-coherent electron-atomic processes, particularly in the study of resonant field-excitation of atomic states, such as the development of dynamically stable configurations of states that are "dressed" by the radiation field. We focused on hydrogen in the first approach, using a compact quantum model of hydrogen that is "complete", meaning that it consists of the engaged $2p$-$3d$ Balmer transition and an energetically-distant ionized state, just three quantum states but with correct hydrogenic energies and transition dipole matrix elements engaged. The model was used to derive an analytic solution of its (very few but transparently relevant) Schrödinger amplitudes. The second method uses the numerically parallel solution for a complete all-states hydrogen atom, thus allowing a direct comparison between a good model and the numerically exact reality. In our recent invited publication [6],

we have contrasted the two approaches and some of the results are shown below). The key to comparison with the model's results are both the clear rate of ionization and the intensity-dependent dressed-state doublets in the photoelectron energy spectrum (see Fig. 1). This theoretical-numerical comparative investigation opens a method that is eligible for significant extension.
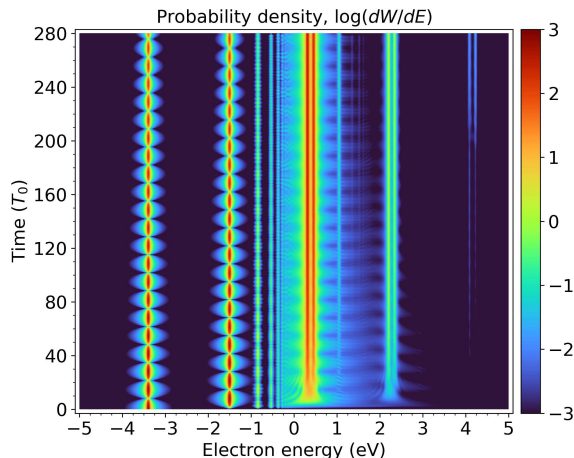

Figure 1: Electron differential-energy probability density (horizontal) versus time (vertical in intervals of the field period, T_0). In our *ab initio* time-dependent Schrödinger equation integration, the hydrogen electron is irradiated by a 150 GW/cm^2, 656 nm field that resonantly dresses the $2p$-$3d$ Balmer transition. Above E=0 in the spectrum the energy doublet is separated by the Rabi frequency of the strong-field $2p$-$3d$ oscillations.

Our development of the innovative Feuerstein-Thumm virtual detector method [3] has been extended substantially by incorporating one or more electrons. Based on non-destructive numerical quantum detections and the propagation of Bohmian-like classical particles, it is allowing us to study in an *ab initio* way the 2-electron nonsequential ionization dynamics of a model atom, in this case with helium character. By interpreting virtual detection signals measured at different points in a 2-electron two-dimensional position space (the time-evolution of the 2-electron probability density is provided below in Fig. 2), we have quantified the relative contributions of single- and double-ionization events to the overall ionization process. Additionally, we are simultaneously developing insights into different ionization and electron recollision pathways by tracking the virtual particles and their dynamical variables in time [8]. We have also extended the method of calculating the photoelectron momentum distribution to atoms with two active electrons, by performing a coherent path-summation over the virtual particles. This is possible because a *single* mathematical solution (wave function) can be reinterpreted to represent a *pair* of electrons interacting classically. This study confirms development toward our next extension, to strong-field multi-electron, and molecular, quantum dynamics.

Future Plans

We will analyze the properties of high-field laser-dressed molecular systems by building from our study of field-dressed states and resonance effects, but now engage the different laser/electron configurations needed. In that case, the dressing process will be treated by a
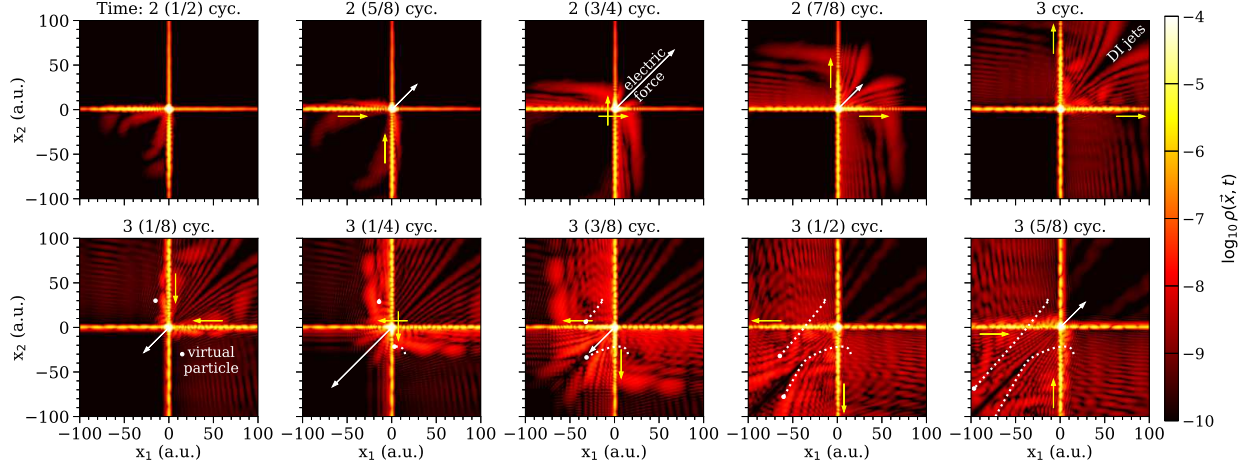
Figure 2: Snapshots of the two-electron probability density $\log_{10}\rho(\vec{x}, t)$ at intervals of 1/8th of the field period. The white arrow represents the instantaneous laser electric force vector, $-(\hat{x}_1 + \hat{x}_2)E(t)$. The yellow arrows signify the direction of on-axis probability current flow. As the field causes ejection of probability into the $x_1 x_2 > 0$ quadrants, double-ionization (DI) packets are formed (see the panels for $t = 2.75$ cyc. and $t = 3$ cyc. for instance). In the first panel at $t = 2\,(1/2)$ cyc., DI jets from the preceding half-cycle of the field are still faintly visible. The trajectories of two virtual particles initiated at $t = 3\,(1/8)$ cyc. and $\vec{x}_d = (\pm 15, \mp 30)$ a.u. are shown, which follow the stream of probability current.

Floquet analysis in contrast to our previous analytic solution involving only three coupled atomic amplitudes. The necessarily new numerical approach will be developed as well.

In this way we will continue to extend our investigation into the correlated behavior of atomic electrons under strong-field irradiation. Having recently demonstrated the extension of the virtual detector method to the two-active-electron case, it is now trivial, from a theoretical standpoint, to add any number of interacting atomic electrons. We aim to study the process of nonsequential triple ionization using the virtual detector method. The utility of the virtual detector method lies in its ability to model the dynamical evolution of the Schrödinger wavefunction in the case of multiple electrons irradiated by high-intensity, low-frequency, and/or long-duration pulses. We will generalize the standard two-dimensional configuration of a "ring" or "square" of numerical detectors to a sphere or cube of detectors, as required for the case of three or more active electrons. In this case time-propagation of the Schrödinger wavefunction coupled with time-resolved numerical detection poses a new computational challenge. We will continue development of our computation codes to make efficient use of more advanced parallel computing architecture.

Peer-reviewed Publications and Presentations from this Project (2020-22):
1. D. Younis and J. H. Eberly, "Benchmark of few-level quantum theory vs *ab initio* numerical solutions for the strong-field Autler-Townes effect in photoionization of hydrogen," (invited), J. Phys. B **55**,164001 (2022).
2. D. Younis, Songbo Xie and J. H. Eberly, "Virtual Detector Theory with Path Summation", invited address to 6th International Workshop on Quantum Coherence, Information and Computing, Stevens Institute of Technology, Hoboken NJ (October 12-14, 2022).

Recent relevant publications (DOE-AMOS support shown by ***).

References

[1] For an introduction to the SENE method, which is the combination of solutions describing the quantum ionization process via the Schrödinger Equation (SE) and the Newton Equation (NE), see ***Xu Wang, Justin Tian and J.H. Eberly, "Extended Virtual Detector Theory for Strong-Field Atonic Ionization", *Phys. Rev. Lett.* **110**, 243001 (2013), and ***Justin Tian, "Theory of Strong-Field Atomic Ionization", Ph.D. Dissertation, Department of Physics and Astronomy, University of Rochester (2017).

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Probing ultrafast XUV/x-ray induced electron correlation in the molecular frame
Award number: DE-SC0021336
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Project Scope:
Electron-electron correlation is a fundamental process where momenta and energies are exchanged in multielectron atomic and molecular systems. This project investigates photo-induced electron correlations in molecules in the time domain and in the molecular frames. Specifically, the investigation focuses on the temporal profile of the energy and momentum redistribution during electron correlations, the impact of the electron-electron correlation dynamics on the consequent chemical bond activities, and the dependence of the electron correlation dynamics on molecular orbital properties and molecular axis alignment or orientation. Three phenomena driven by electron correlation will be studied with direct comparison between experimental data and theoretical calculations: 1) autoionization, 2) single- and two- photon double ionization, 3) shake and core-hole decay processes. To achieve the needed temporal resolution and the multiple-observable measurement, ultrafast (atto- and femto- second) lasers and a reaction microscope (REMI) will be used to retrieve the transient 3-dimensioanl momentum of charge particles as a function of time. The ultrafast lasers to be used include table-top XUV/x-ray attosecond lasers and facility-based free-electron-lasers. The target molecules are prototype or small molecules, such as N_2, CO_2, and C_2H_2.

Recent Progress:
Our 1µm few-cycle high-average-power high-repetition-rate laser has been installed in July 2022. The construction of the high harmonic generation vacuum line has been completed and the pump-probe beam line has been set up. Both configurations of REMI for 3-D momentum imaging with 4π detection and two-sided velocity map imaging (VMI) as an alternative for high energy electron detection with high resolution have been simulated and designed. Based on the spectrometer design, the design of the target chamber has been completed and the custom target chamber has been ordered (expected delivery in late October 2022). We are in progress of designing a stereo ATI carrier envelope phase (CEP) measurement setup. Two graduate students and a postdoc researcher have participated in this project and received instrumental simulation and hands-on training.

Future Plans:
We expect to receive the custom chamber and the spectrometer parts by the end of November 2022 and plan to assemble the spectrometer and install the delay-line detectors by the end of year 2022. We plan to carry out the commissioning of the spectrometer in January – February 2023 and the commissioning of the pump-probe beamline (including XUV beam generation /diagnostics and experiments on noble atomic gases) in March – April. In the Fall 2022, the graduate student will be building a FROG device for few-cycle pulse duration measurement. The postdoc researcher will be building and test the CEP measurement apparatus. We aim to bring the experimental line to operation by May 2023 and carry out experiments on autoionization of N_2 and/or C_2H_2 in summer 2023. Attosecond streaking measurement will be performed. The milestones to achieve include (1) demonstrating operation of REMI spectrometer (as well as the

two-sided VMI at the end of summer 2023); (2) demonstrating generation of attosecond XUV pulses with energy streaking; (3) demonstrating CEP tagging at high repetition rate (200kHz); (4) taking preliminary data on N_2 molecule.

We plan to submit an LCLS beamtime proposal in 2022 for run 22 (beamtime in Oct. 2023-June 2024). According to our communications with LCLS beamline scientists, the DREAM endstation for simultaneous measurement of electron and ion will not be available in the next run (run 22). Therefore, we will propose an experiment on x-ray induced attosecond dynamics of electron correlation without influence from the nuclear motion or orientation, for which detection of electron alone is sufficient. Discussions with potential theorist collaborators is in progress.

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

Physics of Correlated Systems, Award DE-SC0010545
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Project Scope

The interests of this project center on atomic, molecular, and optical systems that involve tightly coupled or *correlated* or entangled degrees of freedom, and are in need of an improved theoretical description, in most cases a quantum mechanical description. Our efforts to treat such systems focus on real atoms and molecules, building in as much of that reality as is feasible into the theoretical treatment. While some projects we've undertaken utilize now-standard techniques such as multiconfiguration Hartree-Fock theory, most involve building analytical and computational tools and capabilities that are less standard, such as hyperspherical coordinate methods, multichannel quantum defect theory, R-matrix theory, or new time-propagation formulations. The types of correlations studied range from the traditional type, electron-electron correlations, that first made the word commonplace in electronic structure theories, to electron-nuclear correlations in diatomics and small polyatomic molecules, and to the correlations between electronic and nuclear (or dissociative) degrees of freedom in molecules.

Our research goals are often aimed at developing an improved understanding or interpretation of experiments that have been carried out or which are feasible for the near future. The theoretical developments can generate ideas for improved control over this class of quantum mechanical phenomena, which have the potential to spark new ideas for controlling energy transfer among atomic or molecular constituents, as well as photoprocesses and chemical reactivity.

Recent Progress

(i) **Multiphoton ionization of strongly correlated atoms**

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

A second major development in the area of multiphoton ionization was also spearheaded by a talented PhD student (subsequently a short-term postdoc) in our group, Dr. Yimeng Wang. Departing from most current studies which have been focusing on the helium atom, Dr. Wang

applied our toolkit consisting of variational R-matrix theory and multichannel quantum defect theory in an effort to understand the phase lag measurement involving interfering one- and two-photon processes in the barium atom, which was carried out more than a decade ago by Dan Elliott's group, and had not previously been understood theoretically. Our treatment[2] achieved good agreement with that complicated experiment, and was one of the first detailed calculations to fully account for the phase lag between competing fragmentation channels in any nontrivial system, going beyond previous theory descriptions that have relied on oversimplified models.

A major new direction in our group has been a collaborative effort with Arvinder Sandhu's experimental group, as a joint experiment-theory collaboration aimed at understanding and extending current control capabilities that arise from pump-probe short pulse absorption and ionization processes in atomic argon. A sequence of two or three ultrafast pulses can produce time-dependent quantum beats between the alternative pathways, and remarkable regularities are emerging in this system. A first article[3] on those joint efforts was published during the past year. Promising avenues have emerged and our multichannel quantum defect toolkit has proven to be well-suited to describing the phenomena they are observing. One interesting finding 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.

Our work has progressed also in treating multiphoton ionization in the unusual and extreme correlation scenarios that exist in the helium atom, owing to its plethora of nearly-degenerate hydrogenic orbitals. As was described in the preceding report, significant progress has been achieved in ramping up our capability to describe ultrafast or strong laser pulses interacting with an atom. The accidental degeneracy of $He^+(n)$ (when one neglects the tiny fine structure splittings) is responsible for modifying the classification of doubly-excited states in helium compared to other atoms with two valence electrons, according to correlated SO(4) group theory quantum numbers $\{K,T\}^A$ formulated long ago in studies by D. Herrick and later by C. D. Lin. Our treatment of helium two-photon ionization considered final state energies in the vicinity of the doubly-excited states near the N=2 and N=3 ionization thresholds.[4] Our study predicted that some of the rules of thumb previously verified for states reached in 1-photon excitation need to be modified for the states reached by two-photon above-threshold absorption. The calculations in [4] also extracted finer details about the ionization, namely the photoelectron angular distributions, characterized by β_k coefficients of the k-th Legendre polynomial with even k only, for either linearly polarized incident light, or for absorption of two opposite circularly polarized incident photons which produces the trefoil polarization field. In particular, rapid variations of the angular distributions occur in the vicinity of autoionizing resonances.

One project we completed involving two-photon ionization of helium in [5] was triggered by the goal of using interference between two or more photon sources to control the electron ejection process. That goal led to our detailed study of angular distributions in the presence of simultaneous photoionization by coherent one-photon and two-photon absorption processes that reach the same energy, i.e., from photon sources of respective frequencies 2ω and ω, respectively. The phase-dependent interference of those two processes, using parallel linearly polarized photon sources along a *z*-axis can produce electron current that is directed preferentially along positive or negative *z*, depending on the phase difference between the photon

sources. Such an experiment is of fundamental interest because the final photoelectron state has broken the parity as a good quantum number. Our publication [5] treats that case, again for the prototype system of atomic helium in the vicinity of doubly-excited final state energies. The calculations predict the angular distribution, and directional asymmetry (strength of positive z current versus negative z current) as a function of final state energy, and its dependence on the atomic and laser phase contributions. It also suggests an alternative way of redirecting the photoelectrons by changing the laser frequency, but with a fixed relative phase and field strength ratio, showing how to use this scheme to redirect photoelectrons by manipulating final state energies across the S-wave $2p^2$ resonance.

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

Our work on molecular physics frame transformation theory did not make any notable advances this year, so the following text summarizes our 2020 publications, namely Refs.[7,8]. Most of the molecular physics problems of current interest in our theoretical treatments are those that involve energy interconversion between electronic and vibrational/dissociative degrees of freedom; such processes are controlled by a breakdown of the Born-Oppenheimer approximation. Dissociative recombination via indirect Rydberg pathways is challenging for standard theoretical methods because there is no simple, direct dissociative pathway to visualize or compute, in contrast to ordinary dissociative recombination or attachment collisions that follow the Bates-type mechanism. A notable system involves an electron collision with HeH^+ at low energies where there is no identifiable direct dissociative Born-Oppenheimer potential curve.

In just the past couple of years, it has become possible to carry out DR experiments with a very cold (<10K) ion storage ring experiment at the Cryogenic Storage Ring (CSR) in Heidelberg. Their dissociative recombination measurement of cryogenic molecular HeH^+ ions that collide with low energy electrons has permitted the sharpest test of theory yet. Specifically, they measured this process at low energy with sufficient energy resolution and sufficiently low rotational temperatures to resolve individual resonances. That experiment pointed out inaccuracies in previous theory published by many groups including our own. Our new variant of the energy-dependent frame transformation theory[8] was implemented to quantitatively test the improved theory, in collaboration with the Prague research group of Roman Curik.

In contrast to the rovibrational frame transformation, which can be viewed as a treatment of correlated electronic and nuclear motions, the correlation of an electron with the fields of two fixed ions or one ion and one atom is a stringent test of theory capabilities, e.g., in unusually high excited states of a diatomic molecule. With former postdoc Teri Price, we continued to work towards developing theory of a class of correlations using the *local* frame transformation, which involves a transformation between spherical and prolate spheroidal coordinates. Some experimental groups have also sought out our collaboration for understanding complex bound and autoionizing spectra of heavy atoms, and we have collaborated with one group to interpret a complicated region of multichannel perturbers in the erbium atom.[6]

Future Plans

Further multiphoton ionization and coherent control studies are underway and should be completed within the coming year. A graduate student, Miguel Alarcon, continues to spearhead our collaboration with the group of Arvinder Sandhu on a class of pump-probe experiments in atomic argon and krypton. That effort is a major jump in complexity, as it involves describing the combination of autoionizing intermediate and final states, whose decay is mediated by the interplay of electron-electron interaction and spin-orbit coupling. We are also collaborating with the group of Thomas Pfeifer at the Max-Planck Institute for Nuclear Physics in Heidelberg, and hope to publish a combined theoretical and experimental study of the simplest above-threshold ionization process in atomic helium, where they have begun a set of impressive measurements at the Hamburg free-electron laser facility that can quantitatively test our theory predictions.

Time permitting, we also hope to develop a new full implementation of rovibrational frame transformation theory for dissociative recombination or photofragmentation processes, in the more complex regime that arises when there are multiple Born-Oppenheimer potential curves of the positively charged molecular target ion. Our efforts will also treat highly excited long-range states of the Sr_2^+ molecule that are beyond capabilities of modern quantum chemistry, by using a recently developed implementation of the spherical-to-spheroidal coordinate frame transformation that interfaces smoothly with generalized quantum defect theory. Other projects that interconnect with research areas of interest to this DOE program will continue to be considered, for possible exploration or collaboration.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

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

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

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Project scope

This project seeks to determine to what extent small molecules can be controllably excited to highly excited states and whether the subsequent dynamics can be controlled as well. To determine this, methods for describing the dynamics of molecules in highly excited states will be developed and tested. These methods will be based on time-dependent perturbation theory and grids designed to describe highly excited and scattering states in molecules. Excitation to highly excited states like Rydberg states, doubly excited states, and other excited configurations will be considered. State-to-state transfers will be among the processes considered to be controlled, along with directed energy flow into specific degrees of freedom. Observables corresponding to those that can be measured in coincidence experiments will also be optimized to provide experimental signatures of the dynamics.

Recent progress

We have continued developing the time-dependent perturbation theory (TDPT) codes that we use to describe the dynamics of molecules including ionization and continuum-continuum interference. This code was developed in Refs. [1, 2] and it is being refined for use in RABBITT calculations [3]. These calculations and the related experiments allow us to determine the attosecond response of molecules to ionization. The testing of the TDPT code has largely been using the molecule CHFClBr. Recent experiments in the group of Hans-Jakob Wörner, however, have allowed us to broaden the testing to additional molecules [4, 5].

This testing has allowed us to make a number of improvements to the TDPT method. One of the most important is increasing the accuracy of the integrals over the laser fields, $\int \mathcal{E}(\tau_1)\mathcal{E}(\tau_2)e^{i(\omega_1\tau_1+\omega_2\tau_2)}\mathrm{d}\tau_1\mathrm{d}\tau_2$. Small inaccuracies in these integrals were causing large qualitative errors by introducing small constant terms to state coefficients at long times that should be zero.

We have used the TDPT method to predict the ionization delays via the RABBITT method for methyl oxirane. For the laser parameters chosen, we predict delays of hundreds of attoseconds that decrease with sideband number (see Fig 1). We should note that these results are using a cc-pVDZ basis, we expect the results to change with both basis size and laser parameters. We are also working to compare these calculations to experimental results.

An undergraduate working in our group has also spent time improving the user features of the TDPT code. Flexibility has been added to the input file structure so that non-experts may use the code to predict RABBITT spectra and other one- or two-photon processes. This will allow other undergraduates and early graduate students in the group to use the
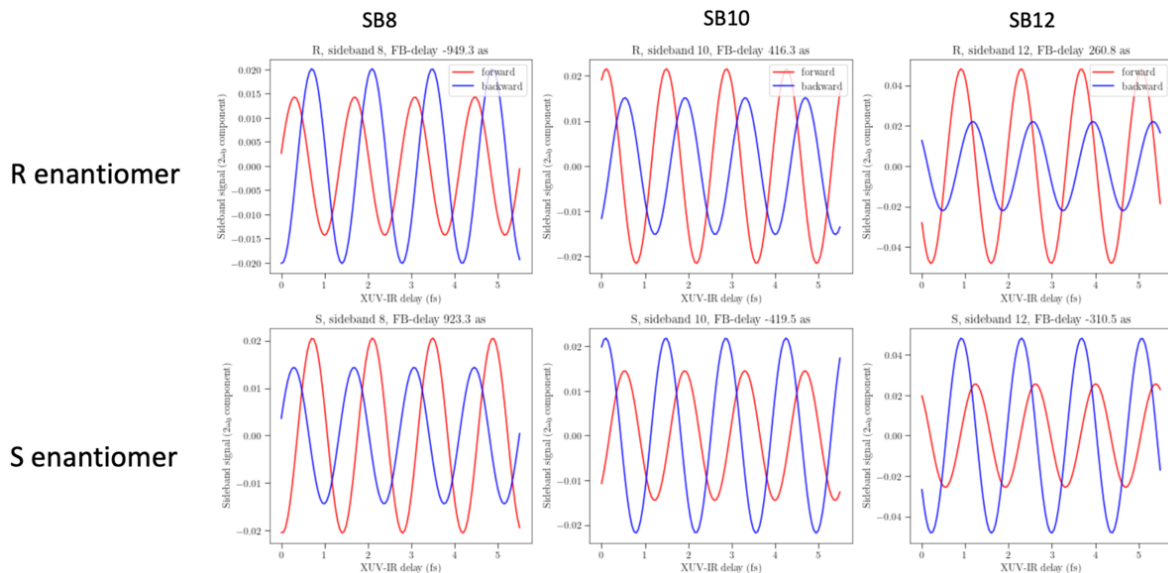
Figure 1: Oscillations of the 2ω component of the RABBITT sidebands for methyl oxirane.

code more easily as a production code. Additionally, it will allow collaborations between experimental groups such as that of Wörner to analyze their results. We plan to use the method to analyze the results of Ref. [4].

The use of coincidence momentum imaging observables to determine the success of our control schemes is a key aspect of this project. Coulomb explosion imaging (CEI) is one such method, and a major goal is determining what aspects of highly excited states can be identified by unique signatures in a CEI experiment. To this end, we have spent effort on the problem of determining a set of possible initial geometries for a given CEI measurement. We have been working with the groups of Daniel Rolles and Artem Rudenko for this, and we are using a data set that was taken for the purpose of aiding this study and determining the sensitivity to laser pulse parameters of the results. The most challenging aspect of determing the geometries is the (possibly strong) perturbations of the molecule during the process of charging. Another difficulty is the accuracy of the inversion of the classical Coulomb dynamics.

To address the first difficulty, we have decided to build a scheme that accounts for the initial kinetic energy of the molecule. This will allow us to identify all of the geometries that may have been perturbed prior to the explosion. The overall procedure partitions the energy determined from the CEI measurement into various degrees of freedom. Initial kinetic energy is one such possibility. Each additional degree of freedom increases the number of matching geometries corresponding to a given measurement. This may be an advantage or a detriment. We believe that it is likely that given a number of possible geometries, only a few will stand out as likely given knowledge of the initial molecules and dynamic processes involved.

To determine the accuracy of the inversion of the Coulomb dynamics, we have engaged in preliminary simulations without the additional complication of initial kinetic energy. While we are still working to improve the method, we have determined that it there is correlation

between relatively low errors in the CEI momentum and the predicted initial geometry (see Fig. 2). We will need to push this threshold lower, however, to be able to make worthwhile predictions.
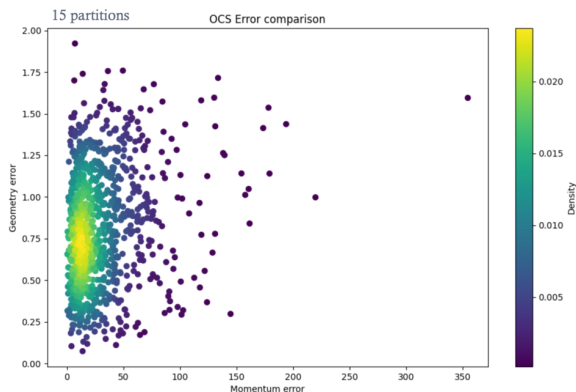

Figure 2: Preliminary simulations of the errors in randomly generated initial geometries and their resulting final momenta by partitioning the energy to invert CEI dynamics.

Finally, we are also preparing our overset grid codes for calculations on bound excited states and improving their use for scattering states. The overset grids work by employing overlapping spherical grids centered on each atom [6, 7]. They avoid the problems of trying to resolve nuclear potentials from atoms far from the grid origin of a single-center grid, but introduce an additional complication of interpolating and separating the functions between grids. In collaboration with the McCurdy and Lucchese groups at Lawrence Berkeley National Laboratory, we have begun exploring different methods of separating the functions between grids. We have developed a purification technique that differs from the Becke switching functions implemented in Ref. [6]. We believe that this technique will allow us to use fewer partial waves in the central grid and therefore speed up the calculations significantly.

Future plans

For the TDPT code, we have a number of applications and methodological improvements we are planning. One application, as mentioned above, is to RABBITT phases in CF_4 following Ref. [4]. The user-facing advancements we have so far made will be important here, as many of these and other future calculations may be performed by experimental students. We are also planning the inclusion of higher-order processes and electron correlation terms into this code. Since we have found that numerical effects can be quite important in these calculations, we will also build some model systems for which TDPT calculations can be done easily and quickly and use these to obtain more accurate and efficient numerical procedures. These model systems will also allow us to explore in greater depth the effect of discretization of the intermediate TDPT states in these calculations. This has been our approach for interfacing with Gaussian-based quantum chemistry codes, and we have been able to converge our calculations [3]. However, models will help us push our understanding of exactly when these techniques fail.

Likewise, the overset grid codes are under development. A key aim of this project is to extend them to bound excited states. Spatially large excited states that are difficult to capture with Gaussians will be targeted, and methods to directly optimize them will be explored. The first step in this process is to implement standard quantum chemistry methods on the overset grids. An implementation in pure matrix form is unlikely to be

performant, and so we will explore methods of iteratively generating efficient functions to solve the quantum chemistry problems. This is analogous to what was done in Ref. [6], where an iterative procedure based on successive terms in the Born series were used to solve the scattering problem. Following implementation of some uncorrelated methods, we can explore the feasibility of multi-configurational self-consistent-field implementations on the overset grids.

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

No publications to report.

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

Award Number DE-SC0022920

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Project Scope

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

Recent Progress

1.1. Using T_1 anisotropy in pulsed electron paramagnetic resonance (EPR) to illuminate a new theory of molecular qubit spin relaxation.

Existing theories of electron spin relaxation in molecular qubits use fluctuations in the magnetic *g*-tensor to define how strongly vibrations induce spin relaxation (spin-phonon coupling).[2,3] While this paradigm has been commonly used to rationalize the results of temperature-dependent spin relaxation (as measured by the T_1 parameter in pulsed EPR) such models typically contain many more theoretical coefficients than experimental data points. To rigorously test the *g*-tensor theory of spin relaxation, we have experimentally acquired T_1 values for molecular qubits over a range of varying magnetic fields in randomly oriented microcrystalline samples. Due to magnetic *g*-tensor anisotropy, measurements at different magnetic fields probe different molecular orientations with their own unique *g* values.[4] The g-tensor spin-phonon coupling model predicts that tetragonal
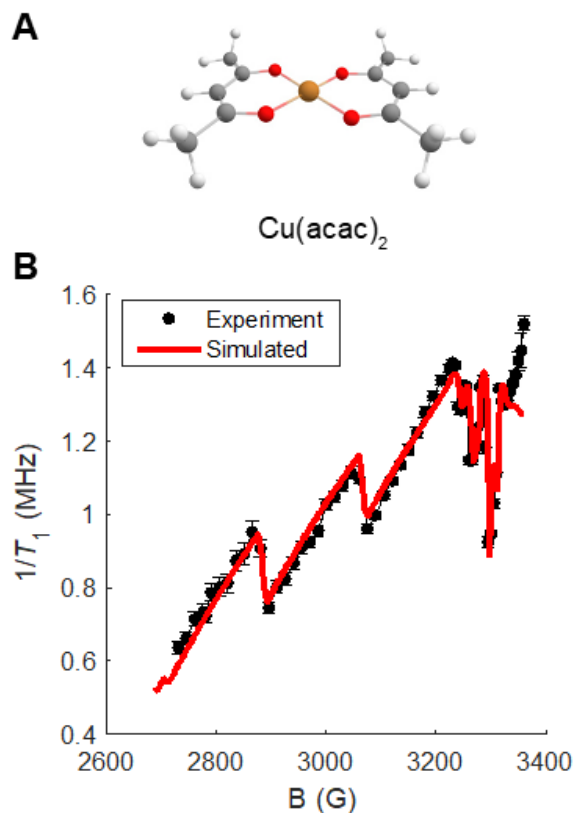
A

Cu(acac)₂

B

molecular qubits should undergo faster relaxation when the molecule's symmetry axis is parallel to the applied magnetic field.[2] We therefore sought to test these spin relaxation predictions with anisotropic T_1 measurements.

Surprisingly, our results demonstrate that spin relaxation in tetragonal Cu(II) qubits proceeds fastest along the perpendicular orientation and slowest along the parallel orientation. **Figure 1** shows pulsed EPR spin relaxation data collected on Cu(acac)₂, where the parallel orientation has a resonant magnetic field of around 2700 G and the perpendicular orientation around 3300 G. Relaxation proceeds around 2.5 times slower at the parallel orientation, indicating that the best molecular spin relaxation models are completely unable to predict the T_1 anisotropy. To rectify this situation, we developed an analysis based on the spin-orbit coupled wavefunctions that leads to the following expression for T_1 anisotropy:

$$\frac{1/T_1(\perp)}{1/T_1(\parallel)} = \frac{\frac{1}{E_{xy}^2}\left(\frac{\partial E_{xy}}{\partial Q}\right)^2 + \frac{1}{8E_{xz}^2}\left(\frac{\partial E_{xz}}{\partial Q}\right)^2 + \frac{1}{8E_{yz}^2}\left(\frac{\partial E_{yz}}{\partial Q}\right)^2}{\frac{1}{4E_{yz}^2}\left(\frac{\partial E_{yz}}{\partial Q}\right)^2 + \frac{1}{4E_{xz}^2}\left(\frac{\partial E_{xz}}{\partial Q}\right)^2}$$

Symbols with E indicate the energies of different electronic excited states, while derivatives with respect to Q indicate the vibronic coupling of those excited states. If we assume that all excited state energies have the same value and all vibronic couplings have the same value, the above expression simplifies into the following numerical form:

$$\frac{1/T_1(\perp)}{1/T_1(\parallel)} = \frac{1+\frac{1}{8}+\frac{1}{8}}{\frac{1}{4}+\frac{1}{4}} = \frac{5}{2}$$

This is in excellent agreement with the experimentally measured T_1 anisotropy and successfully predicts slower relaxation at the parallel orientation. Further extension of this reasoning allowed us to perform a simulation fit of the T_1 anisotropy using only two adjustable parameters, as shown in **Figure 1B**. Our combined experimental and theoretical results indicate major problems in previous spin relaxation models and point the way toward a new paradigm.

1.2. Using resonant inelastic X-ray spectroscopy (RIXS) to quantify ligand–metal covalency contributions to molecular qubit decoherence.

Existing high-performance molecular qubits frequently feature strongly covalent ligand–metal bonds, as exemplified by the copper-sulfur bond motif in compounds such as $[Cu(mnt)_2]^{2-}$, $[Cu(bdt)_2]^{2-}$, and $Cu(dtc)_2$.[4–6] Though the chemical concept of covalency seems intuitive, quantifying the magnitude of covalent bonding presents a challenging experimental spectroscopic
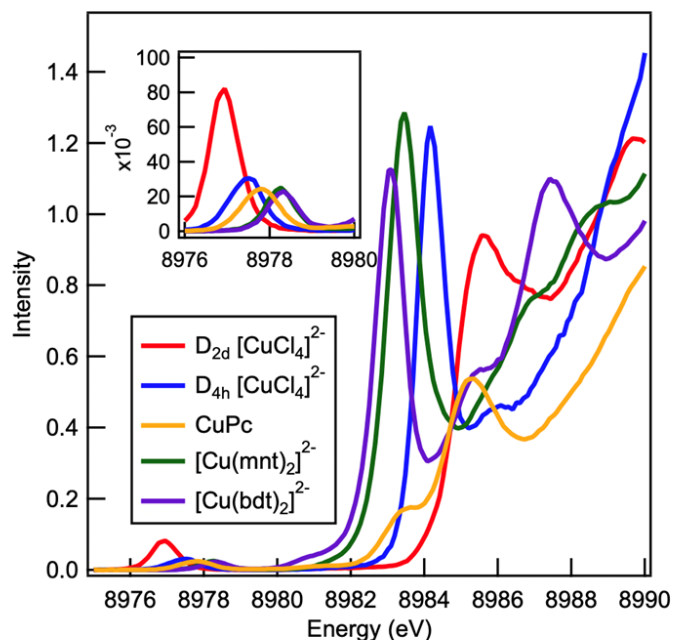
Figure 2: CEE cuts of various Cu(II) model complexes and molecular qubit candidates obtained using 1s2p RIXS at the Cu K-edge. Inset: Zoom in of the 1s → 3d pre-edge transition.

task. While computational metrics for covalency based on spin density delocalization have been employed,[7] experimental metrics for molecular qubit covalency have not been reported.

We have used Cu K-edge 1s2p RIXS spectroscopy to develop new metrics for ligand–metal covalency that can be used to understand molecular qubit decoherence. In addition to the main K-edge absorption features occurring at 8982 eV and higher, Cu K-edge spectroscopy features a diagnostic 1s → 3d pre-edge absorption feature around 8978 eV (**Figure 2**) in the constant emission energy (CEE) cuts. These pre-edge features provide a direct handle on the ligand σ donor strength, which can be directly related to ligand field energies. RIXS additionally affords a constant incident energy (CIE) spectrum, and preliminary results indicate that the width of the CIE cut peaks also serve as an experimental metric for covalency. Notably, X-ray techniques are element-specific. Thus, the 1s2p RIXS metric can be used to quantify the covalency of molecular qubits even when they are embedded in an isostructural diamagnetic matrix, as is often the case for spin relaxation and decoherence studies.

Future Plans

Building on the successes of pulsed EPR T_1 anisotropy and Cu K-edge RIXS, we will seek to develop additional spectroscopic techniques for studying spin relaxation in molecular qubits. Our near-term efforts will focus in two areas: (1) variable-temperature, variable-field (VTVH) magnetic circular dichroism (MCD) spectroscopy to elucidate the unique electronic structure of molecular qubit candidates, and (2) time-resolved Faraday rotation to directly measure the spin relaxation of fast-relaxing molecules.

2.1. MCD spectroscopy.

The equations derived in Section 1.1 indicate the importance of ligand field excited state energies (i.e., excitation of an electron from one d-orbital to another) in determining the spin relaxation rate. However, these energies cannot be easily obtained from conventional UV-vis absorption spectroscopy, as the covalent, conjugated ligands used for molecular qubits facilitate intense charge transfer transitions, which cover nearly all of the ligand field bands in the absorption spectrum. VTVH MCD provides a promising method for finding the positions of the ligand field bands. At low temperature and high magnetic fields, MCD spectra are dominated by the *C*-term intensity mechanism, which preferentially activates ligand field excited states as opposed to charge transfer states. Thus, VTVH MCD provides an experimental spectroscopy for uncovering the positions of the ligand field bands in molecular qubit compounds.

2.2. Time-resolved Faraday rotation.

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. By using a femtosecond pulsed laser system and polarization optics, we will measure ultrafast room temperature spin relaxation dynamics in "non-room-temperature coherent" molecules. This technique will open up entirely new classes of molecules for probing structure-function relationships in spin dynamics, enhancing understanding of how to rationally manipulate the T_1 and T_2 parameters. Ultrafast Faraday rotation additionally promises to give unique insight for spin relaxation in optically addressable qubits. While these compounds possess unique photophysical features that enable initialization and readout of quantum coherence solely using visible light, their relaxation times can only be measured by EPR up to 60 K.[8] Ultrafast Faraday rotation will enable relaxation measurements on optically-addressable qubits at elevated temperatures for the first time.

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Peer-Reviewed Publications Resulting from the Project (Project start date: 07/2022)
No publications to report. One manuscript submitted; one manuscript in preparation.

Attosecond Physics with XFEL sources

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PROJECT SCOPE

In the past few years, the very first attosecond X-ray pulses have been produced at LCLS [1], with additional LCLS experiments planned in the near future [2]. The high energy of XFEL attosecond sources make both inner-core electron dynamics accessible and allow for a single electron to absorb many photons, leading to the break-down of first-order perturbation theory. From a fundamental viewpoint, high field intensities push the study of strong field interactions into the X-ray regime. This allows one to explore a full range of wavelength scaling in strong field ionization, from the mid-infrared to the X-ray.

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

> *1. Develop theoretical framework to interpret attosecond ionization delays in atoms and molecules interacting with high frequency attosecond sources.*
> *2. Explore the scaling of strong field interactions in the high intensity and high frequency regime recently made accessible by XFELs.*

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

As part of broader experimental campaigns, my theoretical physics group's progress on this project will be meaningfully amplified: through our own research, by helping network members make further developments in their own programs and through increased opportunities for dissemination of techniques and results. Finally, NSF recently awarded OSU a mid-scale infrastructure grant to build a National Extreme Ultrafast Science (NEXUS) facility, led by Robert Baker (Chemistry) and Louis DiMauro (Physics), providing additional opportunities for experimental collaboration.

RECENT PROGRESS

Below is a description of the proposed Milestones under the two topics above (Topic A and Topic B, respectively) on which considerable progress has been made since the start of the project.

Topic A

Milestone 1: To derive a formula for the Coulomb-Laser coupling induced time delay for circular polarization. This formula can be used to extract Wigner delays from ionization using circularly polarized light for streaking, such as the current and planned LCLS measurements.

Milestone 2: Implement semiclassical simulations (following the methodology described in the proposal) to simulate orientation resolved single photon ionization delays in molecules. Divide the simulation into two steps, initial quantum ionization (step 1), follow by classical propagation (step 2) to investigate the role of the molecular environment on the departing electron wavepacket.

Milestone 3: Investigate shake-up effects which result from electron correlation. Experimentally such effects can be seen as an additional lower-energy streaking trace. The aim is to better understand multi-electron correlated dynamics accompanying photoionization.

Topic B:

Milestone 1: Obtaining initial conditions for the excited electron wavepacket immediately following strong field ionization using the Strong Field Approximation.

Milestone 2: The results of Milestone 1 are then used to set up Classical Trajectory and Quantum Trajectory Monte Carlo simulations (CTMC and QTMC). These simulations can fully account for the Coulomb potential of the remaining ion. Conduct CTMC and/or QTMC simulations over a scan of ellipticity values.

Progress made on the listed milestones.
Since the start of the project, progress was made on both topics of the proposal, namely single photon ionization regime (Topic A) and the strong field ionization regime (Topic B). In particular, Milestones 1-3 in Topic A were reached and are currently being finalized into a paper. Milestones 1-2 of Topic B were also considerably advanced, and resulted in a Physical Review Letters publication (see "Publications resulting from the project" section). More detail is provided below. Under Milestone 1 (Topic A), we have obtained a formula for the Coulomb-Laser coupling term for circular polarization. This formula can be used by experimentalists who perform angular streaking (using circularly polarized light) of ionization of atoms and molecules. In such experiments, a high-frequency attosecond pulse is combined with a lower frequency circularly polarized pulse to measure the ionization delay, such as was done in a recent LCLS experiment on NO. In particular, the formula for the Coulomb-Laser coupling correction that we obtained can be used to subtract from the measured streaking delay to obtain the Wigner delay in recent LCLS and other similar type of experiments which use circularly polarized light. These results are currently in preparation and will be submitted in the near future. In Milestone 2 (Topic A), we performed

semiclassical simulations (as described in the proposal) and obtained angular- resolved ionization delays in a polyatomic molecule. The results show significant variation of ionization delay with angle, showing that molecular environment exerts a significant influence on the departing electron. These results are currently under review in a journal. In Milestone 3 (Topic A), we investigate the effect of shake-up in a helium atom. To capture electron correlation, we used Dyson orbitals, as detailed in the proposal. These results are currently under review in the same paper as Milestone 2 described above. In regard to Milestones 1 and 2 (topic B), we recently completed a work (Published in PRL) dealing with strong field ionization of a diatomic molecule. In this publication, we introduce a method for determining the ionization site of a diatomic molecule by analyzing the asymmetry in the electron momenta distributions. While this particular work dealt with lower frequency infrared light and ionization of a neutral molecule, the approach that underlies the Quantum Trajectory Monte Carlo (QTMC) simulations can be extended to ionization with X-ray and XUV pulses. For the case of single photon ionization, a similar extraction procedure can be used to extract the ionization site of a molecule. For highly charged ions, it remains an outstanding question whether the non-adiabatic initial conditions used to model the electron wavepacket after strong field ionization are relevant in this regime. Note that the Coulomb interaction, which is easy to account for within classical trajectory simulations, is expected to be particularly strong in this case.

FUTURE PLANS

The focus of this proposal is on investigating ionization delays in atoms and molecules. However, the theory developed in the context of ionization delays will be applicable to the study of other phenomena involving interaction of matter with attosecond high frequency sources. Of particular interest are experiments which use elliptically polarized light, obtaining electron momenta distributions in the plane of polarization. I would like to use these 2D momenta distributions to explore fundamental aspects of the inner-core single photon ionization process, in a manner analogous to how 2D electron momenta distributions were previously used to explore the fundamental aspects of the strong field ionization process using high intensity infrared fields (5,6).

In the future, I would also like to better understand charge migration and the correlated electron dynamics that lead to molecular dissociation following ionization. One question of interest is whether the time evolution of a molecule following single photon absorption and ionization can have a measurable impact on the final momentum of the ionized electron. This opens the possibility of being able to extract the time-evolution of the molecular potential landscape following ionization from the measured electron momenta distributions.

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

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

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

I.   Project Scope

The purpose of this project is to theoretically and computationally study the dynamics of small molecules, which undergo chemical transformations in femtosecond timescales, by using a combination of different strong-field techniques. These techniques include laser-induced electron diffraction (LIED), high-order harmonic generation spectroscopy (HHS), and coincident photoelectron and photoion fragments energy/momentum distribution measurement. By using single laser pulses, previous applications of LIED and HHS have been largely limited to molecules at or near equilibrium geometries. Furthermore, in the molecular retrieval procedure, used in these techniques, nuclei have typically been treated as classical particles. This project aims to overcome these limitations and extend the current capabilities of the strong-field techniques to image ultrafast changes in molecular structures within the pump-probe scheme. The success of this project would make these strong-field molecular imaging techniques applicable to a much broader class of problems. It would also make these techniques more reliable and potentially applicable to larger molecules. The methods and tools developed in this project should also be relevant to other time-resolved spectroscopic techniques such as attosecond transient absorption spectroscopy and time-resolved photoelectron spectroscopy. In all these methods, the electron-nuclear dynamics is at the heart of all the processes involved.

II.   Recent Progress

Strong-field ionization plays an important role in all rescattering processes. For molecules near equilibrium geometries, tunneling ionization rate can be calculated by the SFA or, more conveniently by the molecular Ammosov-Delone-Krainov (MO-ADK) theory. Recently we used *Octopus* code (https://octopus-code.org/) to calibrate the MO-ADK method. This code is based on the time-dependent density functional theory (TDDFT). More importantly, we have now successfully developed a method to calculate accurate molecular structure coefficients for the MO-ADK. We plan to extend this research to molecules away from the equilibrium geometries.

Recently we started developing a semiclassical method to simulate strong-field processes based on the Herman–Kluk (HK) semiclassical propagator. Our preliminary results show that the method leads to significant improvements over other available semiclassical methods that have been used in the strong-field community. In fact, on some standard tests, our results are nearly as good as the numerical solutions of the time-dependent Schrodinger equation (TDSE). We have started collaborating with Professor H. J. Worner group (ETH, Zurich) on the time-resolved photoelectron spectroscopy with N_2.

III. Future Plans

Based on the progress we have made recently, we plan to further develop the semiclassical HK method for applications in strong-field processes. One of the important features is that this method involves calculation with classical trajectories that can be done independently on different computers. Therefore, this method can be extended to larger systems. So, we intend to test our method on simple molecules and compare the results with the TDSE or TDDFT.

We also plan to study LIED and/or HHS within the pump-probe scheme for dissociating molecules. In the first step in the simulation, the time-dependent nuclear wave packet during and after the pump pulse is obtained from the solution of the coupled channel equations, as well as the surface hopping method that we developed recently. In the second step, high-energy photoelectron momentum spectra induced by the probe pulse at each time delay are calculated by using the Quantitative Rescattering (QRS) theory.

Many theoretical and computational tools developed in this project are also relevant to other time-resolved spectroscopic techniques such as attosecond transient absorption spectroscopy (ATAS) and time-resolved photoelectron spectroscopy (TRPES). In particular, the electron-nuclear dynamics is at the heart of all these processes. We therefore plan to perform simulations for other related techniques of current interest to the research community, including the ATAS and TRPES. Together with the LIED and HHS, these techniques provide complementary information about the molecular structure.

IV. Peer-Reviewed Publications Resulting from this Project (Project start date: 08/2022)

No publications to report

Beating electronic decoherence

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Program Scope

This project aims to study and suppress electronic decoherence in molecular systems with two subtasks: (1) developing experimental approaches that will capture the extremely fast decoherence process in time-domain. (2) devising atomistic schemes that can suppress decoherence and produce long-lived electronic coherence in molecular system.

Recent Progress

1. Attosecond imaging of electronic wave packets

In the past year, we have made progress in developing an improved attosecond imaging method to measure the temporal and spatial evolution of electronic wave packets. The method was based on two-electron-angular-streaking (*2eAS*) and addressed an important issue of the previous method. The new method utilizes absolute phase measurement to distinguish the two electrons produced in the double ionization processes. This has allowed the detection range of the method to double to 2.4 fs. This method was applied to probe spin-orbit wave packets in xenon and krypton, in which the yields of double ionization were measured with a time range of 0 and 2.4 fs (Fig. 1). The fully corrected time transients are in good agreement with those obtained from theoretical results (TDCI calculations). The results show the initial peanut-shaped hole was quickly filled at half of the spin-orbit period (1.5 fs) in the xenon cation while the shape remains largely the same at this time delay due to slower dynamics. This is the first time that the spin-
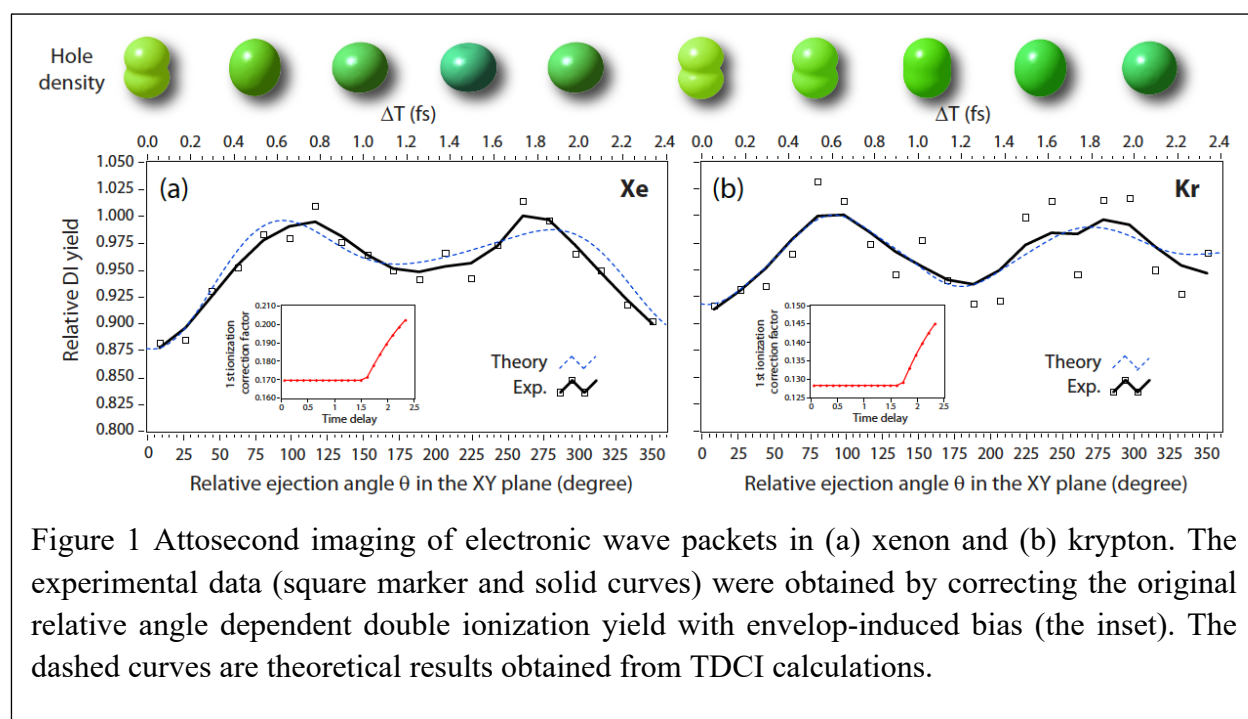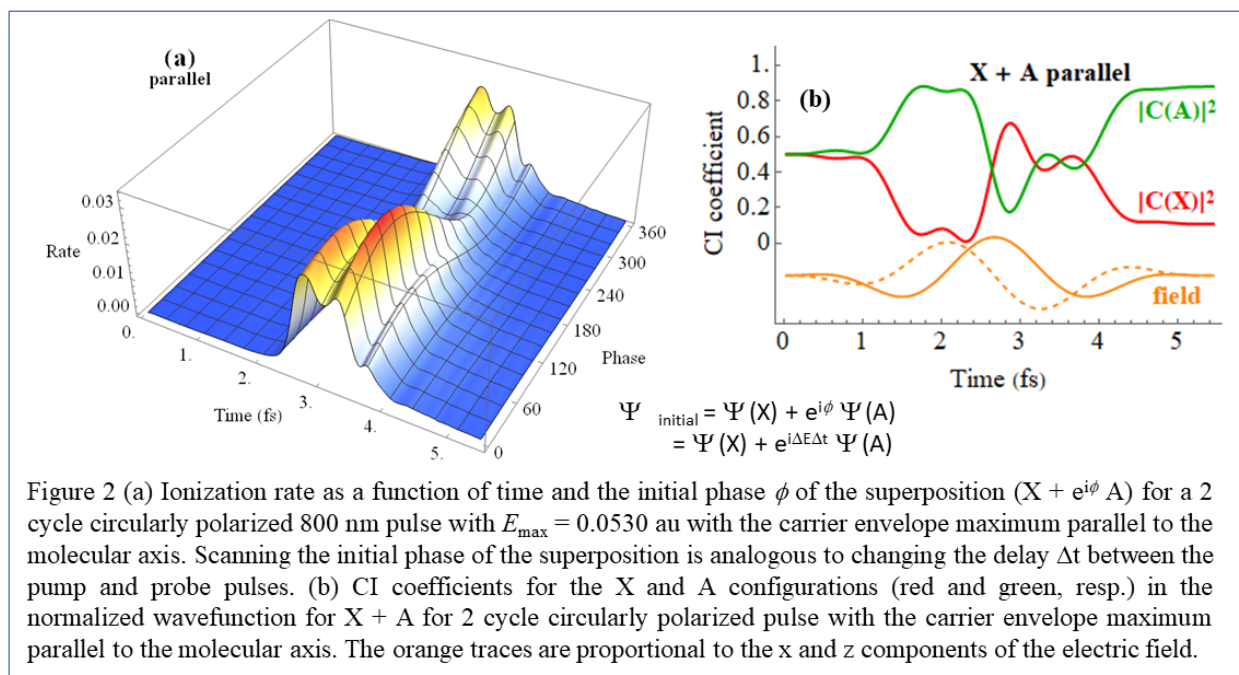

Figure 1 Attosecond imaging of electronic wave packets in (a) xenon and (b) krypton. The experimental data (square marker and solid curves) were obtained by correcting the original relative angle dependent double ionization yield with envelop-induced bias (the inset). The dashed curves are theoretical results obtained from TDCI calculations.

orbit wave packet was detected in the xenon cation. This is because the method can probe coherence in single atom and does not rely on ensemble coherence. The manuscript is currently under review in *Physical Review Letters.*

2. Modeling strong field ionization probing of charge migration

Strong field ionization (SFI) plays an important role in various experimental techniques for studying electronic wave packet dynamics. SFI has been used either as a pump pulse to produce a superposition of electronic states or as a probe to detect wave packet motion. This suggests that SFI could be employed in both steps - to produce electronic wavepackets and to probe their dynamics. Iodoacetylene cation, HCCI$^+$ was chosen for our simulations (this system has been studied previously using high harmonic spectroscopy and advanced modeling). Time dependent configuration interaction calculations were used to simulate strong field ionization as a probe of the electron dynamics of coherent superpositions of the X and A states of HCCI cation produced by SFI. Very short (2 cycle), intense linearly and circularly polarized pulses were used to avoid nuclear dynamic effects. The oscillation of the charge shows two frequencies – the driving frequency of the laser field and the intrinsic frequency due to the energy separation between the X and A states. Strong field ionizations with linear and circularly polarized pulses show marked differences in the ionization rates that depend on the initial phase of the superposition, the polarization direction, and the carrier-envelope phase (Fig. 2). This paper was published in *Frontiers in Chemistry.*

Figure 2 (a) Ionization rate as a function of time and the initial phase ϕ of the superposition (X + e$^{i\phi}$ A) for a 2 cycle circularly polarized 800 nm pulse with E_{max} = 0.0530 au with the carrier envelope maximum parallel to the molecular axis. Scanning the initial phase of the superposition is analogous to changing the delay Δt between the pump and probe pulses. (b) CI coefficients for the X and A configurations (red and green, resp.) in the normalized wavefunction for X + A for 2 cycle circularly polarized pulse with the carrier envelope maximum parallel to the molecular axis. The orange traces are proportional to the x and z components of the electric field.

3. Tutorial on 3D momentum imaging

The Li group recently published a tutorial on 3D momentum imaging technique. The tutorial aims to introduce the most recent development in high performing 3D momentum imaging to researchers and graduate students. Many technical details were discussed to help set up this instrument. A computer program that integrates all components of the system was released to the community. The tutorial was published in J. Phys. B.

4. Multiple vibrational wave packets decohere fast spin-orbit wave packets

Spin-orbit wave packets in molecules are ideal benchmark systems for studying electronic decoherence. Because of the nature of spin-orbit coupling, the potential energy surfaces of these states are considered parallel and thus nuclear dynamics should be perfectly in sync and the electronic coherence is maintained indefinity. The Li group recently carried out an experiment on methyl iodide and detected the coexistence of multiple vibrational wave packets (CH_3 symmetric stretching and CH_3 umbrella motion) and an ultrafast (6.4 fs period) spin-orbit wave packet on the ground states of CH_3I^+ (^2X). It was found that the electronic coherence was lost within the first picosecond (Fig. 3). Further analysis revealed that the vibrational motions vary significantly on the two spin-orbit states, suggesting the non-parallel nature of the potential energy surfaces of the two spin-orbit states. This is different from previous studies carried out in diatomic molecules such as Br_2 and DBr. A manuscript is being prepared for publication.

Figure 3 (a) The Fourier transform spectrum of time resolved methyl iodide dication yields obtained by strong field pump and probe technique. The peak at 0.64 eV is from the spin-orbit states of the ground state cation. The peaks at ~0.35 eV and ~0.15 eV are from CH_3 symmetric stretching and CH_3 umbrella motion, respectively. The doublet feature is due to different vibrational states being populated in the cation by strong field ionization. (b) The time evolution of the FFT amplitude of the spin-orbit wave packets, showing it decays in the first 400 fs.

Future Plans

The Li group will continue to study the electronic coherence dynamics in methyl iodide and explore means to control decoherence time. Other molecular systems will be investigated to detect electronic coherence. We also plan to study whether it is possible to detect conical intersection induced electronic coherence. The Schlegel group will develop theoretical approaches to model electronic decoherence dynamics on multi-dimensional potential energy surfaces.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

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8. 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. Phys. Chem. A. (under review)

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

Award number: DE-SC0017868

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Project Scope

The response of molecules and materials to intense and/or high energy light underpins a wide range of important processes such as light harvesting, radiation damage, and energy storage. At the atomistic level, many of the underlying mechanisms are poorly understood, especially the electron dynamics during and immediately following interaction with a laser pulse. Attosecond transient X-ray absorption, is a power tool for measuring these processes, as the elemental specificity, and corresponding spatial localization, of X-ray absorption can be exploited to probe the time-evolving electronic density in a particular region of a molecule or material. Interpretation of these spectra can be complex, however, as it requires one to relate the intensity and frequency modulations of a spectrum to the underlying dynamics.

First-principles simulations are an ideal tool for "reversing" from time delay to real-time, allowing one to reconstruct electron dynamics from the observed transient spectra. In contrast to simulations of the electron dynamics themselves, there has been less work on computing corresponding attosecond transient X-ray spectra from first-principles. To address this, the goal of this project is to develop quantum chemistry techniques for simulating attosecond electron dynamics and X-ray observables on equal footing, for both solid-state and molecular systems, and to determine relationships between dynamics and the corresponding spectra.

Recent Progress

Under this overarching theme, we made progress on three interconnected efforts: methods for computing transient inner-shell spectra using time-dependent density functional theory (TDDFT) with basis sets, probing valence electron motion in molecules following sudden pump excitations, and transient metallization in insulators.

I. Filtered TDDFT for Transient Absorption Simulations

In the past year we completed implementation and validation of our previously reported method for computing transient spectra using Gaussian basis sets [Yang2022], which can exhibit non-physical "intruder" peaks in their spectrum arising from transitions from an inner-shell level to a poorly-described virtual state [Kadek2015]. Our TDDFT-based approach removes these
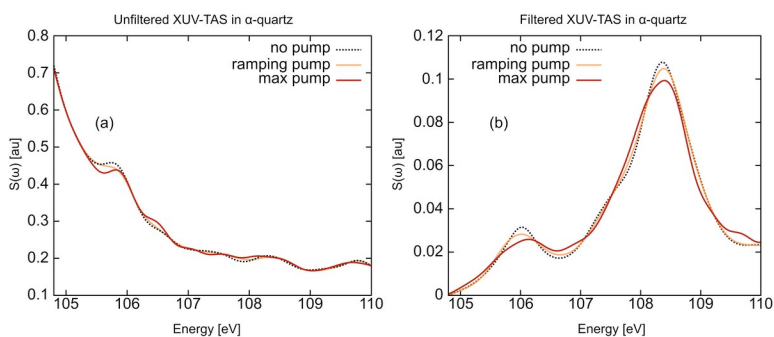

Figure 1: Transient XUV absorption spectra in IR pumped SiO_2 using a bulk-mimicking cluster and Gaussian basis sets. Without correcting for intruder peaks (a), the spectrum is qualitatively incorrect. Using a filtered dipole operator gives a spectrum (b) that correctly exhibits modulations due to varying conduction band population.

deleterious peaks by using a filtered dipole operator, which excludes transitions between these states whilst leaving the interaction with the laser field intact. In addition to molecular cases (reported previously), we recently showed how this type of filtering is essential for computing transient inner-shell spectra in solids when using bulk-mimicking clusters due to the large density of states. Fig. 1 shows an example of this method applied to infrared pumped α-quartz (SiO_2) probed with XUV attosecond transient absorption. The time-delay dependent transient spectrum using standard TDDFT (a) is catastrophically incorrect transient due to intruder peaks, whereas the filtered spectrum (b) correctly shows amplitude modulations associated with conduction band population.

This technique has proven instrumental in our ongoing basis set calculations of transient X-ray absorption in molecules and materials, and is likely to find utility in a wide range of related inner-shell spectroscopy simulations. It has been implemented in the NWChem package, and will be checked into the main development branch soon.

II. X-Ray Transient Absorption for Probing Electron Dynamics in Molecules

Continuing our ongoing efforts to simulate transient X-ray absorption spectroscopy for probing electron dynamics, we have completed our study of valence electron dynamics in 4-aminophenol ($H_2NC_6H_4OH$) following X-ray ionization. Resonant soft X-ray pumped processes are interesting, as the resulting superposition of states can induce complex valence electron dynamics. Moreover, the availability of attosecond X-ray pulses at free electron lasers is making such measurements increasingly feasible. Our simulations show that N K-edge and O K-edge pumped aminophenol result in valence motion across the molecule, both with periods of ~ 0.8 fs. Previously, we reported preliminary results that showed, in agreement with the UV-pumped case [Chen2020], that the X-ray absorption is reduced when there is more electron density around a particular absorbing atom, i.e., the N K-edge absorption is reduced when there is extra density around the N atom.

In the past year, we utilized our filtered dipole TDDFT approach to compute orientationally averaged transient spectra without spurious intruder peaks, and to also decompose the observed spectra into polarization and orbital contributions. This allowed us to interpret the states involved in the modulated X-ray absorption
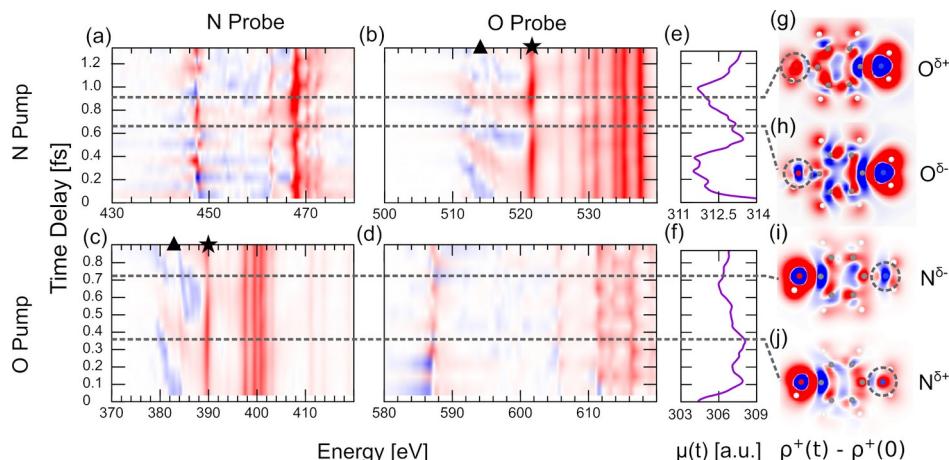
Figure 2: Simulated soft X-ray pump/X-ray probe spectra (a-d) in 4-aminophenol. In both cases, the core-hole induced valence electron dynamics with a period of ~0.7 fs, as shown by the dipole moments (e,f) and snapshots of the difference densities (g-j). Transitions to virtual states (stars) and to occupied states (diamonds) have modulations that correlate with the local density around the absorbing atom (circled).

spectrum, and better understand the nature of the modulations in the spectrum. Fig. 2(a-d) shows the TD-PBE0/def2-TZVP computed transient spectra for aminophenol for all combinations of O/N K-edge pump and O/N K-edge probe, along with the corresponding time-depending dipoles (e,f) and deviations of the electron density from the initial value (g-j). There are three types of signals in the spectrum: 1s probe→virtual, 1s probe→occupied, and occupied→1s. The first two types of excitations are a result of

the superposition created by the core-hole, and their modulations in are correlated with the local electron density around the probe atom, with increased density reducing their intensities. In an orbital picture, the bright low energy peaks (stars) correspond to transitions from O/N 1s to a pump-populated LUMO+1 (π^*), and thus appear modulated positive peaks. The lower energy pre-edge peaks (triangles) correspond to transitions primarily from O/N 1s to a pump-depopulated HOMO and HOMO-2, and alternate positive and negative. Additionally, since the core-hole acts like a broadband pump, there are both low and high frequency dynamics in the molecule, which different probe transitions are sensitive to. The third type of signal, occupied→1s transitions, only occur in the N pump/N probe (a), and O pump/O probe cases (d), manifest as negative peaks, with a complicated time-dependence related to the highly distorted density around those atoms.

Even for this relatively simple study, these transient spectra are highly congested and rich in information, but suggest a general set of rules for X-ray pump/X-ray probe transient absorption. In general, local densities around an absorbing atom appear to reduce the absorption, with different transitions being sensitive to different frequencies of dynamics in the system. Additionally, excitations to depopulated states, and dexcitations to a core-hole encode dynamical information, but interpretation is challenging. Simulations, which can readily decompose peaks in a spectrum into polarization, orbital, and local density dependent quantities are likely to be vital for interpreting future experimental spectra.

III. Strong IR-Induced Transient Metallization in Insulators

In parallel with molecular studies, attosecond experiments on solid-state materials have been the focus of much recent interest, as they can shed light on important processes such as dielectric breakdown and band-gap tunneling. Understanding these processes has implications for energy storage, materials in intense environments, and high density circuitry, but experimental observables such as time-resolved XUV/X-ray absorption can be difficult to interpret without simulations.

Building on our previous success with SiO_2, in the past year we made progress towards simulating transient metallization of diamond via intense IR pulses, and how this processes can be measured via transient carbon K-edge X-ray absorption spectroscopy. To overcome the limitations of grid or planewave methods for inner-shell spectra, we developed a bulk-mimicking cluster model for diamond that allows for use of atom-centered basis sets. This technique, which we previously reported for static field modulated X-ray absorption in TiO_2 [Darapaneni2020], involves truncating the bulk structure and passivating with hydrogen atoms, with the distance chosen such that the optical gap is insensitive to the capping distance. The geometry of this cluster, shown in the inset of Fig. 3, corresponds to a tetramantane-like structure ($C_{22}H_{28}$). Since strong-fields drive the system far-from-equilibrium, we used
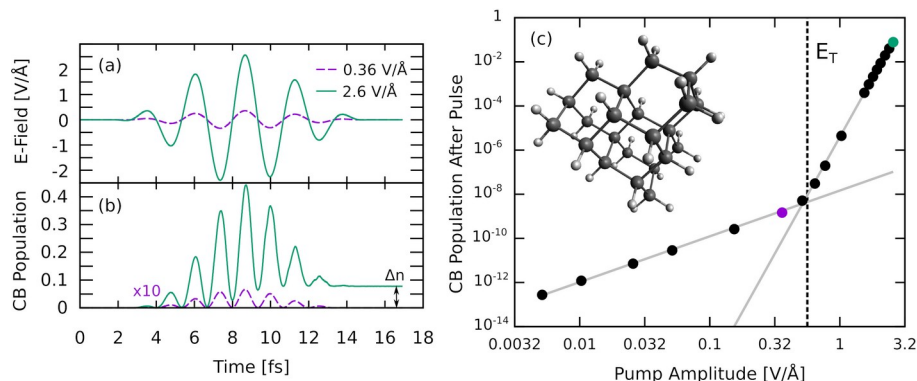

Figure 3: IR-induced strong field breakdown of diamond simulated using TDDFT. (a,b) The conduction band is reversibly populated by a weak field (purple dashed line) and irreversibly populated by a strong enough field (green solid line). The threshold breakdown (ET) of the material can be identified from the qualitative change in final CB population as a function of field amplitude.

Koopmans' tuned range-separated hybrids for the DFT exchange-correlation functional, which are known to give improved dynamics for strong-field processes such as ionization. The resulting ground state properties of this cluster are in good agreement with experiment, including an optical gap of 6.7 eV (6.5 eV for experiment [Armon1982]), and a qualitatively correct carbon K-edge X-ray absorption spectrum.

The corresponding strong-field simulations are also quite promising. Fig. 3 shows the computed conduction band populations for this model diamond system for a range of IR pump intensities. The computed conduction band populations during the pulse (Fig. 3(b)) exhibit two distinct regimes: for low intensities, there is a reversible population of the conduction band (CB), whereas for higher intensities there is irreversible population of the CB. The corresponding breakdown voltage can be computed from the the final CB populations as a function of field amplitude, as shown in panel (c). For diamond, we get a value of 0.5 V/Å, which is excellent agreement with the experimental value of 0.1 V/Å [Balmer2008], and is especially noteworthy since these simulations require absolutely no parametrization from experiment. Simulations of the transient C K-edge spectra for this process are currently underway.

Future Plans

Going forward, on the molecular side of things, we will simulate X-ray pumped valence dynamics in a wider range of molecules, including systems that have been previously shown to exhibit core-hole induced dynamics (e.g., 2-aminophenol, nitrosobenzene). For the materials work, we will complete the transient absorption study of diamond to determine how modulations in the C K-edge encode information about the conduction band population. We will also extend our attosecond strong-field breakdown simulations in diamond and SiO_2 to account for nuclear vibrations using our recently completed (but currently unvalidated) Ehrenfest module in the NWChem software package. This will allows us to determine the role of electron/lattice couplings on the breakdown process.

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Complexity and Correlated Motion of Electrons in Free and Confined Atomic Systems

Award number: DE-FG02-03ER15428
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Project Scope

The goals of the research program are: to further understanding of the interaction of radiation with matter; to provide theoretical support to, and collaboration with, various experimental programs that employ latest generation light sources, particularly ALS, APS and LCLS; and to study the properties (especially photoemission) of free and confined atoms. 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; and seek out new phenomenology, especially in the areas of attosecond time delay in photoemission (including photodetachment), outer-shell photoemission in the vicinity of inner-shell thresholds and confined systems. The primary areas of programmatic focus are: many-body and relativistic effects in photoionization of inner and outer shells of atoms and ions (positive and negative); dynamical properties of atoms endrohedrally confined, primarily in C_{60}; and studies of Wigner time delay on the attosecond time scale in photoemission of free and confined atomic systems. Flexibility is maintained to respond to opportunities as they arise.

Recent Progress

Various aspects of the attosecond dynamics of electrons in the photoemission process, as revealed by Wigner time delay [1-3], have been explored. Time delay of photoemission was scrutinized within a relativistic framework [4] with a focus on the variation of time delay in the vicinity of the Cooper minima, showing that the Cooper minimum in one channel has a strong effect on time delay in other channels *via* interchannel coupling, and that relativistic effects strongly affect the time delay in regions of Cooper minima. In addition, we made a systematic study of the dipole phase and Wigner time delay in inner-shell photoionization [5] and found that the time delay, as a function of photoelectron energy, follows essentially a universal shape. And the angular distribution of Wigner time delay was investigated, revealing a strong angular anisotropy of the time delay occurs near Cooper minima while the spin-orbit splitting affects the time delay near threshold [6]. Near autoionizing resonances, the time delay spectrum can become quite complicated, exhibiting both positive and negative delays across the resonance profile [7,8]. And our work indicates that the angular distribution is also quite complex [9]; at certain energies, the time delay can be positive in one direction of photoemission, and negative in another direction, a very odd result from a physical point of view.

Studies have been initiated to look at attosecond time delay in quadrupole channels, near Cooper minima, where the dipole cross section is small, and at photoemission angles near 90 degrees (with respect to the polarization of the incident photon) where the dipole photoemission for spin-up photoelectrons vanishes for ns states of closed-shell atoms. Preliminary calculations show significant effects of the transition from dipole to quadrupole dynamics in the vicinity of photoemission at 90 degrees with respect to the photon polarization[10].

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

Our program on confined atoms is aimed at mapping out their properties (especially photoemission) to guide experiment and uncover new phenomena. We have found a huge transfer of oscillator strength from the C_{60} shell, near the giant plasmon resonance, to the encapsulated atom for both Ar@C_{60} [15] and Mg@C_{60} [16]. And confinement resonances [19], oscillations in the photoionization cross section of an endohedral atom due to interferences in the photoelectron emission from the cavity, were predicted and confirmed experimentally [14]. Further, in the photoionization of endohedral atoms within nested fullerenes, the multi-walled structure makes the confinement resonances considerably more complicated [18]. And these effects carry over to the photodetachment of fullerene (and nested fullerene) cations which exhibit large resonances and a variety of unexpected properties [19]. Further, to augment the confined atom work, we have performed a density function theory calculation of the photoionization of all 32 valence levels of free C_{60} with full account of the molecular symmetry [20]; the calculation revealed a wealth of detail and is the most accurate calculation to date.

In response to experimental investigations, 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 [21]. It was found that, well above the thresholds, 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 [22]. It has also been demonstrated that the falloff of the branching ratio with energy increases with Z resulting from the relativistic effects that cause the ratio of probability densities of the $(j=l-1)/(j=l+1)$ wave functions for a spin-orbit doublet to behave as Z^2/r^2 for small r. Also, it was demonstrated that the branching ratios are strongly affected in the vicinity of inner-shell thresholds *via* correlation in the final-state wave functions known as interchannel coupling; this showed that the interchannel coupling was different for the two members of a spin-orbit doublet, i.e., it was affected by relativistic interactions. This will be tested experimentally in early 2023.

Since high-Z atoms are excellent laboratories to study the combination of relativistic and many-electron correlation effects dynamics, a new initiative, properties of superheavy elements, has been started [23,24]. We have studied Z=102, 112 and 118 (the heaviest known element) and significant anomalies in the subshell binding energies are found. Also, the photoionization properties show very large differences as compared to lower-Z atoms in the same column of the periodic table. Specifically, the subshell cross sections are completely dominated by relativistic and many-body interactions. More recently, a study of Cooper minima of *ns* states of high-Z atoms has found that relativistic effects can be huge and lead to rather different phenomenology from nonrelativistic predictions [25]. These calculations are of particular interest since experimental studies are now possible [26,27].

Future Plans

We will continue studying attosecond time delay in photoemission, including many-body effects, photodetachment, and nondipole effects and how confinement affects time delay. To provide a "road map" for experimental investigations, we will explore photoionization at high energies (tens of keV) to predict where many-body interactions alter simple behavior; preliminary indications are that this can be very significant. In the area of confined atoms, we will expand on our studies of interatomic Coulomb decay (ICD) and work on ways to enhance the time-dependent local-density approximation to make it more accurate and to include relativistic interactions to be able to deal with heavy endohedrals accurately. In addition, we shall focus on the full molecular symmetry of atomic systems confined in C_{60} to understand the limits of simple models and to deal with off-center endohedral confinement. And we shall respond to new experimental capabilities and results as they occur.

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Resolving femtosecond photoinduced energy flow: capture of nonadiabatic reaction pathway topography and wavepacket dynamics from photoexcitation through the conical intersection seam (DE-SC0020141)

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Project Scope

The dynamics that take place within just tens to hundreds of femtoseconds following the photoexcitation of a molecular chromophore can play a critical role in how the absorbed energy is directed, allowing it to be used for a specific function (photoinduction) or dissipated harmlessly (photoprotection). Underlying these dynamics is the presence of electronic energy degeneracies in the relaxation pathways of the excited chromophores, known as conical intersections (CIs), which mediate nonradiative electronic transitions known as nonadiabatic transitions. These transitions are known to mediate energy flow in natural biological systems, including the highly effective ultraviolet photoprotection mechanism of DNA [1–3], 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. For example, they might be used to enable laser-controlled "molecular motors" at the nanoscale [7,8].

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

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

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

Recent Progress

During this reporting period we have made a major step towards the realization of the ultrafast optical instrumentation needed to demonstrate our proposed spectroscopy method for capturing nonadiabatic transitions.

We report on the development of a novel, highly efficient frequency down- or up-conversion process that can not only handle octave-spanning bandwidths, but can also monolithically manage its own large material dispersion to deliver a pulse with a custom spectral phase [10]. As dispersion management is among the most challenging aspects of optical systems used for ultrafast spectroscopy when approaching the single-cycle limit, this technique may help to push the boundaries of temporal resolution in ultrafast optical spectroscopy, generally. For this program, the technique helps to make feasible the highly ambitious instrument that is required: one that provides synchronized 10-fs light pulses for visible, near-infrared, and mid-infrared spectral ranges.

As a proof of principle, we report the demonstration of an efficient frequency down-conversion stage that transfers pulses from the near-IR (at Ti:sapphire wavelengths, 680–820 nm) to an octave in the mid-IR (2–4 μm) while preserving its absolute bandwidth via an adiabatic frequency conversion process, and also monolithically managing its own large material dispersion to have near-zero net group delay dispersion (GDD). Our goal was to convert a compressed 10-fs pulse at ω_{NIR} to a compressed, passively CEP-stabilized 10-fs pulse at ω_{MIR} with full photon conversion efficiency in the presence of a strong, narrowband pump at $\omega_p = \omega_{NIR} - \omega_{MIR}$. We nearly achieved this, demonstrating conversion of an 11-fs near-IR pulse input to a 12-fs mid-IR pulse output in a single crystal device (Fig. 1).

Ultrafast adiabatic frequency generation employs a slowly changing position-dependent poling frequency $G(z) = 2\pi/\Lambda(z)$ in a chirped quasi-phase matching (QPM) device to efficiently down-convert photons over a wide bandwidth [11]. We have taken the additional step of utilizing the frequency-dependent and localized conversion of ADFG to cancel the material dispersion of a 2-cm device. The total device GDD is determined by a linear function $\tau(\omega) = k'_{NIR}(\omega)z_c(\omega) + k'_{MIR}(\omega)\big(L - z_c(\omega)\big)$, where $z_c(\omega)$ is the conversion position for frequency. That is, the total GDD is the group delay at the input near-IR frequency up to the conversion position plus the group delay at the output mid-IR frequency after the conversion position. A nonlinear $G(z)$ may be chosen to manage the dispersion intrinsically while enabling octave-spanning conversion. GDD functions
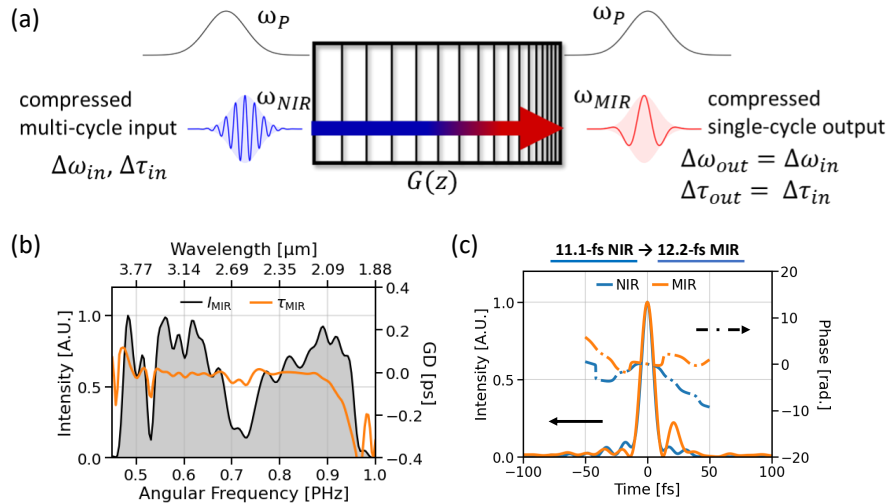
Fig. 1: (a) Concept of demonstrated device: a compressed few-cycle near-IR pulse undergoes bandwidth-conserving down-conversion to a single-cycle mid-IR pulse in a chirped QPM grating with a local poling frequency $G(z)$ designed to impart zero net GDD. (b) Spectrum and phase profile of a generated octave-spanning mid-IR pulse with flat group delay. (c) An 11-fs near-IR input pulse emerges as a 12-fs mid-IR pulse. [10]

can be chosen to suit the application. We chose the group delay profile to be flat, i.e., $d\tau(\omega)/d\omega = 0$, so that negligible GDD would be imparted by the device.

Moreover, we used the recently developed FROSt (frequency resolved optical switching) approach [12] to characterize the octave-spanning mid-IR pulse. Transient absorption is used as a temporal pulse gating mechanism, in which an ultrashort pump pulse changes the temporal absorption profile of a thin semiconductor relative to the moving frame of the pulse to be tested. A ptychographic retrieval algorithm to reconstruct the electric field of the probe pulse. FROSt is particularly suitable for the ultrabroadband transient absorption experiments of our program, as it can be performed *in situ*. And since it does not rely on a nonlinear conversion process, there is no phase-matching bandwidth limiting its applicability for ultrashort pulses, and the test pulse bandwidth can in fact span the full transmission window of the semiconductor medium.

Future Plans

Our next step is to perform a spectroscopy benchmarking experiment on graphene, by observing ultrafast Pauli-blocking using our hyperspectral transient absorption spectroscopy approach. As the sample is much easier to handle than rhodopsin and the spectroscopy signal will have a very high SNR, this is a relatively simple yet scientifically interesting (as it would provide insight into the phenomena of Pauli blocking [13]) stepping stone towards our major program goals of ultrafast transient absorption experiments of the rhodopsins and DNA. The expected change in absorption in the mid-IR lasts only 50 fs. We will collaborate with Dr. Giulio Cerullo and Dr. Eva Pogna of Milano Polytechnic to complete these experiments. We will use the synchronized 11-fs near-IR and 12-fs mid-IR pulses shown in Fig. 1 as the pump and probe, respectively.

We will also design and test the full complement of dispersion-managed adiabatic frequency conversion stages that will be needed for the planned molecular

chromophore experiments, including an adiabatic parametric amplifier for the near-IR (~1200-2200 nm) range, and an adiabatic sum-frequency stage for the visible/near-IR (~500-700 nm) range. Eventually, our system will possess nearly three octaves of near-continuous spectral coverage for probing the dynamical transition energy of the rhodopsin chromophore and DNA UV-absorption photosystem.

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

P. Margules, J. Moses, H. Suchowski, and G. Porat, "Ultrafast Adiabatic Frequency Conversion," J. Phys. Photonics **3**, 022011 (2021).

Theory and Simulation of Nonlinear X-ray Spectroscopy of Molecules

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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, and the development of effective simulation protocols for describing multiple-core excited state energetics and dynamics. Applications are made to detecting strongly-coupled electron-nuclear dynamics in molecules through electronic coherence observed in multidimensional broadband stimulated x-ray Raman signals and ultrafast x-ray diffraction. Attosecond electron dynamics in molecules created by resonant x-ray Raman excitation are proposed to be monitored by x-ray diffraction. Combined time-resolved x-ray and electron diffraction is used to image nuclear wavepacket dynamics.

Recent Progress

Conical Intersection Passages of 4-Thiouracil Probed by X-Ray Diffraction and Stimulated Raman Spectroscopy. As both x-ray stimulated Raman spectroscopy (TRUECARS) and time-resolved x-ray diffraction (TRXD) are sensitive to vibronic coherences generated during conical intersection (CI) passages, we theoretically compared the two techniques by investigating their signals for the CI dynamics in 4-thiouracil [2]. We found that TRUECARS directly probes the timing and the energetic distributions of vibronic coherences, while time-resolved x-ray diffraction gives spatial images of the electron densities as they pass through the CIs. The two techniques thus provide a complementary picture of the chemical dynamics. The signal, pulse requirement, spectroscopic information and difficulties in the experimental implementation was summarized in Table 1 from Ref [2].

Table 1. Comparison of the TRXAS, TRUECARS, and TRXD Techniques

technique	signal	pulse requirement	information	difficulties
TrXAS (established)	$S(\omega_s, T) = -\mathrm{Im}\, \mu_{t'f}\mu_{fe}^* \frac{e_{pr}^*(\omega_s)\varepsilon(\omega_s)\rho_{ee'}(T)}{\omega_s - \omega_{fe'} + i\gamma_{fe'}}$	single probe pulse	precise timing	population background
			state-specific information vibrational coherence	overlapping absorption lines
TRUECARS (proposed)	$S(\omega_s, T) = \mathrm{Im} \int dt \mathcal{E}_B^*(\omega_s)\mathcal{E}_N(t-T)e^{i\omega_s(t-T)}\langle\widehat{\alpha(t)}\rangle$	hybrid pulse (broadband/ narrowband)	energetic profiles	requires two X-ray probe pulses (phase control)
			vibronic coherence structure	
TRXD	$S(\mathbf{q}, T) = N \int dt |\mathcal{E}_X(t-T)|^2 \bar{S}_I(\mathbf{q}, t)$	hard X-ray pulse	spatial information:	extraction of coherences
			electron transition densities at CoIns	from the dominant population background

Ultrafast Valence-Electron Dynamics in Oxazole Monitored by X-Ray Diffraction Following a Stimulated X-Ray Raman Excitation. Ultrafast x-ray diffraction of charge migration dynamics in a neutral molecule was proposed [3]. Using an attosecond soft x-ray pump pulse, a valence-state electronic wavepacket can be prepared via a stimulated resonant x-ray Raman process. The electronic wavepackets induced by resonant excitations at different K-edges are clearly distinct. The created electronic coherence in the vicinity of the selected core, and the subsequent electron dynamics are probed by time-resolved off-resonant single-molecule x-ray diffraction (see Figure 1). The time dependence of the diffraction signal solely originates from the electronic coherence and can be detected by existing experimental techniques, providing a feasible technique for imaging electron dynamics in molecules.
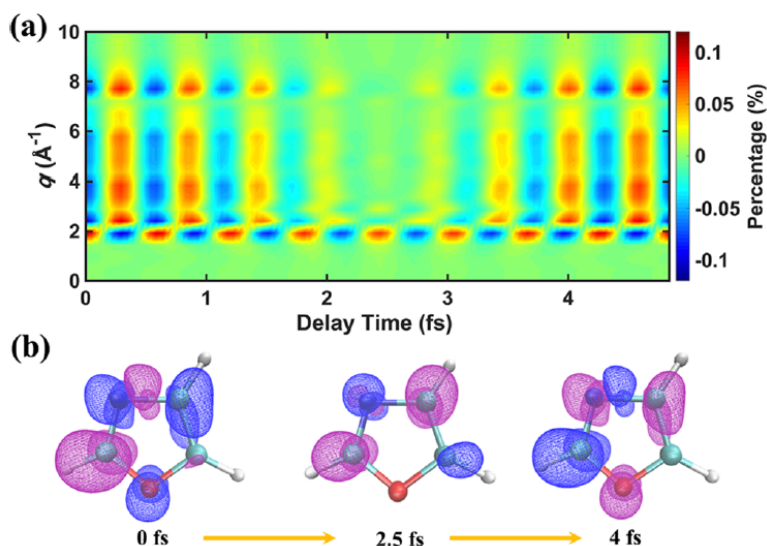

Figure 1. Signals for an x-ray pump pulse tuned to the Oxygen K-edge of oxazole. (a) Rotationally averaged time-resolved x-ray diffraction signal. (b) Isosurfaces of the real-space transition charge densities at t = 0, 2.5 and 4 fs. Blue is negative and purple is positive. [3]

Imaging Purely Nuclear Quantum Dynamics in Molecules by Combined X-Ray and Electron Diffraction. We had demonstrated that by combing time-resolved XRD and UED, the purely nuclear evolving charge density of thiophenol can be directly isolated from the diffraction patterns [5]. This is achieved by subtracting the ultrafast heterodyne-detected x-ray and electron diffraction signals. The time-evolving nuclear charge density of the molecule in real space can be directly reconstructed from the signal, without contribution from more diffuse electronic charge densities (see Figure 2). This technique can thus provide a complete picture of the purely nuclear wavepacket dynamics. The proposed experiment is very challenging as it requires heterodyne detection of both time-resolved XRD and

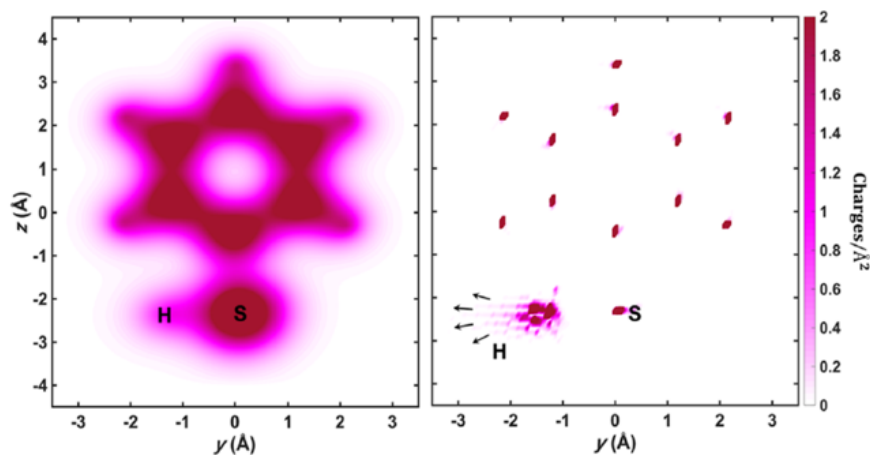*Figure 2. Real-space images of the electronic (left) and nuclear (right) charge densities of thiophenol at t = 5.3 fs. Black arrows in the right panel mark the directions of the nuclear wave-packet momentum as the hydrogen atom dissociates. [5]*

UED. Our study showed that this high-risk/high-gain experiment can reveal chemical information unavailable otherwise.

Future Plans

Time-Resolved X-Ray Photoelectron Circular Dichroism (X-ray trPECD) of molecular chirality. Photoelectron spectroscopy (PES) is widely used to probe photo-induced molecular dynamics. We had recently simulated tr-PES of the uracil photo-relaxation, demonstrating that molecular coherences contribute to the signal that give information about one of the most elementary photochemical events: the passage through conical intersections. Very recently, trPES has been extended to the XUV and to the X-ray domain, opening novel windows into femtosecond molecular dynamics. The full potential of X-ray trPES thus remains to be explored. In general, X-ray probes enable a site-specific interrogation of molecular properties by being resonant to an individual atom within a molecule. We plan to combine the chiral sensitivity of PECD with the site selectivity of X-ray trPES. This is a particularly intriguing possibility, since the global chiral features of a molecule originate from a local site: the chiral center. We plan to employ circularly polarized X-ray pulses in resonance with the chiral center, and record the X-ray trPECD signal as a novel and a highly sensitive probe of molecular chirality. This holds potential to elevate the spectroscopic sensitivity with respect to chiral molecular properties, and potentially reveal new signatures of chemical chirality.

Time-resolved x-ray magnetic circular dichroism (trXMCD) of conical-intersection dynamics. Magnetic circular dichroism (MCD) is a widely applied spectroscopic technique which has demonstrated its superiority over linear absorption spectroscopy in determining electronic transitions and revealing the degeneracy and symmetry of electronic states. MCD is the difference of absorption of left and right circularly polarized light measured when a uniform magnetic field is applied in the same direction as the propagation of light. The magnetic field induce currents in the molecule, giving rise to the CD signal even for achiral molecule. Thus it can be observed in both achiral molecule and chiral molecules in contrast to electronic circular dichroism (ECD) which only applies to chiral molecules. MCD is advantageous in assigning the excited states with the positive/negative sign and magnitude of the peaks in the spectra compared with linear absorption spectra especially when the peak band width is large. We shall use trXMCD as a novel probe for the detection of electronic coherences generated during CI passage. Since trXMCD signal strength is proportional to the applied magnetic field, the signal can be amplified by a strong magnetic field. Besides, it can be measured even for achiral molecules, in contrast to trXCD which only applies to chiral molecules. TrXMCD can depict the evolution of both excited state population and coherence, with distinctive features.

Creation and detection of coherent ring-current dynamics. Ring currents can be induced in cyclic conjugated molecules by applying a static magnetic field, by using circularly polarized light (CPL), or by coupling the molecule to an optical chiral cavity. Magnetic-field-induced ring currents are widely applied in nuclear magnetic resonance, where the static field which is non resonant with electronic excited state perturbs the ground state and creates a ground state ring current. The direction of the magnetic field induced current is determined by the direction of the applied magnetic field and the aromaticity of the molecule; aromatic (antiaromatic) molecules produce a diamagnetic

(paramagnetic) ring current. Using CPL to induce ring currents is receiving considerable current attention. A CPL pulse can induce a ring current in molecules with cyclic conjugated π-bonds. Its direction is controlled by the sense of the CPL. Besides, CPL can create ring currents in selected states by tuning the pulse frequency and bandwidth to specific electronic states. This provides additional control over the ring current generation. Previous studies on light-pulse induced ring currents had only considered a single pair of coherence, where the variation of the ring current at all locations in the molecule is synchronized. We propose to study a novel ring-current dynamics resulting from the superposition of several ring-current pairs created by a broadband circularly pump pulse. Due to the interplay of multiple coherences, we expect to see the ring current evolution at different locations in the molecule with distinctive features resulting in time-resolved ring current migration. TRXCD signal of the created coherent ring-current dynamics will be simulated.

Peer-Reviewed Publications Resulting from the Project (2021-2022)

1. *"Detection of photon statistics and multimode field correlations by Raman processes", Frank Schlawin, Konstantin E. Dorfman, and Shaul Mukamel. J. Chem. Phys. 154, 104116 (2021)*
2. *"Conical Intersection Passages of 4-Thiouracil Probed by X-ray Diffraction and Stimulated Raman Spectroscopy", Yeonsig Nam, Daniel Keefer, Artur Nenov, Irene Conti, Flavia Aleotti, Francesco Segatta, Jin Yong Lee, Marco Garavelli, and Shaul Mukamel. J. Phys. Chem. Lett., 12, 51, 12300-12309 (2021)*
3. *"Ultrafast Valence-Electron Dynamics in Oxazole Monitored by X-Ray Diffraction Following a Stimulated X-Ray Raman Excitation", Haiwang Yong, Stefano M. Cavaletto, Shaul Mukamel. J. Phys. Chem. Lett., 12, 9800-9806 (2021)*
4. *"Femtosecond X-ray Spectroscopy Directly Quantifies Transient Excited State Mixed Valency", Chelsea Liekhus-Schmaltz, Zachary W. Fox, Amity Andersen, Kasper S. Kjaer, Roberto Alonso-Mori, Elisa Biasin, Julia Carlstad, Matthieu Chollet, James D. Gaynor, James M. Glownia, Kiryong Hong, Thomas Kroll, Jae Hyuk Lee, Benjamin Poulter, Marco Reinhard, Dimosthenis Sokaras, Yu Zhang, Gilles Doumy, Anne M. March, Stephen H. Southworth, Shaul Mukamel, Amy A. Cordones, Robert W. Schoenlein, Niranjan Govind and Munira Khalil. J. Phys. Chem. Lett., 13, 378-386 (2022)*
5. *"Imaging Purely Nuclear Quantum Dynamics in Molecules by Combined X-Ray and Electron Diffraction" Haiwang Yong, Daniel Keefer and Shaul Mukamel. J. Am. Chem. Soc., 144, 7796-7804 (2022)*

Modeling of Multidimensional X-ray Probes of Chemical Processes and Dynamics in Molecular Systems

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Project Scope

Emerging X-ray free electron laser (XFEL) beam sources offer novel probes of matter with unprecedented spatial and temporal resolutions. These experimental advances call for the development of robust theoretical and computational tools that could provide predictive modeling capacity of the underlying electronic and structural dynamics. These will be further essential for the design and interpretation of more elaborate multi-pulse experiments.
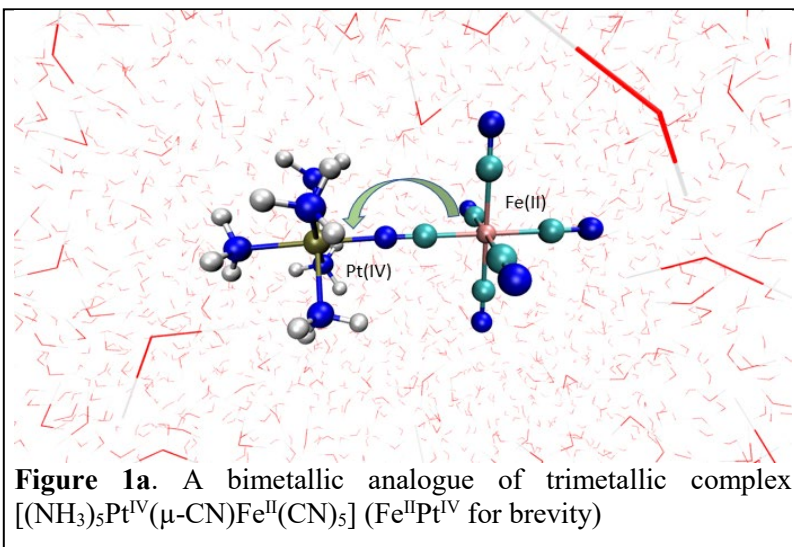
This research effort focuses on developing cutting-edge simulation tools for nonlinear multidimensional X-ray/optical spectroscopies. These techniques combine sequences of ultrafast X-ray and optical pulses to provide a unique experimental toolbox for probing the dynamics of core and valence electronic and vibrational excitations in. molecules as well as material structure. These challenges are addressed by three research thrusts, as outlined below.

The team spans the broad and necessary expertise in theoretical spectroscopy, nonlinear optics, quantum chemistry, molecular non-adiabatic dynamics and code development. In nonlinear spectroscopy, real-time electron dynamics and molecular non-adiabatic dynamics focus on computing the nonlinear response to X-ray pulse sequences, and using multidimensional Raman signals and X-ray time resolved diffraction to study non-adiabatic dynamics at conical intersections. Four-wave mixing techniques will be used to study multi-core excitations and electron correlations. Such experiments were so far reported in the XUV and soft X-rays (at the Fermi facility), providing proof-of-principle for such experiments. LCLS-II will extend these results to the tender and hard X-ray regimes with much finer spatial and temporal resolutions.

This program will create modeling capabilities and make them available to the broad XFEL (e.g LCLS-II) user community to support existing and inspire new innovative experiments. X-ray pulse sequences and experiments for probing core and valence electronic excitations will be designed. Efficient simulation protocols will be developed for the description of multiple-core excited state energetics and dynamics and for the interpretation of their spectroscopic signatures. Nonlinear spectroscopy techniques well established in the visible and the infrared regimes (e.g. time-resolved photoelectron spectroscopy, time-resolved broadband stimulated Raman, and wave mixing) will be extended to the X-ray regime and applied to a broad variety of molecular systems, thus laying out XFEL-based multidimensional spectroscopies as a novel diagnostic tool for tracing electronic and structural dynamics in molecular materials.

Recent Progress

Ultrafast Photoinduced Charge Dynamics in Solvated Transition Metal Complexes (PNNL+UCI): The mixed valence trimetallic complex $[(NC)_5Fe^{II}(\mu\text{-}CN)Pt^{IV}(NH_3)_4(\mu\text{-}NC)Fe^{II}(CN)_5]^{4-}$ ($Fe^{II}Pt^{IV}Fe^{II}$ for brevity) in water has been studied extensively due to its ability to undergo photoinduced, multielectron charge transfer process. Bocarsly and co-workers had synthesized a bimetallic analogue of trimetallic complex $[(NH_3)_5Pt^{IV}(\mu\text{-}CN)Fe^{II}(CN)_5]$ ($Fe^{II}Pt^{IV}$

for brevity) to better understand the electron transfer process of FePtFe complex. In this study, we have modeled the ultrafast electron transfer process in $Fe^{II}Pt^{IV}$ in the presence of explicit water molecules using the quantum mechanics/molecular mechanice (QM/MM) approach in NWChem. We have used time-dependent density functional theory (TDDFT) to study the charge transfer excited state in the $Fe^{II}Pt^{IV}$ complex. In the ground state QM/MM simulations, we have treated the $Fe^{II}Pt^{IV}$ complex with

Figure 1a. A bimetallic analogue of trimetallic complex $[(NH_3)_5Pt^{IV}(\mu\text{-}CN)Fe^{II}(CN)_5]$ ($Fe^{II}Pt^{IV}$ for brevity)

DFT and water molecules are treated using molecular mechanics. We have computed the reorganization energy of $Fe^{II}Pt^{IV}$ system in the excited-state charge transfer process. We are also performing excited-state dynamics at the TDDFT level, starting from a ground-state local minimum, to study the structural evolution and ultrafast scattering of the $Fe^{II}Pt^{IV}$ complex on the metal-to-metal charge transfer (MMCT) excited state. Changes in the hydrogen-bonding interactions between $Fe^{II}Pt^{IV}$ solute and solvent water molecules are also being studied (manuscript in preparation)

Our preliminary calculations on the MMCT excited state show that there are three close lying MMCT excited states in the case of $Fe^{II}Pt^{IV}$. Experimental results have shown that the intervalent transition from $Fe^{II} \rightarrow Pt^{IV}$ is at 2.945 eV for the $Fe^{II}Pt^{IV}$ system. TDDFT calculations show three MMCT states at 2.98 eV, 3.03 eV and 3.08 eV, respectively. The MMCT excitations involve *d-d* transitions from occupied bonding *d* orbitals to unoccupied antibonding *d* orbitals. The initial MMCT excited state relaxation happens within ~50 fs. The relaxation process involves elongation of the M-CN and M-NH$_3$ bond distances in the $Fe^{II}Pt^{IV}$ system. The total reorganization energy of the $Fe^{II}Pt^{IV}$ system is computed to be ~47.63 kcal/mol, which is comparable to the experimental reorganization energy of ~42.50 kcal/mol. Interestingly, the $Fe^{II}Pt^{IV}$ system shows more changes in the solute geometry compared to the $Fe^{II}Ru^{III}$ complex during the relaxation process of the MMCT state that we have studied recently. This can be attributed to the MMCT state being significantly higher in energy for the $Fe^{II}Pt^{IV}$ complex (~3 eV) compared to $Fe^{II}Ru^{III}$ complex (~1.30 eV). Hence, the splitting between the bonding and antibonding orbitals is higher for $Fe^{II}Pt^{IV}$, resulting in significant elongation of Fe-CN and Pt-NH$_3$ bond distances. Our initial computations
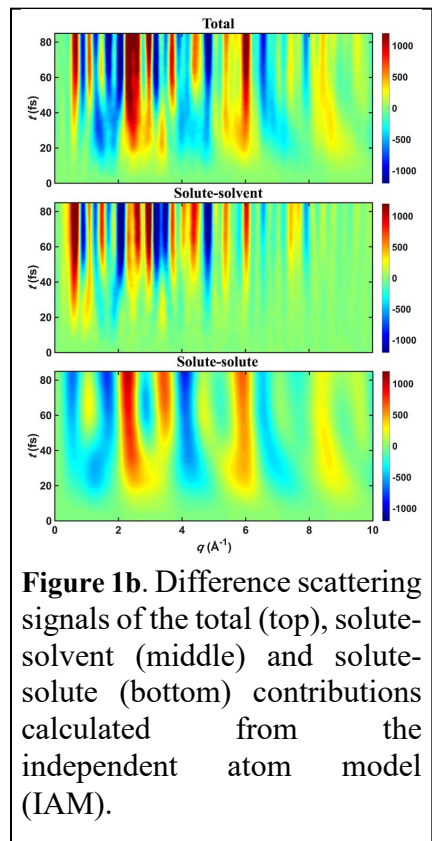
Figure 1b. Difference scattering signals of the total (top), solute-solvent (middle) and solute-solute (bottom) contributions calculated from the independent atom model (IAM).
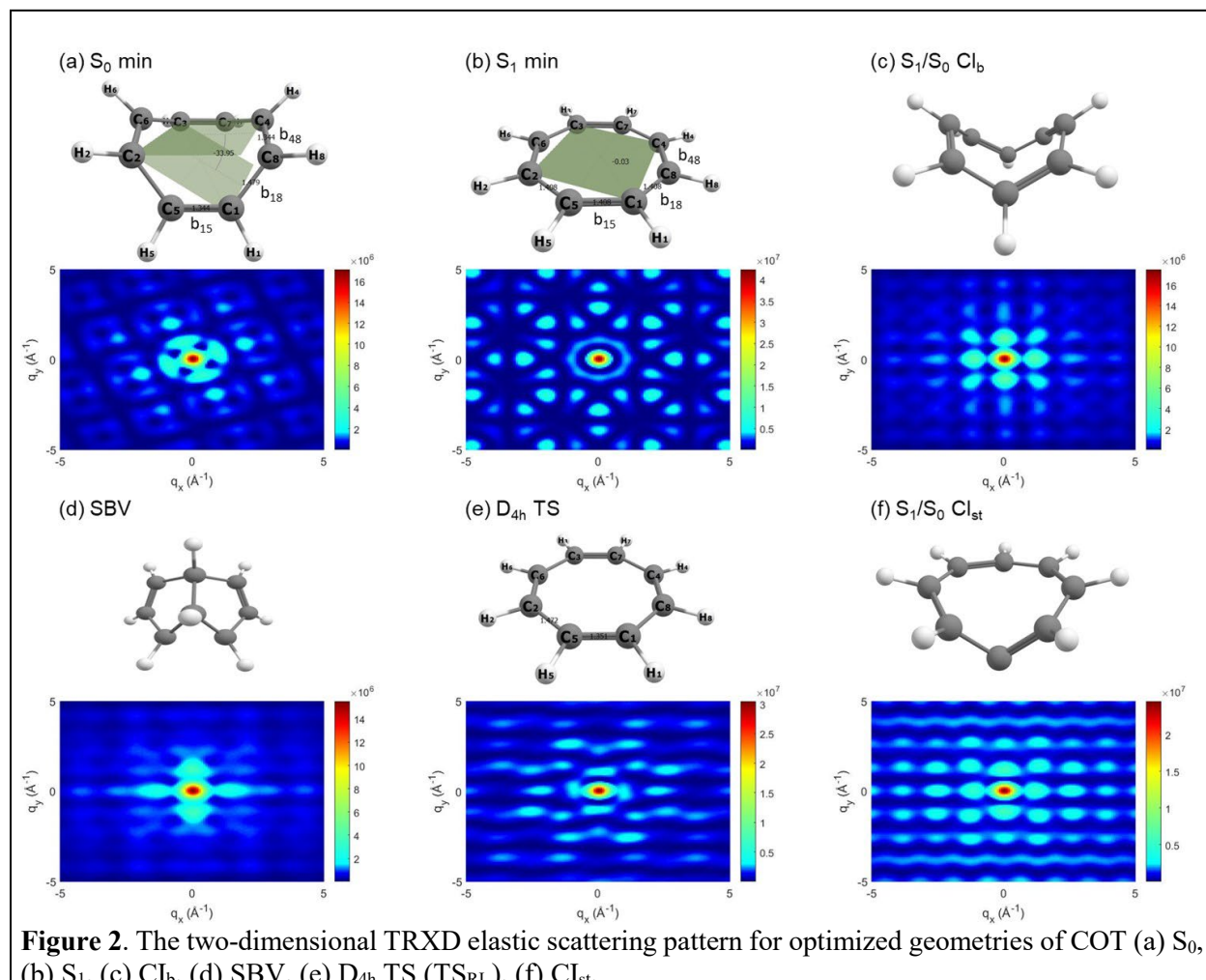
of the difference scattering signals of the total, solute-solvent, and solute-solute contributions are displayed in Figure 1b .These show that although the total signal is contributed mainly by the solute-solvent signal, the solute-solute contribution is noticeable and cannot be ignored. The scattering signals are mainly within 8 Å^{-1}, this is reachable with the high energy hard x-rays available at LCLS-II-HE. The peaks of solute-solvent scattering signal are much narrower compared to solute-solute signal. This is due to the inverse relation between real space and reciprocal (q) space. The effect of broad radial distribution functions of solute-solvent term results in narrow peaks, while relatively narrower radial distribution functions of solute-solute term leads to broader peaks.

Excited State X-ray Circular Dichroism (PNNL+UCI): Circular dichroism spectroscopy is commonly used for measuring enantiomeric excess. In this study, we computationally modeled a UV pump and X-ray probe setup. We are specifically interested in molecules that are achiral in the ground state but become chiral in the first excited state. We have chosen a series of fluorinated amide molecules to study the locality of X-ray CD (XCD) spectroscopy. We have considered three molecules- 2-F-acetamide, 3-F-propanamide and 4-F-butanamide. The first excited states of these amide molecules are nonbonding to π^* excitations. We have used variational excited-state DFT as implemented in NWChem to variationally compute the first excited-states of these molecules. In this approach, orbital occupations are changed to the excited-state electronic configuration during the self-consistent field iterations. Then the excited state density is optimized using the same procedure as the ground state DFT. These variationally optimized excited-state wave functions are used to calculate valence CD and XCD spectra. Our calculations show that structural snapshots of these molecules along the out-of-plane normal mode give rise to oscillation in the sign of the excited-state CD value. For studying the locality of CD spectra, we have calculated excited-state XCD spectra at the fluorine K-edge of three fluorinated amides by taking multiple snapshots from the motion of the out-of-plane normal mode of the three molecules.

Vibronic Coherences and Molecular Aromaticity in Photoexcited Cyclooctatetraene 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 their time-resolved dynamics remains a formidable experimental challenge. In this study, we simulated the photoinduced non-adiabatic dynamics of cyclooctatetraene (COT) involving multiple conical intersections (CIs) ,with the computed relaxation times found in good agreement with experiment. We further investigated the possibility to directly probe the CI passages in COT by off-resonant X-ray Raman spectroscopy (TRUECARS) and time-resolved X-ray diffraction (TRXD). We found that these signals sensitively monitor key chemical features during the ultrafast dynamics involving aromatic and non-aromatic electronic configurations of COT. First, TRUECARS was demonstrated to be capable of distinguishing different CIs along the S3 → S1 relaxation pathway. Second, we found that TRXD, where X-ray photons scatter off electron densities, can resolve ultrafast changes in the aromaticity of COT (Fig .1). It can further distinguish between planar and non-planar geometries explored during the dynamics, as e.g. the D4h transition state facilitating the S1 → S0 relaxation and two different tetraradical-type CIs. The knowledge gained from these measurements can give unique insights into fundamental chemical properties that dynamically change during non-adiabatic passages. A paper has been submitted to Chemical Science and is currently under review.


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}.

Ultrafast Correlation Dynamics between the Qx and Qy Bands in Chlorophyll Molecules (LANL+UCI): The non-radiative relaxation process within the Q-bands of chlorophylls represents a crucial preliminary step during photosynthetic. Despite extensive experimental and theoretical efforts performed in order to clarify the complex dynamics characterizing this stage, a complete understanding of this mechanism is not available. Non-adiabatic excited-state molecular dynamic simulations have been performed to model the non-radiative process within the Q-bands for a model system of chlorophylls. Previous simulation studies based on semi-empirical methods with the fewest switches surface hopping (FSSH) approach showed deviations from experimental measurement due to overestimating the band gap and interband decoherence processes. In this study, we combined the TDDFT method with our newly implemented Ab initio Multiple Cloning (AIMC) approach to overcome the accuracy limitation. Based on a large set of independent trajectories, the population of the Qx and Qy states have been computed as the average of all the trajectories, estimating the rate constant for the process. Finally, by investigating the Qx–Qy

Figure 3. A chlorophyll A molecule (left), calculated nonradiative relaxation timescales and a number of clones per initial condition (right).
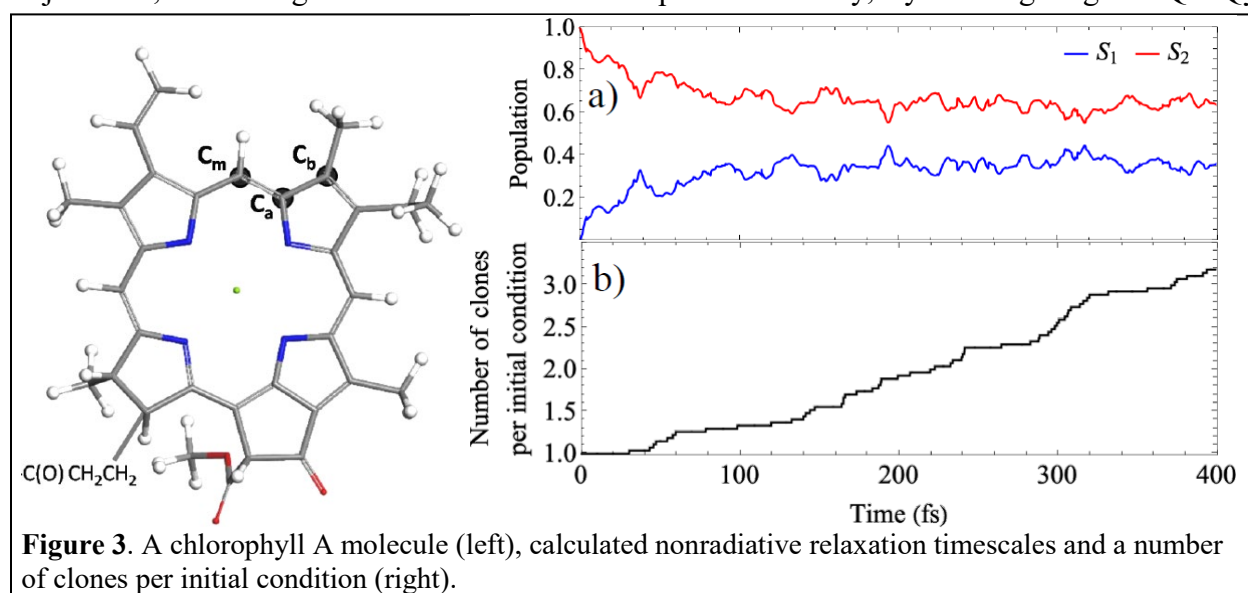
crossing mechanism, we found the most important excited-state dynamics during such relevant photosynthetic process. A manuscript is in preparation.

Comparison of different levels of theory (LANL+UNIBO+PNNL): To extend our X-ray/optical spectroscopies analysis capacity, matching the signal from different levels of theory (CASSCF/CASPT2, TDDFT and semi-empirical) is required. To do so, it would be necessary to have unique characterization of the states. The first task is to align the state between different levels of theory. The LANL and UNIBO groups benchmarked both the valence/excited states, then developed a new algorithm to compute the wavefunction ovelap in a series of geometries along a (symmetry preserving) coordinate. This method can track the photo-induced dynamics between different levels of theory. Currently, we are using the COT system as the testing ground to demonstrate the possibility to automatize the comparison between CASSCF/CASPT2 and TDDFT valence states at a few selected COT geometries. For example, we observed that a state with marked double-excitation character enters the CASSCF/PT2 manifold of states, while being invisible in the TDDFT manifold. Such delineations and identification of states is critical for
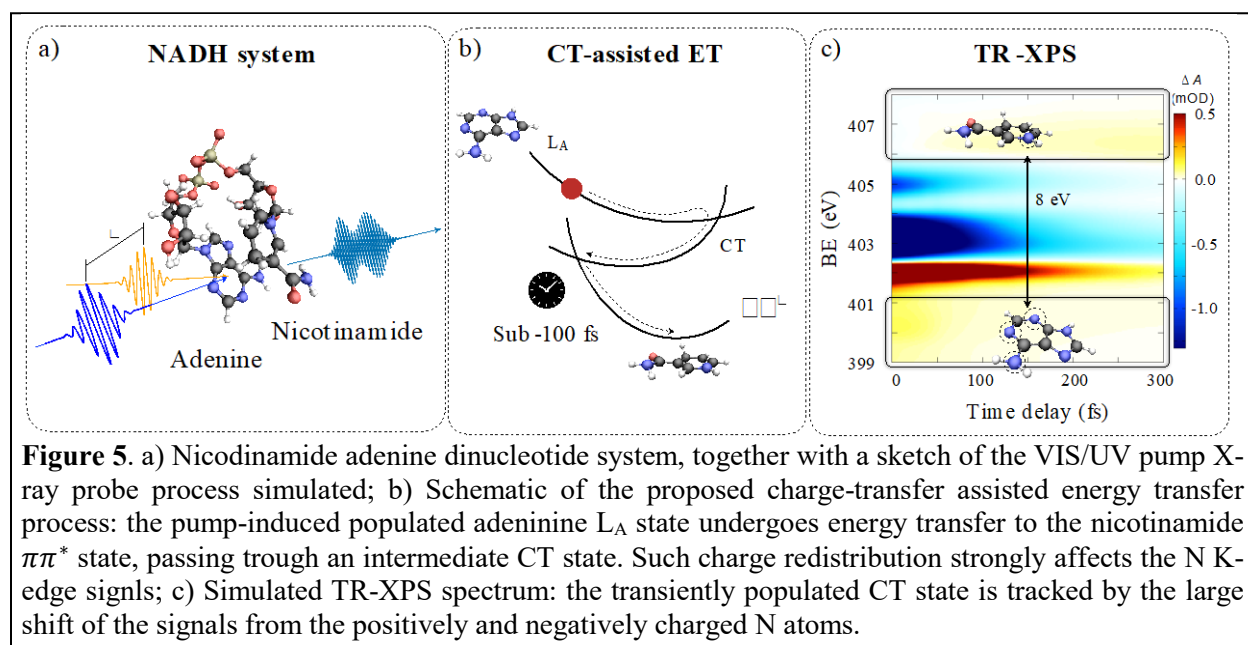
indirect validation of the results for excited state molecular dynamics calculated with lower-level theories.

Figure 4. Compairing the orbitals between CASSCF/CASPT2 (right) vs TDDFT (left) at S_0 min. (DFT).
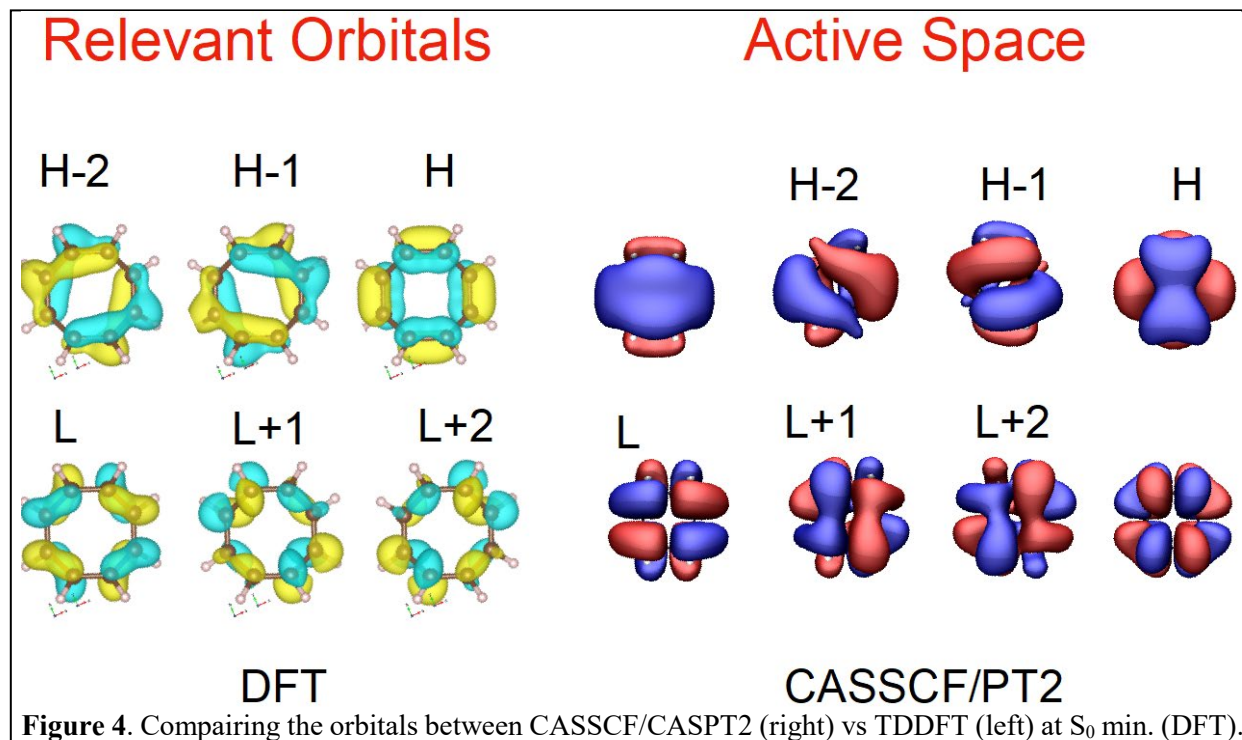
Spectroscopy simulation via MCTDH quantum dynamics (UNIBO): The implementation of an MCTDH (Multi Configuration Time Dependent Hartree) based nonlinear spectroscopy simulation platform has been completed. The UV/VIS transient absorption spectroscopy of the pyrene molecule (with quantum chemical data recently computed at the CASPT2 level of theory) has been employed as a suitable testbed. Here, one can explicitly consider the wave-packet overlap term that shapes the spectral features and determines their broadening and decay due to decoherence. The population dynamics is described exactly (i.e. not relying on rate equation models), and the only approximation lies in the modeling of the potential energy surfaces and their coupling (tipically captured by a linear vibronic model). A non-trivial role of the dynamics along the t_3 time (i.e. after the probe has interacted with the system) has been documented at the highest level of theory. A manuscript is in preparation.

Extending the CASSCF/CASPT2 XAS approach to larger molecules (UNIBO): the recently developed and published protocol [Montorsi2022] for core level CASSCF/CASPT2 spectroscopy simulation has been applied to larger/complex molecular systems. In particular, we computed XPS and XANES signals of azobenzene at both N and C K-edge (where the latter is more complex with respect to the N K-edge, due to the large number of inequivalent carbon centers that should be considered). Moreover, in the framework of the collaboration with Elettra synchrotron in Trieste (Italy), we simulated the XANES at the O, N, C K-edge and the Cl L-edge of the hydroxychloroquine molecule, and compared those with the measurments performed at the BEAR beamline. A manuscript is in preparation.

Resonant ultrafast X-ray spectroscopy of biologically relevant systems (UNIBO): The ultrafast energy transfer (ET) process in the nicotinamide adenine dinucleotide (NADH) dimer has been exploted in different spectral windows: from the VIS/UV (time-resolved PP, TR-PES) to the X-ray (TR-XANES and TR-XPS, at the N-Kedge). See Figure 5 for details of the system and processes. The different techniques were compared to discern which is more suited to follow the charge-transfer mediated ET dynamics (recently computed at the CASPT2/MCTDH level of theory by our group and in collaboration with the Dr. Fabrizio Santoro, CNR, Italy). TR-XPS shows the largest signal shift when the CT state is transiently populated, due to a sudden change of the N partial charges on the two moieties (8 eV shift from the positively charged nicodinamide N to the negatively charged adenine N atoms). A master thesis student has been involved in the quantum chemical calculations and spectroscopy simulations. A paper is in preparation.

Figure 5. a) Nicodinamide adenine dinucleotide system, together with a sketch of the VIS/UV pump X-ray probe process simulated; b) Schematic of the proposed charge-transfer assisted energy transfer process: the pump-induced populated adeninine L_A state undergoes energy transfer to the nicotinamide $\pi\pi^*$ state, passing trough an intermediate CT state. Such charge redistribution strongly affects the N K-edge signls; c) Simulated TR-XPS spectrum: the transiently populated CT state is tracked by the large shift of the signals from the positively and negatively charged N atoms.

Future Plans

Nonlinear Spectroscopy with TDDFT (UNIBO+PNNL): the possibility to compute higher-lying excited states reachable from a given excited state, and the transition dipole moments between these excited states at the TDDFT level was explored in the PBI paper [Segatta2021]. A comparison between these and CASSCF/CASPT2 calculations were performed, and a range of nonlinear spectra of the PBI molecule were simulated and compared with state of the art experiments. This TDDFT approach is being explored with a broader set of molecular systems that have been studied with CASSCF/CASPT2.

Conical Intersections with the Dual-Functional (DF) TDDFT Approach (PNNL+UNIBO+UCI): TDDFT may not be used to represent. conical intersections between ground- and excited- states due to the lack of doubly excited configurations as singly excited configurations do not couple with the reference state. The DF-TDDFT approach of Truhlar and co-workers introduces a coupling between the reference and the first excited state using two different exchange-correlation functionals for the reference calculation and the TDDFT calculation. In this approach, first a ground state calculation is performed for the reference state orbitals using an exchange-correlation functional. A different exchange-correlation functional is then used to perform the TDDFT calculations using the orbitals obtained from the reference state obtained from the ground state calculation with a different functional. As the ground- and excited- state calculations are performed using two different functionals, the couplings between ground- and excited- state do not vanish. This simplified TDDFT-based approach has been demonstrated to properly locate conical intersections. We are implementing this in NWChem. DF-TDDFT will be used to obtain geometries of different organic and transition metal containing systems at the conical intersection between ground and first excited state. Core-level spectroscopic signals will be computed at the conical intersection geometries. These calculations will be compared with wavefunction-based approaches in collaboration with the UNIBO team.

Ab initio Multiple Cloning (AIMC) within the QM/MM framework (PNNL+LANL+UCI): The recently developed *ab initio* multiple cloning (AIMC) approach based on the multiconfigurational Ehrenfest (MCE) method provides a powerful and accurate way of describing the excited-state dynamics of molecular systems. The AIMC method is a controlled approximation to nonadiabatic dynamics with a particular strength in the proper description of decoherence effects because of the branching of vibrational wavepackets at a level crossing. We will extend the AIMC algorithm to the QM/MM framework in the open source NWChem computational chemistry program. This extension will provide a high-level nonadiabatic molecular dynamics framework for simulating photoexcited dynamics of complex molecular systems in realistic solvent environments and experimentally relevant ultrafast spectroscopic probes, such as nonlinear coherent optical and X-ray signals.

State-Specific Solvation and Dynamics of Charge-Transfer States (LANL+PNNL+UCI)
Reaching even a qualitatively correct treatment of CT excitations in molecular systems using *ab initio* electronic structure methods is challenging. The state-specific solvation technique, where the dielectric environment responds to the electronic density of a particular excited state, is critical for a quantitative description of electronic structure since solvent stabilization of charge-transfer

excitations is very signigicant. Performing non-adiabatic dynamics with state-specific solvation is currently an open question, which requires the development of novel methodology. We intend to develop non-adiabatic molecular dynamics framework that incorporates state-specific solvation and implement this method to our both codes, ab initio NWChem and semiempirical NEXMD packages. Since state-specific solvation framework is already implemented in both codes, we will augment it with non-equilibrium solvation models allowing to accoung for solvent dynamics in the non-adiabatic driver. The first implementation will rely on the implicit solvent models with the first application to be done to a small donor-acceptor chromophore using TDDFT technique. Here, calculated dynamics in the electron distribution relevant to the charge transfer transition will be analysed and linked to time-resolved X-Ray electronic diffraction. Subsequently, we will extend this new capability from implicit solvation to the QM/MM framework (described above) that allows much broader application scope.

Extension of the developed MCTDH/spectroscopy platform for X-ray based signals (UNIBO): the platform for nonlinear spectroscopy simulations based on MCTDH quantum dynamics, developed and tested in the UV/VIS window, will be extended for the simulation of UV/VIS pump, X-ray probe experiments (both resonant and non-resonant). The pyrene molecule, whose dynamics has been already parametrized and for which accurate excited state calculations at the C K-edge have been performed, will be the first system to be studied.

SXRS for dark state targeting (UNIBO): the use of SXRS techniques to target valence excited states has been recently proven experimentally at SLAC. We plan to extend that approach to specifically target dark excited states (such as $n\pi^*$ states in nuclebases, whose role in the photo-deactivation is still debated), and possibily to excited states with different spin multiplicities.

Peer-Reviewed Publications Resulting from this Project (2021-2022)

[Rouxel2022] Jérémy R. Rouxel, Daniel Keefer, Flavia Aleotti, Artur Nenov, Marco Garavelli, and Shaul Mukamel. **Coupled electronic and nuclear motions during azobenzene photoisomerization monitored by ultrafast electron diffraction**. JCTC. 2022. DOI: 10.1021/acs.jctc.1c00792

[Montorsi2022] Montorsi, Francesco; Segatta, Francesco; Nenov, Artur; Mukamel, Shaul; Garavelli, Marco. **Soft X-ray spectroscopy simulations with multiconfigurational wavefunction theory: spectrum completeness, sub-eV accuracy and quantitative reproduction of line shapes.** *J. Chem. Theory Comput.* 2022, 18, 2, 1003–1016 DOI: 10.1021/acs.jctc.1c00566

[Gu2021] Bing Gu, Daniel Keefer, Flavia Aleotti, Artur Nenov, Marco Garavelli, and Shaul Mukamel. **Photoisomerization transition state manipulation by entangled-two-photon-absorption**. PNAS (2021) 118 Article Number: e2116868118 DOI: 10.1073/pnas.2116868118

[Cavaletto2022] Stefano M. Cavaletto, Daniel Keefer, and Shaul Mukamel. **Electronic coherences in nonadiabatic molecular photophysics revealed by time-resolved photoelectron spectroscopy**. PNAS, 2022, 119, e2121383119, DOI: 10.1073/pnas.2121383119

[Freixas2022] Victor M. Freixas, Daniel Keefer, Sergei Tretiak, Sebastian Fernandez-Alberti, and Shaul Mukamel. **Ultrafast coherent photoexcited dynamics in a trimeric dendrimer probed by X-ray stimulated-Raman signals.** *Chemical Science*, 2022, **13**, 6373 – 6384

[Nam2022] Nam, Yeonsig; Montorsi, Francesco; Keefer, Daniel; Cavaletto, Stefano Michele; Lee, Jin Yong; Nenov, Artur; Garavelli, Marco; Mukamel, Shaul. **Time-Resolved Optical Pump - Resonant X-ray Probe**

Spectroscopy of 4-Thiouracil; a Simulation Study. Journal of Chemical Theory and Computation (2022) DOI:10.1021/acs.jctc.2c00064

[Keefer2022] Daniel Keefer, Stefano M. Cavaletto, Jérémy R. Rouxel, Marco Garavelli, Haiwang Yong, and Shaul Mukamel. **Ultrafast X-ray Probes of Elementary Molecular Events.** Annual Review of Physical Chemistry (June 2022 submission)

[Segatta2021] Francesco Segatta, Mattia Russo, Daniel Nascimento, Davide Presti, Francesco Rigodanza, Artur Nenov, Andrea Bonvicini, Alberto Arcioni, Shaul Mukamel, Margherita Maiuri, Luca Muccioli, Niranjan Govind, Giulio Cerrulo, Marco Garavelli, **In Silico Ultrafast Nonlinear Spectroscopy Meets Experiments: The Case of Perylene Bisimide Dye**, *Journal of Chemical Theory and Computation*, *17*(11), pp.7134-7145 (2021)

[Nam2022] Yeonsig Nam, Huajing Song, Victor M. Freixas, Daniel Keefer, Sebastian Fernandez-Alberti, Jin Yong Lee, Marco Garavelli, Sergei Tretiak, and Shaul Mukamel, **Monitoring Vibronic Coherences and Molecular Aromaticity in Photoexcited Cyclooctatetraene with X-ray Spectroscopy**, *Chemical Science*, (Submitted)

Structured VUV, EUV and Soft X-ray Light for Probing Quantum Systems

DE-FG02-99ER14982
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Project Scope

The goal of this research is to develop novel short wavelength quantum light sources, and use them to to understand quantum systems. First, we are extending the exquisite control we achieved over structured light (spectral, temporal, polarization, shape, phase and flux) from the extreme UV (EUV) to 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 vacuum UV beams to address challenging applications in molecular and energy systems. Finally, we will use 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 since 2020, with 13 peer-reviewed papers published, accepted or in review in top journals. Students and postdocs from our group have recently moved to DOE Laboratories (Sandia (2), Los Alamos (2), Argonne (1), SLAC (1)). Finally, in other distinct research efforts, we have several collaborations with DOE laboratories, including LBNL and LANL, to probe dynamics in quantum systems using coherent extreme UV (EUV) and soft X-ray (SXR) sources.
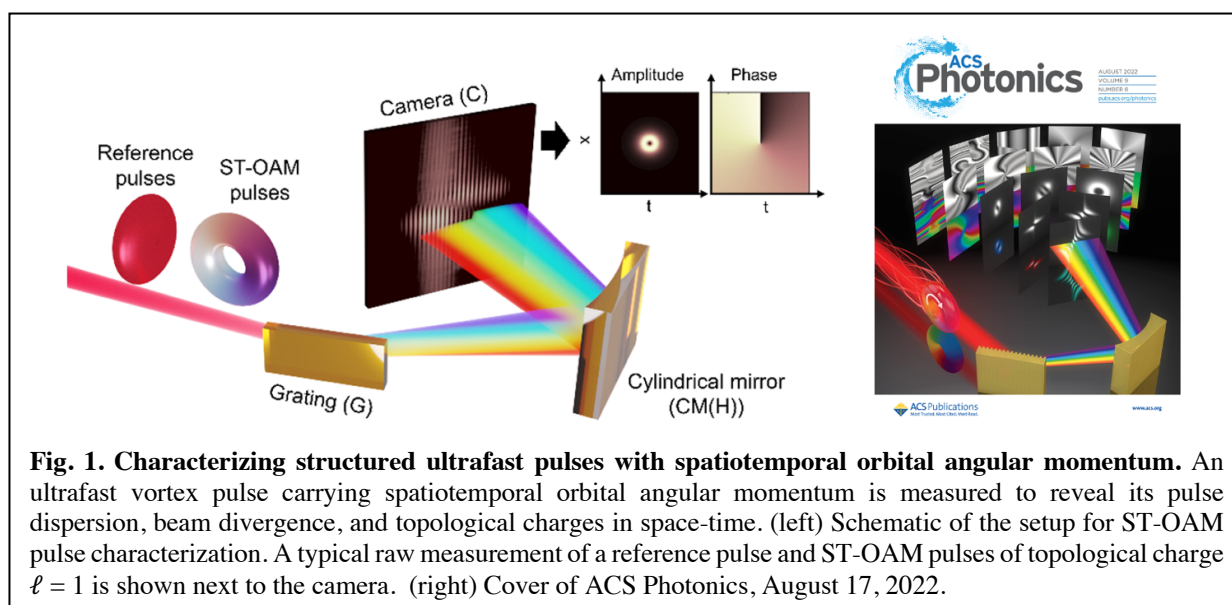
Recent Progress

<u>Tailoring the Spectrum and Structure of Extreme-Ultraviolet and Soft X-Ray Beams [1,2,3,7,13]:</u> The extreme nonlinear optical process of high-harmonic generation (HHG) makes it possible to map the properties of a laser beam onto a radiating electron wavefunction, and in turn, onto the emitted x-ray light. We made significant progress in creating spectral, polarization and phase structured HHG beams (spin and orbital angular momentum, SAM and OAM) that can be used to enhance contrast, and to implement unique excitations and probes of chiral structures in molecules, magnetic materials and nanostructures. In past work we demonstrated the first bright, phase-matched, extreme UV (EUV) and soft X-ray HHG beams with circular (or elliptical) polarization, as well as the ability to generate HHG beams with unique polarization and phase structure. These new HHG capabilities are ideal for a suite of ultrafast X-ray absorption spectroscopies, photoelectron spectroscopies and magneto-optic spectroscopies. Moreover, through selection rules, they allow us to sculpt the HHG spectrum, to tailor the spectral, polarization and phase structure for particular applications.

Bright HHG beams typically emerge from a longitudinal phased distribution of atomic-scale quantum antennae. In recent work just published in Science Advances, we used OAM laser drivers to form a transverse necklace-shaped phased array of linearly polarized HHG emitters, where orbital angular momentum conservation allowed us to tune the line spacing and divergence properties of EUV and soft X-ray high harmonic combs. The on-axis HHG emission exhibits extremely low divergence, well below that obtained when using Gaussian driving beams, which further decreases with harmonic order. This work provides a new degree of freedom for the design of harmonic combs – particularly in the soft X-ray region, where limited options are available.

Very recently we also explored light carrying spatiotemporal orbital angular momentum (ST-OAM), that makes it possible new types of optical vortices arising from transverse OAM. ST-

OAM pulses exhibit novel properties during propagation, transmission, refraction, diffraction, and nonlinear conversion, attracting growing experimental and theoretical interest and studies. However, one major challenge is the lack of a simple and straightforward method for characterizing ultrafast ST-OAM pulses. Using spatially-resolved spectral interferometry, we demonstrated a simple, stationary, single-frame method to quantitatively characterize ultrashort light pulses carrying ST-OAM. Using our method, the presence of an ST-OAM pulse, including its main characteristics such as topological charge numbers and OAM helicity, can be identified easily from the unique and unambiguous features directly seen on the raw data—without any need for a full analysis of the data. After processing and reconstructions, other exquisite features, including pulse dispersion and beam divergence, can also be fully characterized. Our fast characterization method allows high-throughput and quick feedback during the generation and optical alignment processes of ST-OAM pulses. This new method can help advance the field of spatially and temporally structured light and its applications in advanced metrologies.

Fig. 1. Characterizing structured ultrafast pulses with spatiotemporal orbital angular momentum. An ultrafast vortex pulse carrying spatiotemporal orbital angular momentum is measured to reveal its pulse dispersion, beam divergence, and topological charges in space-time. (left) Schematic of the setup for ST-OAM pulse characterization. A typical raw measurement of a reference pulse and ST-OAM pulses of topological charge $\ell = 1$ is shown next to the camera. (right) Cover of ACS Photonics, August 17, 2022.

Enhancing VUV and soft X-ray harmonics using structured waveguides [11,12]: We have made good progress on the use of photonic crystal waveguides for HHG. These structrred waveguides can dramatically decrease waveguide losses for tightly-focused beams of UV, near-IR and mid-IR light compared with the simple capillary waveguides, confining the high-pressure gas, and allowing HHG with lower-pulse-energy and higher repetition rate driving lasers. By confining the HHG driving laser light to a smaller mode area, the pulse energy requirement for bright SXR HHG can be brought down to the sub-mJ level (from ~2-10mJ in past work), or to the ~μJ level for VUV HHG.

Extension of bright high-harmonics via nonadiabatic critical phase matching [5]: Extending the photon energy range of bright high-harmonic generation (HHG) to cover the entire soft X-ray region is important for many applications in science and technology. In past work we showed that the concept of critical ionization fraction is essential, because it dictates the maximum driving laser intensity that can be used while preserving bright HHG emission. In recent work, we revealed a second, nonadiabatic critical ionization fraction that substantially extends the maximum phase-matched high-harmonic photon energy, that arises due to strong reshaping of the intense driving laser field. We validated this understanding through a systematic comparison between experiment and theory, for a wide range of

pulse durations and driving laser wavelengths. We also developed an analytical model that predicts the spectral extension that can be achieved for different driving lasers. These findings are important for the development of high-brightness soft X-ray sources for applications in spectroscopy and imaging.

<u>Probing strong electron-phonon coupling and phase transitions in quantum systems [4,6,8,9,10]:</u> We used photoelectron and other spectroscopies to uncover fundamentally new information about electron-phonon coupling and phase transitions in quantum systems. As sone example, we completed a very unique experimental investigation of warm dense matter (WDM), which is usually very challenging to directly probe because of the transient nature of WDM in the lab, where dynamics can span from femtosecond timescales on up. This makes it difficult to validate advanced theories. Previous studies used high-power lasers, pulsed power, and ion beams at mid and large-scale facilities to excite and probe WDM. These experiments are limited to relatively low repetition rates (<120 Hz), that influence what diagnostic measurements are possible. In recent research we developed a novel approach for overcoming these long-standing challenges. Using intense ultrafast laser pulses, we uniformly heated a sample of isolated ~8 nm metallic nanoparticles to just below the ablation threshold. We then probed the resulting WDM dynamics using velocity-map-imaging photoelectron spectroscopy, which enables uniquely accurate measurements of this exotic state. We can directly measure the instantaneous electron temperature, and use this to accurately extract the electron-ion coupling (G_{ei}) dynamics and hot electron cooling in WD-nanomatter for the first time. We vary the excitation laser fluence to probe the dynamics below and above the melting threshold of the particles to characterize their properties in both solid and WDM phases. By comparing with theories of highly-excited strongly-interacting matter, we find that the state of matter we produce lies at the boundary between hot solids and plasmas. This is evidenced by the fast energy loss of electrons to ions, strong modulation of the electron temperature by variation in volume of the nanoparticle, and the existence of a threshold fluence associated with a change in electron-ion couplings. For example, we extracted higher values of the electron-ion coupling than had been observed in previous experiments, and observed a strong modulation of the electron temperature on ~ 1 ps timescales during cooling, by hundreds of K, that had never been observed before in WDM. These results open a new avenue for experimental WDM research and inform current and future theories. This research benefitted from a theory collaboration with LBNL and LANL.

Future work

We are extending bright structured high harmonic beams from the EUV into the soft x-ray regions of the spectrum. We are also exploring how to use structured light to more sensitively excite and probe strongly-coupled dynamics in quantum, molecular, nano and materials systems. Ultra-broad bandwidth, ultrafast HHG will be used to implement dynamic EUV and soft x-ray spectroscopies in samples excited using mid-IR – UV light. Finally, we are developing VUV sources with ~1 μJ energy per pulse, for applications in transient grating spectroscopies and quantum sensing of molecules and materials (e.g. that can be used to extract the transport and mechanical properties of high-bandgap molecular/layered/energy materials). Methods to make these VUV sources continuously tunable are also being explored.

Peer-Reviewed Publications/Patents Resulting from this Project (2020-2022)

1. *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

2. *Single-frame characterization of ultrafast pulses with spatiotemporal orbital angular momentum*, G. Gui, N. Brooks, B. Wang, H. Kapteyn, M. Murnane, C.T. Liao, ACS Photonics **9**, 2802 (2022). *Featured on cover and also selected as an ACS Editor's Choice Award*. doi.org/10.1021/acsphotonics.2c00626

3. *Ultrashort vortex pulses and their nonlinear frequency conversion*, C.T. Liao, C. Hernández-García, M. Murnane, invited paper, *in press*, Journal of Optics, (2022).

4. *Direct observation of enhanced electron-phonon coupling in copper nanoparticles in the warm-dense matter regime*, Q. Nguyen, J. Simoni, K. Dorney, X. Shi, N. Brooks, J. Ellis, D. Hickstein, J. Knobloch, A. Grennell, D. Morrill, S. Yazdi, E. Campbell, J. Daligault, H. Kapteyn, M. Murnane, responded to reviews (2022). arXiv:2110.14704

5. *Extension of the bright high-harmonic photon energy range via nonadiabatic critical phase matching*, Z. Fu, Y. Chen, S. Peng, B. Zhu, G. Fan, Y. Wang, C. Jin, M. Murnane, H. Kapteyn, Z. Tao, responded to reviews (2022). arXiv:2206.07241

6. *Super-resolved Time-Frequency Measurements of Coupled Phonon Dynamics in a 2D Quantum Material*, C. Gentry, C. Liao, W. You, S. Ryan, B. Varner, X. Shi, T. Gray, D. Temple, M. Raschke, K. Rossnagel, H. Kapteyn, M. Murnane, E. Cating-Subramanian, responded to reviews (2022).

7. *Bright, Single Helicity, Harmonics Driven by Mid-IR Bicircular Fields*, K. Dorney, T. Fan, Q. Nguyen, J. Ellis, D. Hickstein, N. Brooks, D. Zusin, C. Gentry, D. Milošević, C. Hernández-García, H. Kapteyn, M. Murnane, Optics Express **29**(23), 38119-38128 (2021). doi.org/10.1364/OE.440813

8. *Probing and manipulating magnetic and 2D quantum materials using ultrafast laser and high harmonic sources*, M. Murnane, X. Shi, H. Kapteyn, Journal of Physics: Condensed Matter **33**, 353001 (2021), doi: 10.1088/1361-648x/abfe21.

9. *Detection of the keto-enol tautomerization in acetaldehyde, acetone, cyclohexanone, and methyl vinyl ketone with a novel VUV light source*, D. Couch, Q. Nguyen, A. Liu, D. Hickstein, H. Kapteyn, M. Murnane, N. Labbe, Proc. Combustion Institute **38**, 1737–1744 (2021). DOI: 10.1016/j.proci.2020.06.139

10. *Nonequilibrium dissociative dynamics of D2 in two-color, few-photon excitation and ionization*, D. Slaughter, F. Sturm, R. Bello, K. Larsen, N. Shivaram, C. McCurdy, R. Lucchese, L. Martin, C. Hogle, M. Murnane, H. Kapteyn, P. Ranitovic, Th. Weber, Phys. Rev. Research **3,** 033191 (2021).

11. *Optics in 2020: High-Flux MHz Vacuum Ultraviolet Light Source*, D.E. Couch, M. M. Murnane, D. D. Hickstein, and H. C. Kapteyn, Optics and Photonics News **31**(12), 34-34 (2020). DOI: 10.1364/OPN.31.12.000034

12. *A 1 MHz ultrafast vacuum UV source via highly cascaded harmonic generation in negative-curvature hollow-core fibers*, D. Couch, D. Hickstein, S. Backus, D. Winters, J. Ramirez, S. Domingue, M. Kirchner, C. Durfee, M. Murnane, H. Kapteyn, Optica **7**, 832 (2020). doi.org/10.1364/OPTICA.395688

13. *Attosecond light science and its application for probing quantum materials*, Xun Shi, Chen-Ting Liao, Zhensheng Tao, Emma Cating, Margaret Murnane, Carlos Hernandez-Garcia, Henry Kapteyn, Invited paper, JPhys Photonics/JPhys B **53**, 184008 (2020). https://doi.org/10.1088/1361-6455/aba2fb

DYNAMICS OF TWO-ELECTRON ATOMIC AND MOLECULAR PROCESSES

Principal Investigator: Jean Marcel Ngoko Djiokap, Award Number: **DE-SC0021054**

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PROGRAM SCOPE

The goals of this theoretical project are to develop state-of-the-art analytical and numerical tools to describe, understand, control, and image ultrafast correlated two-electron atomic or molecular processes involving energy and spin angular momentum transfers from intense, short-wavelength, ultrashort, arbitrarily polarized, external electromagnetic fields eventually delayed in time to matter. Broadly, our aim is to study the time-dependent correlated dynamics of interacting few-body quantum systems. Investigations of current interest are in the areas of strong field physics, linear attosecond physics, and multiphoton ionization processes. Nearly all projects require large-scale numerical computations, involving, e.g., the direct solution of the full-dimensional time-dependent or time-independent Schrödinger equation for two-electron (or multi-electron) systems interacting with electromagnetic radiation. In some cases, our studies have been stimulated by experimental work carried out by other investigators funded by the DOE AMOS physics program. Principal benefits and outcomes of this research are improved understanding of how to induce and control electron dynamics in atoms and molecules using attosecond pulses, how to transfer energy and spin angular momentum from electromagnetic radiation to matter, how to image electron correlation processes while they occur, and how to characterize the ionizing pulses.

RECENT PROGRESS

A. *Pulse shaping in strong-field ionization: theory and experiments*: Intense ultrafast pulses cause dissociative ionization and shaping the pulses may allow control of both electronic and nuclear processes that determine ion yields. We report on a combined experimental and theoretical effort to determine how shaped laser pulses affect tunnel ionization, the step that precedes many strong-field phenomena. We carried out experiments on Ar, H_2O, N_2 and O_2 using a phase step function of amplitude ¾π that is scanned across the spectrum of the pulse. In addition, we chaged the amount of chirp in the pulses. Semiclassical as well as fully quantum mechanical TDSE calculations are in excellent agreement with experimental results. We find that precise knowledge of the field parameters in the time and frequency domains is essential to afford reproducible results and quantitative theory and experiment comparisons. *This work was a collaboration with the research group of Marcos Dantus from Michigan State University, who is an active DOE-AMOS PI. (See publication [P1] in the list of project publications below.)*

B. *Reversible electron spiral by chirped counter-rotating circularly polarized attosecond pulses at zero time delay:* A novel class of linear, spiral phenomena is discovered in the photoelectron momentum distribution when studying photoionization of S-state atoms by a pair of linearly chirped, oppositely circularly polarized attosecond pulses eventually delayed in time. 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 as well as the binding energy characteristic of an atomic target. Our results indicate potential applications in attochirpmetry and polarimetry. *(See publication [P2] in the list of project publications below.)*

C. Electron photoionization for characterization of a train of attosecond pulses or isolated attosecond pulses with time-dependent polarization state: We study Ramsey interference [1] between a variety of electronic wave packets produced in photoionization of an S-state atom by a train of pulses with arbitrary polarization state and intensity. For a plateau [P4] or Gaussian intensity profile for the pulse train, changing the ellipticity and/or helicity of the composite pulses from pulse to pulse are found to lead to a variety of novel reference interference patterns, including pairs of principal and secondary two-arm spirals, a set of two-arm spirals well separated in energy, a dense two-arm roller coaster spirals, and Newton's rings. *(Author: J.M. Ngoko Djiokap; Manuscript to be submitted to Phys. Rev. A in the project period 2022-2023.)*

D. On the topological charge of the transition amplitude in atomic ionization by short pulses: The concept of electron vortex lines (EVL) [2] is useful in various problems of quantum mechanics. Indeed, it has been shown in [3-9] for instance that EVL can be seen as spiral patterns in the PMD resulting from the ionization of atoms and molecules by a pair of ultrashort laser pulses. These vortices are characterized by the magnitude of the topological charges describing zeros of the transition amplitude. In our work, we use perturbation theory (PT) to analytically evaluate the topological charge in the multiphoton regime. We show that the topological charge calculated from the transition amplitude for the process of atomic ionization depends not only on the helicity of the laser pulses, but also on the atomic initial state, which has well-defined orbital angular momentum quantum numbers l_i, m_i. *(Authors: J.M. Ngoko Djiokap, A.V. Meremianin, and N.L. Manakov; Work in preparation and will be submitted in the project period 2022-2023.)*

E. Interference of photoelectron wave packets in ionization of atoms by two time-delayed crossing arbitrarily polarized ultrashort pulses: Ramsey interference [1] of electron wave packets created by atomic photoionization using two time-delayed, single-color, crossing ultrashort pulses are studied both analytically using first-order perturbation theory (PT) and numerically using ab-initio quantum mechanical calculations. The use of orthogonal pulses is shown to lead to two counterintuitive electron phenomena that are absent for co-propagating pulses (see for instance [3-9]). *(See publication [P3] in the list of project publications below.)*

F. Atomic photoionization by multiple pairs of slits: We study interactions of multiple temporal pairs of slits in coherent control of photoionization of S-state atoms using a pulse train of N+1 pairs evenly delayed in time by τ, in which the two pulses in a pair with a delay τ_0 are counter-rotating CP. For interacting two double-slit experiments, while Ramsey interference [1] between two identical Archimedean spirals yields pairs of principal spirals in the PMD in the polarization plane, interference of two spirals with opposite handedness does not lead to spirals, but instead to crocodile-eye-like patterns with nictares. For more than two interacting experiments, the resulting patterns turn out just to be those two novel reference patterns modulated by different kinds of N-dependent time-energy Fraunhofer functions exhibiting diffraction-grating-like patterns. *(See publication [P4] in the list of project publications below.)*

G. Temporal coherent control of resonant two-photon double ionization of H_2 via doubly-excited states: We use time-delayed, oppositely, CP few-cycle attosecond nonoverlapping pulses to study the temporal coherent control of resonant two-photon double ionization (TPDI) of fixed-in-space H_2 molecule via doubly excited states for light propagating either along or perpendicular to the molecular axis. Our treatment within either the adiabatic-nuclei approximation or fixed-nuclei approximation shows that the latter provides a very good account for this correlated process. *(See publication [P5] in the list of project publications below.)*

FUTURE PLANS

In addition to preparing research described above for publication, we are currently investigating four research problems that should be completed in the remainder of the project period:

(a) *Control of reversible electron spiral by using time-delayed attopulses arbitrarily chirped*. In [P2], reversible spiral originates from the opposite signs for the linear and quadratic terms in the chirp-induced peculiar phase difference between the two electronic wave packets created simultaneously in the continuum. Here, we shall vary the time delay between the two pulses to control the contributions from the linear and quadratic spectral phases. To stimulate more experimental interest in producing this new pattern by manipulating the laser beam group delay dispersion, the general case of arbitrary attochirp shall also be considered. *(This work is being carried out by supervising my graduate student Aqmar Md Yusoff at UNL.)*

(b) **Double-slit effects in double photoionization of the ground state of the H_2 molecule by few-cycle, elliptically polarized pulses in the high-photon soft X-ray regime within the dipole approximation**. The first observable we shall consider is the dynamical electron vortex-shaped momentum distribution produced by time-delayed elliptically-polarized pulses [6], which can be viewed as a temporal two-slit experiment. The second observable is the angular and momentum distributions exhibiting dichroic phenomena by a single pulse [10]. For perturbative weak pulse intensities, various high pulse carrier frequencies, and different molecular orientation with respect to the light propagation direction, we shall search for particular detection geometries and energy sharing configurations that enable direct observation and control of two-slit effects by tuning the pulse ellipticity.

(c) **Resonant harmonic generation (RHG) produced by chirped laser pulses**. In previous work (see, e.g., [11]) on RHG of two-electron atoms (He and Be), electron correlation effects via doubly-excited states were evidenced and isolated only when scanning the laser driving frequency. To avoid any frequency scan, we shall use the concept of chirp as a means to be on resonance with transitions from the ground state to doubly-excited states.

(d) **Effects of the time delay between the two laser fields in RHG of He or Be:** Control the multiphoton regime plateau structure (see, e.g., [11]) will be study by considering overlapping and nonoverlapping driving laser pulses at resonant frequencies.

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PEER-REVIEWED PUBLICATIONS RESULTING FROM THIS PROJECT (2020-2022)

[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).

[P2] N.J. Strandquist Jr, and J. M. Ngoko Djiokap, "*Reversible electron spiral by chirped attopulses at zero time delay,*" Phys. Rev. A, in press (2022). Accepted on 10/23/22.

[P3] J. M. Ngoko Djiokap, A. V. Meremianin, and N. L. Manakov, "*Electron interference in atomic ionization by two crossing polarized ultrashort pulses,*" Phys. Rev. A **103**, 023103 (2021).

[P4] J. M. Ngoko Djiokap, "*Atomic photoionization by multiple temporal pairs of slits,*" Phys. Rev. A **104**, 013115 (2021).

[P5] J.M. Ngoko Djiokap and A.F. Starace, "*Temporal coherent control of resonant two-photon double ionization of the hydrogen molecule via doubly-excited states,*" Phys. Rev. A **103**, 053110 (2021).

"Low-Energy Electron Interactions with Complex Molecules and Biological Targets"
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Project Scope: The primary objectives of this program are to investigate the fundamental atomic and molecular physics involved in low-energy (5-100 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 electrons and the formation of atomic and molecular ionic and neutral fragments. The hole transfer probabilities are enhanced by energy resonances and the inelastic low-energy electron scattering cross sections 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. This program seeks to measure the cross sections, rates, and energy exchange dynamics in weakly coupled complex atomic and molecular targets following ionization and is directly relevant to the Department of Energy, Office of Science commitment to fundamental studies of atoms, and molecules that are the building blocks of the materials of our universe, including DNA, RNA. It is specifically aligned with the Atomic, Molecular and Optical Physics program that supports basic research aimed at understanding fundamental interactions of high energy photons and (low-energy) electrons with atomic and molecular systems to characterize and control their behavior.

Project 1. Electron spin polarization dependent damage of the chiral amino acid L-histidine:

We have examined x-ray and low-energy electron induced damage of adsorbed molecules of biological relevance at the Advanced Photon Source (APS) at Argonne National Laboraotry [1-5]. Specifically, damage and stimulated desorption of monolayer films of L-histidine by low energy spin-polarized electrons (SPE) ejected from a magnetized cobalt substrate has been probed using x-ray photoelectron spectroscopy (XPS). In this case, the x-ray served as both the source of SPEs and the probe. Average damage cross sections for
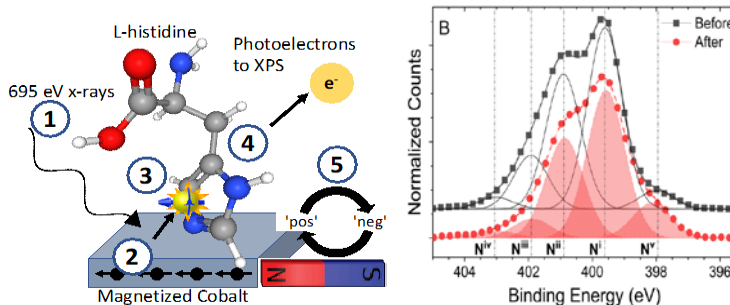

Figure 1: Diagram of the experimental setup where (1) 695 eV x-rays are incident on magnetized Co and (2) eject SPE which then (3) interact with adsorbed L-histidine. (4) The chemical state of the molecules is monitored as a function of ejected electron fluence using XPS, and (5) the magnetization direction of the substrate is reversed in situ. Figure from: M. J. Schaible, R. A. Rosenberg, S. Kundu, and T. M. Orlando, *J. Phys. Chem. Lett.* **11**, 10182 (2020).

N-containing motifs of L-histidine are between 25-30 Mb and 2-5 Mb for zwitterions and neutral molecules, respectively. The magnetization direction of the substrate, which controls the ejected SPE helicity, was reversed in situ, and statistically significant differences in the damage cross sections of 10-30% were measured between positive and negative electron helicities. To our knowledge, this was the first measurement of spin dichroism (SD) in an amino acid. The differential cross sections suggest that inelastic scattering of SPE with chiral molecules could contribute to the persistence of one enantiomer vs. the other under certain irradiation conditions, particularly for the zwitterionic species.

Project 2: Intermolecular Coulomb decay (ICD) at weakly interacting interfaces:

We have completed studies of intra- and inter-molecular Coulomb explosions during low energy (10 - 100 eV) electron interactions with ethane adsorbed on rare gas multilayers. Specifically, positive ion desorption following electron impact dissociative ionization of ethane adsorbed on Ar, Kr, and Xe multilayers has been studied as a function of incident electron energy from threshold to 100 eV. Figure 2 shows that fragment ion yields and identity depend on the type of the rare gas substrate. This, as well as the threshold data, indicate that the majority of ethane molecules undergo indirect ionization following hole transfer from the ionized underlying rare gas. This has been corroborated by density of states calculations by collaborators at the Univ. of Washington showing the energetic alignment of the outer valence states of ethane and the condensed rare gas ionization energies. Due to the near-resonant nature of charge transfer for single-hole states, the ethane molecular ion is excited to different final ionic states on different rare gases, which leads to differences in ion desorption yields and branching ratios. The quantitative yields increase with increasing ionization energy gap between the rare gas and ethane, in the order Ar > Kr > Xe.
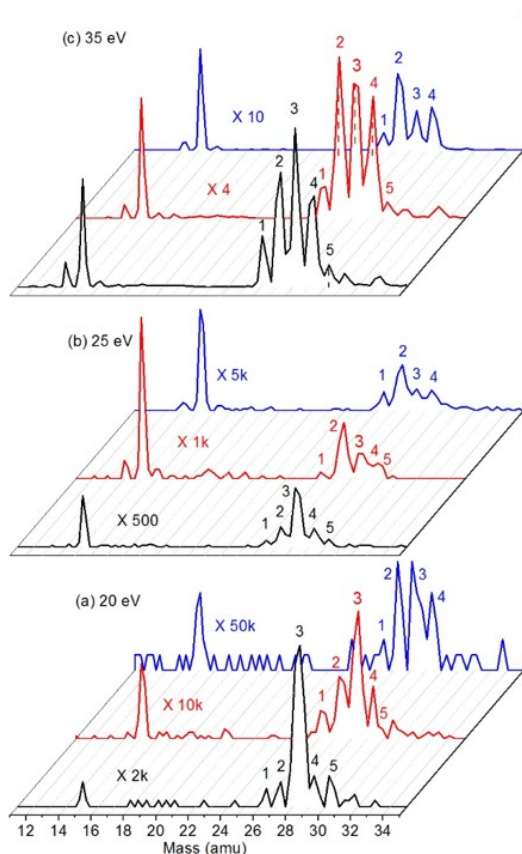
The ICD and ETMD pathways become accessible when the incoming electron has sufficient energy to excite the inner valence ns level of the rare gas to a Rydberg state or ionize it. The large increase in yields from 25 eV onwards for all rare gases is likely due to the formation and decay of two-hole states to two single-hole states on neighboring rare gas and ethane molecules due to interatomic and intermolecular Coulomb decay (ICD) and not electron transfer mediated decay (ETMD).

The experimental findings are supported by calculations of density of states for the final configurations produced by ICD and ETMD and coupling strengths for hole transfer between ethane and rare gases. The ion branching ratios also vary with energy from threshold to

Figure 2. Mass spectra of cation yields from < 1 ML ethane deposited on 50 ML of Ar (black), Kr (red) and Xe (blue) during (a) 20 eV, (b) 25 eV and (c) 35 eV electron beam irradiation. Peaks labelled 1–5 correspond to $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ and $C_2H_6^+$, respectively. Fig. from S. Kundu, H. X. Li, M. Schaible, and T. M. Orlando, *J. Chem. Phys.* (2022) https://doi: 10.1063/5.0099594

about 35 eV, showing the fragmentation pattern changes with the mode of hole transfer and availability

of excess energy. Sigma C-C bonds are more likely to break than C-H bonds in the mid-20 eV range and this effect is most pronounced for Xe, followed by Kr and then Ar.

Future Plans

The future program efforts involve three main tasks that will focus on: 1.) Investigating electron correlated interactions and Coulomb decay channels in condensed molecules and clusters. This includes ICD, ETMD and virtual photon mediated dissociation (VPD). 2.) Probing inelastic electron interactions with hydrated molecules of biological relevance 3.) Examining correlated interactions, Coulomb decay and electron transfer mediated decay in time-resolved x-ray pump: probe of liquid samples containing solvated ions using LCLS-II.

Task 1: ICD and virtual photon mediated ionization and dissociative ionization

This task will be carried out at Georgia Tech. and will focus on:
- Examining the threshold energy to produce tetrahydrofuran dissociation products $HCHO^+$ and $C_4H_8O^+$ adsorbed on water
- Probing the role of proton transfer vs. ICD in systems containing water
- Examining the formation of correlated ion-pairs
- Examining the coverage dependence of the process
- Measuring the kinetic energy distributions of the ejected ions

Task 2. ICD and virtual photon mediated dissociation of molecules

This task will be carried out at Georgia Tech. and will focus on:
- Demonstrating the theoretically predicted virtual photon mediated dissociation (VPD) process for simple H-containing molecules such as water and methane.
- Examining the velocity resolved ion and neutral angular distributions using resonance enhanced multiphoton ionization
- Probing the relative importance/competition of ICD vs. VPD

Task 3. Time resolved ICD and ETMD in ionic liquids

A collaboration with the AMOP group at Argonne National Lab. on strong-field ionization/time-resolved x-ray transient hole absorption and x-ray emission experiments to examine the dynamics of energy exchange and dissipation in complex solutions containing solvated ions will begin. Initial efforts will focus on developing a simple liquid jet system and on examining simple (NaCl) aqueous salt solutions. Joint proposals with the Argonne AMOP group for LCLS-II beam-time will be pursued. Task 3 will focus on:
- What are the hole lifetimes and dynamical responses to core level ionization in aqueous salt solutions containing multiply charged ions?
- Does the water in the solvation shells surrounding cations and anions have different radiation stabilities?
- How important is ICD vs. ETMD in shallow and deep core ionization of salt solutions?

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Recent publications acknowledging support from this program

1. 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

2. M. Schaible, R. A. Rosenberg, S. Kundu, and T. M. Orlando, "Electron Spin-Polarization Dependent Damage to Chiral Amino Acid l-Histidine", *J. Phys. Chem. Lett.* (2020), https://doi: 10.1021/acs.jpclett.0c02855.

3. S. Kindu, M. J. Schaible, A. D. McKee, and T. M. Orlando, "Direct Damage of Deoxyadenosine Monophosphate by Low-Energy Electrons Probed by X-ray Photoelectron Spectroscopy", *J. Phys. Chem. B.* (2020), doi.org./10.1021/acs.jpcb.9b08971 (Supplementary Cover Selected)

4. A. D. McKee, M. Schaible, S. Kundu, R. Rosenberg and T. M. Orlando, "Low energy secondary electron induced damage of condensed nucleotides", *J. Chem. Phys.* 150, 204709 (2019) https://doi.org/10.1063/1.5090491

Presentations acknowledging support from this program

1. T. M. Orlando, "Low-energy electron interactions with complex biomolecules and carcinogenesis", Georgia Tech. Petit Institute for Bioengineering and Biosciences, January 14, 2020. (Recording at https://smartech.gatech.edu/handle/1853/62374)

2. T. M. Orlando, "Low-energy electron interactions with complex molecules and biological targets", DOE Atomic Molecular and Optical Physics PI- Program Meetin.g, Oct. 28-30, 2019.

SISGR: Structure from Fleeting Illumination of Faint Spinning Objects in Flight

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Project Scope

The X-ray Free Electron Laser (XFEL) is a revolutionary tool with wide-ranging applications in physics, chemistry, and the life sciences. The unprecedented ability to record femtosecond X-ray snapshots offers a powerful means to understand, and ultimately control molecular machines and their work cycles at the atomic level on femtosecond timescales.

To realize their full potential, revolutionary experimental tools must be accompanied by powerful theoretical platforms. We have developed a powerful data-driven algorithmic platform combining techniques from scattering physics, Riemannian geometry, graph theory, and AI/ML. These algorithms have demonstrated the capability to extract far more information from the data than hitherto thought possible.

Recent Progress

1. Extracting more information from the data

Our algorithms have demonstrated the capability to extract, from noisy and highly incomplete experimental data recorded with substantial timing uncertainty, the three-dimensional structure [1,2], conformations [2], energy landscapes [3,4], work cycles [3], and structural dynamics [5] of molecular machines in function [6]. Our latest algorithms have extracted few-femtosecond, atomic-resolution structure dynamical information from noisy, 99% incomplete snapshots recorded with 100fs timing uncertainty [7]. At the same time, they have extended the complexity of accessible systems from those consisting of ~10 atoms [8] to systems containing more than 2,000 atoms [7]. As the complexity increases exponentially with the number of atoms, our algorithm opens a new vista in the study of the ultrafast dynamics of molecular systems.

2. New insights

Our results on the ultrafast atomic-level changes associated with the femtosecond de-excitation dynamics of the Photoactive Yellow Protein (PYP) via a conical intersection [7] reveal previously unobserved results, including oscillatory charge dynamics involving often ignored regions surrounding the chromophore. These results are corroborated by independent spectroscopic measurements of PYP [7, 9]. In addition, our results reveal the structure-dynamical trajectories leading to the vicinity of, and "through" the PYP conical intersection, elucidating the properties of the potential energy surfaces involved in PYP de-excitation [7].

Our machine-learning analysis of experimental data enables simple but numerically accurate quantum-dynamical simulations. This approach constitutes a data-driven route to a wide variety of important processes in complex molecular systems hitherto inaccessible to first-principles calculations.

3. Enhancing quantum computing

We have recently demonstrated that the data-driven concepts underlying our work also have important implications for the construction of quantum compilers for classical dynamics [10].

Future Plans

1. Develop, validate & disseminate a suite of easy-to-use algorithms for extracting ultrafast structure-dynamical information from XFEL data.

Our current algorithms are designed for use by experts. As such, they offer little non-expert guidance on how the algorithms are to be used. We plan to develop and disseminate a user-friendly suite of algorithms for extracting structure-dynamical information from noisy, incomplete data recorded with substantial timing uncertainty. The software platform will include online tutorials for non-expert users. This objective will substantially advance the ability of the broad scientific community to extract information from ultrafast data and understand the structure dynamics of molecular systems. Experience with developing cryo-EM algorithms for non-expert use (see e.g., https://github.com/GMashayekhi/ManifoldEM_Matlab) has shown that successful dissemination entails a substantial effort.

Broad access to a powerful, easy-to-use suite of data-analytical algorithms is expected to transform the nature, extent, and quality of information extracted from hard-won experimental data by the broad community Atomic, Molecular, and Optical Sciences (AMOS) community.

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8. Simultaneous observation of nuclear and electronic dynamics by ultrafast electron diffraction, J. Yang, et al., **Science** <u>368</u>, 6493, 885-889 (2020).
9. Probing the early stages of photoreception in photoactive yellow protein with ultrafast time-domain Raman spectroscopy, H. Kuramochi, et al., **Nat Chem** <u>9</u>, 7, 660-666 (2017).
10. Embedding classical dynamics in a quantum computer, D. Giannakis, A. Ourmazd, P. Pfeffer, J. Schumacher, and J. Slawinska, **Physical Review A** <u>105</u>, 5 (2022).

Peer-reviewed Publications Resulting from this Project (5/15/2020 – present)
1. Dynamics retrieval from stochastically weighted incomplete data by low-pass spectral analysis, C. M. Casadei, A. Hosseinizadeh, G. F. X. Schertler, A. Ourmazd, and R. Santra, **Structural Dynamics** <u>9</u>, 044101 (2022).
2. Embedding classical dynamics in a quantum computer, D. Giannakis, A. Ourmazd, P. Pfeffer, J. Schumacher, and J. Slawinska, **Physical Review A** <u>105</u>, 5 (2022).
3. Co-flow injection for serial crystallography at X-ray free-electron lasers, D. Doppler et al., **Journal of Applied Crystallography** <u>55</u>, 1-13 (2022).
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10. Time-resolved serial femtosecond crystallography at the European XFEL, S. Pandey et. al., **Nature Methods** <u>17</u>, 73-78 (2020).
11. Observation of substrate diffusion and ligand binding in enzyme crystals using high-repetition-rate mix-and-inject serial crystallography, S. Pandey et al., **IUCrJ** <u>8</u>, Vol. 6 (2021).
12. Propagation of conformational coordinates across angular space in mapping the continuum of states from cryo-EM data by manifold embedding, S. Maji et. al., **J. Chem. Inf. Model** <u>60</u>, 5, 2484-2491 (2020).

13. Diffraction data from aerosolized Coliphage PR772 virus particles imaged with the Linac Coherent Light Source, H. Li et al., **Scientific Data** <u>7</u>, 404 (2020).
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Control of Molecular Dynamics: Algorithms for Design and Implementation

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A. Project Scope:

Achieving control of quantum phenomena with lasers is a long-standing dream going back to 1960s. Advances in ultrafast laser technology along with flexible pulse shaping capabilities has enabled a rapidly rising number of successes in the control of broad varieties of quantum phenomena. The subject is now open for advanced development, and our DOE grant supported research addresses several key topics in this regard. For example, progress in this area has been hindered by the prohibitive cost of the quantum dynamics simulations needed to explore the principles and possibilities of molecular control. However, the emergence of nascent quantum-computing devices suggests that efficient simulations of quantum dynamics may be on the horizon. The chemical dynamics opportunities that such nascent devices offer will continue to be a focus of our research.

In order to explore the opportunities set out above, one area of particular importance is that current quantum dynamics studies, and especially those seeking to find an optimal control outcome, are limited to only a few particles (i.e., especially of a composite nature, such as with atoms in a polyatomic molecule). Our goal here is to fully explore the utility of artificial neural networks in machine learning aiming to break through this limit. Success of the research in this domain in itself should dramatically accelerate optimal control simulations of complex unimolecular and bimolecular quantum dynamics of current interest in photochemistry and chemical reactions. Beyond the topic of controlled many-body dynamics, the collective studies will make possible the exploration of a number of issues at the foundations of laser control in quantum science, including the critical features of quantum control landscapes.

Finally, the major goal of the project is to develop theoretical concepts and practical algorithms for their transfer into the laboratory to enhance the quality of the experiments as well as to extract greater information from these endeavors. During the current DOE grant period, from November 2021 to September 2022, 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 2021 to September 2022, several research topics were pursued in the general area of understanding and controlling quantum dynamics phenomena. A summary of these accomplishments is provided below:

[1] Sequential optical response suppression for chemical mixture characterization: This study introduced an approach based on quantum tracking control that allows for determining the relative concentrations of constituents in a quantum mixture using a single pulse which enhances the distinguishability of components of the mixture that scales linearly with the number of mixture

constituents. To illustrate the method, we have considered two very distinct model systems: mixtures of diatomic molecules in the gas phase, as well as solid-state materials composed of a mixture of components. A set of numerical analyses were presented showing strong performance in both settings.

[2] Selective photo-excitation of molecules enabled by stimulated Raman pre-excitation: This study showed that double excitation using non-resonant Raman pre-excitation is a viable candidate for selectively promoting molecules to chemically active energy levels. The use of non-resonant Raman pre-excitation is less constraining than resonant Raman, since the choice of Raman pump-Stokes frequencies may be rather freely chosen.

[3] Multilevel evolution strategies for high-resolution black-box control: In this study, we created a multi-level (stage) Evolution Strategy algorithm to address a class of global optimization problems that require complex controls. We considered quantum control problems for which targeted controls may be discretized to increasingly higher resolution (i.e., the multi-level character). An automated scheme facilitated the search over increasingly finer levels of control resolution during optimization. We also presented a laboratory proof-of-concept for the proposed approach.

[4] A Generalized Kernel Method for Global Sensitivity Analysis (GSA): This work described a class of GSA measures which should be of wide importance in many areas of modeling, quantum and beyond. The new GSA method is based on the embedding of the multiple output's joint probability distribution into a reproducing kernel Hilbert space (RKHS). In particular, the distance between embeddings is measured utilizing the maximum mean discrepancy. First, the proposed methodology has easy computability for high-dimensional (e.g., multiple quantum observables) outputs. Second, by utilizing different kernels, or RKHSs, one can determine how the input parameters influence different features of the output distribution. This new class of sensitivity analysis measures, encapsulated into what are called β^k-indicators, were shown to contain both moment-independent and moment-based measures as special cases. Some basic test cases were used to showcase that the β^k-indicators derived from kernel-based GSA provide flexible tools capable of assessing a broad range of applications relevant to chemical physics.

[5] The Promise of Mutation Resistant Small Molecules for Control of SARS-CoV-2 by Interdicting in the Folding of the Spike Protein Receptor Binding Domain: This work exploited our experience in control to now extend it to considering peptides as "controls" of critical protein folding processes. Thus, we proposed that effective molecules aimed at treating the SARS-CoV-2 infection could be developed based on interdicting in the early steps of the folding pathway of key viral proteins, including the receptor binding domain (RBD) of the spike protein. In order to provide for a target on the protein, the earliest contact-formation event along the dominant folding pathway of the RBD spike protein was predicted employing the Sequential Collapse Model (SCM). The segments involved in the predicted earliest contact were suggested to provide optimal folding interdiction target regions (FITRs) for potential small molecule control. The results showed that the identified FITR provides for a mutation-resistant molecular control strategy for the RBD-spike protein.

[6] The optimization landscape of hybrid quantum-classical algorithms: From quantum control to NISQ applications: This work investigated the landscapes of hybrid quantum–classical optimization algorithms that are prevalent in rapidly developing quantum technologies, where the objective function is computed by either a natural quantum system or an engineered quantum ansatz, but the optimizer is classical. Based on noisy intermediate-scale quantum (NISQ) devices, the experimentally growing computational power of quantum hardware may bring quantum

advantages over classical computers, but the classical optimizer is often limited by the available control resources. Here we showed that the landscape's geometry experiences morphological changes from favorable trap-free landscapes to easily trapping rugged landscapes, and eventually to barren-plateau landscapes on which the optimizer can hardly move. This unified view could provide the basis for understanding classes of systems that may be readily controlled out to possible ways to escape traps or plateaus, in particular circumstances.

[7] <u>Machine learning of quantum control utilizing artificial neural networks:</u> This study explored the limit of quantum control simulations of many-body quantum systems utilizing a dual scheme that combined artificial neural networks and the Krylov subspace method for Hilbert space reduction. The dual scheme enables fast, accurate optimal control simulations in a small fraction of the total Hilbert space. We have applied this new scheme for control of long spin-chains. We showed how this dual scheme can identify a working Hilbert space with polynomic scaling with the number of spins, thus, making feasible large-scale optimal control simulations. The study on spin-chain control will be extended to optimal control involving polyatomic systems in the coming year.

C. Future Plans:

In the coming year, in addition to continued study seeking a deeper understanding of the topology of control landscapes, we plan to expand our research on controlling quantum dynamics phenomena. Our immediate plan will be on our ongoing study of N-body quantum control problems, $N>>1$, using the artificial neural network (ANN) machine learning method in conjunction with the Krylov subspace method for Hilbert space reduction, with the aim of demonstrating both mathematically and numerically that the scaling is no longer exponential but rather polynomic in N, at least for practical values of N of chemical interest. It has been shown that the Krylov subspace technique can be applied to facilitate solutions to very large time-dependent quantum problems and to expedite quantum control simulations of complex many-body dynamics. Moreover, we plan to further expedite the implementation of the Krylov subspace method for solving the ANN equation. The adoption of the Krylov method may greatly reduce computational time, thus, making feasible large scale quantum optimal control simulations for a wide range of realistic many-body problems. In addition, we plan to develop a fully optimal Hamiltonian encoding method for speeding up analysis of the mechanism behind the dynamics governing quantum control systems, especially in strongly driven systems. To this end, we plan to formulate new ways to calculate the amplitudes of pathway classes embedded in the Dyson series by using graph theory to exploit patterns in the set of the allowed transitions and greatly reduce the number of transitions that need to be encoded. These improvements should provide an exponential decrease in both computation time and memory usage. These techniques are to be applied to state-to-state transition problems in molecular dynamics and, in particular, quantum gate transformation problems in quantum information science.

D. Peer-Reviewed Publications Resulting from this Project (2020-2022):

[1] Combining the synergistic capabilities of modeling and experiments: Illustration of finding a minimum-time quantum objective, Q.-M. Chen, X. Yang, C. Arenz, R.-B. Wu, X. Peng, I. Pelczer, and H. Rabitz, Phys. Rev. A 101 (2020).
[2] An upper bound on the time required to implement unitary operations, J. Lee, C. Arenz, D. Burgarth, and H. Rabitz, J. Phys. A: Math. Theor. 53, 125304 (2020).

[3] Ultrafast Photofragmentation of Ln(hfac)3 with a Proposed Mechanism for forming High Mass Fluorinated Products, J. Chen, X. Xing, R. Rey-de-Castro, and H. Rabitz, Scientific Reports 10, 7066 (2020).

[4] Optimal control of coupled quantum systems based on the first-order Magnus expansion: Application to multiple dipole-dipole coupled molecular rotors, A. Ma, A. Magann, T.-S. Ho, and H. Rabitz, Phys. Rev. A 102, 013115 (2020).

[5] Amplification of quadratic Hamiltonians, C. Arenz, D. Bondar, D. Burgarth, C. Cormick, H. Rabitz, Quantum, 4, 271 (2020).

[6] Optimal control of coupled quantum systems based on the first-order Magnus expansion: Application to multiple dipole-dipole-coupled molecular rotors, A. Ma, A. Magann, T.-S. Ho, and H. Rabitz, Phys. Rev. A, 102, 013115 (2020).

[7] Assessing three closed-loop learning algorithms by searching for high-quality quantum control pulses, X.-D. Yang, C. Arenz, I. Pelczer, Q.-M. Chen, R.-B. Wu, X. Peng, and H. Rabitz, Phys. Rev. A, 102, 062605 (2020).

[8] Quantum Control Landscapes Beyond the Dipole Approximation: Controllability, Singular Controls, and Resources, B. Russell, R.-B. Wu, and H. Rabitz, Front. Phys., 9, 674794 (2021).

[9] From Pulses to Circuits and Back Again: A Quantum Optimal Control Perspective on Variational Quantum Algorithms, A. Magann, C. Arenz, M. Grace, T.-S. Ho, R. Kosut, J. McClean, H. Rabitz, and M. Sarovar, PRX Quantum, 2, 010101 (2021).

[10] Multilevel evolution strategies for high-resolution black-box control, O. M. Shir, X. Xing, and H. Rabitz, Journal of Heuristics, doi.org/10.1007/s10732-021-09483-z (2021).

[11] Optimization landscape of quantum control systems, X. Ge, R.-B. Wu, and H. Rabitz, Complex System Modeling and Simulation, 1, 77 (2021).

[12] Digital quantum simulation of molecular dynamics and control, A. B. Magann, M. D. Grace, H. Rabitz, and M. Sarovar, Phys. Rev. Research 3, 023165 (2021).

[13] Progress toward favorable landscapes in quantum combinatorial optimization, J. Lee, A. B. Magann, H. Rabitz, and C. Arenz, Phys. Rev. A. 104, 032401 (2021).

[14] Selective photo-excitation of molecules enabled by stimulated Raman pre-excitation, Y. Wang, F. Laforge, A. Goun, and H. Rabitz, Phys. Chem. Chem. Phys., **24**, 10062, DOI: 10.1039/d2c00868h, (2022).

[15] Sequential optical response suppression for chemical mixture characterization, A. Magann, G. McCaul, H. Rabitz, and D. Bondar, Quantum, **6**, 626, DOI: 10.22331/q-2022-01-20-626, (2022).

[16] A Generalized Kernel Method for Global Sensitivity Analysis, J. Barr and H. Rabitz, J. Uncertainty Quantification, 10, 27-54, DOI: 10.1137/20M1354829, (2022).

[17] The Promise of Mutation Resistant Drugs for SARS-CoV-2 that Interdict in the Folding of the Spike Protein Receptor Binding Domain, F. Bergasa-Caceres and H. Rabitz, COVID (MDPI), 1, 288-302, DOI: 10.3390/covid1010023, (2021).

[18] Optimization Landscape of Quantum Control Systems, X.-Z. Ge, R.-B. Wu, and H. Rabitz, IEEE-CSMS, 1, 77-90, DOI: 10.23919/CSMS.2021.0014, (2021) (June 2021).

[19] 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).

"Atoms and Ions Interacting with Particles and Fields"
Award No. DE-SC0012193

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Program Scope

This theory project focuses on the time evolution of systems subjected to either coherent or incoherent interactions represented by fields and particles, respectively. This study is divided into three categories: (1) correlations between two electrons in highly excited states or in double continua, (2) processes for one electron in time dependent or non-separable potentials, and (3) the interaction of atomic electrons with strong electromagnetic fields. Some of the techniques we developed have been used to study collision processes in ions, atoms, and molecules. In particular, we have used these techniques to study the correlation between two (or more) continuum electrons and electron impact ionization of small molecules.

Recent Progress (Publications 10/2021-9/2022)

X-ray physics: The graduate student Akilesh Venkatesh led a project, Ref. [7], to understand the possibility for imaging electron wave packet dynamics using pulsed x-ray scattering. In Ref. [1], we demonstrated a method for modeling non-linear Compton scattering. In Ref. [5], we extended these programs to simultaneously include photons of frequency ω and 2ω to investigate the phase difference that appears in the interference term between these indistinguishable processes. In the new work to be published this year, he led a project to investigate the possibility for detecting properties of electron wave packets using pulsed X-rays. To study the properties of a wave packet, the probe must have a duration smaller than the timescale of the electronic superposition. If the X-rays themselves are pulsed, then the scattering can depend on the phases of the different components of the electron wave packet. Akilesh used the numerical programs developed in Refs. [1] and [5] to calculate the scattering probabilities for different electron wave packets. The goal was to understand what properties of the electron wave packet can be probed with a pulsed X-ray beam. We showed that the x-ray scattering pattern reflects the weighted Fourier transform of the instantaneous electronic wave function if the electronic state of the atom/molecule can be measured after scattering. We explored several cases for the initial electronic wave packet and detected final electronic states to gain an idea of how what the properties that can be detected.

The graduate student supported by this grant, Akilesh Venkatesh, started research in January 2019 and very quickly come up to speed. He has finished three projects involving strong field X-rays to understand non-linear Compton scattering seen at the LCLS and to propose how to use interference in nonlinear Compton scattering. Also, he finished a project involving the orientation and alignment dependence of ionization in collisions between two Rydberg atoms. He is currently investigating basic processes in beyond dipole interaction of light with single electron atoms.

Future Plans

X-ray physics: The graduate student Akilesh Venkatesh is leading a project to investigate the possibility for detecting properties of electron wave packets using X-rays. If the X-rays themselves are pulsed, then the scattering can depend on the phases of the different components of the electron wave packet. We will use the numerical programs developed in Refs. [1] and [5] to calculate the scattering probabilities for different electron wave packets. We will also develop a method based on the perturbative scattering of the X-rays to benchmark these results and understand the origin of different effects. The goal is to understand what properties of the electron wave packet can be probed with a pulsed X-ray beam.

Thermalization in lineland: When two identical particles classically 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, Aanal Shah, and two undergraduates, Colton Griffin and Xinghan Wang, will investigate this process for short range interaction potentials and for Coulomb-like potentials. We will investigate the statistics of how an initial velocity in one electron randomly changes with time. It will be important to understand the systematics of this type of thermalization so we will investigate a variety of short range potentials as well as a variety of initial velocities.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

[1] Akilesh Venkatesh and F. Robicheaux, "Simulation of nonlinear Compton scattering from bound electrons," Phys. Rev. A **101**, 013409 (2020).
[2] P. Giannakeas, M. T. Eiles, F. Robicheaux, and J. M. Rost, "Generalized local frame-transformation theory for ultralong-range Rydberg molecules," Phys. Rev. A **102**, 033315 (2020).
[3] P. Giannakeas, M. T. Eiles, F. Robicheaux, and J. M. Rost, "Dressed ion-pair states of an ultralong-range Rydberg molecule," Phys. Rev. Lett. **125**, 123401 (2020).
[4] Akilesh Venkatesh and F. Robicheaux, "Effect of the orientation of Rydberg atoms on their collisional ionization cross section," Phys. Rev. A **102**, 032819 (2020).
[5] Akilesh Venkatesh and F. Robicheaux, "Interference in nonlinear Compton scattering using a Schrodinger-equation approach," Phys. Rev. A **103**, 013111 (2021).
[6] A. Trautmann, M. J. Mark, P. Ilzhöfer, H. Edri, A. El Arrach, J. G. Maloberti, C. H. Greene, F. Robicheaux, and F. Ferlaino, "Spectroscopy of Rydberg states in erbium using electromagnetically induced transparency," Phys. Rev. Res. **3**, 033165 (2021).
[7] Akilesh Venkatesh and F. Robicheaux, "Simulations for x-ray imaging of wave packet dynamics," Phys. Rev. A accepted for publication (2022).

Light-induced couplings to study and control electronic interactions and electron-nuclear dynamics

Project Scope

This project involves the application of light-induced couplings to study and control correlated and coupled electron and nuclear dynamics in atoms and molecules. Tunable wavelength, multi-pulse, pump-probe techniques, using XUV, NIR, and MIR fields, are employed to investigate the electronic processes. Attosecond transient absorption spectroscopy, four-wave-mixing, and velocity map imaging, represent the main experimental techniques utilized on this project. Specific research topics include 1) the study of polaritons formed through coupling between bright and dark autoionizing states, 2) the control of interferences in ionization pathways to stabilize the autoionizing states, 3) the impact of electron-core interaction on the multiphoton electron angular distributions, 4) the study of electron-nuclear coupling driven dynamics in molecules. The wide range of tunable (600-3400nm) laser fields available for this project have enabled a systematic study of resonant and non-resonant couplings, leading to new strategies for controlling few-body dynamics in atoms and molecules. The use of multi-pulse schemes provides new control possibilities while also providing means to disentangle the role strong fields in standard XUV-IR experiments. Attosecond soft-x-ray pulses will be developed to obtain elemental and chemical sensitivity in the study of correlated charge dynamics.

Recent Progress

In the previous grant period, we demonstrated that by near-resonant coupling between the autoionizing and light-induced states in argon, we can stabilize the atom against ionization, thus confirming a prediction made nearly forty years ago. This stabilization was achieved through the destructive interference between the Auger decay and the radiative ionization of the polaritonic components and depends on the time-delay between XUV and IR pulses. Recently, we explored the intensity dependence of this process and obtained new insights into the optical control of metastable polyelectronic systems. We then extended nonlinear XUV-IR spectroscopy to conduct multi-wave-mixing and transient absorption studies in atoms and molecules, to probe electron dynamics and electron-nuclear couplings. In the case of photoelectron interferometry, we are developing a comprehensive picture elucidating the role of strong fields and electron-core interactions on the phases and angular distributions. Continuing collaborations with UCF, Berkeley, and Purdue groups have been instrumental in these efforts.

Polaritonic structure of autoionizing states: Stabilization and intensity dependence:

Laser-dressed autoionizing states have been studied theoretically since the 1980s, and theoretical work by Zoller and others indicated the possibility of using light pulses to stabilize these states against ionization by causing destructive interferences between the autoionization and radiative-ionization pathways. This quintessential aspect of electron dynamics in the continuum, which has

no counterpart in bound states, had not received experimental confirmation. We employed attosecond transient-absorption spectroscopy in argon to study the formation of a polariton due to coupling between the $3s^{-1}4p$ and several light-induced states. We demonstrated control of autoionization lifetime and stabilization of these polaritons against ionization, in excellent agreement with ab initio theory. These results were published in PRL **127**, 023202 (2021).

Recently, we extended our study to investigate the role of two-photon couplings in formation of multiple polaritons at high IR intensities. Contrary to the traditional approach, our tunable attosecond transient absorption employs an independently adjustable IR probe frequency to resonantly drive or detune the light-induced couplings between excited states. Specifically, the tunability of the dressing-IR field allows us to manipulate the interactions between the $3s^{-1}4p$ bright autoionizing states and several light induced counterparts of the dark autoionizing states ($3s^{-1}3d$, $3s^{-1}5s$, and $3s^{-1}4f$) in argon, thus providing control over the evolution of multiple polaritons. We observed that even under the resonant condition for $3s^{-1}4p - 3s^{-1}4f$ two-photon coupling, the intermediate one-photon couplings with 3d and 5s dark states play an important role, leading to the formation of four polaritonic branches at higher intensities (Fig. 1). We varied the delay, frequency, and intensity of the IR pulse to explore the parameter space and observed excellent agreement with *ab initio* simulations by Argenti group. By selectively including states in simulations, we identified each polaritonic interaction and observed the avoided crossings between branches. These results were published in PRA 105, 063107 (2022).
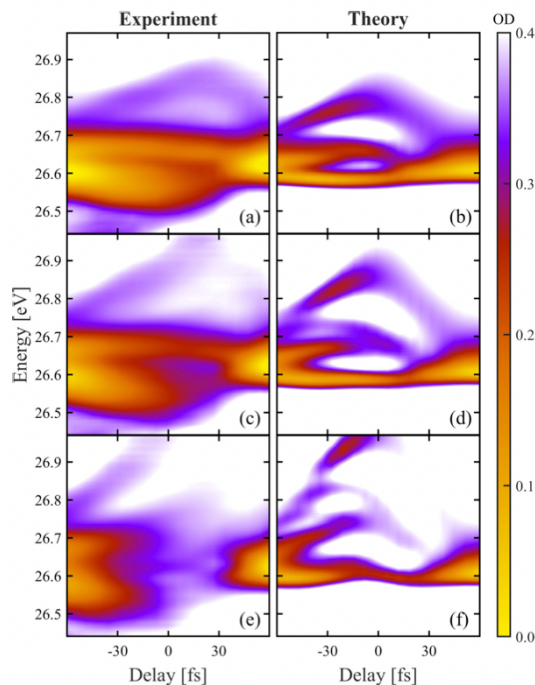

Fig 1. Experimental (left) and theoretical (right) XUV absorption around argon 4p autoionizing state, as a function of the IR pulse delay. Colormap corresponds to the optical density. Different rows illustrate various IR intensities, increasing from top to bottom where (a) 62 GW/ cm^2, (b) 50 GW/cm^2, (c) 110 GW/ cm^2, (d) 100 GW/ cm^2, (e) 205 GW/ cm^2, and (f) 200 GW/ cm^2. Interaction of 4p autoionizing state with 3d and 5s autoionizing light induced states gives rise to the three polariton branches. As intensity increases two-photon couplings with 4f state comes into play, and we observe four distinct polaritonic features.

Probing multielectron excitations and quantum beats through non-linear mixing:

Apart from controlling the lifetime of autoionizing states in Argon, and as an extension of the tunable transient absorption spectroscopy, we have conducted XUV-IR multi-wave mixing studies in neon and krypton. We have obtained two new experimental results, and we are currently working towards their analysis and publication.

The first study investigates the energy regime associated with the formation of doubly excited states in Krypton. Specifically, we found that there exist several doubly excited states around 24 eV, however their electronic configurations are yet to be identified. Using four-wave-mixing, we observed XUV emission that shows beating with a time-period matching the energy difference between a singly and a doubly excited state. The interference between these two pathways is mediated by other resonant states and involves multi-electron transitions. The

identification of doubly excited states requires a full R-matrix treatment, and we are working with the Greene group at Purdue and others to shed some light on this question.

Extending the study of non-linear processes even further, we obtained data on multi-color six-wave mixing in Neon with XUV+NIR+MIR fields. These results are being submitted for publication. In this work, using six-wave-mixing we also obtained a quantum beat between the optically dark spin-orbit split states of neon, and found that this beat shows a non-intuitive phase variation as a function of the final state energy. Our tunable multi-wave mixing also opens the doors for conducting two-dimensional spectroscopy in the XUV regime, which can probe coherences and non-adiabatic couplings between the excited states.

Probing electron-nuclear dynamics with molecular transient absorption studies:

We made progress in the study of transient absorption in O_2 and CO_2 molecules. We have previously focused on molecular transient absorption of autoionizing $nl\sigma_g$ Rydberg series converging to O_2^+ $c^4\Sigma_u^-$ states, where we explored two different aspects: 1) the role of electronic symmetry in determining the transient absorption profile, and 2) the impact of nuclear motion on the autoionization dynamics. These studies involved collaborations with McCurdy group at LBNL, and Leone and Neumark groups at UCB, respectively. In the current period, we obtained the transient absorption spectra for $np\sigma_u$ Rydberg series converging to the $B^2\Sigma_g^-$ and $b^4\Sigma_g^-$ ionic states. To understand the spectral features and the temporal evolution of different series members, we are currently collaborating with Argenti and coworkers, who are working towards computation of of these transient absorption spectra for comparison with the experiment.

To pursue the study of coupled electron-nuclear dynamics and the light induced modification of conical intersections, we employed transient absorption to study the Rydberg series near the conical intersection formed by the $A^2\Pi_u$ and $B^2\Sigma_u^+$ electronic states of CO_2 molecular ion. We used the 11th harmonic to excite these states and observed the signature of several members of the Henning sharp and diffuse series converging to the B ionic limit. This system represents a Rydberg electron attached to an ion

Fig. 2. Attosecond transient absorption spectrogram in CO_2 showing the Henning sharp and diffuse Rydberg series members converging to the B ionic state that forms a conical intersection with the A ionic state.

core that has an electron hole driven between the σ and π orbitals by the bending and asymmetric stretch vibrations of the molecule. Furthermore, the loosely bound Rydberg electron undergoes autoionization which competes with the fragmentation of the ion core. The experimental data (Fig. 2) shows that higher Rydberg states indeed exhibit longer lifetimes. The quantitative evolution of the spectra features however requires detailed simulations and we have initiated a collaboration with a local theorist (Golubev) to model these transient absorption signals. As another window into these interesting many-body dynamics, we invoked a complementary approach of photoelectron spectroscopy to investigate these coupled electron-nuclear dynamics. The preliminary comparison between the photoelectron and transient absorption spectrograms show that the two approaches are sensitive to different Rydberg series, which is a surprising finding.
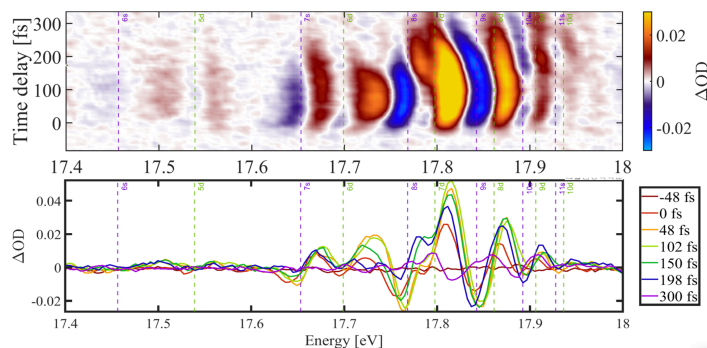
Photoelectron angular distributions in two-color ionization: Electron-core interactions

Photoelectrons emanating from an atom, or a molecule, carry information about the initial and final quantum states, including their angular momentum state. We found that the simple description of photoelectron angular distribution breaks down when the light field can modify the electronic structure or cause transitions to mix the states, thus introducing higher angular momentum components, e.g., beta 8 in Fig. 3. In this study, we created a 3d-5s electronic wavepacket in Argon with XUV, and ionized it with a tunable IR, leading to interference in each of the spin-orbit split continua. The phase of the quantum beat and the beta parameters for the angular distribution in each continua contain information on electron-core interaction and the light induced angular momentum couplings. We collaborated with Greene

Fig. 3. Time-dependent β parameters for the two-photon ionization of XUV excited 3d-5s wavepacket in Argon. The non-zero β_8 signifies introduction of higher angular momentum components due light-induced couplings.

group at Purdue to perform MQDT analysis and calculate time-dependent beat signals and angular anisotropy parameters. We obtained a reasonable agreement between the experiment and theory, and we aim to submit a manuscript on these results. Our comprehensive description improves on the previous understanding of photoelectron angular distributions in two-color ionization.
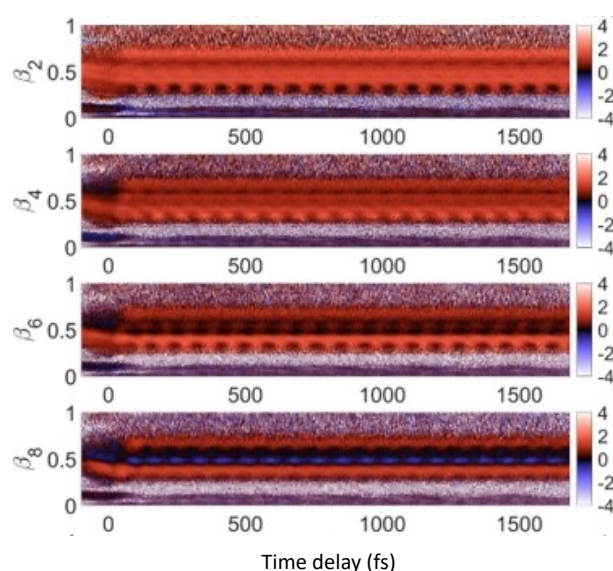
Future Plans:

We will continue our efforts to obtain quantitative understanding of light-induced electronic couplings in atoms and molecules, while publishing the recent results. We will work towards installing a new few-cycle MIR laser that will provide additional tunability of the light field from 1.6 to 3.4 um. The new laser system will also be employed to drive the soft-x-ray generation. The resulting attosecond soft-x-ray capability will allow us to conduct elementally specific probing of charge dynamics in complex molecular systems. The tunable, multi-color and multi-pulse spectroscopy techniques developed in these efforts will enhance the attosecond science toolkit.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

1) Nathan Harkema, Coleman Cariker, Eva Lindroth, Luca Argenti, Arvinder Sandhu, "Autoionizing Polaritons in Attosecond Atomic Ionization", Phys. Rev. Lett. **127**, 023202 (2021).
2) Yen-Cheng Lin, Ashley P Fidler, Arvinder Sandhu, Robert R Lucchese, C William McCurdy, Stephen R Leone, Daniel M Neumark "Coupled nuclear–electronic decay dynamics of O2 inner valence excited states revealed by attosecond XUV wave-mixing spectroscopy", Faraday Discussions **228**, 537 (2021).
3) Sergio Yanez-Pagans, Coleman Cariker, Moniruzzaman Shaikh, Luca Argenti, Arvinder Sandhu, "Multipolariton Control in Attosecond Transient Absorption of Autoionizing States", Physical Review A 105, 063107 (2022).

Coherent Probes of Molecular Charge Migration

Science Using Ultrafast Probes: DE-SC0012462

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Project Scope

In the field of ultrafast science, charge migration (CM) stands out as an important milestone. This correlation driven, multi-electron response is typically initiated 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, and potentially leading to a host of downstream physical or chemical processes such as dissociation, charge transfer and photoelectric energy conversion. Given its ubiquitous and fundamental role, the ability to accurately predict, observe, and potentially control CM stands out as a key goal for ultrafast science. With continued advances in experimental and theoretical tools and techniques, significant progress is being made toward computing and measuring the full evolution of CM-based dynamics, from the primarily electronic response reflected by attosecond changes in the local charge density, to femtosecond coupled electronic-nuclear dynamics. Indeed, reaching this important milestone has become a significant driver of cutting-edge experiment and theory in AMO science.

Since 2015, the ATTO-CM network has worked to establish itself as a resource on fundamental questions related to both the nature of CM in specific families of functionalized molecules, and on the development of experimental techniques needed for its observation. This has been enabled by our emphasis on taking an integrated approach, blending theory and experiment in all phases of the research, as illustrated in Figure 1. The objective of the ATTO-CM team is to advance ultrafast science in the US both at the university laboratory scale and at large facilities, using a concerted effort of theorists and experimentalists. Our emphasis is on the implementation of time-resolve probes of CM, and its interplay with nuclear dynamics, in gas and liquid phases using a versatile toolbox of experimental techniques to initiate and measure CM dynamics. Our ultimate goal is to develop experimental probes that can provide direct access to specific time-resolved information in chemical systems. For practical implementation, our focus has been to identify parameters to probe and control these dynamics, *e.g.*, molecular alignment and/or functionalization of the target.
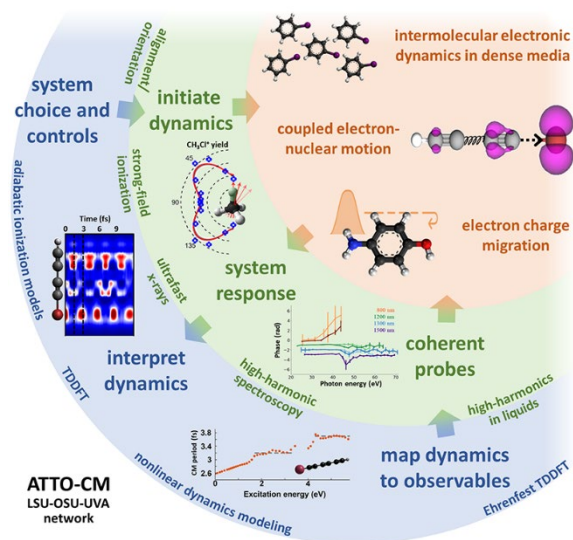

Figure 1: How theory and experiment interact in the ATTO-CM network to address fundamental aspects of charge migration (center). Blue band: theoretical tools; Green band: coherent probes and measurements.

Recent Progress

In our effort to understand and observe CM with ultrafast light fields we have focused on three main thrusts: "Mechanisms of charge migration", "Time resolving charge migration dynamics", and "Expanding the charge migration toolbox". All three nodes of the ATTO-CM network are closely involved in each of the three thrusts defining our program. In brief, our key recent results are:

1. *Thrust 1: Mechanisms of charge migration* –. Building on our identification of simple heuristics for CM modes in halohydrocarbon chains [Folorunso 2021], we performed systematic studies of CM in para-functionalized bromobenzene derivatives. We establish a direct link between the CM contrast and the electron-donating strength of the functional group, as measured with the Hammett sigma value [Folorunso 2022]. We complemented our attochemistry investigations with nonlinear dynamics analysis [Mauger 2022b] of the mechanisms that enable sustained CM modes and found that they emerge as attosecond solitons [Mauger 2022].

2. *Thrust 2: Time resolving charge migration dynamics* –The atto-cm network has established wide-ranging expertise in experimental and theoretical high-harmonic spectroscopy (HHS) [Tuthill 2020, Tuthill 2022]. Building on this, we have pursued several avenues to coherently probe CM with XUV light. Experimentally we have developed (i) attosecond spectroscopy facilitated by a 400-nm driven high-harmonic generation (HHG) source and (ii) HHG from a liquid jet. Theoretically, following our progress with reliably computing HHS signals [Hamer 2021] (iii) we have demonstrated a novel HHS method for probing CM via the high-harmonic sidebands produced when the CM-mode and driving-laser frequencies are incommensurate [Hamer 2022]. (iv) We also have initiated theoretical studies of liquid HHG. At the facility scale, the OSU node has been involved in a series of experiments in the Attosecond Science campaign at LCLS to measure CM in aminophenol using the XLEAP mode of the LCLS.

3. *Thrust 3: Expanding the charge migration toolbox* – We have developed new computational and experimental techniques and expertise to complete an investigation of angle-dependent strong-field ionization of oriented OCS. Through these efforts we have confirmed that OCS molecules are preferentially ionized when the ionizing field points from the S to the O atom, in agreement with our TDDFT and weak-field asymptotic theory (WFAT) calculations, but opposite to that reported previously by other groups [Holmegaard 2010]. On the theory side, we have developed a DFT-based formulation of WFAT for calculating tunneling ionization rates and yields of arbitrary molecules in the adiabatic regime [Wahyutama 2022]. Our DFT-based WFAT can treat multi-electron effects like electron correlation and compares very well with full TDDFT simulations at a fraction of the computational cost. We have also initiated investigations of frequency-matched ionization spectroscopy of CM.

Thrust 1: Mechanisms of charge migration

Thrust 1 of the ATTO-CM network is focused on using first-principles simulations to determine the mechanisms by which CM occurs. To address this, the LSU team leads an ongoing effort to determine the relationship between molecular structure and CM properties to answer key questions such as: Which molecules can be expected to support CM? What chemical properties of a molecule influence the CM? And, can CM be disrupted or enhanced chemically? Understanding the mechanisms for CM is critical for Thrust 2 and 3, and for designing and interpreting future CM experiments.

Attochemistry regulation of charge migration: Building on our previous work developing heuristics for halohydrocarbon chains [Folorunso 2021], we have recently completed a systematic study of CM in para-functionalized bromobenzene derivatives ($Br-C_4H_4-R$), where we determined how the chemical properties of the R group regulate the CM [Folorunso 2022]. To simulate the CM, we used real-time TDDFT with atom-centered basis sets and hybrid DFT functionals. We initialize the hole using constrained DFT and imposing

a +1 charge localized on the Br [Folorunso 2021], which emulates the state of the system following strong-field ionization. Figure 2 (a) shows the hole density dynamics for two representative molecules: one weak electron donor (bromotoluene, left) and one strong electron donor (bromoaniline, middle). While the two compounds have very similar CM time, bromoaniline supports a hole with a more pronounced contrast, which may be of direct relevance to experimental

Figure 2: (a) Hole dynamics plots for bromotoluene (left) and bromoaniline (middle). The -NH_2 functionalized molecule has an enhanced hole contrast. (b) The computed Hammett (electron donating strength) and hole contrast parameters, demonstrating that electron donating functional groups make for good CM hole acceptors.

measures of CM using probes that are sensitive to local charge densities. This contrast enhancement strongly correlates with the Hammett sigma value for the functional group, as shown in Figure 2 (b). The Hammett sigma value is a dimensionless quantity that describes the electron withdrawing/donating strength of the group.

The simple relationship between CM and electron donating strength has numerous implications. It suggests that electron donating functional groups are good regulators for CM, as they enhance the contrast, and thus the observability, of the hole without changing the time scale of the dynamics. Bromobenzene or other conjugated molecules functionalized with strong electron donor groups will be particularly attractive molecules for experimental measurements that probe the local hole/electron density at different ends of the molecule. Amine derivatives like -NH_2, -$NHCH_3$, and -$N(CH_3)_2$ are especially good hole acceptors and thus promising CM-friendly functional groups for such experiments. For interpretation purposes, the fact that the Hammett sigma value predicts so well the hole contrast strengthens the idea that CM can be understood using density-based chemical principles, without invoking complicated beating of states. In a similar line of thought, next we will investigate the role of the initial hole on the CM dynamics by using pseudo-halogens, *i.e.*, hole donor groups, instead of halogens.

Nonlinear dynamics of charge migration: To further investigate the underlying dynamical mechanisms that makes CM modes possible in halohydrocarbon molecules, the LSU node has employed tools from nonlinear dynamics. In [Mauger 2022], using a combination of reduced models and full-dimensional TDDFT simulations, we showed that CM in conjugated carbon chains results from an intricate multi-correlated electron dynamic beyond what can be described via the beating of molecular orbitals. We found that sustained CM modes emerge as attosecond solitons, with a localized hole periodically traveling across the molecule.

More recently, we have focused our efforts on bridging the one-body density dynamics, which we know to be the relevant observable for CM, and the Kohn-Sham orbitals, which are what is being propagated in simulations. To that end, we have identified the canonical Hamiltonian structure of the TDDFT equations we use to describe CM [Mauger 2022b]. We have also identified numerical schemes that simulate TDDFT dynamics for our nonlinear analyses of CM more accurately and with a sizeable speedup compared to [Mauger 2022]. Since phase-space analyses typically require several hundred to over a thousand TDDFT simulations, this will facilitate our future nonlinear investigations. We are currently finalizing a manuscript describing these results [Mauger 2022b]. Moving forward, we aim to use Hamiltonian nonlinear theory to better understand the mechanisms that enable, or disable, CM modes across families of conjugated molecules as well

as their coupling with external degrees of freedom like nuclear motion.

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. While our initial investigations relied on HHS in gas-phase molecules driven by mid-infrared lasers [Tuthill 2020, Hamer 2021, Tuthill 2022], we have expanded the range of our experimental capabilities to cover XUV attosecond spectroscopy and liquid-phase HHG. Theoretically, we have demonstrated a novel high-harmonic sideband spectroscopy approach for probing the types of periodic CM modes identified in Thrust 1 [Hamer 2022]. At the facility scale, we have been closely involved in a series of experiments in the Attosecond Science campaign at LCLS to measure CM in aminophenol using the XLEAP mode of the LCLS.

Attosecond spectroscopy: To study CM, the OSU node uses short pulses with bandwidths broad enough to probe valence-shell electronic dynamics in molecules. HHG-based attosecond sources, however, can lead to spectral congestion when probing molecules: Each harmonic may produce multiple electronic wave packets (one for each ionization channel) which then overlap energetically with those from adjacent harmonic orders. To reduce the spectral congestion of typical 800-nm sources, the OSU team uses a 400-nm generation field leading to an odd harmonic spacing of 6 eV.

To retrieve the ionization phase, we use the RABBITT technique and add a weak copy of the HHG driving field to the HHG light itself, which produces sidebands in the photoelectron spectrum. Figure 3 shows such a photoionization spectrum in CO_2 produced from 400-nm HHG. With the wide harmonic spacing, we clearly resolve the four highest ionization channels, labeled with arrows, as well as three sidebands.

In Figure 3 we also mark with an orange dash-dotted line the theoretical cutoff, corresponding to $3.17\,U_p + I_p$ photon energy for the 400-nm HHG generated in Neon. We retrieve the ponderomotive energy by fitting our HHG phases, measured with RABBITT, to a strong field-approximation model [Scarborough 2018]. Curiously, our harmonic plateau extends at least 5 eV past the theoretical cutoff, outside of the margin of error for our pondero-

Figure 3: Photoionization spectrum of CO_2 from HHG radiation driven by 400 nm, 2.6×10^{14} W/cm^2, in Neon. The X (red), A (green), B (blue), and C (purple) channels from one high-harmonic (sideband) are labeled by solid (dotted) lines. The dash-dotted orange line shows the theoretical cutoff for the X ionization channel.

motive energy retrieval. Overall, we observe that the HHG light extends beyond 70 eV. This extended plateau will further benefit our attosecond spectroscopy investigations as it will allow us to cover a larger energetic search space and to produce shorter attosecond pulses. One may speculate that the extended plateau is due to generation from the neon cation, known as the ultraviolet surprise [Popmintchev 2015]; however, our extended plateau is below the ionization potential of the neon cation. Alternatively, this may be due to the short driving wavelength for which nonclassical effects are enhanced [Lewenstein 1994]. OSU is currently working to further understand the source of this extended plateau.

Soft x-ray pump-probe at the Linac Coherent Light Source (LCLS): The OSU group has continued its participation in the Attosecond campaign at LCLS ("Real -time Observation of Ultrafast Electron Motion using Attosecond XFEL Pulses" – PIs: J. Cryan, A. Marinelli, and P. Walter) with a third experiment in May 2022
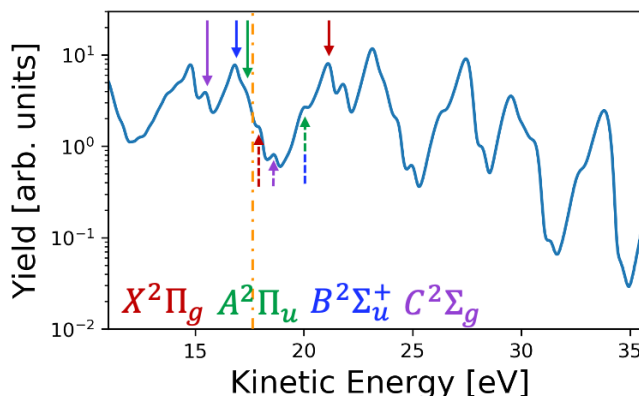
(beamtime LY7220), following their participation in the first two campaigns (beamtimes LV9418 in April 2021 and LW8819 in May 2021). All three experiments aim to directly measure CM in aminophenol using the XLEAP mode of the LCLS, which enables two-color attosecond pump-attosecond probe experiments with isolated soft x-ray pulses [Duris 2020].

The two initial experiments focused on ultrafast charge motion in the para isomer of aminophenol exploiting x-ray absorption spectroscopy (XAS) and x-ray photoelectron spectroscopy (XPS). The XAS technique has revealed a time-dependent absorption signal near 525 eV, slightly below the O K-edge. This matches well with theory simulations of CM in para-aminophenol. The XPS dataset is also under analysis. The most recent experiment investigated CM in the meta isomer to study the effect of molecular linkage on CM.

High-harmonic sideband spectroscopy (HHSS) of charge migration: The LSU node has shown that HHSS is a sensitive probe of CM dynamics in an aligned BrC_4H molecule [Hamer 2022], able to extract both the CM frequency and its second harmonic, and thus the particle-like nature of the dynamics after initiation of a localized hole [Folorunso 2021]. HHSS, as implemented in [Hamer 2022], is based on the beating between the incommensurate frequencies of the CM dynamics ω_{CM}, initiated by a pump laser, and the delayed HHG-driving laser frequency ω_L. It manifests as sidebands in the HHG spectrum and a periodic modulation of the harmonic amplitude and phase. The HHG laser polarization is perpendicular to the molecular backbone to avoid driving the CM signal. In [Hamer 2022] we also showed that HHSS is robust when considering a distribution of alignment angles around perpendicular, as well as a mixture of molecules undergoing CM or not. All calculations are done using TDDFT as implemented in the open-access software Octopus [Tancogne-Dejean 2020]. We have extended this work to focus on the delay-dependent modulation of the harmonic response as it might be implemented in an experiment, for example when tuning the driving laser frequency to $\omega_L = \omega_{CM}/2$, as illustrated in Figure 4. In this frequency-matched configuration, the hole is in the same location along the molecular backbone every half-cycle and any potential aperiodicities in the CM dynamics are averaged out over multiple laser cycles. This leads to improved signal-to-noise in the extraction of CM dynamics from the harmonic amplitudes and phases, and it allows for more flexibility in the HHG-driving-pulse duration in a potential HHSS experiment. This work is ongoing.
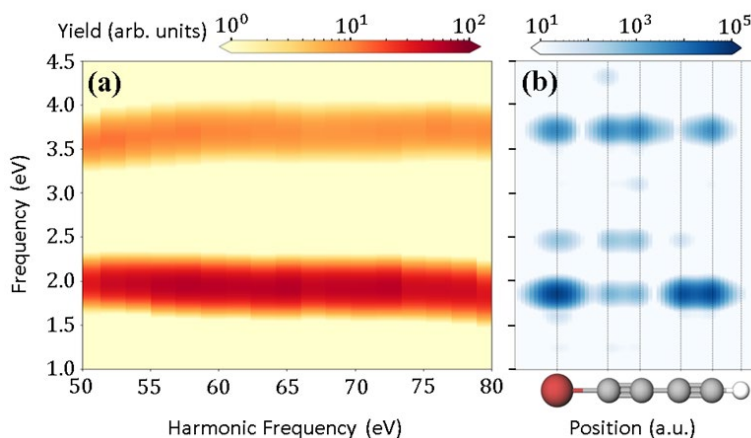

Figure 4: Frequency-domain representation of the CM dynamics: (a) Fourier transform of the collated delay-dependent spectra at 1354 nm, when $\omega_L = \omega_{CM}/2$, vs harmonic energy. (b) Fourier transform of the time-dependent hole density vs position along the molecular backbone.

Liquid high-harmonic spectroscopy: This past year, the liquid harmonics (LHHG) program at OSU has focused on assessing if the harmonic response from solute molecules can be seen in LHHG from a solution mixture, a first step in assessing the fundamental differences between gas-phase and liquid-phase HHG. To this end we have been studying LHHG from solutions of aromatics in isopropanol solvent, using a 1600-nm driving pulse. We chose aromatics as solute molecules for a test case because they have a significantly lower ionization potential than isopropanol and therefore can enhance LHHG at low intensities. So far, our results have indicated that addition of aromatics to isopropanol has little effect on the LHHG spectrum at any intensity

for concentrations below 50%. Figure 5 compares the LHHG yields for two harmonic orders and two aromatic samples. In toluene solutions (left panel), we see little effect on the LHHG yield compared to pure isopropanol below 50% concentration. In fluorobenzene solutions (right), even at 50% concentration we still see little change. Since fluorobenzene interacts more strongly with isopropanol than toluene the difference in the concentration needed to significantly change the LHHG yield points to the importance of intermolecular structure. Our preliminary findings suggest that, at least in polar solvents, it may not be trivial to isolate the solute HHG response from that of the bulk structure.
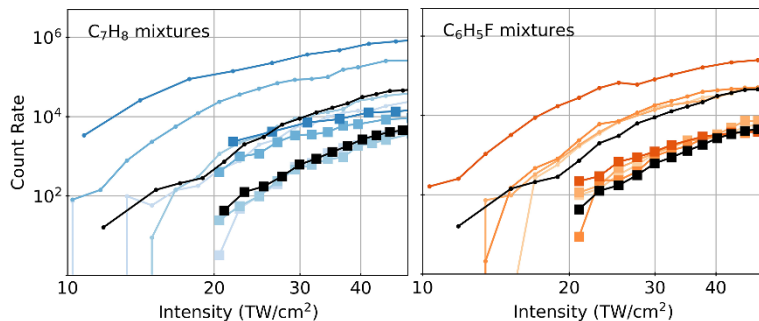

Figure 5: Comparison of experimental liquid HHG yields for orders 17 (dots) and 21 (squares) with various concentration of aromatics in isopropanol. Black curves show the yields with pure isopropanol. Color curves show the yields for the mixtures with the shading labeling the concentration, from 17% (lightest), 33%, 50%, to 100% (darkest) aromatics.

The LSU group has initiated theory studies of LHHG along several different lines, also using Octopus [Tancogne-Dejean 2020]: We are calculating HHG spectra for individual (*i.e.*, gas-phase) molecules that constitute commonly-used solvents and/or solutes, such as benzene derivatives and cyclohexane, and for which some literature data exists for comparison [Alharbi 2015, Wardlow 2016, McGrath 2017], and will next include the molecules being studied at OSU. Our gas-phase results will provide a benchmark for future calculations of HHG from the same molecules in liquid form, when used as either solvents or solutes. We have also initiated studies of liquid-phase laser-matter interaction using the polarizable continuum model (PCM), in which the solvent is considered a continuous polarizable medium characterized by its frequency-dependent dielectric function $\varepsilon(\omega)$ and the solute molecule is hosted by a tight-fitting cavity and treated quantum-mechanically [Mennucci 2012]. The PCM has been extended to treat many different environments, and we are exploring how to use it within Octopus [Delgado 2015] to describe nonlinear laser-driven dynamics.

Thrust 3: Expanding the charge migration toolbox

Our efforts in Thrust 3 focus on the manifold of laser-induced phenomena, including ionization, excitation, and dissociation, that can both initiate CM motion (serving as a "pump") and can be subsequently influenced by CM dynamics (the "probe"). These processes, and what we can learn from them, can be strongly dependent on the relative alignment or orientation of a target molecule relative to the laser polarization. Strong-field ionization is perhaps the most central pump and probe of our CM program, yet highly accurate angle-dependent rates can be difficult and time-consuming to obtain. Accordingly, much of our recent work in this area has centered on developing approximate techniques that can provide angle-dependent strong-field ionization rates with reasonable accuracy at a fraction of the traditional computational cost and then benchmarking those calculations using more accurate numerical methods and experiments.

Angle-dependent strong-field ionization of oriented OCS: The UVA node has measured angle-dependent strong field ionization of OCS using an asymmetric linearly polarized two-color (800-nm+400-nm) laser field and an ensemble of rotationally cooled, but randomly oriented OCS molecules. Due to the strong-field ionization anisotropy, the asymmetric field preferentially ionizes molecules that have particular orientations in the lab frame, relative to the laser polarization. This angle-dependent ionization creates an ensemble of molecular ions with a preferential orientation, characterized by a quasi-coherent superposition of rotational states. The ion rotational wave packet subsequently evolves and exhibits periodic rotational revivals of the initial orientation. The ionization also filters the initially isotropic rotational angular distribution of the neutrals,

effectively creating a hole in the rotational distribution that is characterized by a coherently evolving superposition of neutral rotational states. The neutral rotational wave packet also exhibits periodic orientation revivals. We characterize the post-ionization alignment and orientation of the neutral and ion ensembles using the S^{+3} fragments produced via Coulomb explosion in an intense, time-delayed, 35-fs 800 nm probe. The delay-dependences of the neutral and ion orientation revivals, which peak at different times due to their different rotational constants, reflect the amplitudes of the constituent neutral and ion rotational states in the respective superpositions created by the anisotropic ionization.

To extract the orientation dependence of the strong field ionization process, we use the measured intensity-dependent ionization yield with a trial angle-dependent ionization rate and include (non-ionizing) coherent rotational population redistribution due to stimulated Raman and hyper-Raman processes in the asymmetric field, to compute trial orientation revivals for the neutral and ion. Simulating the rotational dynamics of the ion requires special care. First, due to the coupling of electronic and rotational angular momentum in the ion, the rotational eigenstates and energies differ from those in the neutral. Those differences have a profound effect on the orientational revivals. For example,

Figure 6: (a) Schematic of the model used to compute the ionization-induced orientation revivals for OCS and OCS+. The ionizing field coherently modifies the neutral angular distribution whereas the ion populations created at different times evolve independently. (b) Delay-dependent orientation revival data (dots) and fit (solid line) for OCS and OCS+ probed by Coulomb explosion. (c) Ionization rate vs angle of field relative to molecular dipole moment (integrated over azimuthal angle): (black) extracted from the best fit to the orientation revival structures in (a); (blue) obtained from WFAT calculations; (pink) obtained from TD-DFT calculations.

for the $^2\Pi$ ground state of OCS+, the orientation revival time doubles. Accordingly, upon ionization, the rotational superposition state corresponding to the ionized component of the neutral angular amplitude must first be recast in terms of the rotational states of the ion. In addition, because ionization projects the initial quantum state of the molecule onto an ionic state plus an unmeasured free electron, the molecular ion amplitude created at each instant within the laser pulse has an undefined overall phase. Therefore, it is not coherently connected to the ion amplitude created at any other time. Accordingly, we must independently evolve the ionic rotational wave packets created at each instant throughout the pulse to compute the rotational revival structure for the ions, as illustrated in Figure 6 (a). We adjust the trial ionization rate anisotropy in subsequent calculations to obtain the best simultaneous fit to the neutral and ion orientation revivals. Given the experimental signal to noise, the statistical F-test is applied to determine the number of contributing spherical harmonics that can meaningfully contribute to the best fit anisotropy.

Figure 6 (b) shows the measured and best-fit simulation of the orientation revivals for the neutral and ion at a delay near the second full rotational revival for neutral OCS. The angle-dependent ionization rate corresponding to the simulated revival is shown in black in Figure 6 (c) along with predictions from TDDFT (pink) and WFAT (blue) calculations. The significant differences in the fit and calculated distributions are due primarily to the limited information available from the experiments, with low measurement statistics reducing the
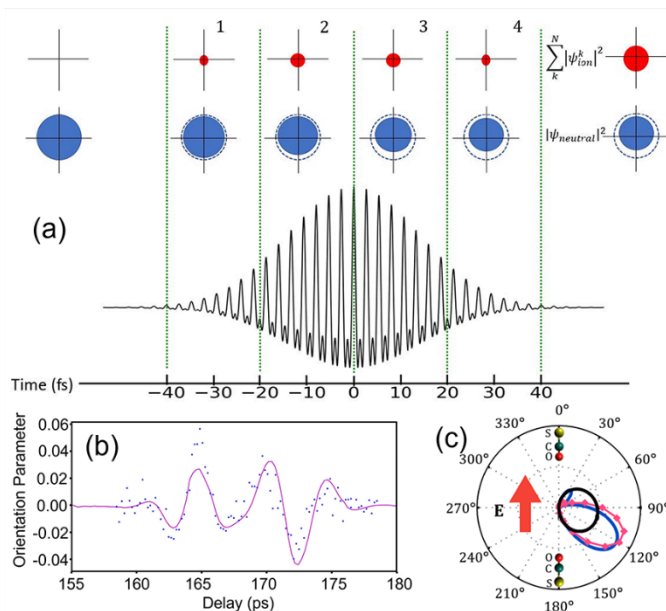
number of meaningful spherical harmonics contributing to the angular structure. Additional measurements might enable a more detailed comparison. However, the current measurements are sufficient to confirm the theoretical prediction that OCS ionizes preferentially when the strong field points from the S to the O atom. This is opposite to the anisotropy reported previously by other groups [Holmegaard 2010].

Weak-field asymptotic theory (WFAT) for ionization simulations: We have developed a DFT-based integral-representation (IR) of many-electron (ME) WFAT from conventional ME-WFAT [Tolstikhin 2014]. We have shown that DFT-based IR-ME-WFAT is an efficient and accurate tool for calculating tunneling ionization (rates and yields in the adiabatic regime) any molecule [Wahyutama 2022].

In our tests, DFT-based IR ME-WFAT can treat multi-electron effects like electron correlation very efficiently, gaining a factor of 100 in computational speed compared to benchmark TDDFT calculations [Wahyutama 2022]. This is because IR ME-WFAT does not require a diffuse basis and does not propagate wave functions or the density in time, which are mandatory ingredients of *ab initio* methods such as the real-time TDDFT. With this efficiency one can use IR-ME-WFAT to quickly scout molecular systems over a large range of parameters. We will use this to screen for candidate for CM-friendly systems over families of molecules. Together with efficiency, we also demonstrated that DFT-based IR ME-WFAT accurately reproduces molecular-alignment dependent ionization as compared with TDDFT [Wahyutama 2022]. This is illustrated in Figure 7 where we see an excellent agreement between the alignment-dependent ionization yields of CH_3Br and CH_3Cl obtained by our method and from RT-TDDFT; we also observed excellent agreement in NO and OCS (not shown). Notably, ME-WFAT yields are in much better agreement with TDDFT and experiment than the one-electron (OE) WFAT calculations, where a single active electron is assumed. We are currently preparing a second manuscript that will outline the complete derivation and analyses of IR ME-WFAT using a general-form wave function. This will enable the extension IR ME-WFAT to multi-configuration methods.
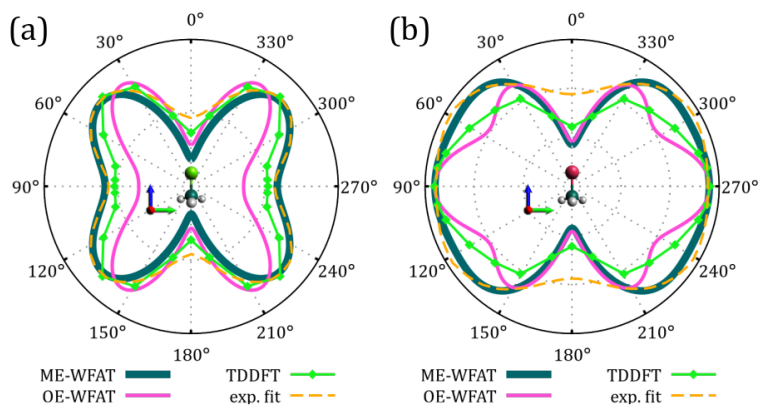

Figure 7: Alignment-dependent ionization yield of (a) CH_3Cl with 64 TW/cm^2 and (b) CH_3Br with 60 TW/cm^2 peak intensity of an 800-nm 37-fs-FWHM pulse. 0° Corresponds to parallel alignment between the laser polarization and molecular C-X bond; the laser is then rotated in the plane of the figure (see inset). Each panel compares the yields obtained with ME-WFAT, OE-WFAT, TDDFT, and experimental measurements from [Sándor 2019].

Frequency-matched ionization (FMI) spectroscopy of charge migration with two-color fields: SFI rates are sensitive to orbital shapes and density distributions, thus a natural question is: can asymmetric two-color ionization be used to measure CM? To answer this, we extended our TDDFT ionization simulations to compute two-color yields as a function of the delay between the initiation of the CM and a two-color ionization probe pulse with the fundamental frequency matching that of the CM. The goal of these studies is to determine how the modulations in the ionization yield can be related to the CM that occurs in the interim.

Our initial FMI studies have focused on bromoacetylene (BrC$_2$H), which we have shown supports CM between the Br and C≡C on a femtosecond time scale [Folorunso 2021], as illustrated in Figure 8 (a). This linear "two site" molecule allows for a simple interpretation of yield modulations in terms of charge densities. Drawing from the attochemistry approach of Thrust 1, we simulate the initial ionization step by creating a local hole on Br with constrained DFT. We then compute the ionization dynamics using real-time TDDFT with

diffuse basis sets, complex absorbing potentials (CAPs), and Koopmans' tuned range-separated exchange-correlation functionals; a procedure we are now well familiar with. We set the two-color ionizing probe field perpendicular to the CM direction to avoid driving the CM. Field-driven CM remains less studied and will be the focus of future work.

Figure 8 (b) shows the result of our FMI simulations in BrC_2H ($\omega_{CM} \approx 2.85$ eV), with the delay-dependent two-color ionizing probe shown in the inset. Compared to panel (a), we clearly see that the $HCCBr^+ \rightarrow HCCBr^{2+}$ yield in (b) oscillates with the same period as the CM. We also see that the ionization yield is highest when the two-color field peaks at the same time as when the hole is on C≡C. This indicates pref-
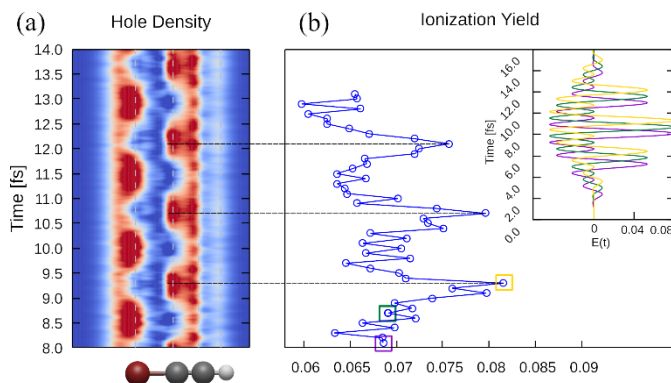

Figure 8: Simulations of FMI spectroscopy of CM in bromoacetylene with a two-color field. (a) Hole dynamics following a sudden ionization on Br. (b) Time-dependent ionization yield as a function of the delay between the CM and a two-color, frequency-matched, pulse (inset) polarized perpendicular to the CM.

erential ionization from the halogen, *i.e.*, ionization is enhanced when the hole is on the triple bond. These results suggest that two-color ionization is a promising probe of CM. We have started investigating how this is related to the hole contrast of Thrust 1 and how robust this effect is for CM-driven and non-frequency-matched cases.

Cross-training and interactions between the network partners

We have maintained continuous communication between all the nodes of the network, including:

- Zoom meetings between all partners, together with frequent, internode email, phone, *etc.* communications between smaller working groups that target specific tasks.
- An intranet website (with content access restricted to members of the ATTO-CM network), featuring results of common interest, all meeting notes, and many relevant papers. The network also has a cloud storage facility to share, archive and back up data.
- In-person ATTO-CM workshop gathering all personnel involved in the collaboration network.

These active exchanges have allowed us to maintain a strong collaborative community among the PIs, students, and postdocs.

ATTO-CM workshop: We have resumed our annual in person ATTO-CM workshop, which took place at OSU on September 26-27, 2022. The workshop included oral presentations from all nodes (PIs, students, and postdocs) of the network. It also featured contributions from three external speakers: Franck Lépine (iLM/CNRS, remotely from Europe), Alexandra Landsman (OSU), and Wen Li (Wayne State University). These external speakers were selected for their expertise in theory/experiments related to ultrafast phenomena in AMO science. The workshop concluded with a PI meeting during which the long-term directions for the network were reaffirmed and the projects for the next 12-to-18 months were refined. The workshop was very successful (a sentiment that was shared by both collaboration members and external visitors) and it will be held again next year, at LSU.

Future Plans

The continued interaction between the three nodes of the ATTO-CM network is a cornerstone of our collaboration. We fully intend to continue our current interactions, *i.e.*, with regular communication (zoom,

emails, shared website, etc.) and exchange visits between the nodes. In what follows, we briefly explain the main avenues we intend to pursue to advance our efforts to coherently probe CM molecules.

Attochemistry regulation of charge migration: LSU will continue its numerical investigations to determine how the chemical properties of a molecule dictate CM dynamics along several avenues: (i) we will study the role of the initial hole on the CM dynamics by using pseudo-halogens, *i.e.*, hole donor groups, instead of halogens; (ii) we will incorporate alternative means of simulating the initial ionization step, including varying the symmetry of the initial hole and directly simulating the laser-field induced ionization step; (iii) in conjunction with simulations of observables (Thrust 2 and Thrust 3), we will determine how the CM hole contrast correlates with the observability of the hole dynamics via HHG and ionization-based probes.

Nonlinear dynamics of charge migration: We will initiate investigations of the effect of nuclear motion on CM. Specifically we will focus on whether nuclear dynamics systematically dooms CM through decoherence or if concerted nucleus-electron CM modes can emerge (as an extension of the attosecond solitons Thrust 1). Building on their success for purely electronic CM modes, we will start these investigations in dimensionally reduced carbon-chains models where only certain bonds (*e.g.*, between the "halogen" and "carbon-chain") are allowed to move and using a semi-classical treatment of nuclear dynamics (Ehrenfest TDDFT).

Attosecond spectroscopy: OSU will study the shape resonance of the C-channel cationic state of CO_2, as a final proof-of-principle for using 400 nm as an HHG driver for attosecond spectroscopy. We will then use sum-frequency of our laser's fundamental 800 nm with the output of an optical parametric amplifier to produce variable wavelengths between 480 nm and 600 nm. While keeping the desired wide harmonic spacing, this will allow us to finely scan the wavelength to increase our spectral resolution [Gorman 2019]. We are also designing an oven for vapor delivery of condensed phase samples to study larger molecules. Combining these efforts, we will study the effect of CM on shape resonance decay in the halogenated benzene series. Based on related species [Despré 2015, Bruner 2017], we expect CM to be present in these molecules. We will use rainbow RABBITT [Gruson 2016] to resolve the decay of the shape resonance in the time domain.

High-harmonic sideband spectroscopy: LSU will explore the extent to which HHSS can be used to map the sub-cycle dynamics of the CM, by taking advantage of the large amount of information contained in the harmonic-energy dependence of the CM probe. For instance, we will explore whether the ionization and rescattering steps of HHG are sensitive to different characteristics of the CM dynamics.

Liquid high-harmonic spectroscopy: OSU will do further studies of aromatic mixtures for LHHG. We will study the aromatic-isopropanol mixtures at higher aromatic concentrations (>50%) to determine when the LHHG of fluorobenzene mixtures deviate from that of pure isopropanol. We will further investigate the importance of intermolecular structure to HHG in mixtures by using n-hexane in place of isopropanol, since this will put the aromatics on equal footing with regards to interactions with the solvent. LSU will calculate HHG spectra from these molecules in the gas-phase. For liquid phase dynamics, LSU will start by calculating the linear and low-order nonlinear response of benzene derivatives within the PCM.

Frequency-matched ionization (FMI) spectroscopy: Previously, the UVA and OSU nodes worked together to perform initial experiments exploring the use of FMI Spectroscopy to detect CM in singly-ionized halogenated hydrocarbon rings, as predicted by TDDFT calculations performed at LSU. Here, the principal concept of FMI spectroscopy is to use strong field ionization, within a single laser pulse, to both create a localized hole and probe the time-dependent modulations in electron density via a second ionization event.

We are currently preparing for next generation FMI experiments based on our preliminary results. First, we will employ ionizing pulses that can allow for FMI in systems with longer CM periods or where the temporal separation between laser field maxima is an integer (or half-integer) multiple of the CM period. We will use a hollow core fiber to broaden the spectrum of our Ti:Sapphire laser pulse, and use spectral filters to create two color fields with tunable central wavelength. Second, we will take advantage of fragment momentum imaging detection to identify molecular fragments, produced through double ionization, that are aligned

perpendicular to the ionizing field, allowing us to focus on molecules for which the CM motion along the primary molecular axis is not significantly influenced by the strong, perpendicular ionizing field.

Strong-field processes with oriented molecules: THz driven field-free molecular orientation has a distinct advantage over optical methods utilizing hyper-Raman transitions in two-color laser fields in that the molecules are not vibrationally or electronically excited (or ionized) by THz pulses. A recent theoretical paper [Tutunnikov 2022] has predicted that substantial orientation can be achieved in room temperature samples using a slightly modified approach to the one previously demonstrated at UVA. We are currently preparing experiments to test the effectiveness of the predicted "orientation echo" technique as a function of rotational temperature. If successful, the method could enable an important class of experiments involving HHS from oriented molecules and will be tested on a HHG beamline at OSU.

Frequency-matched ionization spectroscopy of charge migration: LSU will continue its efforts to simulate two-color ionization using TDDFT and to support two-color measurements at UVA with the computation of angle-, phase-, and intensity-dependent ionization yields. In that vein, we will investigate how two-color ionization can be used to probe CM. Our promising initial results demonstrate that ionization yields are substantially modulated by the location of the hole in the molecule. However, some questions remain concerning the sensitivity and robustness of this effect. To address this, we will determine how the two-color ionization yields vary with the intensity, wavelength, and polarization of the laser.

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[Folorunso 2021] A.S. Folorunso, A. Bruner, F. Mauger, K.A. Hamer, S. Hernandez, R.R. Jones, L.F. DiMauro, M.B. Gaarde, K.J. Schafer, and K. Lopata, "Molecular Modes of Attosecond Charge Migration," Phys. Rev. Lett. 126, 133002 (2021)

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Transient Absorption and Reshaping of Ultrafast Radiation

DE-SC0010431

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Project Scope

Our program is centered on the theoretical study of transient absorption and reshaping of ultrafast extreme ultraviolet (XUV) or X-ray pulses in their interaction with matter. The program emphasizes both fundamental theoretical research [1] and a close connection with experimental groups doing attosecond physics [2–4], [R1-R5]. 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) [5] [R2,R4-5], and through propagation of the emitted radiation in the non-linear medium via the Maxwell wave equation (MWE) [R3]. Although the majority of the system we have considered are rare-gas atoms, we have also recently considered attosecond transient absorption and reflection in condensed phase systems [R1].

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 [R2-R5], [2–4].

(i) Linear and nonlinear reshaping of intense XFEL pulses in rare gases: We have studied the spectral, temporal, and spatial reshaping of intense ultra-short X-ray pulses as they propagate through a neon gas at atmospheric density or above. We study the case in which the X-ray energy is resonant with a core-to-valence transition in the neutral atom, and where transitions between the highly excited core-hole state and several valence-excited states in lead to both X-ray stimulated Raman scattering (XSRS), X-ray lasing (XRL) along with the resonant free-induction decay (FID). This work is done in collaboration with the Young experimental group at Argonne National Lab [R3]. At the theory level, we couple our 3D, cylindrical-symmetry MWE solver to a calculation of the microscopic laser-matter interaction described in terms of few-level systems [R3]. The spatiotemporal profile of the laser pulse is updated after every propagation step with the source terms resulting from the microscopic calculations, providing a real-time evolution in space and time [5].

Several experimental XFEL campaigns have been carried out in 2022, focused on characterizing the reshaping of X-ray pulses by dense gases. In February 2022, Dr. Young was PI of an EU-XFEL campaign to measure the spectral characteristics of the X-ray pulse before and

after interacting with a dense neon or xenon gas. In this campaign, both XRL and XSRS were observed and can be directly compared with simulations as described above, when using SASE input pulses in the calculation rather than isolated attosecond or few-femtosecond pulses. These simulations are individually and collectively time consuming because of the total duration of the SASE pulses and their statistical nature which has to be averaged out through many simulations. Several publications are expected to result from this campaign.

In August 2022, Dr. Siqi Li from SLAC was PI on an LCLS campaign to characterize the temporal structure of attosecond XFEL pulses from the XLEAP before an after interaction with a dense neon gas. The results from this campaign are still under analysis.
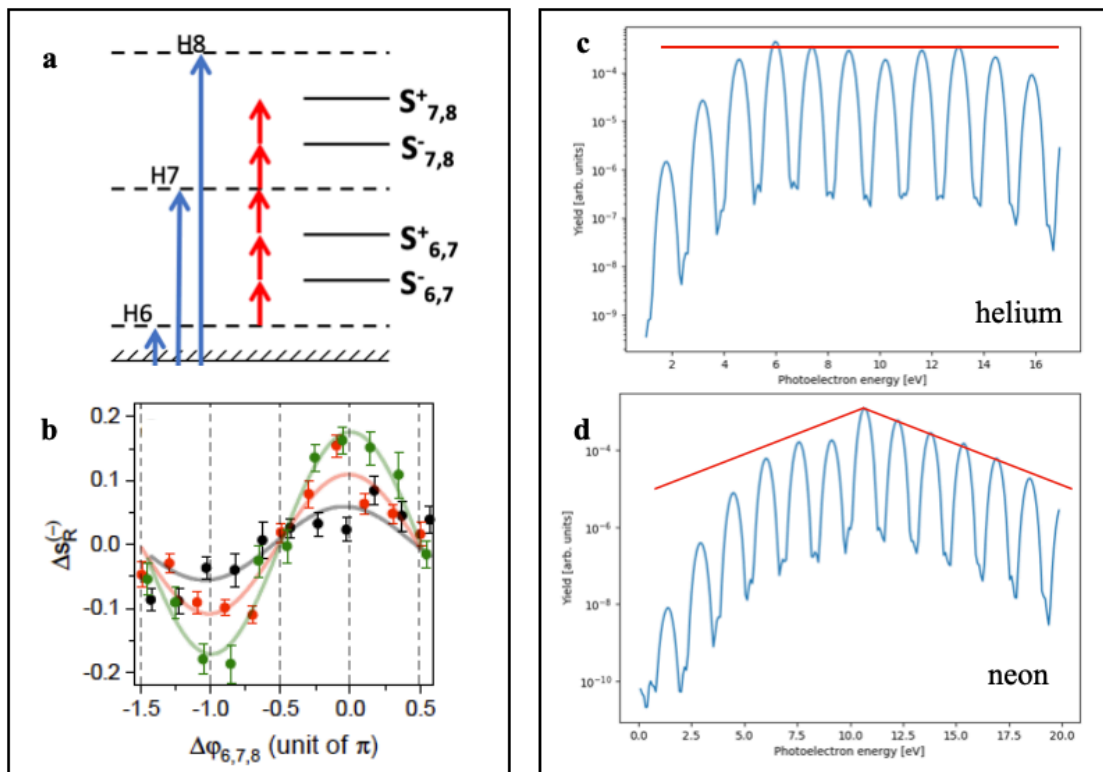

Figure 1: (a) Schematic for probing the intensity dependence of multi-NIR-photon transitions on the oscillations of sidebands $S_{7,8}^{\pm}$. (b) TDSE calculations for the normalised variation of the amplitude $\Delta s_R^{(-)}$ for NIR intensities 1.2, 2.7, and 4.4 TW/cm^2 as a function of the phase difference $\Delta\varphi_{6,7,8}$. (c,d) Photoelectron spectra for a single XUV photon in the presence of an 8 TW/cm^2 NIR field. The XUV photon results in an electron with energy ~ 10 eV.

(ii) Characterization of temporal structure of XUV FEL pulses: The seeded FEL facility FERMI in Trieste, Italy generates high intensity, XUV attosecond pulse trains (APT) that have programmable, reproducible wave forms. In collaboration with the Sansone (U. Freiberg) and Mauritsson (Lund U.) experimental groups we have investigated the characterization of XUV APTs produced at FERMI. Because FERMI is seeded by the third harmonic of an IR laser, the harmonics that make up the APT are spaced by three IR photons. This presents a challenge when characterizing the temporal structure of the XUV pulses, and when determining the shot-to-shot delay between the XUV pulse train and an

accompanying NIR laser field. Having demonstrated a novel timing tool that works by correlating the two NIR sidebands that appear between each pair of XUV harmonics[R4-5], this year we have been involved in the first application of of this tool to study attosecond coherent control of electronic wave packets in two-color photoionization [3]. Figure 1(a) presents a schematic of the experiment in which the sidebands appearing between harmonics 7 and 8 are modulated by changing the phase of the 6th harmonic, which falls just above threshold in helium. Fibure 1(b) shows TDSE calculations of the amplitude modulation of the $S_{7,8}^{(-)}$ sideband as a function of the phase added to harmonic 6. These results, which are in excellent agreement with measurements (not shown) verify that we are able modify the phase of a specific quantum path by selectively acting on the phase of a single XUV harmonic. This is not possible in laser-driven high harmonic generation, where the harmonic phases are not individually addressable. Our TDSE calculations also support that the accuracy with which the XUV-NIR delay can be measured with the novel timing tool is one atomic unit, or 24 attoseconds.

(iii) Resonant perfect absorption of XUV zero-area pulses: The group of Drs. Ott and Pfeifer at the Max Plack Institute in Heidelberg, Germany have recently proposed that an XUV light pulse could be (nearly) perfectly extinguished on resonance [2]. Their scheme works by taking advantage of the combination of temporal reshaping in a macroscopic medium and a delayed infrared pulse which abruptly ends the absorption process by depletion of the ground state, leading to the formation of a zero-area XUV pulse. Our group has contributed large-scale numerical simulations based on the coupled solution of the TDSE (for He atoms, in the single-active-electron approximation) and the MWE, as described in [5], as a supplement to the model calculations shown in the manuscript. This work is currently under review [2].

Future Plans

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

(i) Propagation and reshaping of intense X-ray pulses This work is ongoing, both in terms of systematic calculations for comparison with experimental data, and in terms of analysis of experimental data.

(ii) Complex XFEL waveforms: Continuing our work with the Sansone group using XUV pulses from FERMI, we will continue to collaborate on analyzing recent data on the continuum phase of two IR photon emission/absorption near the ionization threshold of an atomic system. We know from previous work comparing TDSE results to strong field approximation (SFA) simulations that these phases contribute non-trivial effects near threshold [R4] and measuring this effect will be the focus of this. There is the tantalizing suggestion that the continuum phases may show the effect of counter-rotating terms in the two-color XUV+NIR absorption.

We are also pursuing calculations and hopefully experiments using a single XUV harmonic that launches an electron wave packet close to threshold in a rare gas atom. TDSE calculations in Figures 1(c,d) show that there is a notable difference in the photoelectron spectra of different atomic targets when an NIR field is present. This difference is not found at very low intensities, but becomes pronounced at intermediate intensities of a few TW/cm^2. This difference is not found in SFA or "soft photon" calculations that do not take account

of the atomic potential.

(iii) Perfect absorption of zero-area pulses A graduate student from the Ott group at MPI Heidelberg will visit LSU in early 2023, to be trained in the use of our TDSE-MWE code and study how the interaction between space and time influences the formation of the zero-area pulses.

(iv) Condensed-phase ATA: We will be implementing a simple description of laser-exciton dynamics into our coupled TDSE-MWE code. This will be one of the main tasks of a new postdoc arriving in early 2023.

Peer-Reviewed Publications Resulting from this Project (2020-2022)

R1 R. Geneaux, C. J. Kaplan, L. Yue, A. D. Ross, J. E. Bækhøj, P. M. Kraus, H.-T. Chang, A. Guggenmos, M.-Y. Huang, M. Zürch, K. J. Schafer, D. M. Neumark, M. B. Gaarde, and S. R. Leone, *Attosecond time-domain measurement of core-excitonic decay in MgO*, Phys. Rev. Lett. **124**, 207401 (2020)

R2 P. Maroju *et al.*, *Attosecond Pulse-shaping using a seeded Free Electron Laser*, Nature **578**, 386 (2020)

R3 K. Li, M. Labeye, P. Ho, M. B. Gaarde, and L. Young, *Resonant propagation of x-rays from the linear to the nonlinear regime*, Phys. Rev. A **102**, 053113, (2020).

R4 P. Maroju *et al.*, *Analysis of two-color photoelectron spectroscopy for attosecond metrology at seeded free-electron lasers*, New J. Phys. **23**, 043046 (2021).

R5 P. Maroju *et al.*, *Complex attosecond waveform synthesis at FEL Fermi*, Appl. Sci. **11**, 9791 (2021).

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Structural Molecular Dynamics Using Ultrafast Gas X-Ray Scattering

Award # DE-SC0017995

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I. Project Scope

Understanding the structures and chemical dynamics of molecules in their excited states is of great importance for basic energy science and myriad applications within and outside of chemistry and related molecular sciences. This project develops two experimental tools and applies them to explore both the *nuclear dynamics*, i.e. the geometrical arrangement of atomic nuclei in molecules, and *electron dynamics*, i.e. the time evolution of electron probability density distributions during chemical reactions. The experimental approach focuses on ultrafast time resolved gas phase X-ray scattering, which is pursued at the LCLS light source at SLAC National Accelerator Laboratory. The X-ray scattering experiments are prepared and complemented by time-resolved Rydberg fingerprint spectroscopy experiments, which are conducted at Brown University. Both methods are sensitive to the structures of molecules in excited states with a time resolution of <100 fs. Because the experimental methods are complementary, their coordinated application to the same systems provides deeper insights into the molecular dynamics than each technique would give in isolation.
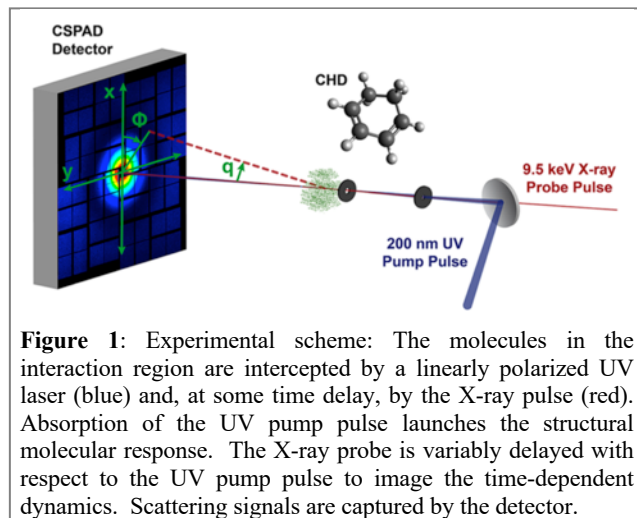
The experiments explore molecular phenomena associated with the nuclear and electron structural dynamics of molecules during reactions. This includes the motions through conical intersections, charge delocalization, the fracture of chemical bonds, vibrational motions and the propagation and spreading of wave packets. Model systems for those investigations include medium-sized organic systems such as cyclohexadiene, trimethyl amine, N-methylmorpholine, N,N-dimethylpiperazine, and 1,2-dithiane. Those systems are deliberately chosen to broaden the investigations beyond standard prototypes. By focusing on structurally well-defined molecules, the project advances our knowledge of molecules in excited electronic states and their chemical reaction dynamics. This aids numerous applications and provides benchmark data that support the continued development of computational methods.

II. Recent Progress

Successful beam times at LCLS have resulted in important advances as reported previously:

- We have expanded our list of molecules for which we studied the ultrafast molecular dynamics by adding cyclopentadiene and quadricyclane to the previous roster that included 1,3-cyclohexadiene, trimethyl amine, N-methyl morpholine and dimethyl piperazine.

- We have measured complete, time-dependent excited state structures of these polyatomic molecules. The structures so obtained are largely experimental, with only the electronic correction terms derived from theory.

- We learned how to determine the spatial orientation of transition dipole moments within the molecular frame from the anisotropy of the pump-probe scattering patterns.

- We worked with our collaborators to develop codes to calculate the total scattering signal from molecules in excited states.

- We uncovered how the passage through conical intersections in 1,3-cyclohexadiene is affected by the initial excitation energy. Subsequent experiments on cyclopentadiene further explore the dependence of the reaction paths on the optical excitation wavelength.

- We disentangled the contributions of electronic and nuclear geometry changes to the x-ray scattering patterns.

Figure 1: Experimental scheme: The molecules in the interaction region are intercepted by a linearly polarized UV laser (blue) and, at some time delay, by the X-ray pulse (red). Absorption of the UV pump pulse launches the structural molecular response. The X-ray probe is variably delayed with respect to the UV pump pulse to image the time-dependent dynamics. Scattering signals are captured by the detector.

The general principle of these experiments is shown in Figure 1: the molecules are excited by an optical laser pulse to an excited state, a process that initiates the reaction. The time-evolving molecular structures are probed by scattering an X-ray pulse that arrives a short time after the excitation pulse. The scattering pattern is measured on the detector, and its analysis leads to the structure as a function of time. By sequencing the time-dependent molecular structures we obtain a 'molecular movie' showing the motions of atoms while reactions proceed.

X-Ray Scattering Beyond the Independent Atom Model

The quality of the x-ray scattering data obtained at the CXI endstation is outstanding. As a result, we are now sensitive to small deviations of the measured signals from the almost universally used independent atom model (IAM).

In the IAM, each atom is deemed independent of the other atoms in the molecule. Thus, the molecular electron density is taken to be a combination of atomic electron densities, centered at the positions of nuclei. For rotationally isotropic samples, the IAM total scattering equation is written as

$$F_{\text{total}}^{\text{IAM}}(q) = \frac{d\sigma_{Th}}{d\Omega} \cdot \left(\sum_{i,j}^{N_{\text{at}}} f_i^0(q) f_j^0(q) \frac{\sin q R_{ij}}{q R_{ij}} + \sum_i^{N_{\text{at}}} S_{\text{inel},i}^0(q) \right),$$

where the pairwise sum stretches over all atoms with relative positions R_{ij}, and $f_i^0(q)$ and $S_{\text{inel},i}^0$ are the elastic and inelastic tabulated atomic form factors, respectively, for the i_{th} atom. While the IAM takes reasonable consideration of the atomic positions in a molecule, the total x-ray scattering signal is intrinsically a property determined by electron density and electron correlation. High quality scattering patterns obtained at LCLS now offer an opportunity to disentangle the approximations inherent in the IAM model used for conventional x-ray studies and offer the opportunity to directly measure the effects of one- and two- electron densities.

The successes and failures of the IAM are apparent in the experimental data, shown as a preliminary analysis in Figure 2. The IAM model predicts the oscillations of the scattering signal nicely, but only in a qualitative way. Electron wavefunctions obtained from DFT calculations yield a much-improved approximation, but it truly requires *ab initio* calculations to reproduce the experimental patterns.

These results demonstrate the exceptional quality of the experimental scattering patterns obtained at CXI. They also show that to model scattering signals of excited and transient molecular states, account must be taken of electron density distributions – as was done in our development of the structural movies. Going forward, it will be rewarding to see is experimental electron density distributions can be determined based on the measured, time-dependent scattering signals.

Conformational Dynamics in N-Methyl Piperidine

In the lab at Brown University, we continue to screen molecular systems for suitable candidates for x-ray and electron scattering experiments. A particularly interesting candidate for future experiments is the N-methyl piperidine C_6NH_{13} (NMP) system. As the related N-methyl morpholine system, which we have investigated in great detail using x-ray scattering, upon excitation NMP undergoes structural oscillations that are observed in the Rydberg electron binding energy (Figure 3). The NMP system is intriguing because it appears that as these structural oscillations centered at the amine group dephase, the molecule can reach a twisted ring structure. The evidence for this is faintly seen in the binding energy distributions of the Rydberg state, but much clearer evidence should come from scattering experiments.

Figure 2: Top: Preliminary analysis of the comparison between experimental and theoretical scattering patterns for quadricyclane C_7H_8 (inset: enlarged scale). Ab initio and DFT: theoretical total x-ray scattering patterns calculated by *ab initio* (CASSCF(2,2)/6-311G) and DFT (B3LYP)/6-311G) electron density distributions. IAM: theoretical total X-ray scattering pattern calculated with the tabulated X-ray atomic form factors and incoherent scattering functions of the elements within the independent atom model approximation. Structural effects: the bandwidths of possible deviations caused by structural effects. Bottom: the percent difference between theoretical and experimental scattering patterns.

In an upcoming MeV beamtime, we plan to perform electron scattering experiments on this system to determine the time-dependent distribution between chair and twisted structures.

Other Endeavors

A rigorous understanding of x-ray scattering is essential for the interpretation of scattering signals from transient and short-lived molecular species. We are collaborating with Prof. A. Kirrander and his team on the development of scattering theory and have written a book chapter, to be published, on the quantum electrodynamic treatment of x-ray scattering.

We have applied the Rydberg photoionization methodology to identify molecular species in flames. The Rydberg spectroscopy is attractive because it can be applied to very hot molecular species, as long as their structural dispersion is reasonably small. This is the case for a dimethyl butane flame, in which we selectively identified 2,3-dimethylbut-2-ene as a transient species in the combustion pathway.

Finally, we have data of x-ray scattering signals at intensities some 2 orders of magnitude higher than we previously used and we are analyzing the results.
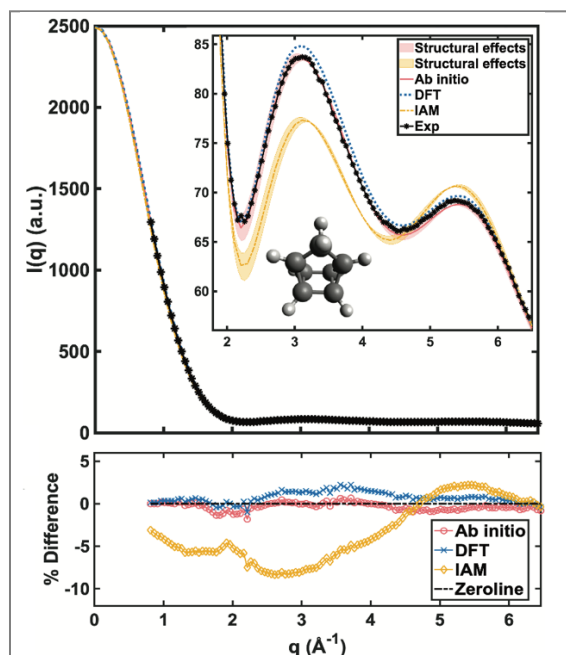
III. Future Plans

We are continuing to analyze data sets obtained at several LCLS beam times. Specifically, we have interesting data on the cyclopentadiene system and are collaborating with Prof. D. Rolles's group on the analysis of quadricyclane and norbornadiene scattering data. In the lab at Brown University, we are conducting photoelectron experiments on these systems to complement the scattering experiments. In particular we hope that time-resolved photoelectron spectra will clarify the reaction pathway of the cyclopentadiene system. In the lab at Brown, we are also constructing a new photoelectron spectrometer with capabilities to match those anticipated for scattering experiments with the future LCLS-II-HE, in particular as it relates to time resolution.

We had an MeV electron scattering beam time scheduled for the summer of 2022, but unfortunately that had to be delayed into the winter. We hope/anticipate that the beam time will take place in December 2022. Once we have new MeV electron scattering data, we will explore to what extent the analysis methods we have developed for x-ray scattering can be applied to electron scattering. In the upcoming year we will also participate in beam times with Prof. D. Rolles at the European XFEL and FLASH.
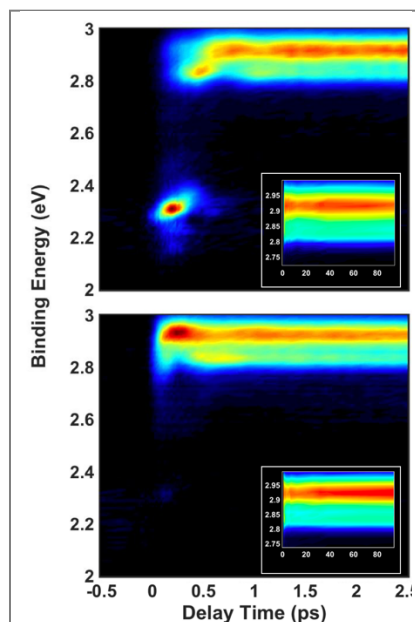

Figure 3: Time-resolved photoelectron spectra of NMP upon 212 nm (top) and 229 nm (bottom) excitation. The insets show the 3s state signals up to 100 ps.

Finally, we will continue working with Prof. A. Kirrander on the theory of x-ray scattering and we will update the scattering cell design that is widely used at the CXI endstation of LCLS.

IV. Peer-Reviewed Publications resulting from this Project (2020-2022)

1. "Observation of the molecular response to light upon photoexcitation" Haiwang Yong et al., *Nature Communications*, 11, 2157 (**2020**). DOI 10.1038/s41467-020-15680-4.
2. "Ultrafast X-ray and Electron Scattering of Free Molecules: a Comparative Evaluation" L. Ma et al, *Structural Dynamics*, **7**, 034102 (**2020**); PMCID: PMC7316516; https://doi.org/10.1063/4.0000010.
3. "Advances in Ultrafast Gas-Phase X-ray Scattering," B. Stankus et al., *J. Phys. B., Atomic, Molecular & Optical Physics*, 53, 23 (**2020**). https://dx.doi.org/10.1088/1361-6455/abbfea.
4. "Determination of Excited State Molecular Structures from Time-Resolved Gas-Phase X-Ray Scattering," H. Yong et al., *Faraday Discussions*, **2021**, 228, 104 – 122. 10.1039/D0FD00118J.
5. "Ultrafast X-Ray Scattering Offers a Structural View of Excited State Charge Transfer," H. Yong et al., *PNAS* 118 (19) e2021714118, **2021**. DOI: 10.1073/pnas.2021714118.
6. "Ultrafast Conformational Dynamics of Rydberg-excited N-Methyl Piperidine," Wenpeng Du, Yan Gao, Brian Stankus, Xuan Xu, Haiwang Yong and Peter M. Weber, *Physical Chemistry Chemical Physics*, **2021**, 23, 27417 - 27427, DOI: 10.1039/D1CP04236J
7. "Transient Symmetry Controls Photo Dynamics near Conical Intersections," Max D.J. Waters, Wenpeng Du, Andres Moreno Carrascosa, Brian Stankus, Martina Cacciarini, Peter M. Weber and Theis I. Sølling, *J. Phys. Chem. Lett*. **2021**, 12, 9220−9225. DOI: 10.1021/acs.jpclett.1c02334
8. "Conformational diversity of 1-phenylpiperidin-4-one in the gas phase," Alexey V. Eroshin, Tran Dinh Phien, Peter M. Weber and Sergey A. Shlykov, *Chemical Physics Letters*, Volume 803, 139851 (**2022**). DOI 10.1016/j.cplett.2022.139851
9. "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.

Combining High Level *Ab Initio* Calculations with Laser Control of Molecular Dynamics (DE-FG02-08ER15983 & DE-FG02-08ER15984)

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1 Project Scope

We use intense, shaped, ultrafast laser pulses to follow and control molecular dynamics and high level *ab initio* calculations to interpret the dynamics and guide the control.

2 Recent Progress

Our scientific focus over the past year has been on coupled electron-nuclear dynamics and correlated electron dynamics in small organic molecules. In the past year we have made significant progress on multiple fronts:

2.1 Excited State Dynamics in Conjugated Systems

A particular focus of the work is combining theory with experiment, where the theory simulates the observables directly and compares to spectra. We have applied time resolved photoelectron spectroscopy (TRPES) measurements and simulations obtained from trajectory surface hopping (TSH) calculations for several molecules in the past, and were able to interpret their dynamics and get important insight about the molecules and the techniques. The most important insights have been compiled in a recent feature article. A comparison of the calculated and measured TRPES signals shows that while our calculations agree qualitatively with the measurements, they do not agree quantitatively on the timescale for decay of the photoelectron signal. We are currently working on understanding this discrepancy, and also carrying out an analysis of UED measurements of the same dynamics. The UED measurements and analysis are carried out in collaboration with the group of Martin Centurion at the University of Nebraska.

2.2 Fourfold Covariance Velocity Map Imaging of Coulomb Explosion

Coulomb explosion imaging (CEI) holds the promise of being a powerful tool for studying ultrafast structural changes in molecules. In order to record all fragment ions from a given explosion event and reconstruct the molecular frame without confusing fragments from different molecules, the measurements are usually carried out by measuring the fragment ions in coincidence, with less than one molecule ionized per laser shot. This can be very time consuming and limits the application of the technique. Covariance measurements allow for much higher count rates (about two orders of magnitude higher), but have so far only been demonstrated for three or fewer particles. In the past year, we have extended covariance measurements to 4 or more particles, and demonstrated our approach on the coulomb explosion imaging of formaldehyde with 6 and 30 fs laser pulses. Figure 1 illustrates this comparison by showing molecular frame covariance measurements for the two different pulse durations.

2.3 Strong Field Molecular Double Ionization

In the past year, we carried out two studies of the strong field double ionization of formaldehyde. One study focused on the surprising production of a stable excited state of the molecular dication, and made use of detailed calculations and measurements in concert. Another study determined the state resolved double ionization yields of formaldehyde by comparing the measured kinetic
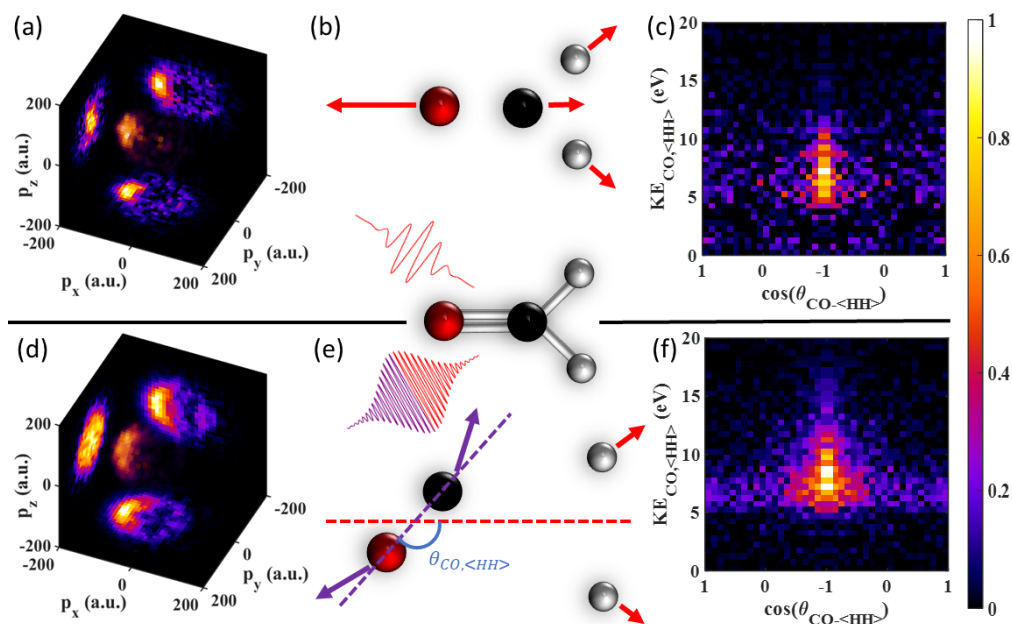
Figure 1: Comparison of CEI with 6 fs 1300 TW/cm² pulses and 30 fs 240 TW/cm² pulses using fourfold covariance velocity map imaging. Panels (a) and (d) show 3D histograms of the O^+ momentum distribution in the molecular frame. Panels (b) and (e) depict possible dynamics of concerted and sequential breakup of the molecule by a short (6 fs) or long (30 fs) pulse. The laser pulse and momentum vectors of the four fragments are are also colored to indicate the time ordering of the breakup process. Panels (c) and (f) show a native frames analysis of panels (a) and (d) by correlating dissociation energy of the CO^{2+} fragment and the native frame angle (CO/ <HH>), assuming the two H^+ ions leave first. The angle axis is mirrored to put the main distribution in the center.

energy release (KER) for different channels with the calculated KER. The measurements made use of covariance velocity map imaging, and the calculations made use of trajectory surface hopping calculations on the first few states of the molecular dication. Figure 2 summarizes our important results on formaldehyde. We believe that this approach of measuring and calculating the differential yield can serve as a powerful tool for understanding strong field molecular ionization.

3 Future Plans
We have several goals for the immediate future:

1. Complete our analysis of the UED measurements for COD to form a complete picture of the excited state dynamics. Extend our TRPES measurements to include 200 nm pump pulses for direct comparison with the UED measurements.

2. Perform pump probe measurements of the dynamics in the formaldehyde dication to study many of the dynamics predicted by the TSH calculations, including the stable parent dication formation on S_1 and the concerted elimination of H_2^+.

3. Interpret the formaldehyde strong field double ionization measurements for both 5 and 30 fs laser pulses with the dynamics calculations in order to obtain a molecular frame, state resolved picture of the strong field double ionization, including non-adiabatic dynamics in the dication.
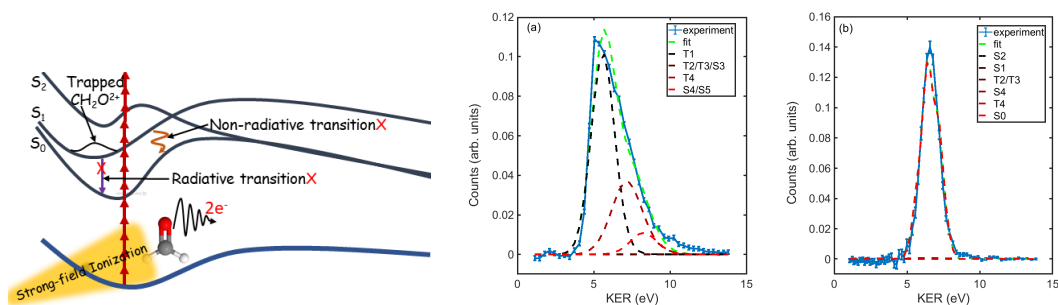
Figure 2: Left: Cartoon of the PES in formaldehyde dication showing how the first excited state has been calculated to be stable with no radiationless decay or fragmentation. Right: Covariance KER spectrum for O^+/D_2C^+ (a) (D^+/DCO^+ in (b)) fitted with calculated KER for different groups of dicationic states using TSH. The blue solid line is the experimental result with error bars computed using a bootstrapping analysis. The green dashed line is the overall fit result. The other dashed lines are individual states' KER distribution weighted by their fit coefficients. Measurements were performed with 6 fs pulses having a peak intensity of 750 TW/cm^2.

4. Perform four particle electron-ion covariance measurements to probe strong field double ionization.

5. Perform TSH dynamics in other molecules in order to understand how low frequency degrees of freedom affect excited state dynamics.

4 Peer-Reviewed Publications Resulting from this Project (2020-2022)

- "The Generality of the GUGA MRCI Approach in COLUMBUS for Treating Complex Quantum Chemistry", Hans Lischka et al., *J. Chem. Phys.*, **152**, 134110, (2020)

- "Excited State Dynamics of cis,cis-1,3-Cyclooctadiene: UV pump VUV Probe Time Resolved Photoelectron Spectroscopy" Yusong Liu, Pratip Chakraborty, Spiridoula Matsika and Thomas Weinacht. *J. Chem. Phys.*, **153**, 074301 (2020)

- "Excited State Dynamics of cis,cis-1,3-Cyclooctadiene: Non-adiabatic Trajectory Surface Hopping" Pratip Chakraborty, Yusong Liu, Thomas Weinacht, Spiridoula Matsika. *J. Chem. Phys.*, **152**, 174302 (2020)

- "Spectroscopic and structural probing of excited state molecular dynamics with time-resolved photoelectron spectroscopy and ultrafast electron diffraction" Yusong Liu, Spencer Horton, Jie Yang, J. Pedro F. Nunes, Xiaozhe Shen, Thomas J. A. Wolf, Ruaridh Forbes, Chuan Cheng, Bryan Moore, Martin Centurion, Kareem Hegazy, Renkai Li, Ming-Fu Lin, Albert Stolow, Paul Hockett, Tamás Rozgonyi, Philipp Marquetand, Xijie Wang, and Thomas Weinacht *Phys. Rev. X*, **10**, 021016, (2020)

- "Simultaneous Observation of Nuclear and Electronic Dynamics by Ultrafast Electron Diffraction", Jie Yang, Xiaolei Zhu, J. Pedro F. Nunes, Jimmy K. Yu, Robert M. Parrish, Thomas J. A. Wolf, Martin Centurion, Markus Guhr, Renkai Li, Yusong Liu, Bryan Moore, Mario Niebuhr, Suji Park, Xiaozhe Shen, Stephen Weathersby, Thomas Weinacht, Todd J. Martinez, Xijie Wang *Science*, **368**, 886, (2020)

- "Angle-dependent strong-field ionization and fragmentation of carbon dioxide using rotational wave-packets" Huynh Lam, Suresh Yarlagadda, Anbu Venkatachalam, Tomthin Nganba Wangjam, Rajesh K. Kushawaha, Chuan Cheng, Peter Svihra, Andrei Nomerotski, Thomas Weinacht, Daniel Rolles and Vinod Kumarappan. *Phys. Rev. A*, **102**, 043119, (2020)

- "Momentum-Resolved Above-Threshold Ionization of Deuterated Water" Chuan Cheng, Ruaridh Forbes, Andrew J. Howard, Michael Spanner, Philip H. Bucksbaum and Thomas Weinacht. *Phys. Rev. A*, **102**, 052813 (2020)

- "Effect of Dynamic Correlation on the Ultrafast Relaxation of Uracil in the Gas Phase", Pratip Chakraborty, Yusong Liu, Thomas Weinacht, and Spiridoula Matsika, *F*araday Disucssions, **228**,266, (2020)

- "Time resolved photoelectron spectroscopy as a test of electronic structure and nonadiabatic dynamics", Pratip Chakraborty, Yusong Liu, Samuel McClung, Thomas Weinacht and Spiridoula Matsika. *J. Phys. Chem. Lett.* 12,21,5099-5104 (2021)

- "Strong-field ionization of water. II. Electronic and nuclear dynamics en route to double ionization" Chuan Cheng, Zachary L. Streeter, Andrew J. Howard, Michael Spanner, Robert R. Lucchese, C. William McCurdy, Thomas Weinacht, Philip H. Bucksbaum, and Ruaridh Forbes. *Phys. Rev. A*, **104**, 023108 (2021)

- "Multi-Particle Three-Dimensional Covariance Imaging: "Coincidence" Insights into the Many-Body Fragmentation of Strong-Field Ionized D_2O" Felix Allum, Chuan Cheng, Andrew J. Howard, Philip H. Bucksbaum, Mark Brouard, Thomas Weinacht, and Ruaridh Forbes. *J. Phys. Chem. Lett.*, **12**, 8302 (2021)

- "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)

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