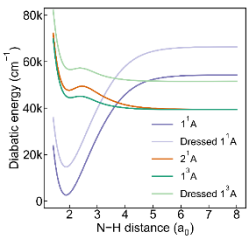
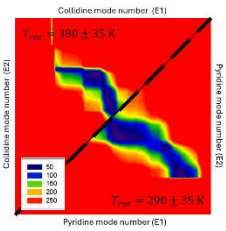
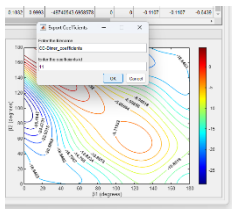
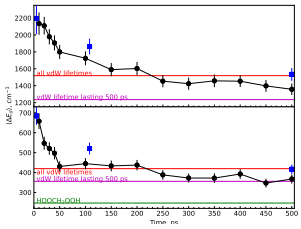
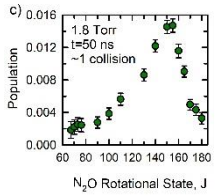
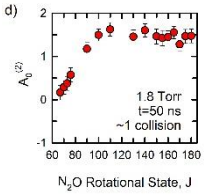


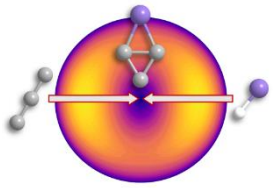


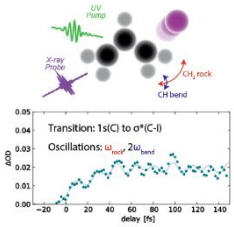


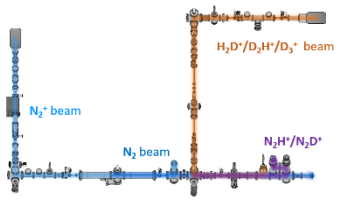


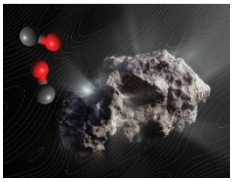










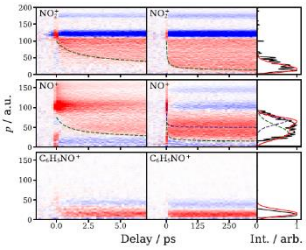


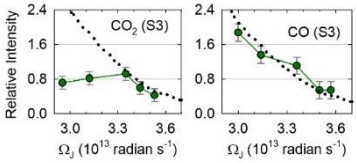
29th Dynamics of Molecular Collisions Conference

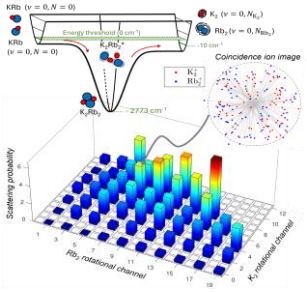
Amy S. Mullin, Chair

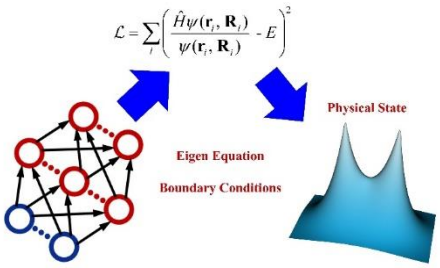
Ahren Jasper, co-Chair

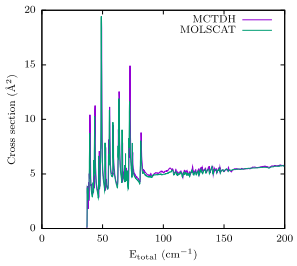
July 6-11, 2025 Snowbird, Utah, USA

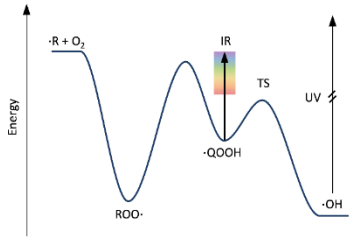


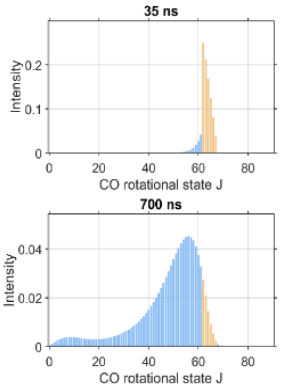


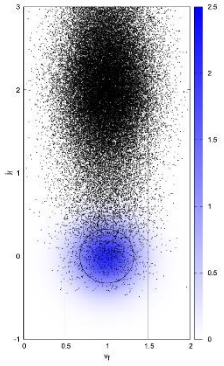


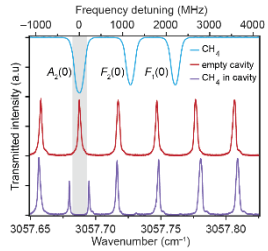


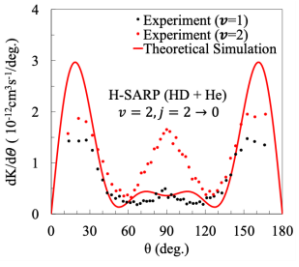


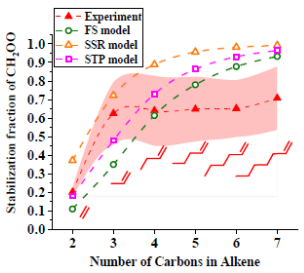


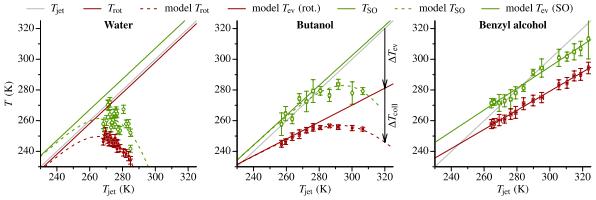












Dynamics of Molecular Collisions (DMC) Conference

We are excited to welcome you to Snowbird, Utah, for the 29th DMC meeting. This conference started in 1965, and has a great history of providing a unique platform and focal point for the gathering of experimentalists and theoreticians in the field of chemical dynamics.

Keynote Speaker

Alec Wodtke
Max Planck Institute for Multidisciplinary Sciences
Institute for Physical Chemistry, University of Göttingen

Herschbach Medals

David W. Chandler
Sandia National Laboratory

Anne B. McCoy
University of Washington

Organizers

Amy S. Mullin
Chair, University of Maryland

Ahren Jasper
co-Chair, Argonne National Laboratory

Featured Sessions

Bimolecular Collision Dynamics
Monday morning

Collision Dynamics in the Condensed Phase
Monday evening

Photodissociation Dynamics
Tuesday morning

Dynamics and Potential Energy Surfaces
Tuesday evening

Dynamics of Interfacial Collisions
Wednesday morning

Spectroscopy, Dynamics, and Electronic Structure
Thursday morning

Quantum Control of Reaction Dynamics
Thursday evening

Applications of Molecular Collisions
Friday morning

The Dynamics of Molecular Collisions (DMC) Conference provides a tremendous opportunity for the gathering of experimentalists and theoreticians in the field of chemical dynamics. At this biannual conference, the latest developments in bimolecular collisional dynamics, dynamics in the condensed phase, photodissociation dynamics, reactions at interfaces, nonadiabatic dynamics, quantum control of reactions, and applications to combustion, atmospheric, and interstellar chemistry are discussed by experts in these fields. Younger scientists are encouraged to present contributed talks as well as posters. The meeting has a Gordon Conference format , leaving afternoons free for the students and scientists to mingle and discuss their work in informal settings. Mornings and evenings are scheduled for talks and every night features a poster session.

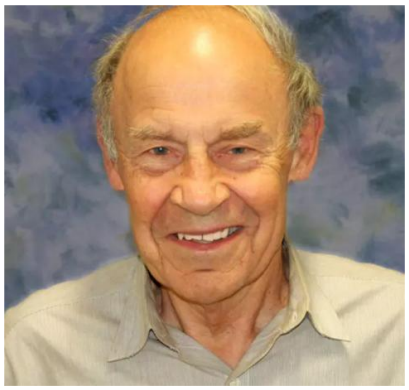
This meeting has had a distinguished history, beginning in 1965 (by Nobel Laureate John Fenn) as a Gordon Research Conference (GRC), and continuing independently when the number of participants grew to exceed the GRC limit. It is held now every two years.

History

1965: New Hampton, New Hampshire; ***John Fenn*** (Yale University).
1968: Andover, New Hampshire; ***John C. Polanyi*** (University of Toronto).
1970: Oak Ridge, Tennessee; ***E.F. Green*** (Brown University).
1972: Plymouth, New Hampshire; ***Sheldon Datz*** (Oak Ridge National Laboratory).
1974: Santa Cruz, California; ***James L. Kinsey*** (Massachusetts Institute of Technology).
1976: Plymouth, New Hampshire; ***Bruce E. Mahan*** (University of California, Berkeley).
1978: Pacific Grove, California; ***Yuan T. Lee*** (University of California, Berkeley).
1981: Plymouth, New Hampshire; ***R. James Cross*** (Yale University).
1983: Gull Lake, Minnesota; ***W. Ronald Gentry*** (University of Minnesota).
1985: Snowbird, Utah; ***Donald G. Truhlar*** (University of Minnesota).
1987: Wheeling, West Virginia, ***Paul Dagdigian*** (The Johns Hopkins University).
1989: Pacific Grove, California, ***William H. Miller*** (University of California, Berkeley).
1991: Lake George, New York, ***James M. Farrar*** (University of Rochester).
1993: Helen, Georgia, ***Joel M. Bowman***, (Emory University).
1995: Pacific Grove, California, ***Daniel Neumark*** (University of California, Berkeley).
1997: Gull Lake, Minnesota, ***George Schatz*** (Northwestern University).
1999: Lake Harmony, Pennsylvania, ***James Valentini*** (Columbia University).
2001: Copper Mountain, Colorado, ***James T. Muckerman*** (Brookhaven National Laboratory).
2003: Tahoe City, California, ***Laurie J. Butler*** (University of Chicago).
2005: Pacific Grove, California, ***Albert Wagner*** (Argonne National Laboratory).
2007: Sante Fe, New Mexico, ***David Chandler*** (Sandia National Laboratories).
2009: Snowbird, Utah, ***Anne McCoy*** (Ohio State University).
2011: Snowbird, Utah; ***David Nesbitt*** (JILA/University of Colorado).
2013: Granlibakken, California; ***Hua Guo*** (University of New Mexico).
2015: Pacific Grove, California; ***Arthur Suits*** (Wayne State University).
2017: Tahoe City, California; ***David Yarkony*** (Johns Hopkins University.
2019: Big Sky, Montana; ***Timothy Minton*** (Montana State University).
2023: Snowbird, Utah; ***Richard Dawes*** (Missouri University of Science and Technology**).**
2025: Snowbird, Utah; ***Amy S. Mullin*** (University of Maryland, College Park).

Herschbach Medal

Outstanding theoretical and experimental contributions to the field are recognized at the DMC conference by awarding the Herschbach Medal, named in honor of Dudley R. Herschbach, Nobel Prize in Chemistry in 1986, and a pioneer of the field.



For bold and architectural work, inspiring and empowering. Such work addresses fundamental, challenging, frontier questions; brings forth new perspectives and capabilities; and typically excites evangelical fervor that recruits many followers.

D. R. Herschbach

The Herschbach Medal tradition was first started in the 2007 meeting chaired by David Chandler, based on a generous donation of funds and artwork designed by Professor Herschbach himself. There are two such awards made, one for experimental and one for theoretical contributions to the field of Molecular Collision Dynamics, broadly defined.

Herschbach Medalists:

2007: Richard N. Zare & William H. Miller
2009: Daniel Neumark & Donald Truhlar
2011: Yuan Lee and George Schatz
2013: Giacinto Scoles, J. Peter Toennies & Joel Bowman
2015: W. Carl Lineberger & Millard Alexander
2017: Hanna Reisler & John Tully
2019: David Yarkony & Kopin Liu
2023: Marsha Lester & Hua Guo
2025: David W. Chandler and Anne B. McCoy

2025 Herschbach Medalists

Dr. Chandler is known for his pioneering work on the development of multiplex detection techniques with molecular beams and for using these techniques to investigate the dynamics of chemical reactions, collisions and electron ejection. His foundational work in ion imaging has ushered in a new era of investigating fundamental physical processes at the microscopic level.

Professor McCoy is known for her work using Diffusion Monte Carlo methods to investigate and interpret the spectral signatures of large amplitude vibrational motions that are not easily characterized with other methods. She works closely with experimentalists, providing predictions and insight into a wide variety of systems, including ions, clusters, and weakly-bound complexes.

Program

Sunday, July 6	
3:00 pm-6:00 pm	Check-in and badge pickup
6:00 pm-7:30 pm	Dinner
7:30 pm-9:00 pm	**Welcome and Keynote Address**
7:30 pm-7:45 pm	Welcome by **Amy Mullin** (University of Maryland)
7:45 pm-8:00 pm	Keynote Introduction by **Art Utz** (Tufts University)
8:00 pm-8:45 pm	Keynote Address by **Alec Wodtke** (Max Planck Institute for Multidisciplinary Science and Institute for Physical Chemistry, Göttingen) "A Golden Age of Quantitative Chemistry: Experiment, Theory and the Dynamics of Molecular Collisions"
8:45 pm-9:00 pm	Discussion
9:00 pm	Reception
Monday July 7	
7:00 am-8:10 am	Breakfast
8:10 am-12:00 pm	**Bimolecular Collision Dynamics**
8:10 am-8:25 am	Session Introduction: **Stephen Klippenstein** (Argonne National Laboratory)
8:25 am-8:55 am	**Richard D Thomas** (Stockholm University) "Probing molecular mutual neutralization reactions of atmospheric importance using the ion storage facility DESIREE"
8:55 am-9:05 am	Discussion
9:05 am-9:35 am	**Jennifer Meyer** (RPTU Kaiserslautern-Landau) "Dynamics of CO_2 action by transition metal ions: Competition between spin-changing and spin-conserving pathways"

9:35 am- 9:45 am	Discussion
9:45 am-10:05 am	**Andrew Petit** (California State University, Fullerton) "New Insights into the Electronic Quenching of NO* with Acetylene: Energy Transfer Versus the Harpoon Mechanism"
10:05 am- 10:10 am	Discussion
10:10 am-10:40 am	Coffee Break
10:40 am-11:10 am	**Richard Dawes** (Missouri University of Science and Technology) "Methods for PES Construction with Applications: Typical and Special Cases, Diabatization, and the Long Range"
11:10 am-11:20 am	Discussion
11:20 am- 11:50 am	**Arthur Suits** (University of Missouri) "New Probes of Kinetics and Spectroscopy in Supersonic Flows"
11:50 am-12:00 pm	Discussion
12:00 pm-1:00 pm	Lunch
1:00 pm-5:00 pm	Afternoon Break
5:00 pm-6:00 pm	**Hot Topic Poster Previews**
	Greta Jacobson (University of Washington) "Machine Learning Approaches for Developing Potential Surfaces: Applications to OH-(H_2O)n (n=1-4) Complexes" **Yang Liu** (University of New Mexico) "Kinetics and Product Branching in Dihydrogen Activation by Gaseous Manganese Oxide Cations" **Olivia Krohn** (Sandia National Laboratory) "Ultrahigh Velocity Resolution for Inelastic Scattering Dynamics" **Chow Shing Lam** (University of Oxford) "Probing the Ultrafast Dynamics of Nitrobenzene through Time-Resolved Coulomb Explosion Imaging" **Chao He** (University of Basel) "Exploring the Chemi-ionization of Carbonyl Sulfide (OCS) with Metastable Neon via Velocity Map Imaging"

	John Hack (University of California, Berkeley) "Coherent Vibrations in C-I Bond Dissociation Studied with Carbon K-edge Transient Absorption" **Simone DeSouza** (University of Maryland) "Dynamics of Optically Centrifuged N_2O in Extreme Rotational States Studied with Transient IR Absorption Spectroscopy" **Madison Foreman** (University of California, Berkeley) "Molecular Beam Scattering from Flat Liquid Jets: Exploring Dynamics at the Aqueous Interface"
6:00-7:15 pm	Dinner
7:15 pm-9:30 pm	**Collision Dynamics in the Condensed Phase**
7:15 pm- 7:30 pm	Session Introduction: **Stephen Bradforth** (University of Southern California)
7:30 pm-8:00 pm	**Ward Thompson** (University of Kansas) "Activation Energies Beyond Arrhenius"
8:00 pm-8:10pm	Discussion
8:10 pm-8:40 pm	**Chris Elles** (University of Kansas) "Ultrafast Dynamics of Manganese Tricarbonyl Coordination Complexes"
8:40 pm-8:50 pm	Discussion
8:50 pm-9:20 pm	**Graham Worth** (University College London) "Simulating Non-adiabatic in Photo-excited Reactions using Direct Quantum Dynamics"
9:20 pm-9:30 pm	Discussion
9:30 pm	**Poster Session 1 (A posters)**

Tuesday, July 8	
7:00 am-8:10 am	Breakfast
8:10 am – 12:00 pm	**Photodissociation Dynamics**

8:10 am-8:25 am	Session Introduction: **Marsha Lester** (University of Pennsylvania)
8:25 am-8:55 am	**Mike Duncan** (University of Georgia) "Infrared and UV-Visible Photodissociation of Organometallic Cations"
8:55 am- 9:05 am	Discussion
9:05 am-9:35 am	**Daniel Neumark** (University of California, Berkeley) "Photodissociation dynamics investigated using XUV and soft x-ray attosecond transient absorption"
9:35 am-9:45 am	Discussion
9:45 am-10:05 am	**Joseph McManus** (University of Oxford) "Tracking ultrafast structural change in photoexcited cis and trans isomers"
10:05 am-10:10 am	Discussion
10:10 am-10:40 am	Coffee Break
10:40 am-11:10 am	**Katharine Tibbetts** "Ultrafast Photodissociation Dynamics in Energetic Molecules"
	Discussion
11:20-11:50 am	**Jingsong Zhang** "Isomer selected photochemistry of C_4H_7 radicals"
11:50 am-12:00 pm	Discussion
12:00 pm- 1:00 pm	Lunch
1:00 pm-5:00 pm	Afternoon Break
5:00 pm-7:15 pm	**Dynamics and Potential Energy Surfaces- In Memory of David Yarkony**
5:00 pm-5:15 pm	Session Introduction: **Hua Guo** (University of New Mexico)
5:15 pm-5:45 pm	**Spiridoula Matsika** (Temple University) "Modeling Ultrafast Excited State Dynamics"

5:45 pm-5:55 pm	Discussion
5:55 pm- 6:25 pm	**Michael Schuurman** (University of Ottawa) "The UV Absorption and Time-Resolved Spectroscopy of Ethylene: A New Theoretical Model"
6:25 pm – 6:35 pm	Discussion
6:35 pm-7:05 pm	**Benjamine Levine** (Stonybrook University) "First Principles Simulation of Coherent Dynamics on Many Electronic States"
7:05 pm-7:15 pm	Discussion
7:15 pm-8:15 pm	Dinner
8:15 pm	**Poster Session 2 (A posters)**

Wednesday, July 9	
7:00 am-8:10 am	Breakfast
8:10 am-12:00 pm	**Dynamics of Interfacial Collisions**
8:10 am-8:25 am	Session Introduction by **Art Utz** (Tufts University)
8:25-8:55 am	**David Nesbitt** (JILA, University of Colorado) "Making a Splash: Chemical Physics at the Gas-Liquid Interface"
8:55 am-9:05 pm	Discussion
9:05 am-9:35 am	**Theofanis Kitsopoulos** "Applying Ion Imaging Methods to Site Specific Elementary Reactions in Heterogeneous Catalysis"
9:35 am-9:45 am	Discussion
9:45 am-10:05 am	**Mihai E. Vaida** "Facet-Dependent Ultrafast Photoinduced Reaction Dynamics of CH_3I Ion TiO_2 Surfaces"

10:05 am-10:10 am	Discussion
10:10 am-10:40 am	Coffee Break
10:40 am-11:10 am	**G. Barratt Park** (Texas Tech University) "State-to-State Scattering of Open Shell Atoms from Surfaces"
10:10 am-10:20 am	Discussion
11:20 am-11:50 am	**George Schatz** (Northwestern University) "Nonadiabatic Dynamics and Ionization in N+ N and N + O Collisions"
11:50 am - 12:00 pm	Discussion
12:00 pm – 1:00 pm	Lunch
1:00 pm – 5:00 pm	Afternoon Break
5:00 pm – 6:00 pm	Business Meeting
6:00 pm – 7:15 pm	Dinner
7:15 pm-9:25 pm	**Herschbach Medal Session**
7:15 pm-7:25 pm	Session Introduction: **Arthur Suits** (University of Missouri)
7:25 pm-7:35 pm	Introduction of David Chandler: **Marsha Lester** (University of Pennsylvania)
7:35 pm-8:15 pm	**David W. Chandler** (Sandia National Laboratory) "Measuring Velocity With High Resolution for Low Energy Molecules and Electrons"
8:15 pm-8:25 pm	Discussion
8:25 pm-8:35 pm	Introduction of Anne McCoy: **Hua Guo** (University of New Mexico)
8:35 pm-9:15 pm	**Anne B. McCoy** (University of Washington)

	"Deciphering spectral signatures of proton delocalization in complexes of hydroxide and hydronium ions with water molecules"
9:15 pm-9:25 pm	Discussion
9:25 pm	**Poster Session 3 (B posters)**

Thursday, July 10	
7:00 am-8:10 am	Breakfast
8:10 am-12:00 pm	**Spectroscopy, Dynamics, and Electronic Structure: In Memory of John Stanton**
8:10 am-8: 25 am	Session Introduction: **Anne McCoy** (University of Washington)
8:25 am - 8:55 am	**Jan Martin** (University of Florida) "Exploiting a Shortcoming of Coupled-Cluster Theory: The Extent of non-Hermiticity as a Diagnostic Indicator of Computational Accuracy"
8:55 am-9:05 am	Discussion
9:05 am-9:35 am	**Rigoberto Hernandez** (Johns Hopkins University) "Classical and Semiclassical Transition State Theory: Old and New"
9:35 am-9:45 am	Discussion
9:45 am-10:05 am	**Yaolong Zhang** (University of New Mexico) SchrödingerNet: A Universal Neural Network Solver for The Schrödinger Equation
10:05 am-10:10 am	Discussion
10:10 am-10:40 am	Coffee Break
10:40 am-11:10 am	**David Tannor** (Weizman Institute of Science) "Two Hundred Years after Hamilton: Exploring New Formulations of Classical and Quantum Mechanics"

10:10 am-11:20 am	Discussion
11:20 am-11:50 am	**Carolin Anna Joy** (Marquette University) "Recent Advances in Mixed Quantum/Classical Theory (MQCT) for Molecule + Molecule Collisions"
11:50 am-12:00 pm	Discussion
12:00 pm -1:00 pm	Lunch
1:00 pm-5:00 pm	Afternoon Break
5:00 pm-7:15 pm	**Quantum Control of Reaction Dynamics**
5:00 pm-5:15 pm	Session Introduction: **Amy Mullin** (University of Maryland)
5:15 pm-5:45 pm	**Marissa Weichman** (Princeton University) "New Platforms for Molecular Polariton Dynamics"
5:45 pm-5:55 pm	Discussion
5:55 pm-6:25 pm	**Helen Chadwick** (Swansea University) "Rotationally controlled hydrogen-surface reactions"
6:25 pm-6:35 pm	Discussion
6:35 pm-7:05 pm	**Yu Liu** (University of Maryland) "Advancing reaction dynamics with ultracold molecules"
7:05 pm-7:15 pm	Discussion
7:15 pm-8:15 pm	Dinner
8:15 pm	**Poster Session 4 (B posters)**

Friday, July 11	
7:00 am-8:10 am	Breakfast
8:10 am - 8:25 am	**Applications of Molecular Collision Dynamics**

8:10 am-8:15 am	Session Introduction: **Ahren Jasper** (Argonne National Laboratory)
8:25 am-8:55 am	**Robert Continetti** (University of California, San Diego) "Hypervelocity Ice Grain Impact Mass Spectrometry and the Search for Extraterrestrial Biosignatures"
8:55 am-9:05 am	Discussion
9:05 am-9:35 am	**Arkke Eskola** (University of Helsinki) "Direct Kinetic Studies of Unimolecular and Bimolecular Reactions of Criegee Intermediates"
9:35 am-9:45 am	Discussion
9:45 am-10:05 am	**Shane Goettl** (University of Hawaii) "Gas-Phase Synthesis of Cyclic Silicon Dicarbide (c-SiC2) and Bicyclic Silicon Tricarbide (c-SiC3) via Single Collision Events from Acyclic Transients"
10:05 am-10:10 am	Discussion
10:10 am-10:40 am	Coffee Break
10:40 am-11:10 am	**Denisia Popolan-Vaida** (University of Central Florida) "Influence of Carbon Chain Length, Functionality, and Reaction Environment on C1-C7 Criegee Intermediates Reaction Networks"
11:10 am-11:20 am	Discussion
11:20 am-11:50 am	**Brandon Rotavera** (University of Georgia) "Bimolecular Reactions of Cyclic Ether Radicals"
11:50 am-12:00 pm	Discussion
12:00 pm-12:05 pm	Thanks and DMC XXX **Ahren Jasper**
12:05 pm-1:30 pm	Box lunches in lobby outside lecture hall

Abstracts for Talks

A Golden Age of Quantitative Chemistry: Experiment, Theory and the Dynamics of Molecular Collisions

Alec Wodtke[1,2]

[1] *Max Planck Institute for Multidisciplinary Sciences, Göttingen, Germany*
[2] *Institute for Physical Chemistry, University of Göttingen, Göttingen, Germany*

ABSTRACT

In this 100-year anniversary of quantum mechanics, we honor a great theoretical breakthrough, from which it became possible to develop essential new ideas that gave birth to the field of chemical physics, ideas like *potential energy surface* and *transition state*. Sadly, these ideas remained poorly appreciated for several decades as the experiments necessary to assess their value could not yet be carried out. With the advent of laser- and molecular beam-based science, newly developed experimental capability proved these concepts to be central to our way of thinking about chemistry. In fact, the situation reversed. For at least four decades starting in the 60's theory lagged behind experiment. Spectacular observations of chemical processes became routine, yet the tools to unlock their meaning were not yet mature, due to the still limited performance of computers. Today, we find theory and experiment as co-equal partners in what one might call a Golden Age of Quantitative Chemistry. Modern electronic structure theory, quantum and classical dynamics as well as reaction rate theory, supercharged with machine learning tools, allow us to compute anything we can imagine. The challenge has now become to construct information-rich experiments capable of providing sufficient observational data that this new theoretical juggernaut remains anchored to reality.

In this talk I will recount a few episodes from my scientific life, emphasizing the failures of the "pre-theory" era as well as the dangers of failure in this new Golden Age.

Probing molecular mutual neutralization reactions of atmospheric importance using the ion storage facility DESIREE

M. Poline[a], A. Dochain[b], S. Rosén[a], M-C. Ji[a], P. Martini[a], M. Larsson[a], H. Cederquist[a], H. Zettergren[a], H. T. Schmidt[a], S. Ndenguéc, E. Quintas-Sánchez[d], R. Dawes[d], S. G. Ard[e], N. S. Shuman[e], A. A. Viggiano[e], and Richard D Thomas[a]

[a] *Department of Physics, Stockholm University, S10691 Stockholm, Sweden. Email: rdt@fysik.su.se*
[b] *ICMN, Université catholique de Louvain, Louvain-la-Neuve, Belgium.*
[c] *Department of Physics and Astronomy, Haverford College, Haverford, 19041, Pennsylvania, USA.*
[d] *Missouri University of Science and Technology, Rolla, 65409, Missouri, USA.*
[e] *AFRL, Space Vehicles Directorate, Kirtland AFB, Albuquerque, New Mexico, USA.*

ABSTRACT

The evolution of plasma environments is defined and governed by balances between ionizing processes, chemical rearrangements, and neutralisation reactions such as mutual neutralisation (MN). Measuring and explaining these processes in detail is fundamental to understanding and modelling non-local thermal equilibrium environments (non-LTE), such as atmospheric plasmas. Until recently, experimental studies of MN involving molecular ions in flow tubes and merged-beams were limited to measurements of overall reactivities without information of the mechanism or the products. The Double ElectroStatic Ion Ring ExpEriment (DESIREE) facility located at Stockholm University, Sweden (a schematic is shown in Fig 1.) uniquely allows for studies of MN interactions between cations and anions at low and well-defined internal temperatures and centre-of-mass collision energies down to about 20 K and ~50 meV, respectively [1-2], makes such studies possible [3-5]. Here, I highlight how this facility can play a crucial role in studying in MN reactions relevant to cool atmospheric plasmas and phenomena such as sprites [6,7]: providing insights into ion balance processes, and, e.g., in the production of F-layer UV airglows. I focus on reactions involving the primary atomic and molecular oxygen and nitrogen ions [3], i.e., $O^- + NO^+$, $O^- + O_2^+$, and $NO_2^- + NO^+$, where I can determine the fractionation into two- and three-body product channels and study the effects of the rovibrational energy of the molecular ion on the reaction process.

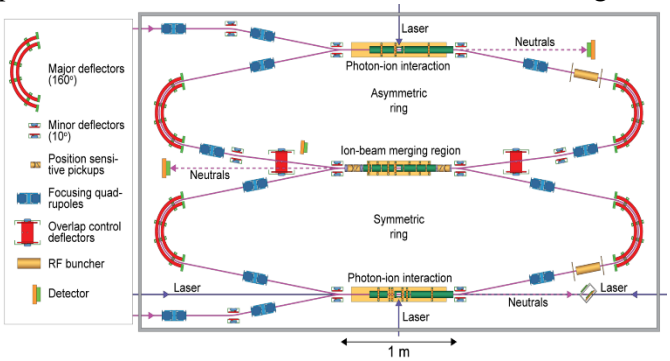


Figure 1: Schematic of the heart of the DESIREE facility: the two cryogenically cooled storage rings.

[1] R. D. Thomas *et al.*, The double electrostatic ion ring experiment: A unique cryogenic electrostatic storage ring for merged ion-beams studies, *Rev. Sci. Instrum.* 82, 065112 (2011).
[2] H. T. Schmidt *et al.*, First storage of ion beams in the Double Electrostatic Ion-Ring Experiment: DESIREE, *Rev. Sci. Instrum.* 84, 055115 (2013).
[3] M. Poline *et al.*, Mutual Neutralization of NO^+ with O^-, *Phys. Rev. Lett.* 132, 023001 (2024).
[4] A. Bogot *et al.*, The mutual neutralization of hydronium and hydroxide, *Science* 383, 285 (2024).
[5] A. Bogot *et al.*, Unravelling non-adiabatic pathways in the mutual neutralization of hydronium and hydroxide, *Nature Chemistry* 17(4), 541 (2025).
[6] N. Liu *et al.*, High-altitude electrical dis charges associated with thunderstorms and lightning, *J. Atmos. Terr. Phys.* 136, 98 (2015)
[7] A. Malagón-Romero *et al.*, Associative electron detachment in sprites, *Geophys. Res. Lett.*, 51, e2023GL107990 (2024).

This material is based upon work supported by the Air Force Office of Scientific Research under award numbers FA9550-19-1-7012; FA8655-24-1-700.

Dynamics of CO_2 action by transition metal ions

Competition between spin-changing and spin-conserving pathways

Jennifer Meyer[a]

[a] *Fachbereich Chemie und Landesforschungszentrum OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger Str 52, 67663 Kaiserslautern, Germany*
jennifer.meyer@chem.rptu.de

ABSTRACT

Steering chemical reactivity to yield a desired product branching ratio is a long-standing quest in chemistry. Single atom catalysts are prominent examples of this endeavor with the aim of combining high selectivity with atom-efficiency. Reactions involving isolated transition metal centers, especially open-shell ones, can follow non-adiabatic reaction pathways, i.e. , switch their spin state during the reaction, leading to the same product species in different electronic states. The reaction can follow a spin-changing or spin-conserving pathway and thereby effect the product state distributions, which in a next reaction step can influence reactivity and/or selectivity. The influence of factors governing the balance between spin-conserving and spin-changing pathways is delicate. The adiabatic pathway is often associated with a barrier, while the corresponding spin changing route is associated to an exothermic intersystem crossing pathway for which the spin-orbit coupling is crucial. Molecular reaction dynamics is a tool to study this competition at the most fundamental level because collision energy dependent differential cross sections and reaction rates are some of the most sensitive tools for probing a reactive potential energy surface.

Here, we present a joint experimental and theoretical study on the possible effects of intersystem crossing on the dynamics of transition metal ion-molecule reactions. Recent crossed beam imaging experiments in our group on the dynamics of the oxygen atom transfer (OAT) reaction $M^+ + CO_2 \rightarrow MO^+ + CO$ (M = Zr, Nb, Ta) showed dominantly indirect dynamics[1,2] despite the thermal rates being close to collision rate and the reactions being highly exothermic. The OAT reactions between M^+ and CO_2 are of multi-state character with the reaction crossing from a ground state surface to a spin surface of lower spin character in the course of the reaction to avoid the higher barrier and endothermic character of the spin-conserving pathway. The question to the nature of the bottleneck along the reaction coordinate arose: A submerged transition state or the intersystem crossing. Further, very specific geometry for the pre-reaction complex $[MCO_2]^+$ is found for all three metals which is dominated by the electrostatic interactions. Recent trajectory calculations confirmed the indirect nature of OAT and the intersystem crossing to be the bottleneck at the investigated collision energies for tantalum and niobium[3,4]. For zirconium, on the other hand, the reaction shows a competion between spin conserving and spin-changing reactions once the endothermic spin-conserving pathway is energetically accessible.

[1]M. Meta *et al.*, Dynamics of the Oxygen Atom Transfer Reaction between Carbon Dioxide and the Tantalum Cation, *J. Phys. Chem. Lett.* 14, 5524, 2023
[1]M. E. Huber *et al.* Ta^+ and $Nb^+ + CO_2$: Intersystem crossing in ion-molecule reactions. *Phys. Chem. Chem. Phys.* 26, 8670, 2024
[3]Y. Liu *et. al.* Multistate dynamics and kinetics of CO_2 activation by Ta^+ in the gas phase: Insights into single-atom catalysis. *J. Am Chem. Soc.* 146, 141182, 2024
[4]Y. Liu *et al.* Intersystem crossing control of the $Nb^+ + CO_2 \rightarrow NbO^+ + CO$ reaction. *J. Phys. Chem. A* 128, 6943, 2024

New Insights into the Electronic Quenching of NO ($A^2\Sigma^+$) with Acetylene: Energy Transfer Versus the Harpoon Mechanism

Celine Diep, Aerin Bridgers, Ken Jones, and Andrew S. Petit[a]

[a] *California State University, Fullerton, Fullerton, CA USA, Email: apetit@fullerton.edu*

ABSTRACT

The electronic quenching of NO ($A^2\Sigma^+$) by molecular partners represents an informative model system for exploring the non-adiabatic dynamics of open-shell molecular systems. A series of previous studies by our group have developed mechanistic pictures for how this electronic quenching occurs for a series of molecular partners, including NO ($A^2\Sigma^+$)+CO, NO ($A^2\Sigma^+$)+H_2O, and NO ($A^2\Sigma^+$)+CO_2.[1-3] In all of these systems, the pathway to a conical intersection between NO ($A^2\Sigma^+$)+M and NO ($X^2\Pi$)+M is facilitated through the harpoon mechanism. In this mechanism, an electron transfers from the 3sσ Rydberg orbital of NO into the LUMO of the molecular partner, creating a transient ion pair with strong intermolecular attractions. In all cases, the electronic quenching process imparts significant vibrational energy to both NO ($X^2\Pi$) and the molecular partner. By analyzing the molecular distortions required to access the conical intersection, we predicted what specific vibrational modes are likely significantly excited by the electronic quenching process. This allowed us to rationalize existing experimental data as well as make predictions for new experiments.[4-5]

Here, we describe our recent efforts to understand the NO ($A^2\Sigma^+$)+C_2H_2 system. Unlike the previous molecular partners we have studied, C_2H_2 has low-lying excited electronic states with energies below that of NO ($A^2\Sigma^+$). As a result, in addition to the harpoon mechanism, there is also the possibility of energy transfer whereby the generation of electronically excited C_2H_2 accompanies the formation of NO ($X^2\Pi$). Using a combination of EOM-EA-CCSD and multireference methodologies, we explore the mechanism for electronic quenching in NO ($A^2\Sigma^+$)+C_2H_2. We demonstrate that collisions between NO ($A^2\Sigma^+$) and C_2H_2 will generate a collision complex with C_2H_2 in its *trans*-bent conformation. Furthermore, we show the existence of a downhill pathway to a conical intersection between NO ($A^2\Sigma^+$)+C_2H_2 and NO ($X^2\Pi$)+C_2H_2. The electronic character of NO ($A^2\Sigma^+$)+C_2H_2 along this pathway is significantly multiconfigurational, with contributions from electronic configurations consistent with both energy transfer and the harpoon mechanism.

---

[1] Guardado, J.S., *et al.* Stereodynamic Control of Collision-Induced Nonadiabatic Dynamics of NO ($A^2\Sigma^+$) with H_2, N_2, and CO: Intermolecular Interactions Drive Collision Outcomes, *J. Phys. Chem. A*, **2021**, *125*, 8803-8815.

[2] Guardado, J.S., *et al.* Reactive Quenching of NO ($A^2\Sigma^+$) with H_2O Leads to HONO: A Theoretical Analysis of the Reactive and Nonreactive Electronic Quenching Mechanisms, *Phys. Chem. Chem. Phys.*, **2022**, *24*, 26717-26730.

[3] Bridgers, A.N., *et al.* Theoretical Study of the Photochemical Mechanisms of the Electronic Quenching of NO ($A^2\Sigma^+$) with CH_4, CH_3OH, and CO_2, *J. Phys. Chem. A*, **2023**, *127*, 7228-7240.

[4] Burgos Paci, M.A., *et al.* Products of the Quenching of NO $A^2\Sigma^+$ (v=0) by N_2O and CO_2, *Phys. Chem. Chem. Phys.*, **2013**, 2554-2564.

[5] Umemoto, H., *et al.* Production Processes of H(D) Atoms in the Reactions of NO ($A^2\Sigma^+$) with C_2H_2, C_2H_4, H_2O, and their Isotopic Variants, *Chem. Phys.*, **2000**, 39-47.

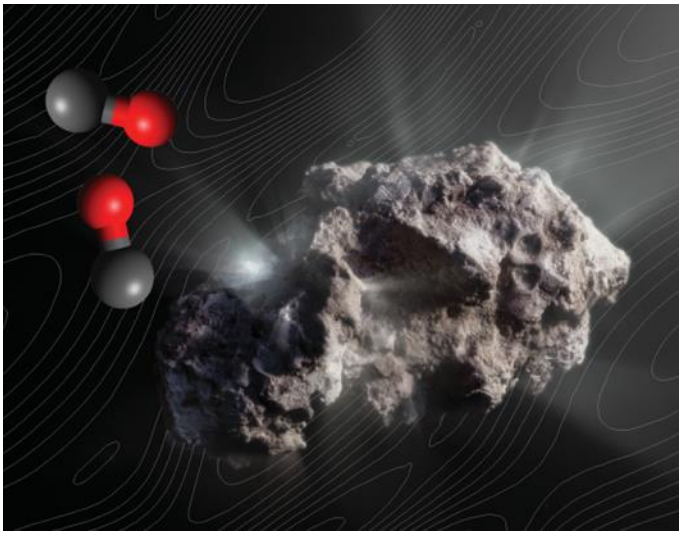
Methods for PES construction with applications: typical and special cases, diabatization, and the long range

Richard Dawes,[a] Ernesto Quintas-Sánchez,[a] Adrian Batista-Planas[a]

[a] *Missouri S&T, Rolla, MO 65409, dawesr@mst.edu*

ABSTRACT

This talk will present methods to construct PESs useful for dynamical studies of bimolecular collisions. Some details of our automated IMLS-based approach to PES construction will be presented for a variety of applications. The applications will illustrate different classes of systems and their associated challenges. These include some "routine" cases, as well as others such as systems with extreme anisotropy, ions, (ro)vibrationally excited monomers, and open-shell systems that require diabatization. A special software package developed to implement a rigorous treatment of the long range will also be presented.



New Probes of Kinetics and Spectroscopy in Supersonic Flows

Yanan Liu[a], Abbas Behzadfar[a], Nicolas Suas-David[b], Arthur G. Suits[a]

[a] *Department of Chemistry, University of Missouri, Columbia MO 65211 USA*
Email: suitsa@missouri.edu
[b]*Univ Rennes, Institut de Physique de Rennes - UMR 6251, F-35000 Rennes, France*

ABSTRACT

We will highlight two new experimental directions in our laboratory involving application of uniform supersonic flows produced by Laval nozzles. In the first, we report the first example of *Supersonic Photacoustic Spectroscopy*. Photoacoustic spectroscopy (PAS) is a sensitive broadband absorption technique relying on simple and inexpensive components. Despite this, PAS has never been applied in a cold supersonic environment. The reason for this is clear: how can one detect an acoustic signal under supersonic conditions? The flow provided by a Laval nozzle expansion offers a solution: such flows are thermal collisional environments propagating much faster than the local speed of sound, but inside which one may produce a photoacoustic signal by suitably chopped laser excitation of molecules in the flow. Downstream, a microphone can respond to the pressure oscillations induced by the laser excitation as the flow sweeps by after the absorbed radiation has been converted to translational energy of the molecules. Such a strategy offers a near-universal approach to spectroscopy and low-temperature kinetics in uniform flows. We will show application to methane and acetylene detection in the mid-nfrared and discuss issues of sensitivity and prospects of the method.

In the second example, we will apply Chirped-Pulse Fourier-Transform mm-wave (CP-FTmmW) rotational spectroscopy in a supersonic flow (CPUF) to perform kinetics inside an *extended* Laval nozzle.[1] The initial expansion inside the nozzle is then followed by a second supersonic expansion. This permits low temperature kinetics measurements *inside* the nozzle, while the secondary expansion takes the sample to low density and low temperature optimal for CP-FTmmW detection. We will present the first low temperature kinetics measurements for reaction of vinoxy (C_2H_3O) and cyanomethylene (HCCN) radicals with molecular oxygen, and discuss implications of these results for astrochemistry and the chemistry of Earth's atmosphere.

---

[1] S. Thawoos, N. Suas-David, R. M. Gurusinghe, M. Edlin, A. Behzadfar, J. Lang, and A. G. Suits, "Low temperature reaction kinetics inside an extended Laval nozzle: REMPI characterization and detection by broadband rotational spectroscopy," J Chem Phys **159,** 214201, 2023.

Activation Energies Beyond Arrhenius

Zeke A. Piskulich, Anjali Radhakrishnan, Elizabeth R. Bartlett, and Ward H. Thompson,[a]

Department of Chemistry, University of Kansas, Lawrence, KS 66045.
[a]*Email: wthompson@ku.edu*

ABSTRACT

How the dynamics of a reaction, or other chemical process, changes with temperature is one of the most fundamental measures of its behavior. This is most directly characterized by its activation energy, obtained through an Arrhenius analysis involving measurements or simulations of the dynamics at different temperatures. Here, recently developed methods that enable the activation energy to be determined from simulations at a single temperature will be described. A key advantage of these approaches is that they enable separation of not only energetic and entropic driving forces: They also offer mechanistic insight into these driving forces through a rigorous decomposition of the activation energy into contributions associated with the different motions and interactions. This is information that is not available in any other way. These methods are providing new understanding of dynamics from diffusion to reorientation to chemical reaction to spectroscopy. Examples of the approach will be discussed in the context of the structure and dynamics of water, including in osmolyte solutions.

Ultrafast Dynamics of Manganese Tricarbonyl Coordination Complexes

Christopher G. Elles

Department of Chemistry, University of Kansas, Lawerence, Kansas 66045, USA
Email: elles@ku.edu

ABSTRACT

The optical activation of metal coordination compounds plays an important role in applications ranging from photocatalysis to photodynamic therapy. The efficiency of any given compound for the intended use often depends on the initial relaxation dynamics of a metal-to-ligand charge-transfer (MLCT) state, which can be difficult to measure due to the strong correlation of electronic and nuclear motions and the complexity of the potential energy landscape in metal coordination compounds. Here, we examine the solution-phase relaxation dynamics of MLCT excited states for a series of light-sensitive manganese coordination compounds using femtosecond optical and x-ray absorption spectroscopy with ~50 fs time resolution. The compounds have the form $Mn(CO)_3(^{R}bpy)Br$, where ^{R}bpy is either the common 2,2'-bipyridine ligand (R = H) or a 4,4'-disubstituted analogue with stronger electron withdrawing character (R = CF_3 or NO_2). Changing the electron withdrawing character of the ^{R}bpy ligand alters the electronic properties of the compound, and provides insight into the relaxation dynamics of the MLCT excited states.

Transient absorption measurements reveal rapid relaxation of the MLCT states of the ^{H}bpy and ^{CF3}bpy compounds within ~300 fs due to the photolysis of an equatorial CO ligand, whereas the excited-state lifetime of ^{NO2}bpy is much longer and no release of CO is detected.[1] However, optical spectroscopy only probes the evolution of delocalized valence orbitals and lacks structural sensitivity that is necessary to determine a detailed mechanism of the dynamics. Therefore, we also apply time-resolved x-ray absorption spectroscopy (TR-XAS) to directly probe the dynamics with elemental specificity. Ultrafast measurements of the x-ray absorption near-edge spectra (XANES) at the Mn and Br K-edges reveal a series of electronic and nuclear changes that are associated with the initial electronic relaxation dynamics and the ensuing nuclear dynamics that ultimately result in either CO release for the ^{H}bpy and ^{CF3}bpy compounds, or a stabilized MLCT excited state for the ^{NO2}bpy substituted compound. These measurements reveal new details about the excited-state dynamics, including the role of concerted electronic and nuclear dynamics.

---

[1] Henke, W. C.; *et al.* Ultrafast Spectroscopy of $[Mn(CO)_3]$ Complexes: Tuning the Kinetics of Light-Driven CO Release and Solvent Binding. *Inorg. Chem.* 59, 2178-2187, 2020.

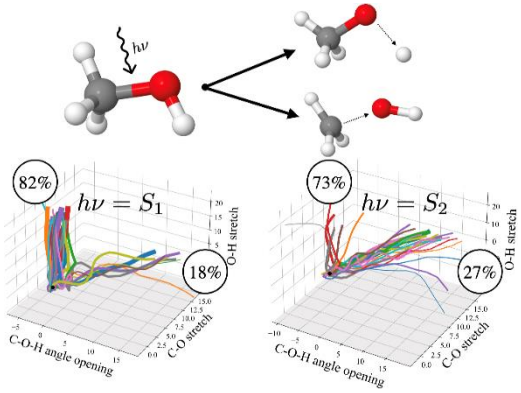
Simulating Non-adiabatic Effects in Photo-excited Reactions using Direct Quantum Dynamics

Graham Worth

University College London. g.a.worth@ucl.ac.uk

ABSTRACT

To describe the reactivity of molecules after photo-excitation often requires the inclusion of non-adiabatic effects due to the coupling between electronic and nuclear motion in the manifold of excited-states. These are needed as, when potential surfaces cross, vibronic coupling leads to an instantaneous rearrangement of the electronic configuration, making new channels available for, e.g. dissociation. This provides a challenge for simulations as, not only do quantum effects need to be included, but also a number of potential energy surfaces and the couplings between them are needed. One approach to solve this problem is to use "direct dynamics" in which the time-dependent Schrödinger equation is solved for the evolution of an initial wavepacket over potential surfaces calculated on-the- fly using quantum chemistry calculations. This removes the need to pre-compute surfaces. Quantum chemistry for excited-states is, however, still not straightforward. This is particularly true for dissociation reactions due to the need for a multi-configurational ansatz. In this contribution, the progress we have made in this area using the direct dynamics variational multi-configurational Gaussian (DD-vMCG) method [1] will be shown, with a focus on describing the dissociation of molecules such as formamide [2] , methanol [3] and phenol[4].



---

[1] G. W. Richings, *et al.* Quantum dynamics simulations using gaussian wavepackets: The vMCG method. Int. Rev. Phys. Chem., 34:269–308, 2015.
[2] K. E. Spinlove, *el at.* Curve crossing in a manifold of coupled electronic states: Direct quantum dynamics simulations of formamide. Farad. Discuss., 212:191–215, 2018.
[3] L. L. E. Cigrang and G. A. Worth, Modelling photodissociation: Quantum dynamics simulations of methanol. J. Phys. Chem. A, 128:7546–7557, 2024.
[4] G. Christopoulou, T. Tran, and G. A. Worth, Direct nonadiabatic quantum dynamics simulations of the photodissociation of phenol. Phys. Chem. Chem. Phys., 23:23684 – 23695, 2021.

Infrared and UV-Visible Photodissociation of Organometallic Cations

Michael A. Duncan

Department of Chemistry, University of Georgia, Athens, GA 30602. Email: maduncan@uga.edu

ABSTRACT

Cold cations of metal ion-acetylene and metal ion-benzene complexes are produced in a pulsed supersonic molecular beam by laser vaporization. These ions are mass-selected and studied with infrared and UV-visible laser photodissociation spectroscopy and photofragment imaging. Infrared spectra are compared to the predictions of theory to elucidate the structures of these ions and their electronic states. Transition metal (Fe, V, Co, Pt) complexes with acetylene are studied in the C–H stretching region, revealing the formation of cation-π complexes or cycloaddition products.[1] The spectra reveal coordination numbers, ligand vibrational shifts as a function of cluster size, and the occurrence of intracluster cyclization reactions to form benzene. UV-visible laser spectroscopy reveal specific electronic states for Ag^+(benzene) and Mg^+(benzene) complexes, but continuous spectra for Fe^+(acetylene) and Fe^+(benzene).[2-4] The threshold for photodissociation in the latter cases provide the determination of the bond energies.[2,3] Photofragment images also probe dissociation energies for Fe^+(acetylene), Fe^+(benzene) and Mg^+(benzene).[2-4] Computational studies at the DFT level complement all of these experiments.

---

[1] A. D. Brathwaite, J. H. Marks, I. J. Webster, A. G. Batchelor, T. B. Ward, M. A. Duncan, "Coordination and Spin States in $Fe^+(C_2H_2)_n$ Complexes Studied with Infrared Spectroscopy," *J. Phys. Chem. A* **126**, 9680–9690 (2022).

[2] J. E. Colley, N. J. Dynak, J. R. C. Blais, M. A. Duncan, "Photodissociation Spectroscopy and Photofragment Imaging to Probe the Dissociation Energy of the Fe^+(Acetylene) Complex," *J. Phys. Chem. A* **127**, 1244–1251 (2023).

[3] J. E. Colley, N. J. Dynak, J. R. C. Blais, M. A. Duncan, "Photodissociation Spectroscopy and Photofragment Imaging to Probe the Dissociation Energies of the $Fe^+(Benzene)_{1,2}$ Complexes," *J. Phys. Chem. A* **127**, 2795–2804 (2023).

[4] J. E. Colley, N. J. Dynak, J. R. C. Blais, M. A. Duncan, "Photodissociation Spectroscopy and Photofragment Imaging of the Mg^+(Benzene) Complex," *J. Phys. Chem. A* ***128***, 10507–10515 (2024).

Investigating photodissociation dynamics with XUV and soft x-ray attosecond transient absorption

Daniel Neumark

Department of Chemistry, University of California, Berkeley, CA 94720
Email: dneumark@berkeley.edu

ABSTRACT

Attosecond transient absorption using XUV or soft x-ray pulses provides a unique window into the photodissociation dynamics of benchmark systems. In these experiments, a molecule is photodissociated with an ultrafast UV pulse, and the resulting transient absorption spectrum is measured with a broadband attosecond probe pulse that can excite core-to-valence electronic transitions in the dissociating molecule. As the energies of these transitions are element-specific, these experiments probe the evolving electronic structure around specific atoms as a molecule dissociates. Examples will include CH_3I, where an XUV pulse probes core-to-valence transitions in the I atom while a higher energy soft x-ray pulse probes corresponding transitions in the C atom. The two experiments provide complementary information; the XUV experiment tracks bifurcation at the conical intersection that governs spin-orbit branching of the I atom, whereas the soft x-ray experiment is sensitive to the evolving geometry of the CH_3 group.

Tracking ultrafast structural change in photoexcited *cis* and *trans* isomers

Joseph. W. McManus,[1]* Avijit Duley,[2] Huynh V. S. Lam,[2] Anbu S. Venkatachalam,[2] Keyu Chen,[2] Shalauddin,[2] Artem Rudenko,[2] Daniel Rolles[2] and Mark Brouard[1]

[1] *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford, UK.*
[2] *James R. MacDonald Laboratory, Kansas State University, Manhattan, Kansas, USA.*
* *Email: joseph.mcmanus@chem.ox.ac.uk*

Molecular photoswitching is a process that is important in nature for the conversion of photons to mechanical energy. The simplest possible molecular photoswitch is ethylene, which undergoes photoinduced *cis-trans* isomerization.[1] The molecule is planar in its ground electronic state, but excitation to the (π, π*) excited state removes the restriction on rotation about the C–C bond axis, resulting in ultrafast torsion to a twisted geometry.

This work explores the photoinduced molecular dynamics of a simple, substituted derivative of ethylene. We have applied time-resolved Coulomb explosion imaging[2] to track the structural change in the *cis* and *trans* forms of 1,2-dichloroethylene (DCE) after exciting their (π, π*) absorption bands. This technique uses two femtosecond laser pulses. First the 'pump' pulse photoexcites the target molecule, then after some delay the 'probe' pulse induces rapid multiple ionisation and subsequent breakup into many fragment ions. Recording the relative momenta of the fragment ions then provides an intuitive visualisation of the molecular structure at the instant of fragmentation.[3] For example, Figure 1(a) plots the momenta of C^+ and Cl^+ ions from the Coulomb explosion of *trans*-1,2-DCE in its ground electronic state.

By varying the delay between the pump and probe laser pulses, a series of snapshots of the evolving molecular structure can be captured. Similar to ethylene, we observe that π* ← π excited 1,2-DCE undergoes ultrafast structural rearrangement to an out-of-plane geometry, which acts as a precursor to dissociation. This is well illustrated by the shift in the recoil angle of the Cl^+ ion pair, shown in Figure 1(b). In the *trans* geometry the Cl^+ ions recoil back-to-back, but a rapid decrease in their recoil angle follows photoexcitation because, as the molecule twists, the Cl atoms no longer occupy positions facing opposite one another.

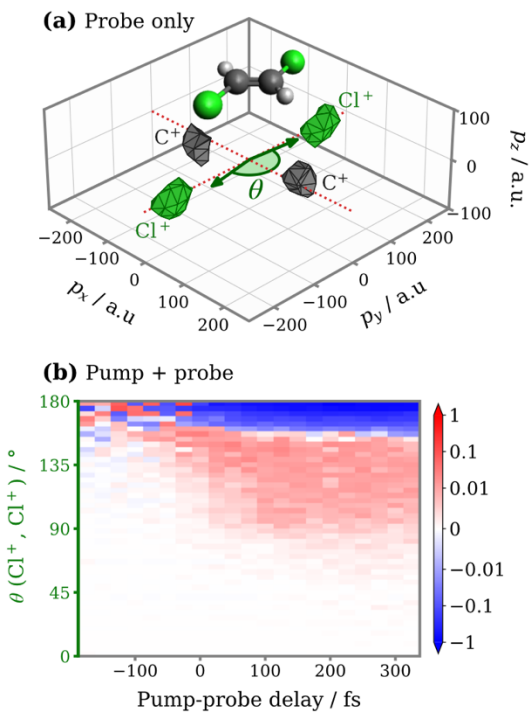


Figure 1. (a) Three-dimensional representation of the correlated momenta of $2C^+$ (*black*) + $2Cl^+$ (*green*) from the Coulomb explosion of *trans*-1,2-DCE in its ground electronic state. (b) The recoil angle between the Cl^+ ion pair plotted as a function of delay between the pump and probe pulses, where positive delay corresponds to the pump pulse arriving before the probe pulse. The average signal when the probe pulse arrives before the pump pulse has been subtracted from all delays in order to highlight which regions are enhanced (*red*) and which are depleted (*blue*).

[1] M. Ben-Nun and T.J. Martinez, *Ab initio molecular dynamics study of cis–trans photoisomerization in ethylene*, Chem. Phys. Lett, 298, 57-65, 1998.

[2] H. Stapelfeldt, E. Constant, H. Sakai and P.B. Corkum, *Time-resolved Coulomb explosion imaging: A method to measure structure and dynamics of molecular nuclear wave packets*, Phys. Rev. A, 58, 426-433, 1998.

[3] M. Pitzer *et al.*, *Direct determination of absolute molecular stereochemistry in gas phase by Coulomb explosion imaging*, Science, 341**,** 1096-1100, 2013.

Ultrafast Photodissociation Dynamics in Energetic Molecules

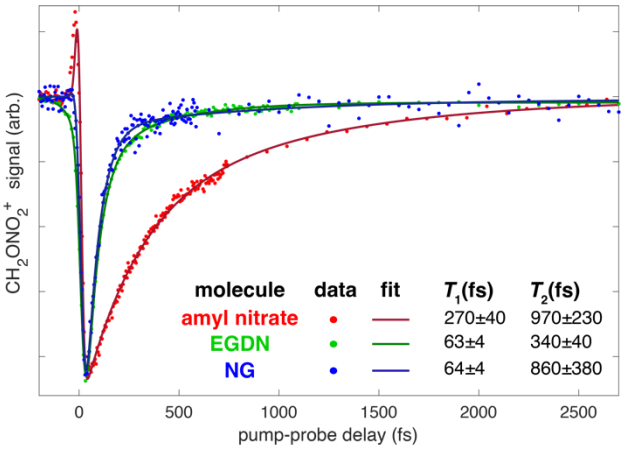
Hugo López Peña, Erica Britt, Madison Minvielle, and Katharine Moore Tibbetts

Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284, United States.
Email: kmtibbetts@vcu.edu

ABSTRACT

Ignition of energetic materials such as high explosives can initiate decomposition reactions on atomic length scales within femtoseconds. Pump-probe spectroscopy techniques like femtosecond time-resolved mass spectrometry (FTRMS) can capture photodissociation dynamics with sub-50 fs resolution, which is ideal for investigating the initial decomposition dynamics of energetic molecules when coupled to high-level quantum chemical calculations and *ab initio* molecular dynamics simulations.

FTRMS is particularly suited to probing photodissociation dynamics in ionized energetic molecules because energetic molecules can be metastable to dissociation upon removal of one or more electrons. For instance, *para*-nitrotoluene (PNT), a model for the high explosive TNT, is stable upon removal of a single electron but undergoes spontaneous Coulomb explosion within 200 fs or 90 fs, respectively, when two or three electrons are removed.[1] Nitromethane undergoes spontanteous nitro-nitrite rearrangement and dissociation to NO^+ within 500 fs when ionized into an excited electronic state.[2] Compared to these model systems, nitrate esters are particularly sensitive energetic materials that are metastable to dissociation whern ionized. FTRMS measurements show that the lifetimes of metastable nitrate ester cations depend on molecular structure, as shown in the Figure for the transient signals of the $CH_2ONO_2^+$ (*m/z* 76) ion from amyl nitrate (a fuel additive) and the sensitive explosives ethylene glycol dinitrate (EGDN)[3] and nitroglycerin (NG). Whereas the initially depleted $CH_2ONO_2^+$ signal from amyl nitrate recovers over several hundred femtoseconds, the signals from the explosives EGDN and NG are nearly recovered within ~100 fs. This fast signal depletion and recovery indicates a much shorter cation lifetime in the explosives (EGDN and NG) compared to the non-explosive fuel additive (amyl nitrate). The faster dissociation of ionized EGDN and NG compared to amyl nitrate raises the intriguing possibility that bulk properties of energetic materials such as impact sensitivity could be related to the rates of initial dissociation reactions triggered by photoionization.



---

[1] J. M. Shusterman, G. L. Gutsev, H. A. López Peña, B. R. Ramachandran, and K. M. Tibbetts, "Coulomb Explosion Dynamics of Multiply Charged para-Nitrotoluene Cations", J. *Phys. Chem. A* **2022** *126* 6617-6627

[2] M. D. Word, H. A. López Peña, D. Ampadu Boateng, S. L. McPherson, G. L. Gutsev, L. G. Gutsev, K. U. Lao, and K. M. Tibbetts, "Ultrafast Dynamics of Nitro-Nitrite Rearrangement and Dissociation in Nitromethane Cation", *J. Phys. Chem. A* **2022** *126* 879-888

[3] E. Britt, H. A. López Peña, J. M. Shusterman, K. Sangroula, K. U. Lao, and K. M. Tibbetts, "Ultrafast Dissociation Dynamics of the Sensitive Explosive Ethylene Glycol Dinitrate", *J. Phys. Chem. Lett.* **2025** *16* 882-888

Isomer selected photochemistry of C_4H_7 radicals

Michael Lucas,[a] Yuan Qin,[a] Lei Yang,[a] Ge Sun,[a] and Jingsong Zhang[a,b]

[a] *Department of Chemistry, University of California, Riverside, CA 92521, USA*
[b] *Air Pollution Research Center, University of California, Riverside, CA 92521, USA*
Email: jingsong.zhang@ucr.edu

ABSTRACT

C_4H_7 radicals are common intermediates in combustion. 1-Methylallyl (CH_2=CH–•CH-CH_3) and 2-methylallyl (CH_2=C(CH_3)–•CH_2) are methyl-substituted allyl and resonance-stabilized radicals, while 2-buten-2-yl (CH_3–•C=CH-CH_3) and 2-methyl-1-propenyl (•CH=C(CH_3)^2) are methyl-substituted propenyl radicals. These four isomers serve as an ideal system for studying isomer-dependent photochemistry. Each isomer, representing a local minimum on the global ground-state potential energy surface, provides unique access points to different regions of the excited-state surfaces, leading to distinct dissociation pathways. In this work, ultraviolet (UV) photodissociation dynamics of the four C_4H_7 radicals are investigated at λ = 220-250 nm using high-*n* Rydberg atom time-of-flight technique.

All four C_4H_7 radicals exhibit broad UV absorption in the 220-250 nm region, attributed to 3s/3p Rydberg states. For 1-methylallyl, 2-methylallyl, and 2-buten-2-yl, the translational energy distributions of H-atom product channel, $P(E_T)$'s, show bimodal distributions and two dissociation pathways. The dominant pathway has isotropic product angular distribution and small fraction of average translational energy in the total excess energy, $\langle f_T \rangle$~0.15, corresponding to unimolecular decomposition of highly vibrationally excited hot radical following internal conversion, to different products, 1,3-butadiene + H (1-methylallyl), methylenecyclopropane + H (2-methylallyl), and 2-butyne + H and 1,2-butadiene + H (2-buten-2-yl). The minor pathway is anisotropic and has a large $\langle f_T \rangle$~0.4-0.7, from non-statistical direct H-atom dissociation on the repulsive excited-state surface to form 1,3-butadiene + H (1-methylallyl and 2-methylallyl) and 1,2-butadiene + H (2-buten-2-yl). For 2-methyl-1-propenyl, the $P(E_T)$'s show only one slow component ($\langle f_T \rangle$~0.14) and isotropic angular distribution, from statistical dissociation of hot radical to methylenecyclopropane + H.

Modeling Ultrafast Excited State Dynamics

Spiridoula Matsika

Department of Chemistry, Temple University, Email: smatsika@temple.edu

ABSTRACT

Nonadiabatic processes play an important role in photophysics and photochemistry involved in chemistry, materials, and biology. A focus of our work is to develop our understanding of excited state processes and nonadiabatic events in molecular systems. We achieve this by a closely collaborative approach between theory and experiment, where we calculate time resolved observables, such as photoelectron spectra, ultrafast electron diffraction or kinetic energy release signals, and compare to the corresponding experimental pump-probe signals. Recently, we have focused on examining how different pump or probe energies affect the dynamics or the signals. In nitrophenol we have shown that excitation at different wavelengths leads to different pathways in the dynamics, even though excited state decay times appear very similar. This is a cautionary story that we cannot rely on decay time constants alone to study the dynamics, and a better approach is to use a combination of experimental techniques and theory for interpretation.

The UV Absorption and Time-Resolved Spectroscopy of Ethylene: A New Theoretical Model

Simon Neville, Martha Yaghoubi Jouybari, Michael Schuurman

Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, Ontario, Canada, email: Michael.Schuurman@uOttawa.ca

ABSTRACT

The excited state dynamics of ethylene following excitation into the energetically lowest lying absorption band, nominally understood as arising from the ππ* and π3s states, have been the focus of numerous theoretical and computational studies for many decades. Here, we present new quantum dynamics computations and spectroscopic simulations that indicate the non-adiabatic population dynamics can be better understood as arising from strong vibronic coupling between the ππ* and σπ* states, and separately, between the π3s and σ3s electronic states. This model is shown to offer a clear explanation for previously unassigned bands in the UV absorption spectrum and is the basis for the interpretation of recent time-resolved photo-electron spectroscopic results.

First Principles Simulation of Coherent Dynamics on Many Electronic States

Benjamin G. Levine, Jiri Suchan, Andrew S. Durden, Fangchun Liang, and Michael P. Esch

Department of Chemistry and Institute for Advanced Computational Science, Stony Brook University, Stony Brook, NY 11733. Email: ben.levine@stonybrook.edu

ABSTRACT

Many important problems in chemistry and materials science involve nonadiabatic dynamics on large numbers of electronic states. Phenomena important for strong-field physics, energy conversion, hot carrier cooling, and relaxation of plasmonic excitations fall into this category. Some of these phenomena involve long lived coherences, which are challenging to accurately model with many mixed quantum-classical methods. We will present recent theoretical developments towards an accurate and broadly applicable simulation method for modeling dynamics in this regime. Specifically, we will present the development of the Ehrenfest with collapse to a block (TAB) method and a derivative designed for dense manifolds of states (DMS). The primary achievement of TAB-DMS is that it is able to accurately describe decoherence effects without requiring explicit computation of individual electronic eigenstates. Coupling to graphics processing unit accelerated time-dependent configuration interaction software to TAB and TAB-DMS enables ab initio nonadiabatic molecular dynamics simulations on many electronic states, in full nuclear dimensionality, and without prior knowledge of reaction mechanism. We apply our approach to investigate long-lived electronic coherences observed in recent ultrafast experiments on thiophene excited by a strong, non-resonant laser pulse.

Making a Splash: Chemical Physics at the Gas-Liquid Interface

Mikhail Ryazanov[a], Timothy Livingston Large[b], David J. Nesbitt[c]

[a]JILA, University of Colorado, Boulder, CO 80309
[b] Combustion Research Facility, Sandia National Lab, Livermore, CA, 94550
[c] JILA, University of Colorado, Boulder, Department of Chemistry and Biochemistry, Department of Physics, University of Colorado, Boulder, CO 80309, USA, email: djn@jila.colorado.edu

ABSTRACT

We often teach in freshman Chemistry that there are three phases of matter: gas, liquid and solid – with the order reflecting increasing complexity and strength of interaction between the molecular constituents. But there is also an additional "phase" of matter associated with the microscopically thin interface (a few molecules thick) *between* the gas and liquid, which is poorly understood and yet plays a crucial role in fields ranging from atmospheric aerosol chemistry to passage of gases through alveolar sacs in our lungs. This talk will report some new directions for this emerging field, each embracing a rovibronically quantum state-resolved perspective. Specifically, we exploit molecular beams and laser spectroscopy to address two fundamental questions. At the microscopic level, do molecules in all internal quantum states (e.g., vibrational, rotational, electronic) colliding with the gas-liquid interface "stick" with unit probability? Can reactive, scattering, and/or evaporating molecules at the gas liquid interface avoid collisions with other species and thereby reflect a "nascent" collision-free distribution? We present results from three experimental applications: i) reactive scattering dynamics of F atoms with wetted wheel gas-liquid interfaces, ii) inelastic scattering of HCl from self-assembled monolayers (SAMs) via resonance-enhanced photoionization (REMPI)/velocity map imaging (VMI) methods, and iii) quantum state resolved evaporation dynamics of NO at the gas-water interface. As a recurring theme, we find that molecules reactively, inelastically, or evaporatively scatter from the gas-liquid interface into internal quantum state distributions substantially ***out of equilibrium*** with respect to the bulk liquid (T_S). From detailed balance considerations, the data unambiguously indicate that molecules exhibit a clear rovibronic state dependence to how they "stick" to and eventually solvate into the liquid. These results serve to underscore the importance of ***non-equilibrium thermodynamics*** in energy transfer/chemical reactions at gas-liquid interfaces. Such non-equilibrium behavior makes this rapidly emergent field more complicated but also provides extremely interesting targets for further experimental/theoretical exploration.

Applying Ion Imaging Methods to Site Specific Elementary Reactions in Heterogeneous Catalysis

Theofanis Kitsopoulos

School of Mathematics and Natural Sciences, University of Southern Mississippi, Hattiesburg MS 39402, USA. Email: Theofanis.Kitsopoulos@usm.edu

ABSTRACT

Heterogeneous catalysis, a linchpin of modern industry, lies at the forefront of global efforts to secure sustainable energy sources and develop eco-friendly technologies. In this talk I will present the adoption of Ion Imaging—and its innovative variants—to quantify catalytic rates for site-specific elementary reactions, presenting an unparalleled opportunity to deepen our foundational comprehension of this pivotal field.

Velocity Resolved Kinetics (VRK) [1, 2] emerges as a transformative tool poised to revolutionize our understanding of site-specific chemical reaction mechanisms in heterogeneous catalysis. It allows rigorous exploration to characterize the pivotal factors shaping the kinetics of elementary reactions at surfaces. By scrutinizing the chemical nature of catalysts and the intricate geometries of active sites (stereodynamics), we aim to elucidate the intricate interplay between molecular structure and catalytic activity. Our investigations focus on elementary reactions involving carbon, hydrogen, oxygen, and nitrogen—cornerstones of numerous industrial processes including methane reforming, syngas production, fuel cell technologies, Fischer-Tropsch synthesis, and the Haber-Bosch process.

Employing a "bottom-up" approach to catalysis, we endeavor to decipher the complexities of heterogeneous chemical catalysis by unraveling the site-specific kinetics of elementary building block reactions. Our integrated experimental and computational methodologies offer a comprehensive suite of tools to probe and dissect catalytic processes at unprecedented levels of detail. By operating within the microsecond regime and spanning temperatures from 200 to 1000 K, our methodology faithfully replicates industrial conditions, ensuring real-world relevance and applicability.

---

[1] Neugebohren, J.; Borodin, D.; Hahn, H. W.; Altschäffel, J.; Kandratsenka, A.; Auerbach, D. J.; Campbell, C. T.; Schwarzer, D.; Harding, D. J.; Wodtke, A. M. Velocity-resolved kinetics of site-specific carbon monoxide oxidation on platinum surfaces. *Nature* 2018, *558* (7709), 280-283.

[2] Fingerhut, J.; Lecroart, L.; Schwarzer, M.; Horandl, S.; Borodin, D.; Kandratsenka, A.; Kitsopoulos, T. N.; Auerbach, D. J.; Wodtke, A. M. Identification of reaction intermediates in the decomposition of formic acid on Pd. *Faraday Discuss*, 251 (0), 412-434, 2024.

Facet-Dependent Ultrafast Photoinduced Reaction Dynamics of CH_3I on TiO_2 Surfaces

Aakash Gupta[a], Tian Wang[b], Keith Blackman[a], Corine M. Smith[a], Xiaosong Li[b], and Mihai E. Vaida[a]

[a]Department of Physics and Renewable Energy and Chemical Transformations Cluster, University of Central Florida, Orlando, Florida 32816, USA
[b]Department of Chemistry, University of Washington, Seattle, Washington 98195, USA
mihai.vaida@ucf.edu

ABSTRACT

The detection of intermediate species during surface photoinduced reactions and the correlation of their ultrafast dynamics with the properties of the surface is crucial to fully understand and control heterogeneous reactions at the gas-solid interfaces. In this study, a technique that combines time-of-flight mass spectrometry with laser spectroscopy and fast surface preparation with molecules is employed to investigate the mechanism of photoinduced CH_3I reactions on TiO_2(100) and TiO_2(110) surfaces through the direct detection of intermediate species and final products.

On TiO_2(100), the photoinduced reaction dynamics of CH_3I exhibit similar trends observed on other metal oxide surfaces.[1-3] A portion of the initial intermediates produced on a freshly prepared surface is trapped to passivate the surface. On the passivated TiO_2(100) surface, adsorbed CH_3I molecules are excited into the dissociative A-band by a 266 nm pump laser pulse, generating CH_3 and I intermediates that can recombine to regenerate CH_3I. Subsequently, the probe laser pulse ionizes the intermediate and final products, which are detected by a mass spectrometer as a function of the pump-probe time delay. The short minimum dissociation time of CH_3I obtained by monitoring the CH_3^+ fragment, which is 110 fs, and the rapid rise of the CH_3^+ signal indicate that CH_3I is adsorbed with the I atom facing the surface. The reformation time of CH_3I is much longer than the dissociation time of CH_3I and reflects the time required for the CH_3 and I intermediates to lose the excess translational energy released from photodissociation.

In contrast, on the TiO_2(110) surface, the photochemistry diverges significantly. On the freshly prepared surface, a fraction of the initial intermediates is not only trapped to passivate the surface, but CH_3 fragments can also react with undissociated CH_3I molecules to form CH_3ICH_3 species. Upon the formation of CH_3ICH_3, the pump laser pulse excites this species into a vibrational level of a bound electronic state. Subsequently, the probe pulse further excites this species into a dissociative cationic state, producing CH_3^+ and CH_3I. The CH_3^+ signal exhibits oscillations with a periodicity of 100 fs, attributed to coherent wave packet motion on the bound electronic state of CH_3ICH_3. The transient evolution obtained by monitoring CH_3I^+ reflects both the reaction between the CH_3 and I intermediates as well as the dissociation of CH_3ICH_3 species. This investigation reveals how changes in the surface structure can lead to dramatically different chemical behavior at the nanoscale.

---

[1]M. A. K. Pathan, A. Gupta and M. E. Vaida, J. Phys. Chem. Lett., **13**, 9759-9765, 2022.
[2] K. Blackman *et al, Rev.Sci. Instrum. 95,* 083003, 2024.
[3]M. E. Vaida and T. M. Bernhardt, in Ultrafast Phenomena in Molecular Sciences: Femtosecond Physics and Chemistry, eds. R. de Nalda and L. Bañares, Springer International Publishing, Cham, pp. 231-261, 2014.

State-to-State Scattering of Open Shell Atoms from Surfaces

Zibo Zhao[a], Ximei Yang[a], Yingqi Wang[b], Jiamei Quan[c], Xueming Yang[d,e], Alec M. Wodtke[a,f], Hua Guo[b], G. Barratt Park[a,g]

[a] *Max Planck Institute for Multidisciplinary Sciences, Göttingen, Germany*
[b] *University of New Mexico, Albuquerque, NM, USA*
[c] *Institute of Advanced Science Facilities, Shenzhen, China*
[d] *Dalian Institute of Chemical Physics, Dalian, China*
[e] *Southern University of Science and Technology, Shenzhen, China*
[f] *University of Göttingen, Institute for Physical Chemistry, Göttingen, Germany*
[g] *Texas Tech University, Lubbock, TX, USA; barratt.park@ttu.edu*

ABSTRACT

In this work, VUV radiation obtained from tabletop laser systems and from the Dalian Coherent Light Source (DCLS) were used to generate controlled beams of open-shell atoms for surface scattering experiments. The incidence energy can be tuned by changing the photolysis wavelength. Atoms in different electronically excited states scatter from the surface at different times and can be distinguished unambiguously with the help of ion imaging. I will discuss two scattering systems. First, we performed state-resolved scattering of O-atom beams in the ^{3}P and ^{1}D electronic states from a highly-oriented pyrolytic graphite (HOPG) surface [1]. We characterized a spin non-conserving ^{1}D→^{3}P scattering channel and gained insight into the role of intersystem crossing in the oxidation of graphite by atomic oxygen. Measurement of the sticking coefficients reveals that O(^{1}D) is more reactive to graphite than O(^{3}P), due in part to the low probability of spin transitions at the surface. In a second study, we scattered atomic carbon beams from Au(111) and characterized C(^{1}D→^{3}P) and C(^{3}P→^{3}P) scattering channels. The C(^{3}P→^{3}P) channel exhibits two peaks in the scattering kinetic energy distribution. The possible mechanism for bimodal scattering may involve charge transfer. If time allows, I will also introduce some preliminary results on the mechanisms of methanol reactions at Pt and Ag surfaces.

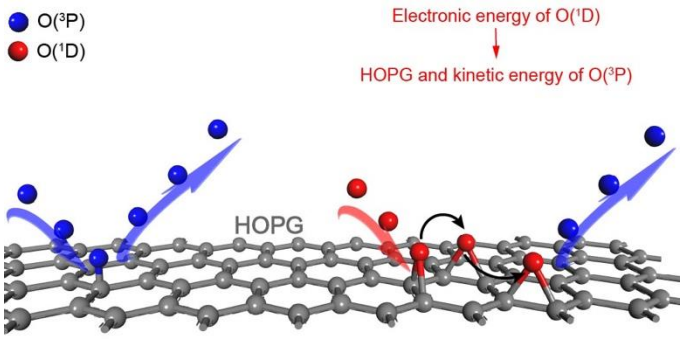


Figure 1. O(^3P→^3P) scattering on HOPG at incidence energies from 0.2−1.2 eV occurs without intersystem crossing near the surface. O(^1D→^3P) scattering over the incidence energy range studied (0.06−0.23 eV) is accompanied by a spin transition at the seam of crossing, which occurs with low probability.

---

[1] [3] Zhao, Z. et al. Spin-dependent reactivity and spin-flipping dynamics in oxygen atom scattering from graphite *Nat. Chem.* **15**, 1006–1011, (2023).

Nonadiabatic Dynamics and Ionization in N+ N and N + O Collisions

George C. Schatz[a]

[a] *Department of Chemistry, Northwestern University, Evanston IL 60208-3113 USA*
Email: g-schatz@northwestern.edu

ABSTRACT

Excited atomic nitrogen and oxygen play an important role in plasma formation in hypersonic shock-waves, as happens during spacecraft reentry and other high velocity vehicle applications. In this talk I describe studies aimed at providing collision induced excitation and associative ionization (dissociative recombination) cross sections for two of the most important processes leading to plasma formation, the N + N and N + O systems using high quality potential energy surfaces from multireference configuration interaction, quantum scattering and complex basis function calculations. One project involving Yanze Wu (postdoc) and Madji Hochlaf was recently published for the case of N + N collisions[1] leading to transitions involving N(^{4}S), N(^{2}D) and N(^{2}P) states at N+ N energies up to 6 eV, and the results are in good agreement with experiment where comparisons are possible. These results reveal that both spin-orbit and derivative coupling nonadiabatic processes play important roles that depend on the spin and orbital symmetry of the states considered. For processes involving spin-orbit coupling, we have developed a scaling method for treating transitions between different fine-structure components with a method that only requires calculations with two coupled states, and with the cross sections being scaled to include all contributing components. In addition we have defined accurate degeneracy factors for determining cross sections and rate coefficients that include all symmetry factors.

Studies of associative ionization (AI) and dissociative recombination (DR) in N + N collisions in collaboration with Abhisek Ghosal(postdoc) are based on the use of spin-flip coupled-cluster calculations (SF-EOM-CCSD) with complex basis functions (CBF) to determine the rates of ionization as a function of the internuclear separation, followed by scattering calculations that convert these rates into cross sections. In this case there are seven important excited states of N_2 that are accessible to ionization, and our results, for states that are well described using a single reference wavefunction, are in good agreement with earlier results from Guberman[2] who modeled autoionization widths.

---

[1] Yanze Wu, Majdi Hochlaf and George C. Schatz, Modeling of collision-induced excitation and quenching of atomic nitrogen, J. Chem. Phys. 161, 014104 (2024).

[2] S. L. Guberman, Spectroscopy above the ionization threshold: Dissociative recombination of the ground vibrational level of N_2^+ J. Chem. Phys. 137, 074309 (2012).

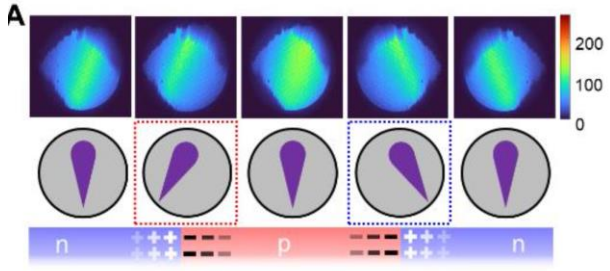
Measuring Velocity With High Resolution for Low Energy Molecules and Electrons

David W. Chandler, Olivia Krohn, Eric Smoll, Frank Alcorn, Suhas Kumar, Chris Kliewer

Sandia National Laboratory. Email: chand@sandia.gov
Livermore Ca, 94550

ABSTRACT

The progress of science is ensured when each generation of scientists improves upon the previous generations work. To stand on their shoulder to reach higher. The march is to generate the highest quality science and that relies on making better and better quantitative measurements of physical species and phenomena to understand them at a fundamental level. Measurements of species and phenomena that have not been able to previously be studied due to lack of technology are of particular interest. Many times this is a question of technology advancing such as the ever-improving laser technologies that provide us with higher frequency resolution and faster time resolution light sources. A similar evolution in the detection of charged species by various imaging techniques has taken shape over the last ~40 years since the first Ion Imaging paper was published in 1987. Velocity mapped ion imaging has become the "go to" method for measuring the velocity distribution of everything from photochemistry produced fragments, bimolecular reaction products, photo-electrons kinetic energies, electron interferences in molecules, and orientation and alignment of molecules produced by various processes to name just a few of the applications. These advancements have been made through the efforts of an army of researchers through the world. As the ability to image has improved through improvements in ion optics, techniques such as "slice imaging", and clever techniques to measure the position and arrival time of all the species the scope of interesting problems to solve has expanded. I report here on my efforts to image low-energy electrons from a secondary electron microscope in a manner that lets one see the electron plume respond to a PN junction, the fast evolution of laser induced plasma electrons for quantitative measurement of electron temperature, the imaging of species coming from a surface in a manner that lets me determine the position on the surface that the reaction product was formed and the production and detection of ultra-high velocity resolution molecular beams for precise low energy scattering experiments.



Chandler DW. Houston PL, J Chem. Phys. 87(2) pp 1445-1447 (1987)

Deciphering spectral signatures of proton delocalization in complexes of hydroxide and hydronium ions with water molecules

Anne B. McCoy

Department of Chemistry, University of Washington, Seattle, WA 98195 USA.
Email: abmccoy@uw.edu.edu

ABSTRACT

One class of system where explorations of larger complexes is particularly instructive involves complexes of ions with water molecules. In these systems the cooperative nature of the hydrogen bond that are formed leads to large changes in the strengths of the ion-water interactions as more water molecules are introduced, and this, in turn, has a large effect on the spectroscopy. This talk will focus on work in our group exploring the most fundamental ion-water complexes, those between water molecules and hydronium or hydroxide ions. This work employs an array of theoretical and computational approaches, ranging from analysis of the couplings of the vibrations at the harmonic level through analysis of the wave functions using diffusion Monte Carlo approaches. The work is motivated by the studies of the vibrational spectra of complexes of hydronium and hydroxide ions with up to five water molecules, performed by Mark Johnson, Knut Asmis and Michael Duncan and their groups. Interestingly, as the number of solvating water molecules is increased from one to three, the frequency of the OH bond involved in the ion/water interaction experiences a large blue-shift with very similar spectral contours being observed for the complexes of hydroxide and hydronium ions with water.

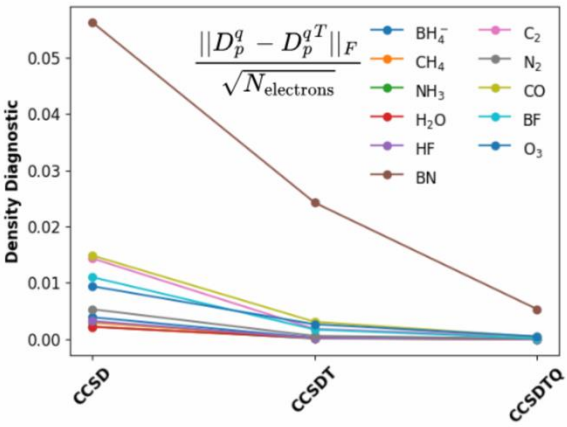
Exploiting a Shortcoming of Coupled-Cluster Theory: The Extent of non-Hermiticity as a Diagnostic Indicator of Computational Accuracy

Kaila E. Weflen,[a] Megan R. Bentley,[a] James H. Thorpe,[b] Peter R. Franke,[a] Jan M.L. Martin,[a,c] Devin A. Matthews,[b] and John F. Stanton[a,d]

[a] *Quantum Theory Project, University of Florida, Gainesville, FL 32611.*
[b] *Department of Chemistry, Southern Methodist University, Dallas, TX 75275*
[c] *On sabbatical from: Dept. of Molecular Chemistry and Materials Science, Weizmann Institute of Science, 234 Herzl Street, 7610001 Reḥovot, Israel. Email: gershom @weizmann.ac.il*
[d] *Senior author. Deceased March 21, 2025*

ABSTRACT

The fundamental non-Hermitian nature of the forms of coupled-cluster (CC) theory widely used in quantum chemistry has usually been viewed as a negative, but the present letter shows how this can be used to advantage. Specifically, the non-symmetric nature of the reduced one-particle density matrix (in the molecular orbital basis) is advocated as a diagnostic indicator of computational quality.[1]



In the limit of full coupled-cluster theory (which is equivalent to full configuration interaction (FCI)), the electronic wavefunction and correlation energy are exact within a given one-particle basis set and the symmetric character of the exact density matrix is recovered. The extent of the density matrix asymmetry is shown to provide a measure of "how difficult the problem is" (like the well-known T_1 diagnostic[2] and others[3,4]), but its variation with level of theory also gives information about "how well this particular method works", irrespective of the difficulty of the problem at hand. The proposed diagnostic is described and applied to a select group of small molecules, and an example of its overall utility for the practicing quantum chemist is illustrated through its application to the beryllium dimer (Be_2). Future application of this idea to excited states, open-shell systems, symmetry-breaking problems and extension of the method to the two-particle density are then proposed.

---

[1] Weflen, K. E. *et al.* Exploiting a Shortcoming of Coupled-Cluster Theory: The Extent of non-Hermiticity as a Diagnostic Indicator of Computational Accuracy. *J. Phys. Chem. Lett.* 16, 5121-5127, 2025.
[2] Lee, T. J. and Taylor, P. R. A Diagnostic for Determining the Quality of Single-Reference Electron Correlation Methods. *Int. J. Quantum Chem. Symp.* 23, 199-207, 1989.
[3] Xu, X. *et al.* An All-Purpose Measure of Electron Correlation for Multireference Diagnostics *Int. J. Chem. Theory Comput.* 20, 721-727, 2024.
[4] Martin, J. M. L., Santra, G., and Semidalas, E. An exchange-based diagnostic for static correlation *AIP Conf. Proc.* 2611, 020014, 2022 and references therein.

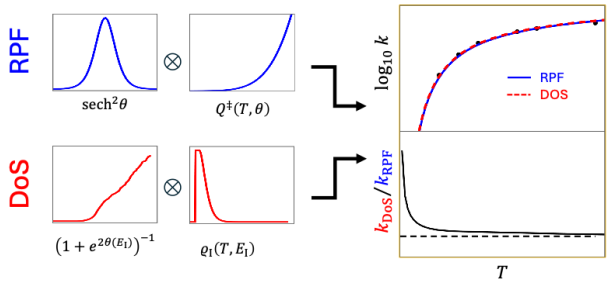
Classical and Semiclassical Transition State Theory: Old and New

Rigoberto Hernandez[a,c,d] and Alexander Popov[b]

[a]*Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218.*
Email: r.hernandez@jhu.edu
[b]*Department of Chemistry,* [c]*Department of Chemical and Biomolecular Engineering and Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, MD 21218*

ABSTRACT

The rates of chemical reactions (or any activated process) are by definition determined by the flux of reactants (or initial states) that end up as products (or final states). Through the last hundred years of studies on reaction rate theory, it has become clear that this can be equated to the flux through any surface that divides reactants from products as long as only those trajectories that end up as products are included in the flux. Transition state theory (TST) ignores this last clause. That is, it overestimates the rate if any of the trajectories recross the dividing surface. However, its advantage is that it replaces a dynamical calculation with a geometric one. Through a variational principle or perturbation theory, however, one can construct non-recrossing dividing surfaces that lead to exact rates.[1] These approaches are limited by the nature of the search space of surfaces and the reference dividing surface, respectively. We will discuss recent advances for determining such dividing surfaces geometrically using non-perturbative approaches.[2] Moreover, we can also address reactions under conditions far from equilibrium in so-called complex environments.[3] Semiclassical transition state theory (SCTST) offers the posibility of retaining the geometic advantages of TST while including quantum corrections. Stanton and coworkers,[4] for example, exploited high accuracy electronic structure gradients of the transition state in obtaining reaction rates, and thereby showed the applicability of semiclassical transition state theory. One alternative of the canonical SCTST rate formula introducted by Hernandez and Miller[5] is written as a convolution of a kernel and the so-called restricted partition function (RPF) over the action associated with the reaction coordinate. The argument of this trace is a function of the Hamiltonian operator which can be resolved over the Hilbert space of quantum states orthogonal to the reaction coordinate.[6] In principle, it can be resolved using the nonperturbative phase space approaches developed recently, making it useful for renewed attention. Meanwhile, the density-of-states (DoS) SCTST has also reframed the rate formula in terms of the instanton's density of states (DoS).[7] We will show the relationship between RPF-SCTST and DoS-SCTST, and derive the latter from the former. In this way, we help to unify these branches of SCTST, and provide a clearer formalism for future advances.[8]



---

[1] R. Hernandez, T. Bartsch and T. Uzer, "Transition state theory in liquids beyond planar dividing surfaces," *Chem. Phys.* **370**, 270-276 (2010).
[2] M. Feldmaier, R. Bardakcioglu, J. Reiff, J. Main, and R. Hernandez, "Phase-space resolved rates in driven multidimensional chemical reactions," *J. Chem. Phys.* **151**, 244108 (2019).
[3] Y. Nagahata, R. Hernandez and T. Komatsuzaki, "Perspective: Phase Space Geometry of Isolated to Condensed Chemical Reactions," *J. Chem. Phys.*, 155, 210901 (2021).
[4] T. L. Nguyen, J. F. Stanton, and J. R. Barker, "Ab initio reaction rate constants computed using semiclassical transition-state theory: HO + H_2 →H_2O + H and isotopologues," *J. Phys. Chem. A* 115, 5118–5126 (2011).
[5] R. Hernandez and W. H. Miller, "Semiclassical transition state theory – a new perspective," *Chem. Phys. Lett.* **214**, 129 (1993).
[6] R. Hernandez; "A combined use of perturbation theory and diagonalization: application to bound energy levels and semiclassical rate theory," *J. Chem. Phys.* **101**, 9534 (1994).
[7] J. E. Lawrence and J. O. Richardson, "Improved microcanonical instanton theory," *Faraday Discuss. Chem. Soc.* **238**, 204 (2022).
[8] A. V. Popov and R. Hernandez, *J. Chem. Phys.* (2025), submitted.

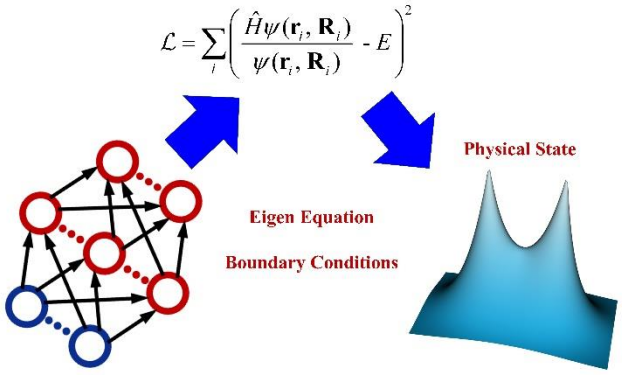
SchrödingerNet: A Universal Neural Network Solver for The Schrödinger Equation

Yaolong Zhang[a], Bin Jiang[b], and Hua Guo[a]

[a] Department of Chemistry and Chemical Biology, Center for Computational Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, USA Email: ylzhangch@unm.edu
[b] Key Laboratory of Precision and Intelligent Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

ABSTRACT

Recent advances in machine learning have enabled numerically accurate solutions of the electronic Schrödinger equation (SE) by integrating neural network (NN)-based wavefunction ansatzes with variational Monte Carlo (VMC) methods[1-2]. However, existing NN-based approaches typically rely on the Born–Oppenheimer approximation (BOA) and require separate, computationally intensive training for each nuclear configuration. In this work, we introduce SchrödingerNet, a novel NN wavefunction ansatz designed to solve the full electronic-nuclear SE by minimizing a loss function aiming to equalize local energies across the system[3]. Our approach proposes a new wavefunction ansatz inspired by quantum chemistry methods, incorporating multiple orbital types with configuration-dependent coefficients and an explicit electron–electron correlation term. This design combines physical interpretability with the expressive power of NNs, enabling the accurate description of multi-reference systems across a wide range of nuclear geometries using a few Slater determinants and significantly fewer parameters. Moreover, it naturally incorporates non-BOA effects. Benchmark results on molecular systems validate the accuracy and efficiency of SchrödingerNet.



---

[1] Hermann, J.; Schätzle, Z.; Noé, F., Deep-neural-network solution of the electronic Schrödinger equation. Nat. Chem. 12, 891-897, 2020.
[2] Pfau, D.; Spencer, J. S.; Matthews, A. G. D. G.; Foulkes, W. M. C., Ab initio solution of the many-electron Schrödinger equation with deep neural networks. Phys. Rev. Res. 2, 033429, 2020.
[3] Zhang, Y.; Jiang, B.; Guo, H., Schrödingernet: A universal neural network solver for the Schrödinger equation. J. Chem. Theory Comput. 21, 670-677, 2025.

Two Hundred Years after Hamilton: Exploring New Formulations of Classical and Quantum Mechanics

David J. Tannor

Department of Chemical and Biological Physics, Weizmann Institute of Science, 76100 Rehovot, Israel, Email:David.Tannor@weizmann.ac.il

ABSTRACT

This talk has three parts. The first part is an introduction to Hamilton's two monumental papers from 1834-1835, which introduced the Hamilton-Jacobi equation, Hamilton's equations of motion and the principle of least action [1]. These three formulations of classical mechanics became the three forerunners of quantum mechanics; but ironically none of them is what Hamilton was looking for -- he was looking for a "magical" function, the principal function $S(q_1, q_2, t)$ from which the entire trajectory history can be obtained just by differentiation (no integration) [2]. In the second part of the talk I argue that Hamilton's principal function is almost certainly more magical than even Hamilton realized. Astonishingly, all of the above formulations of classical mechanics can be derived just from assuming that $S(q_1, q_2, t)$ is additive, with no input of physics [3]. The third part of the talk will present a new formulation of quantum mechanics in which the Hamilton-Jacobi equation is extended to complex-valued trajectories [4], allowing the treatment of classically allowed processes, classically forbidden process and arbitrary time-dependent external fields within a single, coherent framework. The approach is illustrated for barrier tunneling, wavepacket revivals, nonadiabatic dynamics, optical excitation using shaped laser pulses and high harmonic generation with strong field attosecond pulses [5].

1. W. R. Hamilton, On a General Method in Dynamics, Philosophical Transactions, Part 2, p. 247 (1834); ibid., Second Essay on a General Method in Dynamics, Part 1, p. 95 (1835).

2. M. Nakane and C. G. Fraser, The Early History of Hamilton-Jacobi Dynamics 1834-1837, Centaurus 44, 161 (2002); C. Lanczos, The Variational Principles of Mechanics (Oxford, 1949)

3. D. J. Tannor, New derivation of Hamilton's three formulations of classical mechanics (preprint); ibid, Duality of the Principle of Least Action: A New Formulation of Classical Mechanics, arXiv:2109.09094 (2021).

4. Y. Goldfarb, I. Degani and D. J. Tannor, Bohmian mechanics with complex action: A new trajectory based formulation of quantum mechanics, J. Chem. Phys. 125, 231103 (2006); J. Schiff, Y. Goldfarb and D. J. Tannor, Path integral derivations of complex trajectory methods, Phys. Rev. A 83, 012104 (2011); N. Zamstein and D. J. Tannor, Overcoming the root search problem in complex quantum trajectory calculations, J. Chem. Phys. 140, 041105(2014).

5. N. Zamstein and D. J. Tannor, Non-adiabatic molecular dynamics with complex quantum trajectories. I. The adiabatic representation, J. Chem. Phys. 137, 22A518 (2012); W. Koch and D. J. Tannor, Wavepacket revivals via complex trajectory propagation, Chem. Phys. Lett. 683, 306 (2017); W. Koch and D. J. Tannor, A three-step model of high harmonic generation using complex classical trajectories, Annals of Physics, 427, 168288 (2021).

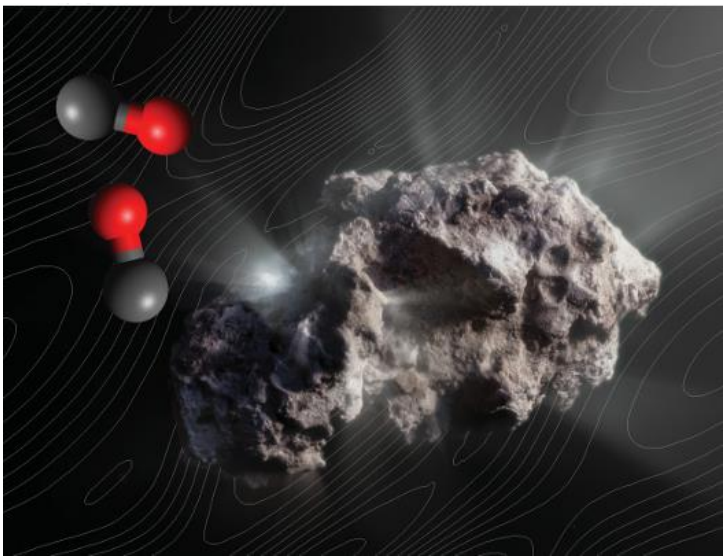
Recent Advances in Mixed Quantum/Classical Theory (MQCT) for Molecule + Molecule Collisions

Carolin Anna Joy, Dulat Bostan, and Dmitri Babikov

Chemistry Department, Marquette University, Milwaukee, WI, 53201-1881
Email: carolin.joy@marquette.edu

ABSTRACT

Collisional energy transfer plays a critical role in numerous physical processes, from atmospheric chemistry to interstellar medium dynamics. However, full quantum mechanical treatments of molecular collisions become computationally prohibitive for molecule + molecule systems, particularly those involving two heavy collision partners and higher collision energies, when the number of partial waves required for the description of scattering increases substantially. This presentation highlights recent developments in the Mixed Quantum/Classical Theory (MQCT), which combines quantum mechanical treatment of internal ro-vibrational motion with classical descriptions of scattering, providing an optimal balance between accuracy and computational efficiency. Our implementation employs time-dependent Schrödinger equation for the internal molecular states while using Ehrenfest mean-field trajectories for translational motion. This approach preserves essential quantum phenomena including state quantization, zero-point energy, selection rules, and quantum interference — while achieving significant computational speedup compared to fully quantum methods. Recent algorithmic improvements and massive parallelization have permitted us to extend MQCT to previously inaccessible complex systems. We present applications to challenging molecule-molecule collisions of heavy partners, including H_2O + H_2O, CO + CO, and HCN + H_2O.[1-3] Comparisons with available benchmark quantum calculations demonstrate that MQCT provides reliable predictions across broad energy range, while offering unique time-dependent insights into collision dynamics. Our results show that for complex polyatomic systems, MQCT accurately captures state-to-state transitions, even when incorporating large rotational basis sets that would be computationally intractable with fully quantum approaches. These advances position MQCT as a powerful predictive tool for modeling energy transfer in complex molecular systems relevant to astrophysical and atmospheric environments.



---

[1] Mandal, B.; Babikov, D. Rate Coefficients for Rotational State-to-State Transitions in H_2O + H_2O Collisions for Cometary and Planetary Applications, as Predicted by Mixed Quantum-Classical Theory. *Astron. Astrophys* 671, A51, 2023.

[2] Mandal, B.; Babikov, D. Improved Temperature Dependence of Rate Coefficients for Rotational State-to-State Transitions in H_2O + H_2O Collisions. *Astron Astrophys* 2023, *678*, A51

[3] Bostan, Dulat, et al. "Mixed quantum/classical calculations of rotationally inelastic scattering in the CO + CO system: a comparison with fully quantum results." *Physical Chemistry Chemical Physics* 26(8), 6627-6637, 2024

New Platforms for Molecular Polariton Dynamics

Marissa L. Weichman

Department of Chemistry, Princeton University, Princeton, NJ, Email:weichman@princeton.edu

ABSTRACT

Polaritons are hybrid light-matter states that arise from strong interactions between a molecular ensemble and the confined electromagnetic field of an optical cavity. Cavity-coupled molecules can demonstrate reactivity and photophysics distinct from their free-space counterparts, but the mechanisms and scope of these phenomena remain uncertain. I will discuss new experimental platforms that we are developing to observe and understand molecular dynamics under cavity strong coupling.

While polaritons are well-established in solution-phase and solid-state systems, they had not been previously reported in isolated gas-phase molecules, where attaining sufficiently strong light-matter interactions is a challenge. We are able to access the strong coupling regime in an intracavity cryogenic buffer gas cell optimized for the preparation of simultaneously cold and dense ensembles. We recently reported a proof-of-principle demonstration in methane where we strongly cavity-coupled individual rovibrational transitions and explored a range of conditions, including coupling strengths and detunings. We are extending this platform to achieve state-resolved electronic strong coupling in molecular iodine and to perform nonlinear spectroscopy of strongly-coupled systems when optically pumped either along the cavity axis or orthogonal to it. We will harness this setup as a testbed for fundamental studies of polariton photophysics and chemistry.

We are also searching for signatures of cavity-altered dynamics in benchmark condensed-phase systems with the goal of understanding how and when reactive trajectories may be influenced by strong light-matter interactions. We recently examined ultrafast radical hydrogen (H)-abstraction processes under vibrational strong coupling and found a conspicuous absence of cavity-altered dynamics in these low-barrier reactions. In ongoing work, we are targeting reactions with higher barriers where vibrational dynamics may be more likely to be perturbed by cavity coupling. We are also examining ultrafast dynamics in molecules under electronic strong coupling in order to examine prospects for cavity control of photochemistry.

Rotationally controlled hydrogen-surface reactions

Helen Chadwick

Department of Chemistry, Swansea University, Singleton Park, Swansea, SA2 8PP, United Kingdom.
Email: h.j.chadwick@swansea.ac.uk

ABSTRACT

Hydrogen is the most abundant molecule in the universe, and its interaction with surfaces underpins a huge range of processes, from the industrial manufacture of chemicals to developing a hydrogen economy. Understanding collisions of hydrogen with surfaces at a fundamental, molecular level therefore has great value. One property of ground-state H_2 that it was particularly difficult to control was its rotational orientation with respect to the surface, which classically corresponds to whether it is rotating like a helicopter (rotational plane parallel to the surface) of like a cartwheel (rotational plane perpendicular to the surface). Using a unique magnetic molecular interferometry technique (MMI)[1], which combines homogeneous and inhomogeneous magnetic fields, we can control and manipulate the rotational orientation of the H_2 molecule before it collides with a surface and explore what effect it has on the outcome of the molecule-surface collision. In this presentation I will introduce the MMI technique and present recent results[2] showing the effect that rotational orientation has on the dissociation of H_2 when it collides with a single crystal surface.

---

[1] O. Godsi *et al*. A general method for controlling and resolving rotational orientation of molecules in molecule-surface collisions, *Nat. Comm.*, 8, 15357, 2017.
[2] H. Chadwick *et al.* Quantum state control of a ground state ortho-H_2 dissociation reaction, *Nat. Comm.*, accepted, 2025.

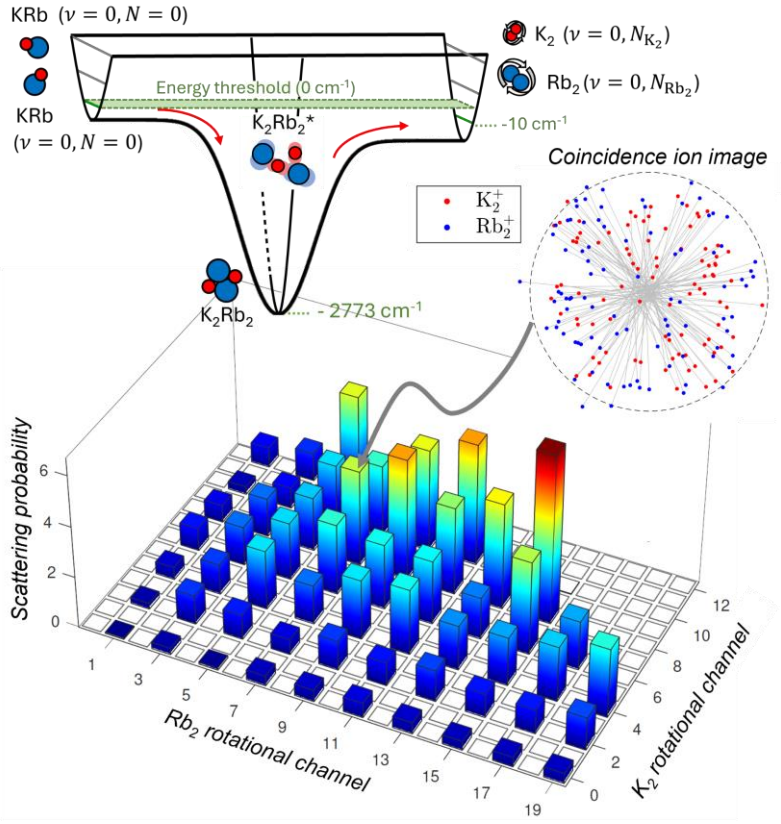
Advancing reaction dynamics with ultracold molecules

Yu Liu[a, b, c] , Jingchen Zhang[b,c] , Paul Julienne

[a] *Institute for Physical Science and Technology, University of Maryland, College Park*
[b] *Department of Chemistry and Chemical Biology, University of Maryland, College Park*
[c] *Joint Quantum Institute, University of Maryland and NIST*
Email: yuliu@umd.edu

ABSTRACT

Over the past few decades, concurrent advances in experimental techniques in both atomic, molecular, and optical (AMO) physics and physical chemistry have enabled unprecedented control over simple molecules, both in terms of their translational motion and their internal states. In this talk, I will discuss the potential for these fully-controlled molecules to advance our understanding and control of reaction dynamics at the quantum level. I will present a series of studies[1] on the reaction KRb + KRb → K_2 + Rb_2 initiated at T < 1 μK[2], including the direct observation of a long-lived reactive complex[3], the demonstration of product rotational state control via conserved nuclear spins[4], and a test of the statistical model using the pair-correlated quantum state distribution of the products[5]. These initial experiments paved the way for a new project in my group at the University of Maryland, where we are aiming to study isotope exchange reactions between Li atoms and diatomic molecules (e.g., ^{7}Li + ^{6}Li$_2$ → ^{6}Li^{7}Li + ^{6}Li, ^{6}Li^{7}Li + ^{6}Li^{7}Li → ^{6}Li$_2$ + ^{7}Li$_2$) at ultralow temperatures, and at the state-to-state level. I will present the prospect of this system as a playground for investigating quantum effects in reaction dynamics, such as interference between reaction pathways, entanglement between reaction products, and coherent control of bimolecular reactions. Finally, I will present our recent theory work on possible pathways to generate the ultracold reactants, specifically the formation of ultracold Li_2 dimers from laser cooled Li atoms.



---

[1] Liu, Y., & Ni, K.-K. Bimolecular Chemistry in the Ultracold Regime. *Annual Review of Physical Chemistry*, 73(1) (2022).
[2] Hu, M. G., Liu, Y., … Ni, K. K. Direct observation of bimolecular reactions of ultracold KRb molecules. *Science* (New York, N.Y.), 366(6469), 1111–1115 (2019).
[3] Liu, Y., Hu, M. G., … Ni, K. K. Photo-excitation of long-lived transient intermediates in ultracold reactions. *Nature Physics* (2020).
[4] Hu, M. G., Liu, Y., … Ni, K. K. Nuclear spin conservation enables state-to-state control of ultracold molecular reactions. *Nature Chemistry* (2020).
[5] Liu, Y., Hu, M.-G., Nichols, M. A., Yang, D., Xie, D., Guo, H., & Ni, K.-K. Precision test of statistical dynamics with state-to-state ultracold chemistry. *Nature*, 593(7859), 379–384 (2021).

Hypervelocity Ice Grain Impact Mass Spectrometry and the Search for Extraterrestrial Biosignatures

Robert E. Continetti

Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, La Jolla CA 92093-0340 USA Email: rcontinetti@ucsd.edu

ABSTRACT

One proposed spaceflight instrument for the detection of biosignatures in small icy particles – like those ejected from ocean worlds like Saturn's moon Enceladus or Jupiter's moon Europa – is an impact ionization mass spectrometer. Laboratory validation of proposed flyby sampling missions is needed to show that biosignature molecules can survive an impact at hypervelocity speeds. We developed an Aerosol Impact Spectrometer that makes use of charge-detection mass spectrometry to enable studies of the impact dynamics for single mass- and charge-selected submicron particles.[1,2] This provides a tool in the laboratory for validating the approach of sampling ocean world ice grain plumes in a flyby missions for the detection of specific biosignatures. Previously, we have applied this approach to study the impact dynamics of ice grains from 40 m/s to 2.4 km/sec, examining the coefficient of restitution and post-impact behavior including rebound, adhesion and fragmentation.[3,4] Now, using a 41-element linear accelerator (615 keV/q), this technique has been extended to allow particle velocities up to 4.2 km/sec, well above the ~2 km/sec threshold for impact ionization. Time-of-flight mass spectra obtained from the impact of single ~0.8 μm charged ice grains using the Hypervelocity Ice Grain Impact Mass Spectrometer following impact have now been measured. This technique replicates the hypervelocity impact of organic-laden submicron ice grains for in-situ mass spectrometric characterization in space missions. It is found that amino acids entrained in ice grains can be detected intact after impact at speeds up to 4.2 km/s and that the presence of salt reduces their detectability, providing an important benchmark for future missions to ocean worlds in our solar system to search for evidence for life beyond our planet.[5]

Acknowledgment: This work was supported by the Air Force Office of Scientific Research award MURI-22 FA9550-22-1-0199.

---

[1] B.D. Adamson, M.E.C. Miller, R.E. Continetti, The aerosol impact spectrometer: a versatile platform for studying the velocity dependence of nanoparticle-surface impact phenomena. *EPJ Tech. Instrum.* **4**, 1–17 (2017).

[2] S.E Burke and R.E. Continetti, Submicron particle impact dynamics and chemistry, Annual Review of Physical Chemistry, **75**, 67-88 (2024).

[3] M.E.C. Miller, S.E. Burke, R.E. Continetti, Production and impact characterization of Enceladus ice grain analogues. *ACS Earth Sp. Chem.* **6**, 1813–1822 (2022).

[4]S.E. Burke, M.E.C. Miller, R.E. Continetti, Velocity dependence of submicron ice grain rebound, sticking, particle fragmentation, and impact ionization up to 2.4 km/s. *ACS Earth Sp. Chem.* **7**, 764–773 (2023).

[5]S.E. Burke, Z.A. Auvil, K.A. Hanold, R.E. Continetti, Detection of amino acids with a hypervelocity ice grain impact mass spectrometer, Proc. Nat'l Acad. Sci., 120, e2313447120 (2023).

Direct Kinetic Studies of Unimolecular and Bimolecular Reactions of Criegee Intermediates

Jari Peltola, Petri Heinonen, Timo Pekkanen, and Arkke Eskola

Department of Chemistry, University of Helsinki, PO. BOX 55 (A.I. Virtasen aukio 1), FIN-00014, Finland. Email: arkke.eskola@helsinki.fi

ABSTRACT

Some time ago we designed and constructed a time-resolved, broadband cavity-enhanced absorption spectrometer (TR-BB-CEAS) instrument operating in the UV-range to perform direct kinetic measurements of stabilized Criegee Intermediates (sCIs). Both uni- and bimolecular reactions can be investigated over wide temperature (200–600 K) and pressure (5–500 Torr) ranges.[1] In our first experiments, we introduced a novel method to produce the smallest sCI by 213 nm laser photolysis of CH_2IBr to produce the CH_2I radical, which then reacts with O_2 to form formaldehyde oxide and an iodine atom ($CH_2I + O_2 \rightarrow CH_2OO + I$). By utilizing this new method in the unimolecular kinetic measurements of CH_2OO, we found that obtained unimolecular-decay rate coefficient is significantly larger compared to previous measurements employing the more widely used CH_2I_2 precursor.[1] In our view, *gem*-diiodo precursors introduce reaction pathways that lead to the regeneration of sCIs under some conditions, but these pathways are not present with the *gem*-bromoiodo precursors. This view is consistent with our and others observation for the unimolecular decay of acetone oxide, $(CH_3)_2COO$. By employing $(CH_3)_2CIBr$ as the precursor, our measured unimolecular-decay rate coefficient is in excellent agreement with previously reported indirect measurements, but not with a previous direct measurement that used $(CH_3)_2CI_2$ as the precursor. Our kinetic measurements for $(CH_3)_2COO$ also revealed that its unimolecular-decay reaction is faster than the previous direct measurement suggested, and bimolecular loss channels are actually unable to compete with the fast unimolecular reaction under atmospheric conditions. More recently, we have introduced another method to produce sCIs; the 193 nm photolysis of CH_2ICl to produce $CH_2I + Cl$ in presence of O_2. This new method will be useful in resolving the disagreement between the results obtained with *gem*-bromoiodo and *gem*-diiodo precursors. We also present unpublished results obtained with a laser photolysis – photoionization mass-spectrometer instrument that shed light on the secondary-chemistry problem discussed above.

Very recently we have investigated the unimolecular-decay reactions of $(C_2H_5)_2COO$[4] and *cyclic*-$(CH_2)_5COO$[5] sCIs utilizing $(C_2H_5)_2CIBr$ and *cyclic*-$(CH_2)_5CIBr$ precursors and 213 nm laser photolysis, respectively. To our knowledge, the latter experiments are the first-ever direct experimental observation and kinetic measurement of a *cyclic*-sCI. We look to build on this work and eventually investigate *cyclic* sCIs formed by the ozonolysis of *β*-pinene. Currently, we also work on sCI + perfluoro-compound reactions. More generally, our aim is to find chemical species, whose atmospheric degradation chemistry the sCIs may play an important role.

---

[1] Peltola J. *et al*., Time-resolved, broadband UV-absorption spectrometry measurements of Criegee intermediate kinetics using a new photolytic precursor: unimolecular decomposition of CH_2OO and its reaction with formic acid, *Phys. Chem. Chem. Phys.* 22, 11797-11808, 2020.

[2] Peltola J. *et al.,* Solving the discrepancy between the direct and relative-rate determinations of unimolecular reaction kinetics of dimethyl-substituted Criegee intermediate $(CH_3)_2COO$ using a new photolytic precursor, *Phys. Chem. Chem. Phys.,* 24, 5211-5219, 2022.

[3] Franzon L. *et al.,* An Experimental and Master Equation Investigation of Kinetics of the CH_2OO + RCN Reactions (R = H, CH_3, C_2H_5) and Their Atmospheric Relevance, *J. Phys. Chem. A*, 127, 477−488, 2023.

[4] Peltola J. *et al*., An experimental and computational study of the unimolecular-decay reaction of diethyl-substituted Criegee intermediate $(C_2H_5)_2COO$, *Phys. Chem. Chem. Phys.* 26, 28244-28258, 2024.

[5] Peltola J. *et al*., Direct Kinetic Measurements of a Cyclic Criegee Intermediate; Unimolecular Decomposition of *c*-$(CH_2)_5COO$, *J. Phys. Chem. Lett.*, 15, 5331-5336, 2024.

Gas-Phase Synthesis of Cyclic Silicon Dicarbide (c-SiC_2) and Bicyclic Silicon Tricarbide (c-SiC_3) via Single Collision Events from Acyclic Transients

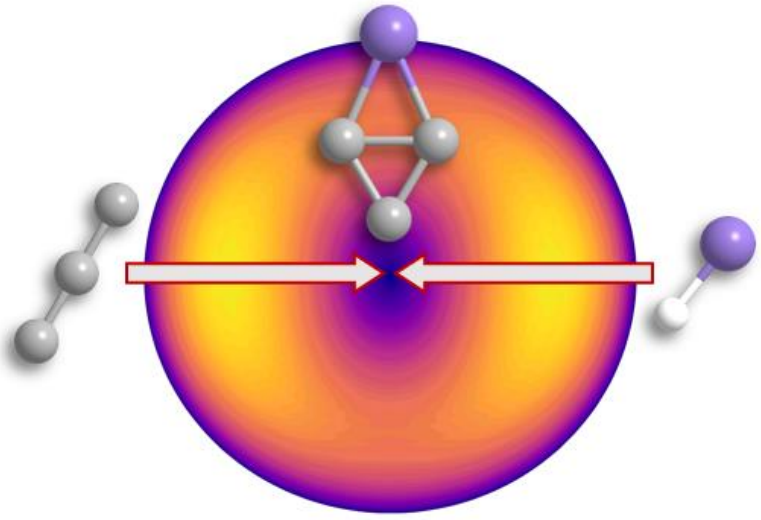
Shane J. Goettl,[a] Breno R. L. Galvão,[b] Rui Sun,[a] and Ralf I. Kaiser[a]

[a] *Department of Chemistry, University of Hawai'i at Mānoa, Honolulu, HI 96822, USA. Email: sgoettl@hawaii.edu*

[b] *Centro Federal de Educação Tecnológica de Minas Gerais, Belo Horizonte, Brasil 30421-169*

ABSTRACT

The gas-phase preparation of two silicon carbide molecules—cyclic silicon dicarbide (c-SiC_2, X^1A_1) and bicyclic silicon tricarbide (c-SiC_3, X^1A_1)—was accomplished under controlled experimental conditions via the bimolecular reactions of dicarbon (C_2, $X^1\Sigma_g^+/a^3\Pi_u$) and tricarbon (C_3, $X^1\Sigma_g^+$) with silylidyne radicals (SiH, $X^2\Pi$) under single-collision conditions. The combination of crossed molecular beams experiments with electronic structure calculations revealed barrierless entrance channels with addition of the silicon atom of the silylidyne radical to one or both terminal carbon atoms of dicarbon/tricarbon involving the formation of one or two rings in a single collision event with eventual hydrogen atom ejection leading to the cyclic silicon dicarbide (c-SiC_2) and the carbon–carbon bisected bicyclic silicon tricarbide (c-SiC_3) molecules. Quasi-classical trajectory (QCT) simulations as conducted for the tricarbon–silylidyne system provide excellent agreement with the experimental results. The overall barrierless and exoergic nature of these bimolecular reactions provides a directed synthesis of c-SiC_2 and c-SiC_3 even at ultralow temperatures as in cold molecular clouds such as G+0.693−0.0027 in the Galactic Center, where the former molecule was observed recently. Compared to the bicyclic silicon tricarbide molecule (c-SiC_3, X^1A_1), the isovalent tetracarbon molecule (C_4, $X^3\Sigma_g^-$) is not only linear, but also holds a triplet ground state. Therefore, the replacement of a single carbon atom with silicon results in a profound effect on stability, chemical bonding, and molecular structure, thus providing rare insights into the unique reaction mechanisms of silicon and carbon, where stability and chemical bonding diverge between isovalent systems.



Influence of Carbon Chain Length, Functionality, and Reaction Environment on C_1-C_7 Criegee Intermediates Reaction Networks

Denisia M. Popolan-Vaida,[a] Alec C. DeCecco,[a] Yitong Zhai,[a] Nils Hansen,[b] and Ahren W. Jasper[c]

[a] *Department of Chemistry, University of Central Florida, Orlando, FL 32816, Email: denisia.popolan-vaida@ucf.edu*

[b] *Combustion Research Facility, Sandia National Laboratories, Livermore, CA 94551, USA*

[c] *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA*

ABSTRACT

Reaction networks that govern the complex chemistry of combustion and atmospheric systems are often driven by reactive intermediates, which typically exist in low concentrations. Accurately identifying and quantifying these transient species within complex mixtures is crucial for developing a chemically accurate understanding of these systems. Among important intermediates, Criegee intermediates (CIs) - carbonyl oxides formed during the ozonolysis of unsaturated organic compounds - play a significant role. CIs exhibit fascinating chemical properties, participating in complex reaction networks that involve both unimolecular and bimolecular pathways. Their reactivity is dependent on factors such as carbon chain length, functional groups, and the nature of co-reactants. CIs possess the unique ability to incorporate both carbon and oxygen atoms into co-reactants via 1,3-dipolar cycloaddition or insertion mechanisms, leading to the formation of high-molecular-weight, low-volatility products. These products are closely associated with the rapid formation of secondary organic aerosols.

The reaction networks of C_2 CIs of different functionality and C_1 to C_7 CIs of different carbon number formed during the ozone-assisted oxidation of crotonaldehyde, crotyl alcohol, and a series of C_2 to C_7 acyclic and endocyclic alkenes, respectively were studied in an atmospheric pressure jet stirred reactor to understand the impact of the functionality, carbon number and reactive environment on product distribution and the formation of high-molecular-weight, low-volatility compounds. Molecular beam high-resolution mass spectrometry and tunable synchrotron single photon ionization, along with ab initio ionization energy calculations, were used to detect and identify gas-phase reactive intermediates and final products. Additionally, temperature-dependent analysis using DART ionization-Orbitrap mass spectrometry facilitated the detection of high-molecular weight, low-volatility reaction products. The ozone-assisted oxidation of acyclic C_1 to C_7 alkenes were observed to lead to complex CIs reaction networks that involve both CIs unimolecular and bimolecular reactions. For instance, formaldehyde oxide CIs formed in the ozone-assisted oxidation of ethylene, 1-propene, and 1-butene are observed to dominate the reaction networks, and products corresponding to sequential CIs additions to co-products like water, alkenes, aldehydes, alcohols, and carboxylic acids are detected. However, oligomerization does not appear to be favored by increasing the CIs carbon number. No evidence for the formation of bimolecular products is observed in the case of long chain CIs formed in the ozone-assisted oxidation of endocyclic alkenes, i.e., C_5 to C_7 alkenes. Instead, long chain CI are observed to undergo unimolecular decomposition followed by autooxidation. C_2 Criegee intermediates formed during the ozone-assisted oxidation of crotonaldehyde and crotyl alcohol, specifically acetaldehyde oxide (CH_3CHOO), glyoxal oxide (CHOCHOO), and glycolaldehyde oxide ($CH_2OHCHOO$), were found to exhibit similar reactivity patterns. Their reactions predominantly lead to products associated with interactions involving aldehydes, alkenes, and alcohols.

The results of our studies represent an important step towards understanding the CIs reactive behavior in complex reactive environments where several co-reactants are present. It provides valuable information for future kinetic modeling work that can add to a better understanding of the role and reactivity of CIs in the gas-phase to heterogeneous environments.

Bimolecular Reactions of Cyclic Ether Radicals

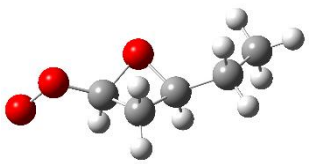
Brandon Rotavera

Department of Chemistry, University of Georgia. Email: rotavera@uga.edu

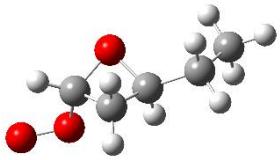
ABSTRACT

Alkyl-substituted cyclic ethers including alkyloxiranes and alkyloxetanes are isomer-specific proxies for reaction mechanisms of carbon-centered hydroperoxyalkyl radicals (ȮOOH). Subsequent bimolecular reactions of cyclic ethers include H-abstraction, which creates strained, carbon-centered radicals that may form peroxy radicals following O_2-addition. The length of the alkyl substituents and the proximity of the localized electron relative to the ether group affects the propensity for intramolecular hydrogen transfer to form a ȮOOH radical that retains the cyclic ether structure. In addition, stereochemical effects, namely the position of the substituents relative to the plane of the ether group, creates stereoisomer-specific reaction pathways, some of which involve chain-branching via formation and decomposition of organic acids (e.g. performic acid) and some involve the formation of metastable dicarbonyls (e.g. 2,4-pentanedione) that, prior to Doner et al.[1] were ascribed to form exclusively via decomposition reactions of ketohydroperoxides formed from second-O_2-addition (ȮOOH + O_2).

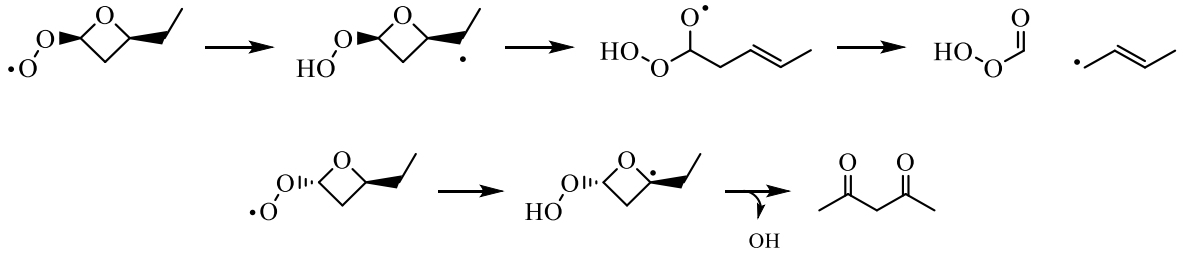
The importance of accurate and complete description of the chemical kinetics of cyclic ether lies in the ubiquitous, inadequate description of the aforementioned bimolecular reactions and the associated uncertainty that arises from mechanism truncation error[2]. Ongoing efforts to produce high-fidelity sub-mechanisms for cyclic ethers are outlined. The approach involves isomer-resolved speciation measurements from gas-phase oxidation experiments of cyclic ethers in a jet-stirred reactor in addition to high-level quantum-chemical computation of rate coefficients and thermochemical properties of species.



cis-2-ethyloxetanyl-4-peroxy



trans-2-ethyloxetanyl-4-peroxy



---

[1] Doner, A. C., J. Zador, Rotavera, B. Stereoisomer-Dependent Rate Coefficients and Reaction Mechanisms of 2-ethyloxetanylperoxy Radicals. *Proc. Comb. Inst.* 40, 105578, 2024.

[2] Dewey, N. S. and Rotavera, B. Reaction mechanisms of alkyloxiranes for combustion modeling. *Combustion Flame* 252, 112753, 2023.

[3] Copan, A. V., Moore III, K. B., Elliott, S. N., Mulvihill, C. R., Pratali Maffei, L., Klippenstein, S. J. Radical Stereochemistry: Accounting for Diastereomers in Kinetic Mechanism Development. *J. Phys. Chem. A* 128, 3711-3725, 2024.

Abstracts for Posters

Poster A13

Internal Conversion and Intersystem Crossing in Ammonia Photodissociation Manipulated by a Light-Induced Conical Intersection

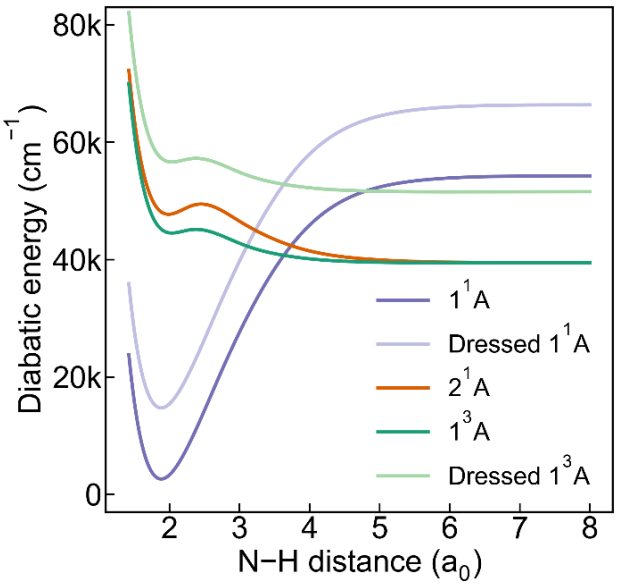
Chris Avanessian

Department of Chemistry, Johns Hopkins University, Baltimore, MD. Email: cavanes1@jhu.edu

ABSTRACT

Conical intersections (CIs) play an important role in photochemistry, allowing for ultrafast radiationless decay in processes such as photodissociation.[1] In addition to these natural CIs, light can give rise to seams of light-induced conical intersection (LICI), as the dipole–field interaction can significantly change the topography of the coupled potential energy surfaces.[2] This work explores the effect of LICIs on the photodissociation channels of ammonia, where a CI is known to play an important role. The radical channel, which yields NH_2 + H, is dominant. The molecular channel, which yields NH + H_2, is much rarer, and sometimes involves intersystem crossing to the triplet state.[3]

An approximate Floquet Hamiltonian was used to simulate the nonadiabatic molecular dynamics of ammonia photodissociation in the presence of an external laser field.[4] Quasiclassical surface-hopping trajectories were performed with SHARC using recently reported diabatic potential energy matrices, dipole matrices, and spin-orbit coupling matrices which were fitted using neural networks.[5]



The product branching ratios were drastically altered by the laser–dipole interaction, which is a signature of nonadiabatic effects induced by light. Without the electric field, 27% of trajectories throughout the entire energy range yielded excited-state NH_2. With the electric field present, this value decreased to below 1%, and the excited-state population lifetime decreased.[4] Significant changes were also observed in the molecular channel. With the field off, 0.04% of trajectories with a total energy of 8.4 eV yielded triplet NH. With an electric field strength of 0.02 Ha/ea_0, over 0.3% of trajectories yielded triplet NH (an 8-fold increase), and this value was even larger for higher field strengths.

---

[1] Guan, Y., Xie, C., Yarkony, D. R., and Guo, H. High-fidelity first principles nonadiabaticity: diabatization, analytic representation of global diabatic potential energy matrices, and quantum dynamics. *Phys. Chem. Chem. Phys.* 23 (44), 24962–24983, 2021.

[2] Fábri, C., Csehi, A., Halász, G. J., Cederbaum, L. S., and Vibók, Á. Classical and quantum light-induced non-adiabaticity in molecular systems. *AVS Quantum Sci.* 6 (2), 023501, 2024.

[3] Wang, Y., Guo, H., and Yarkony, D. R. Internal conversion and intersystem crossing dynamics based on coupled potential energy surfaces with full geometry-dependent spin–orbit and derivative couplings. Nonadiabatic photodissociation dynamics of NH_3(A) leading to the NH($X^3\Sigma^-$, $a^1\Delta$) + H_2 channel. *Phys. Chem. Chem. Phys.* 24 (24), 15060–15067, 2022.

[4] Avanessian, C., Wang, Y., and Yarkony, D. R. Floquet-Engineered Photodissociation Simulated Using Coupled Potential Energy and Dipole Matrices. *J. Phys. Chem. Lett.* 15, 9905–9911, 2024.

[5] Wang, Y., Guan, Y., Guo, H., and Yarkony, D. R. Enabling complete multichannel nonadiabatic dynamics: A global representation of the two-channel coupled, 1,2^{1}A and 1^{3}A states of NH_3 using neural networks. *J. Chem. Phys.* 154 (9), 094121, 2021.

Poster A12

Profiling Near-Resonant Vibration-to-Vibration Energy Transfer in the Collisional Deactivation of Vibrationally Excited Pyridines

Benjamin W. Baldwin, Pierce E. van Mulbregt, and Amy S. Mullin

Department of Chemistry and Biochemistry, University of Maryland, College Park, USA
Email: baldwbe@umd.edu

ABSTRACT

Transient state-resolved IR spectroscopy of CO_2 in the (00^01) antisymmetric stretch following collisions with highly vibrationally excited pyridine molecules (E_{vib}=37,500 or 41,670 cm^{-1}) is used to investigate near-resonant vibrational energy transfer. Two vibrational energy donors, pyridine and collidine (2,4,6-trimethylpyridine), are prepared via UV absorption at λ=266 or 240 nm, followed by rapid radiationless decay using a tunable OPO. The experiments show that the CO_2 (00^01) collision products have modest amounts of recoil energy for both donors. Differences are seen in the extent of rotational excitation, with the methylated donor imparting more rotational energy to the CO_2 (0001) products. Energy transfer rate constants show how the donor energy and extent of methylation affect vibration-to-vibration (V-V) efficiencies. For a given excitation wavelength, the addition of 3 methyl groups to the donor molecule shifts the donor vibrational distribution to low frequency hindered rotor modes, which are likely responsible for the increased CO_2 (00^01) rotation.

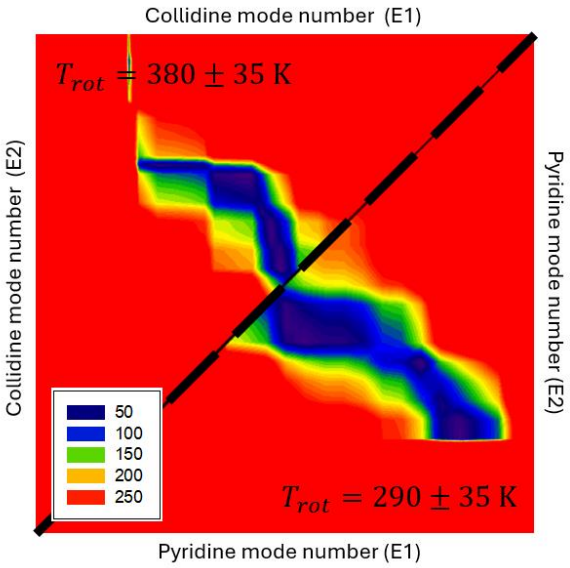


Figure 1. Heat map of energy mismatch (up to 250 cm^{-1}) between CO_2 (00^01) vibrational energy and donor combination modes. T_{rot} values are the observed nascent rotational temperature of scattered CO_2 (00^01). Inset values have units of cm^{-1}.

The primary energy transfer pathway for pyridine relaxation results in rotational and translational (V-R/T) excitation of CO_2 (00^00) and the product distributions show evidence of an impulsive collision mechanism.[1,2] In contrast, the V-V pathway occurs through long-range interactions, wherein CO_2 gains 2349 cm^{-1} of vibrational energy. The difference in CO_2 rotational energy gain is explained by differences in the possible donor combination modes with energies near 2349 cm^{-1}. Figure 1 shows a heat map of the donor combination mode energies (up to 250 cm^{-1}) that are in excess of the CO_2 (00^01) vibrational energy. Statistically, the methylated donor has a smaller window for near-resonant energy transfer, and its collisions lead to CO_2 (00^01) products with more rotational energy.

---

[1] J. Du, N. A. Sassin, D. K. Havey and A.S. Mullin, Full State-Resolved Energy Gain Profiles of CO_2 from Collisions with Highly Vibrationally Excited Molecules. II. Energy-Dependent Pyrazine (E = 32 700 and 37 900 cm^{-1}) Relaxation, *J. Phys. Chem. A* 117, 12104, 2013.

[2] J. Park, L. Shum, A. S. Lemoff, K. Werner, and A. S. Mullin, Methylation effects in state-resolved quenching of highly vibrationally excited azabenzenes (E_{vib}~38 500 cm^{-1}), *J. Chem. Phys* 117, 5221, 2002.

Poster A21

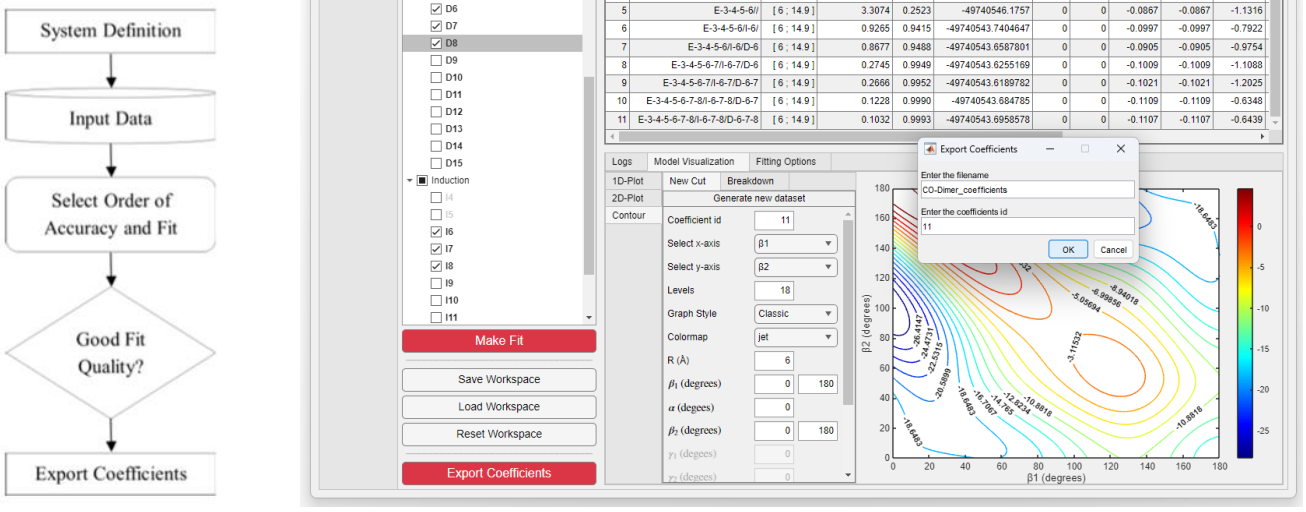
Long-Range-Fit: A program to fit long-range interactions

Adrian Batista-Planas, Ernesto Quintas-Sánchez and Richard Dawes

Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409-0010
Email: albgzz@mst.edu

ABSTRACT

Understanding intermolecular forces is fundamental to modeling and predicting the behavior of molecular systems, with applications spanning atmospheric chemistry, astrochemistry, and beyond. In particular, long-range molecular interactions—with electrostatics, induction, and dispersion as its main components—play a critical role, especially at low temperature and density regimes. Long-range interactions are often described through perturbation theory, expanding the electronic charge distribution via multipolar series. However, while the theory is well-established,[1] obtaining the resulting analytical expressions (and its practical implementation) is a highly complex and system-dependent task. To address this challenge, we developed Long-Range-Fit (LRF), an interactive and user-friendly software package designed to automate the generation and fitting of long-range interaction terms for systems composed of two rigid molecules. By just specifying the symmetry and net charge of each molecular fragment, users can efficiently obtain an accurate representation of the long-range region of the potential energy surface up to fifteenth order in the multipolar series. LRF complements existing tools such as AUTOSURF,[2] offering a robust and physically rigorous framework that bridges sophisticated theoretical formulations with practical computational modeling.



---

[1] A. Stone, The Theory of Intermolecular Forces, 2nd ed., Oxford University Press, United Kingdom, 2013.
[2] E. Quintas-Sánchez and R. Dawes, AUTOSURF: A Freely Available Program to Construct Potential Energy Surfaces. J. Chem. Inf. Model. 59, 262-271, 2019.

Poster B12

Isomers and band assignments in the cryogenic vibrational spectra of protonated formic acid complexes with D_2, N_2, and H_2O using two color, IR-IR photobleaching

Erica L. Bocanegra,[a] Abhijit Rana,[a] Anne B. McCoy,[b] and Mark A. Johnson[a]

[a]*Sterling Chemistry Laboratory, Department of Chemistry Yale University, New Haven, 06511 CT. Email: erica.bocanegra@yale.edu*

[b]*Department of Chemistry, University of Washington, Seattle, 98195 WA*

ABSTRACT

Protonated formic acid (PFA) is purported to be an active species involved in accelerated condensation reactions at the interface of microdroplets. Here we analyze cryogenic ion vibrational spectra of tagged PFA with electronic structure and anharmonic vibrational calculations to establish the isomers generated by electrospray ionization (ESI) followed by buffer gas cooling to ~25 K. Two isomers are identified (the trans form (E,Z), and the cis form (E,E)) and generated in comparable abundance at low temperature despite the fact that the calculated E,E structure lies 6.40 kJ mol^{-1} above the E,Z form. A large (~60 kJ mol^{-1} barrier separates them such that the E,E form can be kinetically trapped upon cooling in the ion trap. The anticooperativity between the H-bonds of the OH groups is explored by measuring the shift in the D_2 and N_2 tag-bound OH fundamentals when a second tag is attached. Analysis of the isotopomer-specific patterns displayed by the H/D isotopically labeled PFA-H_2O-D_2 isomers reveal the strong degree of coupling between the water-bound OH stretch and the water bending modes. Two distinct, non-interconverting rotamers arise from the orientation of the D_2-bound OH taking on the E or Z form, while the water exclusively binds to the E OH. This assignment scheme corrects a previous theoretical analysis that invoked a scenario in which structures with E- and Z-bound water molecules interconvert at low (20 K) temperature.

Poster A1

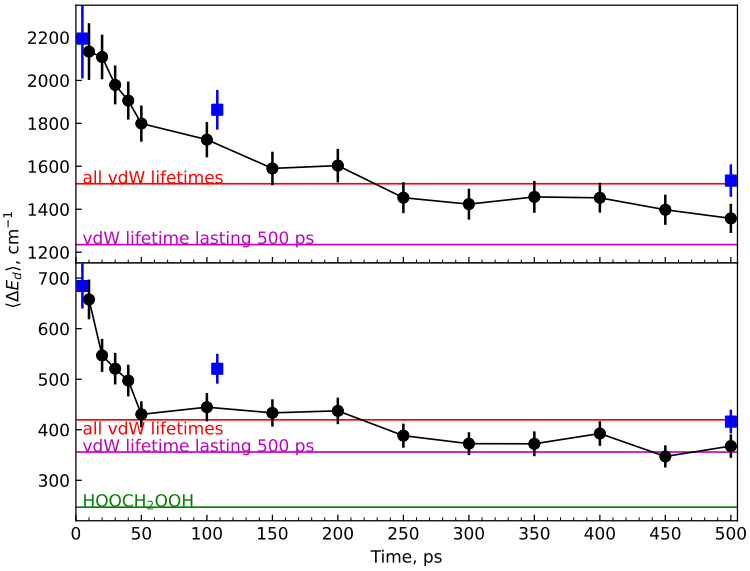
Collisional Energy Transfer in Transient van der Waals Complexes of the Simplest Criegee Intermediate and Hydrogen Peroxide

Ashley K. Borkowski,[a] Rebecca L. Caravan,[a] and Ahren W. Jasper[a]

[a] *Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439*
Email: aborkowski@anl.gov

ABSTRACT

When alkenes undergo ozonolysis in the atmosphere, this leads to the formation of zwitterionic reactive intermediates known as carbonyl oxides or more commonly known as Criegee intermediates (CIs). The simplest CI is formaldehyde oxide, CH_2OO. Recent experimental studies revealed that CH_2OO reacts significantly faster with H_2O_2 in the presences of water versus dry conditions.[1] Explaining this enhanced reactivity demands an understanding of collisional energy transfer in the transient van der Waals (vdW) complex, $CH_2OO\cdots H_2O_2$, for various third-body bath gases. The present study introduces water as a new third-body bath.[1,2] Classical trajectories describing CH_2OO + H_2O_2 collisions were simulated and categorized according to the duration for which the CI remained next to the peroxide, *i.e.*, according to the lifetimes of the transient vdW complexes. These structures were used to initiate trajectories describing third-body collisions, which were analyzed to answer the question: *What $CH_2OO\cdots H_2O_2$ configurations promote collisional energy transfer with third-body bath gases?* We find that the average energy transferred in downward collisions decreases with increased lifetime of the transient complexed species. This study explores the underlying chemical physics of this trend and connects with the experimental, and potential atmospheric significance of these phenomena.



The material in this study is based in part on work at ANL supported by the U.S. Department of Energy (USDOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences under DOE Contract Number DE-AC02-06CH11357 through the Argonne-Sandia Consortium on Pressure Dependent Chemistry, FWP 59044.

[1] Percival, C. J., Winiberg, F. A. F., Chao, W., Zou, M., Vansco, M. F., Borkowski, A. K., Khan, M. A. H., Markus, C. R., Osborn, D. L., Jasper, A. W., Lester, M. I., Shallcross, D. E., Klippenstein, S. J., Taatjes, C. A. & Caravan, R. L., *In preparation*, 2025.

[2] Caravan, R. L., Bannan, T. J., Winiberg, F. A. F., Khan, M. A. H., Rousso, A. C., Jasper, A. W., Worrall, S. D., Bacak, A., Artaxo, P., Brito, J., Priestley, M., Allan, J. D., Coe, H., Ju, Y., Osborn, D. L., Hansen, N., Klippenstein, S. J., Shallcross, D. E., Taatjes, C. A. & Percival, C. J. Observational evidence for Criegee intermediate oligomerization reactions relevant to aerosol formation in the troposphere. *Nat. Geosci.* **17**, 219-226, 2024.

Dynamics of Optically Centrifuged N_2O in Extreme Rotational States Studied with Transient IR Absorption Spectroscopy

Simone A. DeSouza, Michael E. Ritter, Christopher R. Lukowski, and Amy S. Mullin

Department of Chemistry and Biochemistry, University of Maryland, College Park
Email: sdesouz1@umd.edu

ABSTRACT

Molecules in high energy rotational states are observed as products of reactions and collisional energy transfer, but they are not easily prepared by traditional experimental methods. High rotational states can be prepared using an optical centrifuge, which is an ultrafast laser-based method that selectively populates molecules in high J states with inverted rotational distributions. In this project, an optical centrifuge is used to prepare N_2O molecules with J=67-180 and rotational energies up to 18,500 cm^{-1}. High-resolution polarization-sensitive transient IR absorption spectroscopy is used to characterize the properties and collision dynamics of the centrifuged molecules using ν_3 fundamental transitions near $\lambda = 4.4\,\mu$m at a pressure of 1.8 Torr.[1,2]

A tunable optical centrifuge prepares an ensemble of N_2O molecules with J≤180 by limiting the angular frequency Ω_{OC} of the optical trap. Fig 1a compares a full-bandwidth trap S1, which has enough intensity at $\Omega_{OC} = \Omega_{J=180}$ to drive molecules into higher states, with a reduced-bandwidth trap S2 that has one-tenth the S1 intensity at $\Omega_{J=180}$. Transient IR absorption signals for J=150 are shown in Fig. 1b using s- and p-polarized IR probing. The nearly-nascent population distribution peaks near J=150, as shown in Fig. 1c. The J=160-180 states have population decay rates that are one-third the collision rate. Alignment parameters for the J=90-180 states have values near $A_0^{(2)} = 1.5$, and alignment decay rates that are one-tenth the collision rate. The J=67-76 states have alignment parameters approaching $A_0^{(2)} = 0$, showing that they correspond to bath collision products. Transient Doppler profiles show that the high-J states are scattered with low recoil velocities, while the low-J states gain substantial amounts of translational energy. Evidence is also seen for significant Doppler broadening in the J=100 state, which together with its large alignment parameter, shows that this state originated from superrotor states and superrotor-bath collisions. Overall, we learn that that optically centrifuged N_2O molecules are initially aligned by the optical field, undergo inhibited population decay, and maintain their alignment through many collisions. In contrast, energy transfer and substantial loss of alignment occur on essentially every collision for low-J molecules. These results are compared with dynamics studies on optically centrifuged CO and CO_2.[3,4] This project has been funded through the NSF.

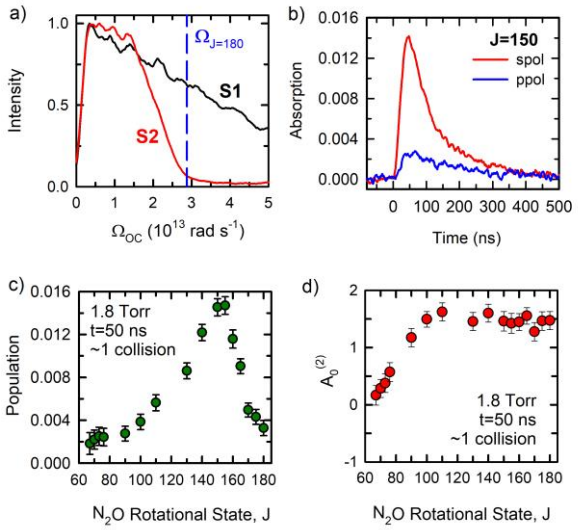


Figure 1. a) Optical centrifuge trap profiles. b) Transient absorption signals for N_2O J=150. C) N_2O populations at 50 ns. d) N_2O alignment moments $A_0^{(2)}$ at 50 ns.

---

[1] Yuan, L., Toro, C., Bell, M., and Mullin, A.S. Spectroscopy of Molecules in very High Rotational States using an Optical Centrifuge. *Faraday Discussions* 150, 101-111, 2011.
[2] Ogden, H.M., Michael, T.J., Murray, M.J., and Mullin, A.S. Transient IR (00^01–00^00) Absorption Spectroscopy of Optically Centrifuged N_2O with Extreme Rotation up to J=205. *JSQRT* 246, 106867, 2020.
[3] Laskowski, M.R., Michael, T.J., Ogden, H.M., Alexander, M.H., and Mullin, A.S. Rotational Energy Transfer Kinetics of Optically Centrifuged CO Molecules Investigated through Transient IR Spectroscopy and Master Equation Simulations. *Faraday Discuss.,* 2022, **238**, 87-102.
[4] Ritter, M.E., DeSouza, S.A., Ogden, H.M., Michael, T.J., and Mullin, A.S. Transient IR spectroscopy of optically centrifuged CO_2 (R186-R282) and collisional dynamics for the J=244-282 states. *Faraday Discuss.,* 2024, **251**, 140-159.

Poster B9

Tracking the Morphology and Optical Properties of Aerosol Particles in an Electrodynamic Balance

Arden M. Floyd, Cole R. Sagan, and Marissa L. Weichman

Department of Chemistry, Princeton University, Princeton, NJ, 08544.
Email: amfloyd@princeton.edu

ABSTRACT

Nano- to micrometer scale aerosol particles play a significant role in the chemistry and radiative balance of the atmosphere. At the same time, large uncertainty exists concerning the interactions of these particles with solar radiation and their role in heterogeneous chemistry in the troposphere and stratosphere. For example, there are still many open questions concerning how the physical and chemical properties of aerosol particles are altered as they interact with radiation and reagents in the atmosphere. The unique environment of the microdroplet surface often leads to chemistry that is distinct from the bulk material. These considerations highlight the demand for a platform which is able to precisely measure the physical and chemical properties of single microdroplets over extended timescales.

I will report on a new apparatus under construction in the Weichman Lab at Princeton University for spectroscopic investigations of single aerosol particles levitated in a linear quadrupole electrodynamic balance. We demonstrate trapping of micron-scale aqueous 1,2,6-hexanetriol particles produced from a droplet-on-demand device, which are charged and injected *via* an induction electrode into a vertically oriented quadrupole trap. Particles are levitated by an electrode held at opposite polarity to the induction electrode, which balances the downward forces of gravity and drag from a flow of nitrogen. 532 nm continuous wave laser light scattered by the particle is collected by an objective positioned at 90 degrees, from which we observe Mie scattering fringes characteristic of the particle size and refractive index. Fitting the observed angular scattering intensity distribution to predictions from Mie theory allows extraction of the particle size.

In ongoing work, we are installing an incoherent broadband, cavity-enhanced spectrometer to interrogate the size, refractive index, and morphology of single micron-scale, electrodynamically levitated sulfate particles. I will report on progress towards tracking the broadband extinction of these particles over time when exposed to gas-phase biomass burning marker species such as oxalic acid, elucidating the impact of VOC condensation on radiative transfer. Additionally, by fitting the broadband spectra of particles to predictions from homogeneous and core-shell Mie theory, we will be able to determine the presence and thickness of an outer organic shell on the core sulfate aerosol. These structural details are key for determining the effect mixing with organics has on the rates of reagent uptake and heterogeneous reactions on sulfate aerosol particles.

Poster A6 Hot Topic

Molecular Beam Scattering from Flat Liquid Jets: Exploring Dynamics at the Aqueous Interface

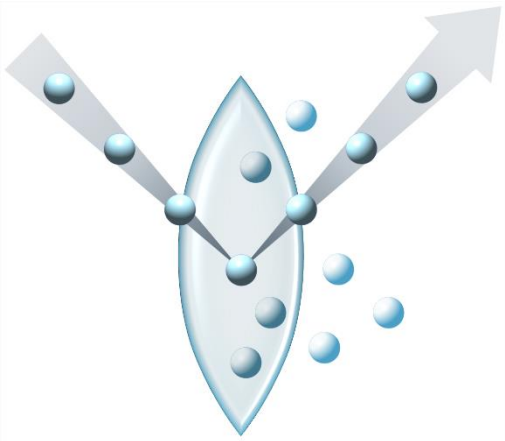
Madison M. Foreman,[ab] Walt Yang,[a] Tiffany C. Ly,[a] and Daniel M.Neumark[ab]

[a] *Department of Chemistry, University of California, Berkeley, CA Email: mmforeman@berkeley.edu*
[b] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA*

ABSTRACT

Gas–liquid surface interactions represent the critical first steps in adsorption, dissolution, and unique interfacial reactions. Multiphase chemistry on aqueous surfaces is especially prevalent, driving processes from atmospheric carbon cycling to industrial catalysis. Molecular beam scattering experiments employing novel flat liquid jet techniques offer a powerful probe into the fundamental dynamics and mechanisms of gas-phase particles colliding with a liquid surface. [1,2]

Here we present the first translational energy distributions of molecular beams (He, Ne, Ar, CD_4, and ND_3) scattered from a flat jet of cold salty water, collected through a range of deflection angles and analyzed with kinematic modeling. We find that the aqueous interface facilitates a high degree of collisional energy transfer compared to hydrocarbon surfaces, consistent with observed super-specular scattering patterns. Different gaseous species exhibit variations in scattering behavior, with ND_3 appearing to undergo complete surface trapping. Interactions between He and the liquid surface are weak, allowing He scattering to serve as a probe for surface roughness.



---

[1] Yang, W. *et al*. Molecular beam scattering from flat jets of liquid dodecane and water. *Nat. Sci.* 4, e20240009, 2024
[2] Yang, W. *et al*. Molecular Beam Scattering of Neon from Flat Jets of Cold Salty Water. *ChemRxiv*, doi.org/10.26434/chemrxiv-2025-lqh8b, preprint, 2025

Poster A7

The Breakdown of the Electrical Double Layer Model in Polar Aprotic Solvents

Amanda Souna,[a] Siddharth Singh,[a] Ovuokenye Omadoko,[a] Jason D. Tran,[a] John T. Fourkas,[a] Jake W. Polster,[b] Savannah Silva,[b] Rachel A. Lucas,[b] Ethan Cao,[b] Zuzanna Siwy,[b] Mohammad Hossein Motevaselian,[c] and Narayana Aluru[d]

[a] *University of Maryland, College Park, MD 20742. Email: fourkas@umd.edu*
[b] *University of California at Irvine, Irvine, CA 92697*
[c] *University of Illinois, Urbana-Champaign, IL 61801*
[d] *University of Texas, Austin, TX 78712*

ABSTRACT

The electrical double-layer (EDL) model is foundational to our understanding of interfacial electrochemistry and related phenomena. This model, which assumes that the solvent is a featureless continuum and that the ions are point charges, has proven to be highly successful in predicting the organization of aqueous electrolyte systems near polar and charged interfaces. We have found, through spectroscopic and electrochemical experiments, as well as through molecular dynamics (MD) simulations, that solutions in polar aprotic liquids do not adhere to the EDL model. Polar surfaces induce substantial ordering in such liquids, creating a structure that is akin to that of a supported lipid bilayer. In acetonitrile, for instance, this ordering has remarkable thermodynamic stability even at elevated temperatures or in the presence of large mole fractions of water.

Our studies show that the lipid-bilayer-like (LBL) organization of acetonitrile at a silica surface persists even at high salt concentrations. The LBL organization not only determines the surface potential at low ionic concentrations, but also controls the favored positions of cations and anions even at high ionic strengths, in direct opposition to the predictions of the EDL model. Accordingly, there is nothing resembling a Debye length in this system. Our simulations further show that even at a 1 M salt concentration the LBL organization and the charge density profile of the acetonitrile are virtually the same as those in the neat liquid.

The details of the behavior of salt solutions in acetonitrile at a silica interface depend to some extent on the identities and sizes of the anions and cations, but the general behavior persists. We have also observed similar behavior for other polar, aprotic liquids. These results have significant implications for technologies in which such solutions are used, such as batteries and ion-selective separations.

Poster A9

Gas-Phase Synthesis of Cyclic Silicon Dicarbide (c-SiC_2) and Bicyclic Silicon Tricarbide (c-SiC_3) via Single Collision Events from Acyclic Transients

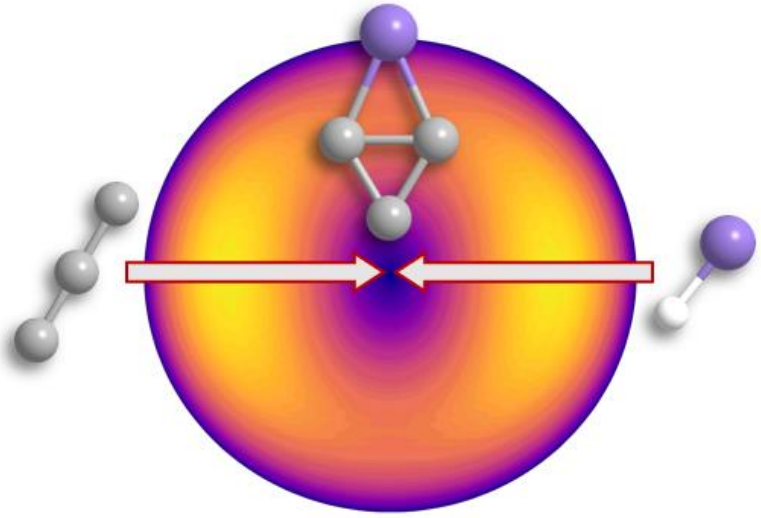
Shane J. Goettl,[a] Breno R. L. Galvão,[b] Rui Sun,[a] and Ralf I. Kaiser[a]

[a] *Department of Chemistry, University of Hawai'i at Mānoa, Honolulu, HI 96822, USA. Email: sgoettl@hawaii.edu*

[b] *Centro Federal de Educação Tecnológica de Minas Gerais, Belo Horizonte, Brasil 30421-169*

ABSTRACT

The gas-phase preparation of two silicon carbide molecules—cyclic silicon dicarbide (c-SiC_2, X^1A_1) and bicyclic silicon tricarbide (c-SiC_3, X^1A_1)—was accomplished under controlled experimental conditions via the bimolecular reactions of dicarbon (C_2, $X^1\Sigma_g^+/a^3\Pi_u$) and tricarbon (C_3, $X^1\Sigma_g^+$) with silylidyne radicals (SiH, $X^2\Pi$) under single-collision conditions. The combination of crossed molecular beams experiments with electronic structure calculations revealed barrierless entrance channels with addition of the silicon atom of the silylidyne radical to one or both terminal carbon atoms of dicarbon/tricarbon involving the formation of one or two rings in a single collision event with eventual hydrogen atom ejection leading to the cyclic silicon dicarbide (c-SiC_2) and the carbon–carbon bisected bicyclic silicon tricarbide (c-SiC_3) molecules. Quasi-classical trajectory (QCT) simulations as conducted for the tricarbon–silylidyne system provide excellent agreement with the experimental results. The overall barrierless and exoergic nature of these bimolecular reactions provides a directed synthesis of c-SiC_2 and c-SiC_3 even at ultralow temperatures as in cold molecular clouds such as G+0.693−0.0027 in the Galactic Center, where the former molecule was observed recently. Compared to the bicyclic silicon tricarbide molecule (c-SiC_3, X^1A_1), the isovalent tetracarbon molecule (C_4, $X^3\Sigma_g^-$) is not only linear, but also holds a triplet ground state. Therefore, the replacement of a single carbon atom with silicon results in a profound effect on stability, chemical bonding, and molecular structure, thus providing rare insights into the unique reaction mechanisms of silicon and carbon, where stability and chemical bonding diverge between isovalent systems.



Poster B13 Hot Topic

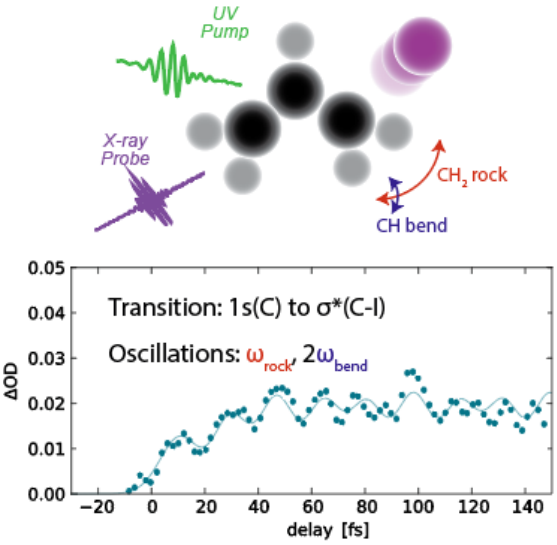
Coherent vibrations in C-I bond dissociation studied with carbon K-edge transient absorption

John H. Hack,* Christian A. Schröeder, Eric A. Haugen, Daniel M. Neumark, and Stephen R. Leone

Lawrence Berkeley National Laboratory and University of California, Berkeley.
**Email: johnhack@berkeley.edu*

ABSTRACT

Femtosecond photochemical dissociation and ionization can induce rapid structural changes in molecules, launching coherent vibrations that can influence resulting product distributions.[1,2] Experimentally, core-level transient absorption spectroscopy has been shown to be a highly sensitive probe of vibrational motion, able to resolve changes in bond distances on the order of 100 femtometers.[3] Using high-order harmonic generation it is possible to generate sub-femtosecond pulses of x-ray radiation, allowing for the tracking of vibrational and electronic motion with few-femtosecond time resolution. In X-ray transient absorption, molecular vibrations are read-out as oscillations in the core-to-valence transition, induced by changes in the core excited state potential along the vibrational coordinate. Alkyl and allyl iodides provide a well-studied platform for photochemical nonadiabatic state crossing and dissociation, initiated by excitation at 266 nm. In small alkyl iodides, UV excitation results in an excited state curve crossing on a femtosecond timescale followed by C-I bond dissociation.[4] We investigated the nuclear and electronic dynamics of allyl iodide dissociation using transient absorption at the carbon K-edge (1s core level), following UV excitation at 266 nm. Preliminary results resolved the CH out-of-plane bending and CH_2 wagging at the primary carbon atom, resulting from a change in the equilibrium nuclear geometry between the neutral to allyl radical. Notably, the bending vibration appears at the fundamental frequency, while the wagging is imparted onto the core-level transition at the overtone frequency, suggesting that the core-excited potential has even symmetry with respect to the wagging coordinate.



X-ray transient absorption of allyl iodide following 266 nm excitation. The 1s(C) to σ*(C-I) transition oscillates with two components at characteristic CH_2 rocking and CH bending frequencies.

---

[1] Ridente, E., *et* al. Femtosecond symmetry breaking and coherent relaxation of methane cations via x-ray spectroscopy. *Science*, 380, 713-717, 2023.
[2] Tibbetts, K. M. Coherent Vibrational and Dissociation Dynamics of Polyatomic Radical Cations. *Chem. Eur. J.* 25, 8431-8439, 2019.
[3] Rupprecht, P., *et* al. Resolving vibrations in a polyatomic molecule with femtometer precision via x-ray spectroscopy. *Phys. Rev. A*, 108, 032816, 2023.
[4] Chang, K. F., *et* al. Conical intersection and coherent vibrational dynamics in alkyl iodides captured by attosecond transient absorption spectroscopy. *J. Chem. Phys*, 156, 114304, 2022.

Poster B8

Using Vibrational Perturbation Theory to Elucidate the Contributions to Shifts in CO Stretching Frequency and Assign the OD Stretching Region of $[Py^+\text{-}(CH_2)_n\text{-}COOH]_2$ $[NTf_2^-]$ (n=1-9) Ionic Liquids

Yarra Hassan[a], Payten A. Harville[b], Olivia C. Moss[b], Anne B. McCoy[a], and Mark A. Johnson[b]

[a] *Department of Chemistry, University of Washington, Seattle, Washington 98195, United States. Email: yarramh@uw.edu*

[b] *Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06520, United States*

ABSTRACT

Ionic liquids have many interesting properties that have numerous applications, for example as green solvents and rocket fuel. In this work we examined the vibrational spectra of $[Py^+\text{-}(CH_2)_n\text{-}COOH]_2[NTf_2^-]$ (n=1-9) cluster ions, which were obtained using gas phase cryogenic ion spectroscopy. Specifically, we examined the size-dependent CO stretching frequency, which red shifts by approximately 30 cm^{-1} as the value of n increases. In previous work that focused on the isolated cation ($Py^+\text{-}(CH_2)_n\text{-}COOH$), similar red shifts in the CO stretching frequency were observed. These were attributed to two effects: through-bond and through-space electrostatic effects.[1] The through-bond effects occur because of the electron-withdrawing nature of the pyridinium ring. The through-space effects are caused by the response of the CO frequency to the charge on the Py^+ ring through the vibrational Stark effect. Here we explore how these two effects are manifested in the spectra of the ternary $[Py^+\text{-}(CH_2)_n\text{-}COOH]_2[NTf_2^-]$ complexes. In this work, we use harmonic and second-order vibrational perturbation theory (VPT2) calculations based on electronic structure calculations that were performed at the B3LYP/6-31+G** level of theory/basis set to explore the changes in the CO stretching frequencies with chain length. The VPT2 calculations recover the observed 30 cm^{-1} shift in the CO frequency seen in the measured spectra. We find that in these larger complexes the shifts can be traced to both through-space and through-bond effects, as were identified for the isolated $Py^+\text{-}(CH_2)_n\text{-}COOH$ ion. We also investigate the OD region of the spectrum to gain a better understanding of the hydrogen-bonding environment in the ternary complex. In the OD region of the spectra there are three observed peaks with consistent frequencies across the different alkyl chain lengths. Using VPT2 calculations we investigate what vibrational modes give rise to the spectral features that appear in the OD region of the spectrum.

---

[1] P.A. Harville, O.C. Moss, Y. Hassan, L. Hunger, R. Ludwig, A.B. McCoy, M.A. Johnson. Intramolecular Polarization Contributions to the pK_a's of Carboxylic Acids Through the Chain Length Dependence of Vibrational Tag-Shifts in Cryogenically Cooled Pyridinium-$(CH_2)_n$-COOH (n = 1-7) Cations. J.Phys. Chem. A. **2024**, 128,47,10159-10166.

Poster A2 Hot Topic

Exploring the Chemi-ionization of Carbonyl Sulfide (OCS) with Metastable Neon via Velocity Map Imaging

C. He, X. Zhang, A. Mishra, L. Ploenes, P.Straňák and S. Willitsch

Department of Chemistry, University of Basel, Klingelbergstrasse 80, 4056, Basel, Switzerland.
Email: chao.he@unibas.ch

ABSTRACT

Chemi-ionization (CI) reactions are fundamental in high-energy environments such as plasmas, planetary atmospheres and interstellar space[1,2] and have become valuable tools for probing quantum effects in reactive collisions.[3] Here, we report a new velocity map imaging (VMI) crossed-molecular-beam experiment for studies of gas-phase CI reactions.[4,5] An electrostatic deflector is integrated into the setup to enable the spatial separation of different conformers or individual rotational states of molecules according to their different effective dipole moments, while the ionic products are probed using time-sliced VMI technique. As the pioneer application of this new method, we first studied rotational-state-dependent CI reaction of carbonyl sulfide (OCS) with metastable neon atoms at collision energy of 0.3 eV via time-of-flight mass spectrometer (TOF-MS). The experimental results reveal that OCS molecules in the rotational ground state J = 0 are about a factor 2.5 more reactive in dissociative ionisation (yielding S^+) ions than in Penning ionisation (producing OCS^+) in comparison to the J = 1.[4]

Here, time-sliced VMI technique is utilized to detect the products OCS^+ and S^+. For OCS^+, strong forward scattering and minor backward scattering were observed. The total kinetic energy distribution exhibited a peak near 0.16 eV, with the distribution extending up to approximately 0.5 eV. These experimental results are reminiscent of the angle-energy distributions of Penning ions (Ar^+) in the CI reaction of metastable helium with argon.[6] The product S^+ exhibits a nearly isotropic angular distribution, and analysis of the total kinetic energy distribution suggests that the lowest dissociation channel $S^+(^4S) + CO(X^1\Sigma^+)$ is formed. These findings are in agreement with previous comprehensive studies on photodissociation dynamics of OCS^+ in its $A^2\Pi$ and $B^2\Sigma$ electronic states.[7,8] We are currently acquiring additional velocity map images of OCS^+ and S^+ to further investigate any posible rotational state-specific influence on product branching ratios in the CI reaction of carbonyl sulfide (OCS) with metastable neon.

---

[1] Siska, P. E. Molecular-beam studies of penning ionization. *Rev. Mod. Phys.* 65, 337-412, 1993.
[2] Gordon, S. D. *et al*. The stereodynamics of ion forming reactions. *Int. Rev. Phys. Chem.* 39, 109-134, 2020.
[3] Margulis, B. *et al*. Tomography of Feshbach resonance states. *Science* 380, 77-81, 2023.
[4] Ploenes, L. *et al*. A novel crossed-molecular-beam experiment for investigating reactions of state- and conformationally selected strong-field-seeking molecules. *Mol. Phys.* 119, e1965234, 2021.
[5] Ploenes, L. *et al*. Collisional alignment and molecular rotation control the chemi-ionization of individual conformers of hydroquinone with metastable neon. *Nat. Chem.* 16, 1876-1881, 2024.
[6] Longley, E. J. *et al.* Angle-energy distributions of Penning ions in crossed molecular beams. III. Angle-energy coupling in He*(2 ^{1}S,2 ^{3}S) + Ar→He+Ar^+ + e^-. *J. Chem. Phys.* 106, 6365-6375, 1997.
[7] Chang, C. *et al.* Imaging the mode-selected predissociation of $OCS^+[(v_1v_2v_3)B^2\Sigma^+]$. *J. Phys. Chem. A* 109, 1022-1025, 2005.
[8] Wang, Y. *et al.* High-resolution imaging study on photodissociation of $OCS^+[A^2\Pi_{\Omega=1/2,3/2}(v_1\ 0\ v_3)]$. *J. Phys. Chem. A* 128, 4765-4774, 2024.

Poster B10

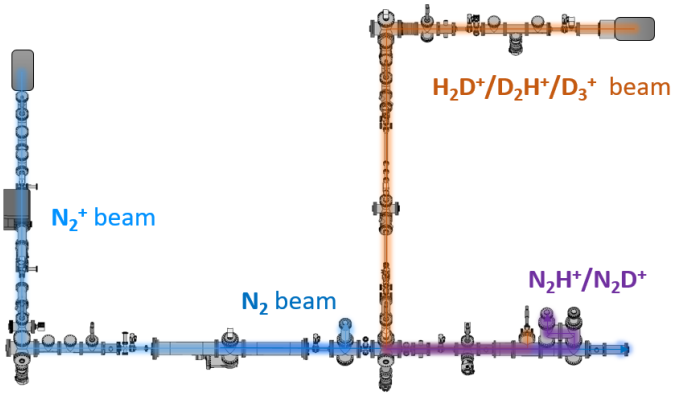
Formation of N_2H^+ and N_2D^+ in Collisions of N_2 with H_3^+ Isotopologues

Dmitry Ivanov,[a] Caixia Bu,[a] Pierre-Michel Hillenbrand,[b,c] Leonard W. Isberner,[b] Daniel Schury,[a]
Xavier Urbain,[d] and Daniel W. Savin [a]

[a] *Columbia Astrophysics Laboratory, Columbia University, New York, NY 10027, USA.*
Email: di2224@columbia.edu
[b] *I. Physikalisches Institut, Justus-Liebig-Universität, 35392 Giessen, Germany*
[c] *GSI Helmholtzzentrum für Schwerionenforschung, 64291 Darmstadt, Germany*
[d] *Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, B-1348 Louvain-la-Neuve, Belgium*

ABSTRACT

We used a dual-source, ion-neutral, merged-fast-beams apparatus[1, 2] to investigate reactions of N_2 with H_3^+ isotopologues leading to the formation of N_2H^+ and N_2D^+. These ions are of great interest for astrochemistry. The properties of prestellar cores and the outer midplane of protoplanetary discs can be inferred using observations of deuterated molecules.[3, 4] In particular, the N_2D^+-to-N_2H^+ abundance ratio is a commonly used diagnostic, the accuracy of which requires an understanding of the underlying chemical processes forming these ions. The schematic of our instrument along with the six reactions studied are presented below.



$$N_2 + H_3^+ \rightarrow N_2H^+ + H_2 \quad (1)$$
$$N_2 + H_2D^+ \rightarrow N_2H^+ + HD \quad (2)$$
$$N_2 + H_2D^+ \rightarrow N_2D^+ + H_2 \quad (3)$$
$$N_2 + D_2H^+ \rightarrow N_2H^+ + D_2 \quad (4)$$
$$N_2 + D_2H^+ \rightarrow N_2D^+ + HD \quad (5)$$
$$N_2 + D_3^+ \rightarrow N_2D^+ + D_2 \quad (6)$$

Fast ion beams of N_2^+ and H_3^+ isotopologues were produced in duoplasmatron sources. The N_2^+ ions were neutralized to the $X^1\Sigma^+_g$ ground electronic state by electron capture from N_2 in a gas cell at room temperature. The H_3^+ isotopologues ions were then merged onto the neutral beam. The N_2H^+ and N_2D^+ daughter products were detected using an electrostatic energy analyzer. This procedure allowed us to measure the integral cross section for the ion-molecular reaction and determine thermal rate coefficients, both to an accuracy of ~ 20%. These results can be used in astrochemical models to describe the processes taking place at dense cold regions found in prestellar cores and protoplanetary disks.

This work was supported, in part, by a grant from the U.S. National Science Foundation Division of Astronomical Sciences Astronomy and Astrophysics Grants Program.

---

[1] O'Connor A *et al.* Reaction studies of neutral atomic C with H_3^+ using a merged-beams apparatus. *Astrophys. J. Suppl. Ser.* 219, 6, 2015.
[2] Hillenbrand P-M. *et al.* Experimental and theoretical studies of the isotope exchange reaction D + H_3^+ → H_2D^+ + H. *Astrophys. J.* 877, 38, 2019.
[3] Aikawa, Y. *et al.* Multiple paths of deuterium fractionation in protoplanetary disks. *Astrophys. J.* 855, 119, 2018
[4] Sipilä, O. and Caselli, P. Hydrodynamics with gas–grain chemistry and radiative transfer: comparing dynamical and static models. *Astron. Astrophys.* 615, A15, 2018.

Poster A3 Hot Topic

Machine Learning Approaches for Developing Potential Surfaces: Applications to $OH^-(H_2O)_n$ (n=1-4) Complexes

Greta M. Jacobson and Anne B. McCoy

Department of Chemsitry, University of Washington, Seattle, WA 98195, USA. Email: gretaja.edu

ABSTRACT

An approach for obtaining high-level ab initio potential surfaces is described.[1] The approach combines a molecular orbital-based machine learning model[2] with the development of a neural-network potential, where the sampled geometries and energies that provide the training data for the potential are obtained using a diffusion Monte Carlo (DMC) calculation. Protocols are developed to make full use of the structures that are obtained from the DMC calculation in the training process. These approaches are used to develop potentials for $OH^-(H_2O)$ and $H_3O^+(H_2O)$, which are used for subsequent DMC calculations. The results of these calculations are compared to those performed using previously reported potentials. Overall, the results of the two sets of DMC calculations are in good agreement for these very floppy molecules. Potentials are also developed for $OH^-(H_2O)_{2\text{-}4}$, for which there are not available potential surfaces. The results of DMC calculations for these ions are compared to those for the corresponding $H_3O^+(H_2O)_n$ ions. It is found that the level of delocalization of the shared proton is similar for a hydroxide or hydronium ion bound to the same number of water molecules. This finding is consistent with the experimental observation that these sets of ions have similar spectra.

---

[1] Jacobson, G. M.; Cheng, L.; Bhethanabotla, V.; Sun, J., McCoy, A. B. Machine Learning Approaches for Developing Potential Surfaces: Applications to $OH^-(H_2O)_n$ (n = 1 − 3) Complexes. *J. Phys. Chem. A* 129, 2958–2972, 2025.

[2] Lu, F.; Cheng, L.; DiRisio, R. J.; Finney, J. M.; Boyer, M. A.; Moonkaen, P.; Sun, J.; Lee, S. J.; Deustua, J. E.; Miller III, T. F.; McCoy, A. B. Fast Near Ab Initio Potential Energy Surfaces Using Machine Learning. *J. Phys. Chem. A* 126, 4013–4024, 2022.

Poster B2

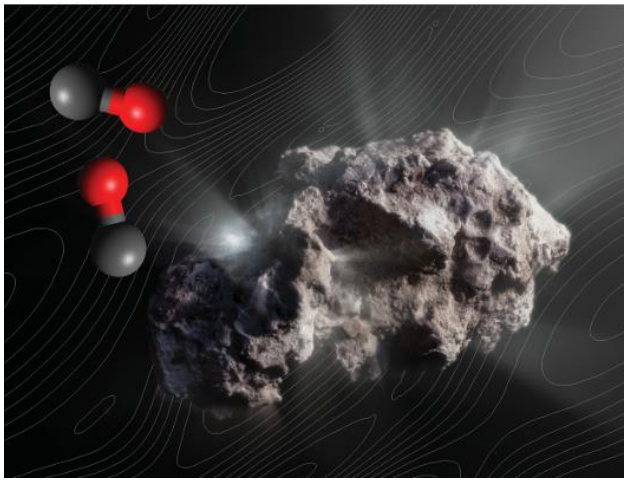
Recent Advances in Mixed Quantum/Classical Theory (MQCT) for Molecule + Molecule Collisions

Carolin Anna Joy, Dulat Bostan, and Dmitri Babikov

Chemistry Department, Marquette University, Milwaukee, WI, 53201-1881
Email: carolin.joy@marquette.edu

ABSTRACT

Collisional energy transfer plays a critical role in numerous physical processes, from atmospheric chemistry to interstellar medium dynamics. However, full quantum mechanical treatments of molecular collisions become computationally prohibitive for molecule + molecule systems, particularly those involving two heavy collision partners and higher collision energies, when the number of partial waves required for the description of scattering increases substantially. This presentation highlights recent developments in the Mixed Quantum/Classical Theory (MQCT), which combines quantum mechanical treatment of internal ro-vibrational motion with classical descriptions of scattering, providing an optimal balance between accuracy and computational efficiency. Our implementation employs time-dependent Schrödinger equation for the internal molecular states while using Ehrenfest mean-field trajectories for translational motion. This approach preserves essential quantum phenomena including state quantization, zero-point energy, selection rules, and quantum interference — while achieving significant computational speedup compared to fully quantum methods. Recent algorithmic improvements and massive parallelization have permitted us to extend MQCT to previously inaccessible complex systems. We present applications to challenging molecule-molecule collisions of heavy partners, including H_2O + H_2O, CO + CO, and HCN + H_2O.[1-3] Comparisons with available benchmark quantum calculations demonstrate that MQCT provides reliable predictions across broad energy range, while offering unique time-dependent insights into collision dynamics. Our results show that for complex polyatomic systems, MQCT accurately captures state-to-state transitions, even when incorporating large rotational basis sets that would be computationally intractable with fully quantum approaches. These advances position MQCT as a powerful predictive tool for modeling energy transfer in complex molecular systems relevant to astrophysical and atmospheric environments.



---

[1] Mandal, B.; Babikov, D. Rate Coefficients for Rotational State-to-State Transitions in H_2O + H_2O Collisions for Cometary and Planetary Applications, as Predicted by Mixed Quantum-Classical Theory. *Astron. Astrophys* 671, A51, 2023.

[2] Mandal, B.; Babikov, D. Improved Temperature Dependence of Rate Coefficients for Rotational State-to-State Transitions in H_2O + H_2O Collisions. *Astron Astrophys* 2023, *678*, A51

[3] Bostan, Dulat, et al. "Mixed quantum/classical calculations of rotationally inelastic scattering in the CO + CO system: a comparison with fully quantum results." *Physical Chemistry Chemical Physics* 26(8), 6627-6637, 2024

Poster B11

Photo-oxidation Dynamics of Phenolate Anion Studied by Extreme Ultraviolet Time-resolved Photoelectron Spectroscopy in Liquid Jets

Do Hyung Kang,[a] Jaydeep Basu,[a] Masafumi Koga,[a] Neal Haldar,[a] and Daniel M. Neumark[a, b]

[a] *Department of Chemistry, University of California, Berkeley, CA 94720, USA.*
Email: sonar112@berkeley.edu
[b] *Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

ABSTRACT

The UV-induced photo-oxidation dynamics of phenolate anion (PhO^-) were investigated using femtosecond time-resolved photoelectron spectroscopy with an 21.7 eV extreme ultraviolet (XUV) probe pulse in liquid (flat) jets.[1,2] Upon excitation to the S_1 ($1^1\pi\pi^*$) state by a 4.3 eV UV pump pulse, we observed two decay components of the phenolate S_1 state with lifetimes of ~7 ps and ~21 ps. These lifetimes are broadly consistent with previous measurement from transient absorption (TA) experiments,[3-4] where they were attributed to electron detachment from the vibrationally hot and cold S_1 state, respectively. A key distinction between our time-resolved photoelectron spectra and the TA results is the significantly weaker photoelectron signal associated with the hydrated electron in our experiment. This contrasts sharply with observations from the iodide (I^-) charge-transfer-to-solvent (CTTS) state, where the hydrated electron signal is much stronger. This may suggest that the ejected electron undergoes strong interaction with the phenoxyl radical ($PhO\cdot$) pair, facilitating recombination to regenerate ground state phenolate anion within the contact pair region.[5] Only a small fraction of the reaction flux generates a hydrated electron, which subsequently undergoes geminate recombination with the radical on the nanosecond timescale. We also examine excitation to the higher-lying S_2 ($2^1\pi\pi^*$) excited state using a 5.1 eV UV pump. In this case, the time-resolved photoelectron spectrum displays a sharp spectral shift within ~300 fs, indicative of ultrafast internal conversion from S_2 to S_1. The subsequent dynamics largely mirror those observed following direct S_1 excitation but with an increased portion of hot S_1 component. These results provide evidence for a geminate recombination pathway during the photo-oxidation process, underscoring the inherently low quantum yield for hydrated electron generation in aromatic chromophores possibly arising from the strong interaction between the ejected electron and polar neutral radical.

---

[1] M. Koga, D. H. Kang, Z. N. Heim, P. Meyer, B. A. Erickson, N. Haldar, N. Baradaran, M. Havenith, and D. M. Neumark, Extreme ultraviolet time-resolved photoelectron spectroscopy of adenine, adenosine, and adenosine monophosphate in a liquid flat jet, *Phys. Chem. Chem. Phys.,* **26**, 13106-13117, 2024.
[2] D. H. Kang, M. Koga, N. Haldar, and D. M. Neumark. Dynamics of photoexcited 5-bromouracil and 5-bromo-2'-deoxyuridine studied by extreme ultraviolet time-resolved photoelectron spectroscopy in liquid flat jets. *Chem. Sci.*, **15**, 17245-17255, 2024.
[3] X.Chen, D. S. Larsen, S. E. Bradforth and I. H. M. van Stokkum, Broadband Spectral Probing Revealing Ultrafast Photochemical Branching after Ultraviolet Excitation of the Aqueous Phenolate Anion. *J. Phys. Chem. A*, **115**, 3807-3819, 2011
[4] K. Robertson, W. G. Fortune, J. A. Davies, A. N. Boichenko, M. S. Scholz, O. Tau, A. V. Bochenkova, and H. H. Fielding, Wavelength Dependent Mechanism of Phenolate Photooxidation in Aqueous Solution, *Chem. Sci.*, **14**, 3257-3264, 2023.
[5] A. L. Tyson, and J. R. R. Verlet, On the Mechanism of Phenolate Photo-Oxidation in Aqueous Solution, *J. Phys. Chem. B*, **123**, 2373-2379, 2019.

Poster A14

Electron-ion coincidence imaging of Associative Ionization: Fundamental studies for Hypersonics

Jai Khatri and Arthur G. Suits

Department of Chemistry, University of Missouri, Columbia, Missouri, USA

jaikhatri1997@gmail.com

We are developing a novel instrument for associative ionization studies. The main goal is to use electron-ion coincidence imaging methods to obtain associative ionization cross sections and excitation functions for a variety of relevant atomic species. This method will allow us to identify electronic states of reactants and determine rovibrational distribution of the product ions via electron-ion coincidence imaging. Here, we are investigating associative ionization of nitrogen and oxygen using intrabeam collisions in fast beams. This reaction ($N+O \rightarrow NO^+ + e^-$) is generally considered the most important regrading plasma formation for hypersonics in pure air due to its low activation energy. We use a pulsed discharge in N_2 and O_2 to produce N^+ and O^+ beams at 1-3 keV. Selective acceleration of the O^+ beam, followed by charge transfer neutralization of both atomic ions, enables precise velocity matching between neutral nitrogen and oxygen atoms in the interaction region, allowing fine control over their relative collision energies. We will provide a progress report on the characterization of the beams and development of this instrument.

Poster B6 Hot Topic

Ultrahigh velocity resolution for inelastic scattering dynamics

Olivia Krohn and Dave Chandler

Combustion Research Facility, Sandia National Laboratory, Livermore, California
okcarls@sandia.gov

The study of inelastic collisions in the gas-phase remains an excellent probe of the fundamental potential energy surface of the interacting molecules. Such studies are often involve measuring the differential cross section of the scattered products as a function of energy and quantum state of the final product. These studies are typically conducted within molecular beams, which provide rotationally cold molecules, and with velocity map ion imaging (VMII), which enables state-selective and velocity sensitive detection of one the final scattering product states. These tools have been prolific in studies of atomic-molecular systems; however, the detection resolution of both final products states in bi-molecular collisions has been historically impeded by the velocity width of the molecular beam, which blurs the kinetic energy resolution of the products. For this reason, an approachable method to achieve excellent velocity resolution is extremely impactful to studies of molecular collisions. We present a technique to utilize co-linear mid-infrared (MIR) and molecular beams to prepare molecules in a chosen ro-vibrational quantum state with extremely high velocity resolution. The MIR laser counter-propagates to the molecular beam, such that the center wavelength and linewidth dictate the center velocity and velocity width, respectively, of the excited molecules. With the achieved velocity resolution[1], studies of bimolecular collisions with full information of both final products will be achievable. Our first system is the study of vibrational energy transfer between singly vibrationally excited nitric oxide, i.e. NO(v=1) + NO(v=1) → NO(v=2) + NO(v=0).

---

[1] O. A. Krohn and David W. Chandler. J. Phys. Chem. Lett. 2024 15 (50), 12455-12463. DOI: 10.1021/acs.jpclett.4c02927

Poster B3 Hot Topic

Probing the Ultrafast Dynamics of Nitrobenzene through Time-Resolved Coulomb Explosion Imaging

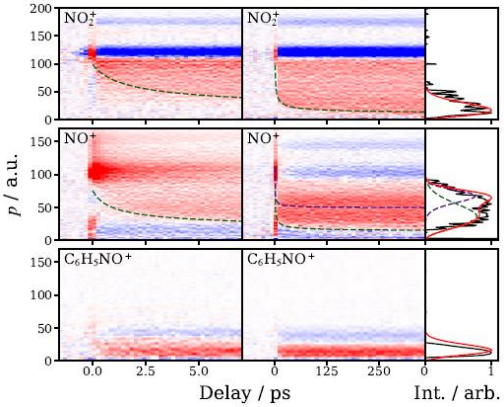
Chow-Shing Lam, Tai-Che Chou, Joseph McManus and Mark Brouard

[a] *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford OX1 3TA, United Kingdom*
Email: chow-shing.lam@chem.ox.ac.uk

ABSTRACT

Recording the real-time nuclear positions of molecules during structural transformations has long been a goal in reaction dynamics. Visualizing photo-induced structural changes is essential for advancing our understanding of photochemistry; however, the ultrafast timescales involved pose significant challenges.[1] Ultrafast techniques have advanced our ability to track transient electronic and geometric evolution, but they often fall short of providing definitive structural details.

Coulomb explosion imaging (CEI) with coincidence detection has emerged as a powerful approach to capturing such dynamics by correlating multiple charged fragments to reconstruct molecular structure based on the measured fragment momenta. However, its use has been limited by low count rates required to avoid false coincidences. Covariance analysis overcomes this limitation by statistically analyzing the joint variability of fragment momentum distributions at high count rates, significantly speeding up data acquisition.[2]



In this work, we demonstrate the power of time-resolved covariance CEI using nitrobenzene, which serve as a prototypical model for nitro-aromatic compounds, a class widely applied in photoswitches, photolabile protecting groups, and NO-donors in vasodilators.[3] We explore the photochemistry of nitrobenzene by exciting it with UV pulse at 240 nm into its S_4 electronically excited singlet state, followed by ionization with an intense 800 nm pulse. This setup allows us to identify and characterize photofragmentation channels leading to NO_2, NO, and O formation. Remarkably, NO_2 photofragments exhibit bimodal rise times of ~8 ps and ≥2 ns and can be detected within the first picosecond after excitation. NO is produced through two distinct pathways: (i) slow, prompt and (ii) fast, delayed fragments, with rise times of ~8 ps and ~14 ps, respectively. NO^+ is detected in covariance with $C_6H_5O^+$, corresponding exclusively to pathway (ii). Intriguingly, the covariant momenta of ($C_5H_5^+$, NO^+) are observed only for the fast NO fragments, suggesting that the secondary dissociation of $C_6H_5O \rightarrow C_5H_5 + CO$ uniquely follows pathway (ii). Experimental data, complemented by simulations, provide new insight into the dissociation mechanisms and offer a possible explanation for discrepancies in previous literature.[4,5] By combining femtosecond pump-probe spectroscopy with universal detection methods, this study opens up new possibilities for exploring the time-resolved photochemistry of complex molecules in the gas phase.

[1] Zewail, A. H. Femtochemistry: Atomic-Scale Dynamics of the Chemical Bond. *J. Phys. Chem. A* 104, 5660-5694, 2000.
[2] Allum, F. *et al.* Multi-Particle Three-Dimensional Covariance Imaging: "Coincidence" Insights into the Many-Body Fragmentation of Strong-Field Ionized D_2O. *J. Phys. Chem. Lett* 12, 8302-8308, 2021.
[3] Fukuhara, K. *et al.* Photochemical Generation of Nitric Oxide from 6-Nitrobenzo[a]pyrene. *J. Am. Chem. Soc.* 123, 8662, 2001.
[4] Lin, M. *et al.* Photodissociation dynamics of nitrobenzene and nitrotoluene. *J. Chem. Phys.* 126, 064310, 2007.
[5] Hegazy, K. *et al.* Investigating dissociation pathways of nitrobenzene via mega-electron-volt ultrafast electron diffraction. arXiv:2308.03996, 2024.

Poster B5

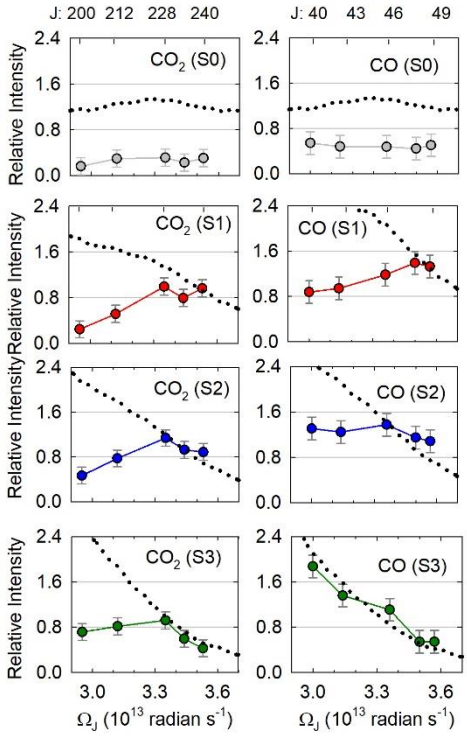
Comparing How CO and CO_2 Are Optically Centrifuged

Rachel Mingxin Lei, Simone A. DeSouza, Hannah M. Ogden, Tara J. Michael, Matthew Laskowski, and Amy S. Mullin

Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742
Email: mingxin@terpmail.umd.edu

ABSTRACT

The optical centrifuge is an ultrafast laser-based technique that uses pairs of chirped pulses and sequential Raman excitation to prepare gas-phase molecules with high rotational energies. The extent of rotational excitation is controlled by varying the optical bandwidth of the chirped pulses. Here we use a tunable optical centrifuge to selectively optimize population of CO (J=41–49) and CO_2 (J=200–240), which both have rotational angular frequencies of $\Omega_J = (2.8 - 3.5) \times 10^{13}\ rad\ s^{-1}$. Nascent rotational distributions for CO_2 and CO are measured with high resolution transient IR absorption near λ=4.4 μm at 300 mTorr with four different optical centrifuge traps, each with a distinct pulse spectrum.[1] The nascent distributions at t=100 ns are shown as symbols in the figure. The S0 trap uses the full bandwidth of the optical centrifuge pulses and very few molecules are released from the optical trap. The trap intensity is large enough that molecules instead are driven into higher J states. The bandwidth is sequentially reduced for the S1-S3 optical traps, leading to the increased population release of lower J states. The dotted lines in the figure show the relative intensity of the optical traps. Both CO and CO_2 are optically centrifuged because they have non-uniform polarizability (i.e. cigar-shaped electron density). However, for the same optical trap, CO_2 and CO have different rotational distributions. These differences result directly from the interactions of the molecules with the optical field and the ladder of rotational states that are populated through sequential Raman excitation. The polarizability anisotropy of CO_2 is four times larger than CO's. As a result, CO_2 is held more tightly in the optical trap, for a given optical centrifuge spectrum and angular frequency. This behavior is most notable for the S3 optical trap.



The capture and rotational acceleration of molecules in an optical trap, and their subsequent release, is characterized by the transient IR absorption signals and the overlap geometry of the optical centrifuge and IR laser beams. The interaction region in the experiments includes a tightly focused optical centrifuge beam with a beam waist of 52 μm and a gently focused IR beam with a beam waist of 230 μm that overlaps the pulsed beam 11 times. A geometric correction factor of 13.2 is used along with Beer's Law to convert transient IR absorption signals to absolute number densities. The number densities for CO_2 are 40% larger than for CO, consistent with its larger polarizability anisotropy. Furthermore, as much as 70% of the sample is optically centrifuged in the interaction region, which increases the likelihood of superrotor-superrotor collisions. This project was funded by the National Science Foundation.

---

[1] Ritter, M.E., DeSouza, S. A., Mullin, A. S, Transient IR spectroscopy of optically centrifuged CO_2 (R186-R282) and collisional dynamics for the J=244-282 states. *Faraday Discuss.* **251**, 140-159, 2024.

Poster B14

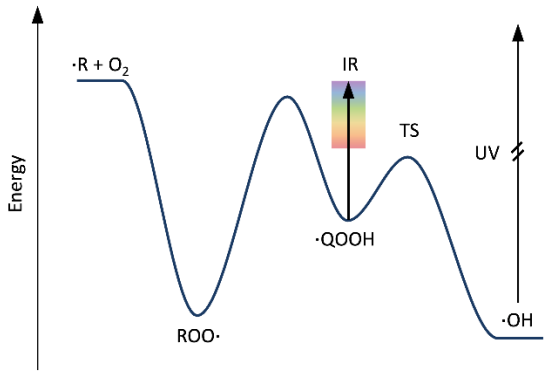
Unimolecular Dynamics of Hydroperoxyalkyl (•QOOH) Intermediates

Yujie Qian, Lilyana R. Walsh, and Marsha I. Lester

Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19103-6323 USA
Email: milester@sas.upenn.edu

ABSTRACT

Hydroperoxyalkyl (•QOOH) intermediates are important carbon-centered radicals formed during alkane oxidation in atmospheric and low-temperature combustion chemistry. Yet, direct observation of •QOOH intermediates has been challenging due to their transient nature and low steady-state concentration. The •QOOH intermediates can decay by unimolecular dissociation to hydroxyl (OH) radicals and cyclic ether products or undergo bimolecular reaction with O_2 leading to low-volatility organic compounds or autoignition. An alternative synthetic method has been developed to generate stabilized •QOOH radicals under jet-cooled and collision-free conditions.[1-3] Most recently, the •QOOH intermediates formed in isopentane oxidation are being characterized through their infrared (IR) fingerprint across the 3500-7100 cm^{-1} spectral region. IR activation also initiates the energy- and time-resolved unimolecular dissociation dynamics of •QOOH to OH products, which are detected by UV laser-induced fluorescence. The experimental kinetics study is supported by theoretical characterization of the transition state (TS) region to compute energy-dependent and thermal decay rates. The combined experimental and theoretical approaches provide new insights on the unimolecular reaction dynamics, including heavy atom tunneling, of transient •QOOH intermediates under controlled laboratory conditions as well as their impact in realistic atmospheric and combustion chemistry.



---

[1] Hansen, A. S. *et al.*, "Watching a hydroperoxyalkyl tadical (•QOOH) fissociate" *Science* **373**, 679-682, 2021.
[2] Qian, Y. *et al.*, "Isomer-tesolved unimolecular fynamics of the hydroperoxyalkyl tadical (•QOOH) in vyclohexane oxidation", *Proc. Natl. Acad. Sci.* **121**, e2401148121, 2024.
[3] Qian, Y. *et al.*, "Infrared fingerprint and unimolecular decay dynamics of the hydroperoxyalkyl intermediate (•QOOH) in cyclopentane oxidation", *J. Phys. Chem. A* **128**, 9240–9250, 2024.

Poster A10

Kinetic analysis to determine the mechanistic foundations of the sequential activation of methane by Ta^+

Tucker W.R. Lewis[a], Albert A. Viggiano[a], Brendan C. Sweeney[a], Jennifer Meyer[b], Shaun G. Ard[a], Nicholas S. Shuman[a]

[a]Air Force Research Laboratory, Space Vehicles Directorate, Kirtland AFB, Albuquerque, New Mexico 87117, United States

[b]RPTU Kaiserslautern-Landau, Fachbereich Chemie und Forschungszentrum OPTIMAS, Erwin-Schrödinger Str. 52, 67663 Kaiserslautern, Germany

ABSTRACT

The kinetics of $Ta^+ + CH_4$ and related reactions $TaC_nH_m^+ + CH_4$ (n=2-4, m = n, 2n, 3n) are measured from 300 – 600 K using a selected-ion flow tube apparatus. The reaction kinetics feature a complex network of 38 competing unimolecular, bimolecular, and ternary processes, each requiring the estimation of a rate constant and its uncertainty to evaluate. The Differential Evolution algorithm was employed to optimize rate constants and the initial concentrations of each species to find the best fit to experimental data. Distributions of parameter values were calculated by Bootstrap Sampling the data sets and refitting the sampled data with Differential Evolution. Analysis of these distributions yielded the most probable values for the rate constants as well as estimations of their uncertainties. The results confirm that Ta^+ efficiently dehydrogenates methane through a non-spin conserved process. Sequential chemistry leads to the dehydrogenation of up to four methane molecules per tantalum center through the competing processes of $TaC_nH_m^+ + CH_4 \rightarrow TaC_{n+1}H_{m+2}^+ + H_2$ (dehydrogenation) and $TaC_{n+1}H_{m+4}^+$ (association). Supported by density functional calculations, the distinct mechanisms and product structures of the sequential reactions are derived.

Poster A18

Photoacoustic Spectroscopy in a Supersonic Flow

Yanan Liu,[a] Jai Khatri,[a] Shameemah Thawoos,[b] Nicolas Suas-David,[c] and Arthur G. Suits[a]

[a]*Department of Chemistry, University of Missouri, Columbia, Missouri 65211, USA*
[b]*Department of Natural Sciences and Mathematics, University of Olivet, Olivet, Michigan 49076, USA*
[c]*Univ Rennes, CNRS, Institut de Physique de Rennes - UMR 6251, F-35000 Rennes, France*
Email: ylmdw@missouri.edu

Photoacoustic spectroscopy (PAS) is a sensitive absorption technique widely used for trace gas detection. It is inherently broadband because the detection system, usually a microphone or tuning fork, does not depend on the frequency of the absorbed radiation. Furthermore, the required components are relatively simple, robust, and inexpensive. Despite this, PAS has never been applied in a cold supersonic environment. The reason for this is obvious: how could one detect an acoustic signal under supersonic conditions? The supersonic flow provided by a Laval nozzle expansion offers a solution. Such flows are thermal collisional environments propagating much faster than the local speed of sound, but inside which one may produce a photoacoustic signal by suitably chopped laser excitation of molecules seeded in the flow. Downstream from the laser excitation a microphone can respond to the pressure oscillations induced by the laser excitation as the flow sweeps by after the absorbed radiation has been converted to translational energy of the molecules. Sensitive lock-in techniques can pick out the photoacoustic signal even at the low pressure in the flow environment. High-resolution, high-power mid-infrared laser sources are now widely available offering near universal detection when coupled with PAS. Such a strategy offers a novel approach to the spectroscopy and low-temperature kinetics of molecules and radicals. Here we show preliminary results demonstrating the feasibility of this approach and outline plans to enhance the sensitivity of the method and bring applications to low temperature kinetics and spectroscopy.

Poster A19

Kinetics and Product Branching in Dihydrogen Activation by Gaseous Manganese Oxide Cations

Yang Liu,[1] Milan Ončák,[2] and Hua Guo[1]

[1]*Department of Chemistry and Chemical Biology, Center for Computational Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, United States*

[2]*Universität Innsbruck, Institut für Ionenenphysik und Angewandte Physik, Technikerstraße 25, 6020 Innsbruck, Austria*

Abstract

The activation of dihydrogen by transition-metal monoxide cations (MO^+) in the gas phase offers valuable mechanistic insight into muti-state reactions. We present here a mixed quantum–classical trajectory surface hopping and two-dimensional (2D) ring-polymer molecular dynamics (RPMD) study of the $MnO^+ + H_2$ reaction, based on newly developed full-dimensional coupled potential energy surfaces (PESs) for both the lowest-lying quintet and septet spin states. The PESs, with CCSD(T)/AVDZ-level accuracy, are developed using a Δ-machine learning approach based on a set of low-level density functional theory (DFT) PESs, corrected by a limited set of CCSD(T)/AVDZ energy points. The rate coefficients calculated for the $MnO^+ + H_2$ reaction using classical trajectory and 2D RPMD methods are in close agreement with each other, and both are slightly lower than the experimental values. This consistency between the two methods suggests that quantum tunneling is not significant in this reaction. While the reactivity is controlled by an entrance channel barrier in the quintet state, post-transition state intersystem crossing as well as multiple adiabatic reaction channels lead to branching in product formation. The calculated product branching fractions for the $MnOH^+ + H$ and $Mn^+ + H_2O$ channels are in good agreement with experimental observations. Finally, isotope effects on branching fractions are reasonably reproduced, although quantitative discrepancies remain.

Poster B20

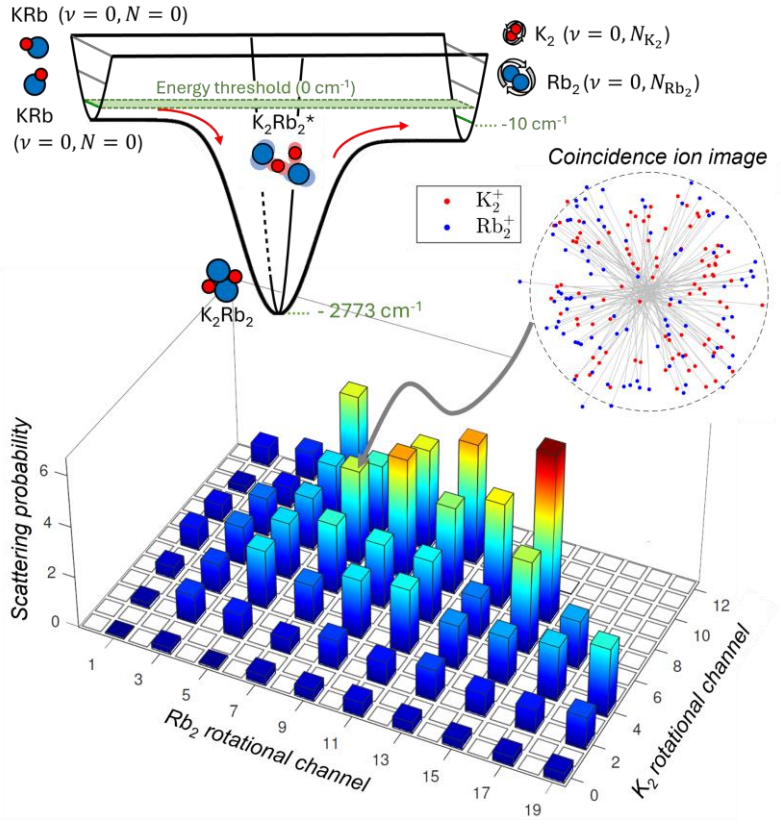
Advancing reaction dynamics with ultracold molecules

Yu Liu[a, b, c] , Jingchen Zhang[b,c] , Paul Julienne

[a] *Institute for Physical Science and Technology, University of Maryland, College Park*
[b] *Department of Chemistry and Chemical Biology, University of Maryland, College Park*
[c] *Joint Quantum Institute, University of Maryland and NIST*
Email: yuliu@umd.edu

ABSTRACT

Over the past few decades, concurrent advances in experimental techniques in both atomic, molecular, and optical (AMO) physics and physical chemistry have enabled unprecedented control over simple molecules, both in terms of their translational motion and their internal states. In this talk, I will discuss the potential for these fully-controlled molecules to advance our understanding and control of reaction dynamics at the quantum level. I will present a series of studies[1] on the reaction KRb + KRb → K_2 + Rb_2 initiated at T < 1 μK[2], including the direct observation of a long-lived reactive complex[3], the demonstration of product rotational state control via conserved nuclear spins[4], and a test of the statistical model using the pair-correlated quantum state distribution of the products[5]. These initial experiments paved the way for a new project in my group at the University of Maryland, where we are aiming to study isotope exchange reactions between Li atoms and diatomic molecules (e.g., ^{7}Li + ^{6}Li$_2$ → ^{6}Li^{7}Li + ^{6}Li, ^{6}Li^{7}Li + ^{6}Li^{7}Li → ^{6}Li$_2$ + ^{7}Li$_2$) at ultralow temperatures, and at the state-to-state level. I will present the prospect of this system as a playground for investigating quantum effects in reaction dynamics, such as interference between reaction pathways, entanglement between reaction products, and coherent control of bimolecular reactions. Finally, I will present our recent theory work on possible pathways to generate the ultracold reactants, specifically the formation of ultracold Li_2 dimers from laser cooled Li atoms.



---

[1] Liu, Y., & Ni, K.-K. Bimolecular Chemistry in the Ultracold Regime. *Annual Review of Physical Chemistry*, 73(1) (2022).
[2] Hu, M. G., Liu, Y., … Ni, K. K. Direct observation of bimolecular reactions of ultracold KRb molecules. *Science* (New York, N.Y.), 366(6469), 1111–1115 (2019).
[3] Liu, Y., Hu, M. G., … Ni, K. K. Photo-excitation of long-lived transient intermediates in ultracold reactions. *Nature Physics* (2020).
[4] Hu, M. G., Liu, Y., … Ni, K. K. Nuclear spin conservation enables state-to-state control of ultracold molecular reactions. *Nature Chemistry* (2020).
[5] Liu, Y., Hu, M.-G., Nichols, M. A., Yang, D., Xie, D., Guo, H., & Ni, K.-K. Precision test of statistical dynamics with state-to-state ultracold chemistry. *Nature*, 593(7859), 379–384 (2021).

Poster B18

Stereodynamics of cold molecules in collision with rare gas atoms

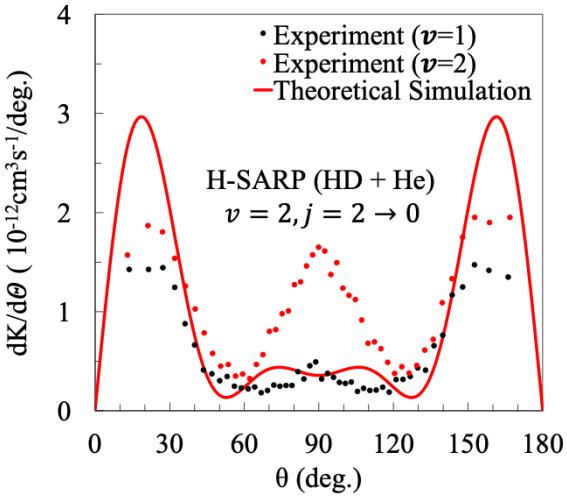
B. Mandal,[a] C. Sanz-Sanz,[b] P. G. Jambrina,[c] K. Patkowski,[d] F. J. Aoiz,[e] and N. Balakrishnan [a]

[a] *Dept. of Chemistry, University of Nevada, Las Vegas, USA*
[b] *Departamento de Química Física Aplicada, Modulo 14, Universidad Autonoma de Madrid, Spain*
[c] *Departamento de Química Física, University of Salamanca, Spain*
[d] *Department of Chemistry and Biochemistry, Auburn University, Alabama, USA*
[e] *Departamento de Química Física, Universidad Complutense, Madrid, Spain*
Email: bikramaditya.mandal@unlv.edu

ABSTRACT

The quest to control the outcomes of molecular collisions has long been a cherished goal of chemists and physicists alike. The advent of cold and ultracold molecules has improved the prospect of acheiving this goal as quantum effects dominate in this regime and small perturbations introduced by external electric or magnetic fields alter the collision outcome. Indeed, ultracold polar molecules are currently being explored for many applications in quantum sciences, including quantum computing, quantum sensing, and quantum information processing. There is growing interest in ultracold chemistry to explore reaction mechanisms and control reaction outcomes through quantum interference.

While most of the current experimental studies of ultracold molecules for quantum science applications are focused on dipolar molecules of alkali metal dimers or open-shell molecules involving alkaline-earth metals (SrF, CaF, YbF), collisions of simple diatomic molecules such as H_2, HD, and D_2 have also gained considerable interest from a fundamental perspective. Indeed, cold collisions of HD with He, H_2, and D_2 as well as D_2 with He, Ne, and D_2 have been reported by Mukherjee, Zare, and collaborators. For these systems, cold collisions are achieved by co-propagating the collision partners in a molecular beam combined with the Stark-induced adiabatic Raman passage (SARP) techniques to prepare the initial molecular quantum state and molecular alignment.



Here we present a comprehensive quantum mechanical study of stereodynamic control of molecule + atom collisions that have been probed experimentally by Perreault *et al.* using the SARP techniques, namely, collisions of HD($v = 2$) + He, $D_2(v = 2)$ + He, and $D_2(v = 4)$ + Ne.[1,2] For HD + He and D_2 + He,[3] our calculations utilize a highly accurate full-dimensional H_2 + He interaction potential with diagonal Born-Oppenheimer correction (DBOC) appropriate for the HD and D_2 isotopomers. Our analysis shows that rotational quenching of HD from $j = 2 \rightarrow j' = 0,1$ in $v = 2$ and $j = 2 \rightarrow j' = 0$ in $v = 2$ for D_2 is dominated by an $l = 1$ shape resonance. Despite improvements in the development of the potential energy surfaces (PESs), a good agreement with SARP experiments for $v = 2$ is achieved only when contributions from collision energies below 1.0 cm^{-1} were excluded in the computation of velocity averaged differential rate coefficients for both systems.

For D_2 + Ne,[4] our results on a new Ne-H_2 PES show reasonable agreement with experiments but differ in the assignment of specific angular momentum partial waves to key features of the measured angular distribution.

[1] Perreault, W. E. *et al.*, Quantum controlled cold scattering challenges theory. *J. Phys. Chem. Lett.,* **13**, 10912, 2022.
[2] Perreault, W. E. *et al.*, Resonant cold scattering of highly vibrationally excited D_2 with Ne. *J. Chem. Phys.,* **157**, 144301, 2022.
[3] Mandal, B. *et al.*, Stereodynamics of cold HD and D_2 collisions with He, *J. Chem. Phys.,* **162**, 104201, 2025.
[4] Mandal, B. *et al.*, Cold collisions of highly vibrationally excited and aligned D_2 with Ne, *J. Chem. Phys.,* **162**, 000000, 2025.

Poster A4

The Stereodynamics of Two Orientated Molecules

Joseph. W. McManus,* Matthew Strutton, Max McCrea, Alexander Crosby, Joshua Featherstone and Mark Brouard

Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford, UK.
** Email: joseph.mcmanus@chem.ox.ac.uk*

ABSTRACT

Orienting a molecule prior to a collision acts as a direct probe of the relevant potential energy surface(s), and has been of particular interest in recent years.[1,2] Here presented is a novel theory, as well as its application to experimental and simulated data, that describes collisions between two molecules that are both oriented. This represents complete control over a collision, allowing selective rotational excitation, with potential applications towards favouring certain reactive pathways.

Our experiment involves a crossed molecular beam apparatus. Both collision partners experience hexapolar electric fields as they travel towards each other, allowing for focussing and state selection. Laser excitation via REMPI and velocity-mapped imaging are employed to detect the velocity distribution of scattered products, one final internal state at a time. The molecules experience a dipolar electric field as they collide, allowing orientation of their bond axes. To complement these data, full quantum calculations are performed,[3] as well as mixed quantum-classical trajectories.[4]

---

1. C.G. Heid, V. Walpole, M. Brouard, P.G. Jambrina and F.J. Aoiz, *Side-impact collisions of Ar with NO*, Nat. Chem., 11, 662-668, 2019.
2. V. Walpole, C.G Heid, P.G. Jambrina, F.J. Aoiz, and M. Brouard, *Steric effects in the inelastic scattering of NO(X) + Ar: Side-on orientation*, J. Chem. Phys. A, 123, 043401, 2019.
3. M.H. Alexander, P.J. Dagdigian, H.-J. Werner, J. Kłos, B. Desrousseaux, G. Raffy and F. Lique, *Hibridon: A program suite for time-independent non-reactive quantum scattering calculations*, Comput. Phys. Commun., 289, 108761, 2023.
4. B. Mandal, D. Bostan, C. Joy and D. Babikov, *MQCT 2024: A program for calculations of inelastic scattering of two molecules (new version announcement),* Comput. Phys. Commun., 294, 108938, 2024.

Poster B21

Towards high-energy Collision Applications: A Non-adiabatic Dynamics study on the Thirteen-State $^1A'$ Manifold of N_2O

Qinghui Meng, Yinan Shu, Zoltan Varga, Dayou Zhang, and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN
Email: meng0260@umn.edu

ABSTRACT

Calculations of collisions involving excited electronic states play an important role in many high-energy environments, for example in simulating thermal energy content and heat flux in flows around hypersonic re-entry vehicles, and useful data is usually not available from either experiment or theory. In this work, compatibilization by deep neural network (CDNN) – an automatic coupled potential energy surface (PESs) learning method[1]– is used to discover and fit an underlying adiabatic-equivalent compatible potential energy matrix (CPEM) for singlet oxygen collisions with N_2 in the $^1A'$ manifold of N_2O. The procedure yields not only a fit to the CPEM and its gradient but also analytic representations of the adiabatic surfaces, and their gradients. The problem is challenging because we consider high-energy collisions involving a 13-state dense manifold of electronic states. Using the resulting representation of the PESs and their analytic gradients, we calculated electronically nonadiabatic cross sections for $N_2(X\,^1\Sigma_g^+)$ + $O(^1S)$ collisions for various initial conditions by using a new asymptotically extended formulation of the curvature-driven coherent switching with decay of mixing (κCSDM) semiclassical dynamics method[2,3],[4] which needs only the adiabatic potential energy surfaces to compute the coupling between electronic states and resolves the conflict between differing symmetries of the interacting atom-diatom system and the completely separated final states. This application also opens the way for treating other difficult problems involving electronic energy transfer and reactions of electronically excited species at high energy for various applications in chemistry, physics, materials, and engineering.

We present simultaneous diabatization and adiabatic potential energy surface fitting of the thirteen-state $^1A'$ N_2O system including the corresponding N_2 + O and NO + N asymptotes. We further showed that we could decrease the size of the neural network architecture for more affordable simulations while suffering less than 10% increase in the error of energetic fitting. We used the fitted surfaces and couplings to calculate cross sections for electronic energy transfer and chemical reactions in singlet oxygen collisions with N_2. Previous modeling of high-enthalpy gases had to use simple models for electronic energy transfer because data were not available either experimentally of theoretically.

---

[1] Shu, Y.; Varga, Z.; Zhang, D.; Meng, Q.; Parameswaran, A. M.; Zhou, J.-G.; Truhlar, D. G. Learning Multiple Potential Energy Surfaces by Automated Discovery of a Compatible Representation. *J. Chem. Theory Comput. 21*, 3342-3352, **2025**.

[2] Jasper, A. W.; Zhu, C.; Nangia, S.; Truhlar, D. G. Introductory lecture: Nonadiabatic effects in chemical dynamics. *Faraday Discuss. 127*, 1–22, **2004**.

[3] Zhu, C.; Nangia, S.; Jasper, A. W.; Truhlar, D. G. Coherent switching with decay of mixing: An improved treatment of electronic coherence for non-Born-Oppenheimer trajectories. *J. Chem. Phys. 121*, 7658-7670, **2004**.

[4] Shu, Y.; Zhang, L.; Chen, X.; Sun, S.; Huang, Y.; Truhlar, D. G. Nonadiabatic dynamics algorithms with only potential energies and gradients: Curvature-driven coherent switching with decay of mixing and curvature-driven trajectory surface hopping. *J. Chem. Theory Comput. 18*, 1320-1328, **2022**.

Poster B7

Computational study of the low-resolution IR spectrum of CH_5^+ and its isotopologues in the CH stretching region

Pattarapon Moonkaen,[a] Anne B. McCoy[a]

[a] *Department of Chemistry, University of Washington, Seattle, WA 98195 USA*
Email:moonkp@uw.edu

ABSTRACT

CH_5^+ has been of interest to spectroscopists for many years because of its interesting properties that result from its high permutational symmetry and the low energy barriers that separate the 120 equivalent minima on the potential surface. Indeed, the zero-point level has been shown to have comparable amplitude at the 120 equivalent minima as well as the 180 transition states that separate these minima.[1] Electronic structure calculations predict that the minimum energy structure corresponds to a CH_3^+ cation making a three-center two-electron bond (3c2e) with H_2. The resulting large-amplitude motions displayed by CH_5^+ has made assignment of the rotationally resolved spectrum challenging.[2]

Recently the Vilesov group has reported low-resolution spectra of CH_5^+ and CH_4D^+ in helium nanodroplets.[3] The spectrum of CH_5^+ in the CH stretching region consists of two broad peaks, while the spectrum of CH_4D^+ in this region contains a single sharp peak. This motivated us to revisit the vibrational spectra of CH_5^+ and its isotopologues. In this work we will expand an approach that was previously developed in our group for a study of the spectrum of the bioxalate anion, $C_2O_4H^-$ in the OH stretching region.[4] In that work, geometries were randomly sampled from the harmonic ground state probability distribution, the OH bond is optimized, and the spectrum was obtained by convoluting the harmonic spectrum of the OH oscillator at each of the sampled geometries. In this work, we will expand the method to an anharmonic five-dimensional calculation of the spectrum in the CH stretching region for CH_5^+, and by using diffusion Monte Carlo (DMC) to obtain ground state probability distribution used to sample geometries of CH_5^+ or its isotopologues. For these calculations, the five CH or CD stretching vibrations are described using an anharmoically coupled harmonic oscillator (HCAO) model. The comparison between the theoretical spectra and experimental and the effect of full and partial deuteration on IR spectra will be discussed as well.

---

[1] Huang, X. *et al*. Quantum Deconstruction of the Infrared Spectrum of CH_5^+. *Science* 311, 60-63, 2006
[2] Asvany, O. *et al*, Experimental ground-state combination differences of CH_5^+. *Science* 347, 1346-1349, 2015
[3] Singh, A. *et al*, Infrared Spectroscopy of CH_5^+ Cations in Helium Nanodroplets. *J. Phys. Chem. Lett.* 15(44), 10931-10936, 2024
[4] Wolke, C. T. *et al*. Diffuse Vibrational Signature of a Single Proton Embedded in the Oxalate Scaffold $HO_2CCO_2^-$. *J. Phys. Chem. A* 119(52), 13018-13024, 2015

Poster A20

Applications of the MCTDH approach to rigid rotor scattering: achievements, challenges and perspectives.

Steve Ndengue,[a] Richard Dawes,[b] and Fabien Gatti[c]

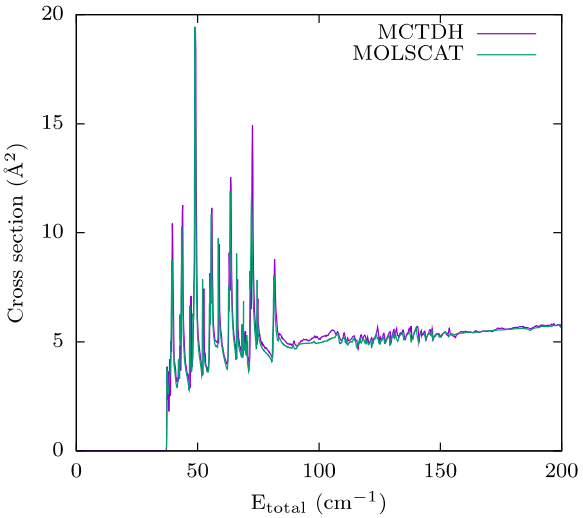
[a] *Department of Physics and Astronomy, Haverford College, Haverford, 19041 PA. Email: sndengue@haverford.edu*

[b] *Institut Carnot de Bourgogne, Universite Bourgogne Europe, Dijon, France.*

[c] *Department of Chemistry, Missouri S&T, Rolla, 65401 MO.*

ABSTRACT

The Heidelberg MCTDH (MultiConfiguration Time Dependent Hartree[1]) package is a powerful and versatile computational tool for simulating molecular quantum dynamics, with broad applications in chemical physics. Over the past several years, we have employed the MCTDH framework to investigate a range of rigid rotors scattering scenarios, beginning with systems composed of two linear molecules and extending to more complex interactions involving asymmetric and linear rotor combinations. In this work, we present selected recent results that highlight the capabilities of MCTDH in modeling inelastic molecular collisions, particularly in regimes where traditional close-coupling methods are computationally prohibitive or fail to converge. We illustrate the efficacy of this approach through the case studies[2,3] of $PO^+ + H_2$, H_2O + Ar, CH_3COOH + He, and H_2O + H_2. These examples demonstrate that MCTDH can accurately capture inelastic cross-sections, even at low collision energies. Despite its strengths, certain systems remain challenging. For instance, the scattering of two asymmetric rotors—exemplified by H_2O + H_2O—proves to be computationally demanding, even when using the Multi-Layer MCTDH (ML-MCTDH) extension. We discuss these limitations and identify potential directions for improvements. Finally, we present ongoing efforts to extend the methodology toward the treatment of open-shell systems, outlining preliminary developments and offering practical resources, including custom scripts and auxiliary codes, to facilitate similar investigations by interested researchers.



---

[1] Meyer, H.-D. *et al*. The multi-configurational time-dependent Hartree approach. *Chemical Physics Letters* 165.1, 73-78, 1990.

[2] Ndengue, S. *et al.* Atom-Triatom rigid rotor inelastic scattering with the Multiconfiguration Time Dependent Hartree approach. *Chemical Physics Letters* 668, 42-46, 2017.

[3] Ndengue, S. *et al.* State-to-state inelastic rotational cross sections in five-atom systems with the multiconfiguration time dependent Hartree method. *The Journal of Chemical Physics* 151, 134301, 2019.

Poster A15

Probing molecular polariton dynamics in the gas phase for optical control of chemistry

Jane Nelson, Trevor Wright, and Marissa Weichman

Dept. of Chemistry, Princeton University, Princeton, NJ 08544.
Email: janenelson@princeton.edu

ABSTRACT

Polaritons, hybrid light-matter states that arise from strong cavity coupling of molecular transitions, represent a compelling platform for optical control of chemistry.[1] Altered chemical reaction rates have been reported under strong coupling of a molecular vibration to the photonic mode of an optical cavity. However, prior demonstrations lack the mechanistic explanations necessary to guide the expansion of the field. Different from the liquid-phase state of most polariton chemistry studies, the gas phase presents an environment free of solvent effects conducive to simple molecular dynamics and reactive surfaces. In this context, gas-phase experiments on vibrational polaritons could dramatically impact fundamental understanding of light-matter interactions and routes toward reaction control. We have demonstrated the first gas-phase molecular polaritons by coupling rovibrational transitions of methane (CH_4) in a variety of cavity geometries and molecular conditions.[2,3] Representative transmission spectra of extra-cavity methane (blue), an empty cavity 8.36 cm in length (red), and the same cavity containing methane (purple) are shown in Figure 1; the cavity mode splits into two polariton peaks with gas present. We achieve strong coupling at both cryogenic and room temperatures. And, with sufficient molecular number density, we achieve multimode coupling between multiple cavity modes and one or more molecular transitions. Our apparatus enables quantum state-specific cavity coupling, optical access via an orthogonal axis, and greater overall experimental control that prior polariton chemistry efforts have not accessed.

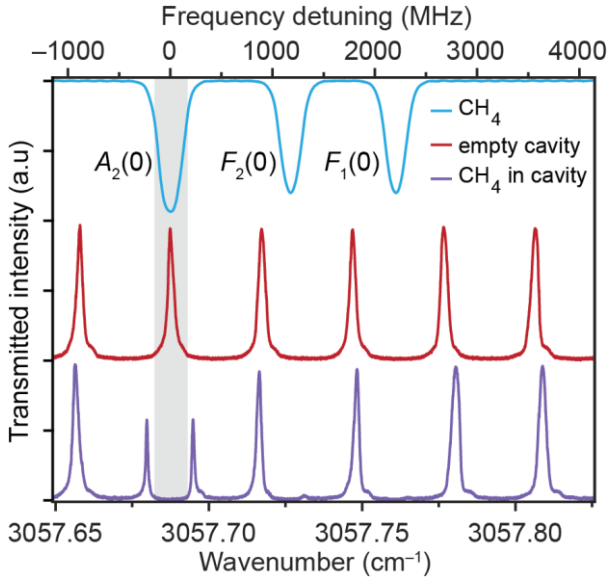


Figure 1: Transmission spectra of polariton system in CH_4

In ongoing work, we are considering a range of benchmark molecular processes to study under strong cavity coupling in our unique gas-phase apparatus.[4] We are currently pursuing nonlinear spectroscopy experiments to probe the dynamics of methane under strong cavity coupling to disentangle the bulk molecular response from that of the polaritonic states. We are also building towards studies of infrared-driven unimolecular gas-phase processes including isomerization and intramolecular vibrational energy redistribution. In turn, our work will help connect experimental and theoretical understanding of polariton chemistry and influence technologies in precision spectroscopy and chemical reaction control.

---

[1] Dunkelberger, A. *et al*. Vibration-cavity polariton chemistry and dynamics. *Ann. Rev. Phys. Chem.* 73, 429-451, 2022.
[2] Wright, A. *et al*. Rovibrational polaritons in gas-phase methane. *J. Am. Chem. Soc.* 145, 5982-5987, 2023.
[3] Wright, A. *et al*. A versatile platform for gas-phase molecular polaritonics. *J. Chem. Phys.* 159, 164202, 2023.
[4] Nelson, J and Weichman, M. More than just smoke and mirrors: gas-phase polaritons for optical control of chemistry. *J. Chem. Phys.* 161, 74304, 2024.

Poster B4

Matrix Dependent Conformer Specific Sublimation Dynamics Probed by Chirped-Pulse Mm-Wave Rotational Spectroscopy

Kyle T. Renshaw[a], Quentin D. Borengasser[a], Emily Hayden[a], and Bernadette M. Broderick[a]

[a] Broderick Lab, University of Missouri-Columbia, 125 Chemistry Building Columbia, MO 65211. Email: ktr29p@missouri.edu

ABSTRACT

The sublimation dynamics of mixed ices of astrochemical interest have been investigated utilizing CPICE, an instrument which combines chirped-pulse mmWave spectroscopy with buffer gas cooling of molecules desorbed from an ice surface. Recent incorporation of a Fourier-Transform Infrared Spectrometer permits in-situ monitoring of the ice via reflection-absorption infrared spectroscopy (RAIRS) prior to temperature-programmed desorption (TPD). While RAIRS can in some cases reveal distinct conformer-features,[1] the broadband rotational spectra provide an inherently structure specific probe, allowing for determination of branching ratios with conformer specificity. The sublimation of condensed *n*-propanol (PrOH) and *n*-propyl cyanide (PrCN), with five and two symmetry unique structures respectively, have been previously determined to be highly conformer specific.[2,3] This work investigates the effects of intermolecular interactions introduced by formation of binary ice mixtures. Candidate species have been chosen to investigate a range of intermolecular interactions including hydrogen bonding (PrOH + H2O) and dipole-dipole interactions (PrCN + H2O). Of additional interest are the effects of ice structure, with neat PrCN ices having experimentally accessible glass and crystalline states which have previously been shown to alter the conformer distributions, promoting conversion from *anti*-PrCN to *gauche*-PrCN following annealing of the amorphous phase.[1]

---

[1] Durig, J *et al.* Infrared and Raman spectra, conformational stability, ab initio calculations of structure and vibrational assignment of butyronitrile. *Phys. Chem. Chem. Phys.* 3, 766-775, 2001.

[2] Borengasser, Q *et al.* Conformer-Specific Desorption in Propanol Ices Probed by Chirped-Pulse Millimeter-Wave Rotational Spectroscopy. *J. Phys. Chem. Let.* 14, 6550-6555, 2023.

[3] Kanaherarachchi, A *et al.* Conformer Distributions of n-Propyl Cyanide in the Gas Phase and Following Ice Sublimation Measured by Broadband Rotational Spectroscopy. *ACS Earth Space Chem.* 8, 14-20, 2024

Poster B19

Evaporation of Nitric Oxide from Water, Butanol, and Benzyl Alcohol Liquid Microjets: Non-Equilibrium Effects and Collisions

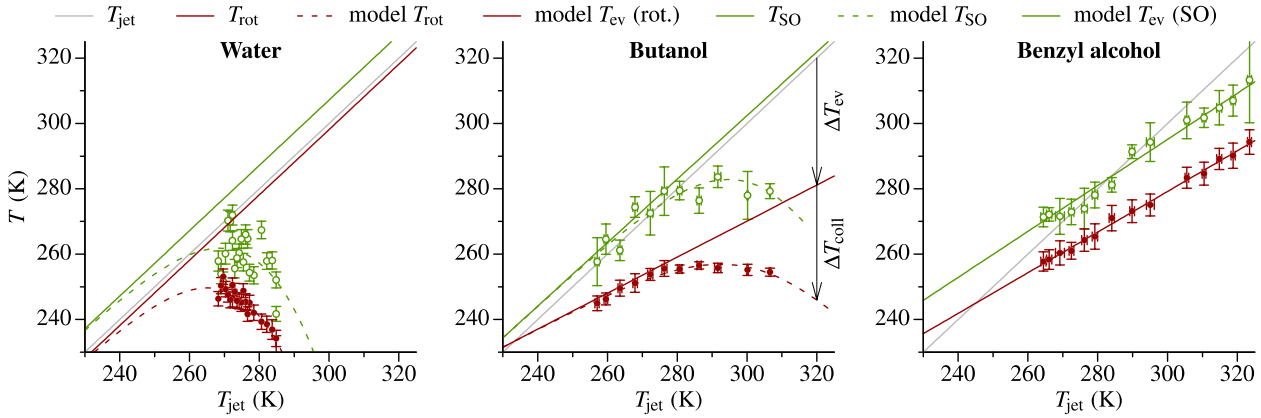
Mikhail Ryazanov[a,b] and David J. Nesbitt[a]

[a] *JILA, National Institute of Standards and Technology and University of Colorado, Boulder, Colorado 80309, USA.*

[b] *Email: mikhail.ryazanov@jila.colorado.edu*

ABSTRACT

Evaporation of nitric oxide (NO) dissolved in liquid water[1], butanol[2], and benzyl alcohol[3] has been studied experimentally by exploiting the combination of liquid microjets in high vacuum with laser-induced fluorescence detection for quantum-state-resolved measurements of NO rotational and spin–orbit distributions. The rotational populations in each case obey Boltzmann distributions corresponding to temperatures T_{rot} significantly (10–50 K) *lower* than the liquid microjet temperature T_{jet}. Systematic studies of the dependence of T_{rot} on T_{jet} indicate that, despite using microjets of the smallest practical diameter (4–9 μm), we observe significant effects due to NO collisions with the "co-evaporant" solvent vapor: in the case of water – at all temperatures above its freezing point, and for butanol – at temperatures above ~270 K. Conversely, benzyl alcohol over the entire temperature range investigated (265–325 K) has sufficiently low vapor pressure to make such collisional effects entirely negligible. However, both T_{rot} and effective spin–orbit temperature T_{SO} of NO evaporating from liquid benzyl alcohol unambiguously demonstrate non-equilibrium behavior. Specifically, the observed NO rotational and spin–orbit temperatures differ systematically from the liquid microjet temperature, showing a linear trend with $dT_{NO}/dT_{jet} \approx 2/3$. These findings resemble results previously seen in NO desorption from and scattering at surfaces of other liquids and solids. Combining this linear evaporation model (T_{ev}) with our previously developed theory for subsequent NO cooling in collisions with the co-evaporating solvent, we are able to reproduce the experimental results for all three liquids and thus provide insights into the differences and similarities between liquid–solute interactions involving NO rotational and spin–orbit degrees of freedom.



This experiment is currently moving into quantum-state-resolved collision dynamics of HCl/DCl at the gas–self-assembled monolayer (SAM) interface, exploiting REMPI and 3D VMI methods for vector momentum, isotope, rovibrational (v, J) quantum-state studies of inelastic energy transfer and H/D exchange kinetics.

---

[1] Ryazanov, M. and Nesbitt, D. J. Quantum-state-resolved studies of aqueous evaporation dynamics: NO ejection from a liquid water microjet. *J. Chem. Phys.* 150, 044201, 2019.

[2] Ryazanov, M. and Nesbitt, D. J. Non-equilibrium and collisional effects in nitric oxide evaporation from 1-butanol liquid microjet, compared with water and benzyl alcohol. *In preparation*, 2025.

[3] Ryazanov, M. and Nesbitt, D. J. Non-equilibrium dynamics at the gas–liquid interface: State-resolved studies of NO evaporation from a benzyl alcohol liquid microjet. J. Chem. Phys. 158, 144703, 2023.

Poster A17

Investigating Kinetics of Messenger Tag Rearrangement in Cryogenically Cooled Pyridinium-(CH_2)-COOH

Payten A. Harville, Erica L. Bocanegra, Madeeha Salik, and Mark A. Johnson

Sterling Chemistry Laboratory, Yale University, 225 Prospect St, New Haven, CT
Email: madeeha.salik@yale.edu

ABSTRACT

Cryogenic ion traps have been used to study kinetics of molecular interactions, such as proton migration on hydrated 4-aminobenzoic acid and Eigen-Zundel interconversion in $H^+(H_2O)_6$. Here we utilize carboxyl-functionalized ionic liquids [HOOC-(CH_2)n-Py^+] (n = 1-7) to study the kinetics of messenger tag rearrangement in a cryogenically cooled 3D Paul trap. In investigating the chain-length dependent intramolecular polarization contributions to the pKa's of carboxylic acids, two features arose in the OH stretch region. Isomer-specific double resonance confirmed that the two features are due to two isomers associated with different tag locations. The redshifted OH feature arises from the isomer in which the tag molecule is attached to the OH group. The higher energy OH stretch is due to the isomer in which the tag is bound closer to the pyridinium ring, leaving the OH free. While these two isomers can be isolated using isomer specific double resonance in a Wiley-McLaren time-of-flight, experiments in trap reveal that depletion of one isomer resulted in depletion of the other isomer as well. We report the kinetics of this tag rearrangement on $Py^+(CH_2)COOH$.

Poster A5

Machine Learning to Extend Photochemical Dynamics Simulations with High Fidelity: Case study Uracil

Juan Carlos San Vicente Veliz and Spiridoula Matsika

Department of Chemistry, Temple University, Email: j.sanvicente@temple.edu

ABSTRACT

Photochemical processes play a key role in numerous critical yet poorly understood phenomena, such as radiation damage, photosynthesis, and vision. Some of the fundamental challenges in this field lie in the complexity of excited-state systems and the high computational costs associated with accurately simulating their dynamics. We present an ad-hoc approach to address these limitations by extending the time scale of photochemical dynamics simulations using a machine-learned model. Using high-fidelity dynamics data from uracil [1], we train an equivariant neural network model that captures energies, forces, and non-adiabatic couplings. The machine-learned model is then used to run ML-based dynamics simulations at a fraction of the computational cost, with accuracy comparable to traditional methods. This approach opens the door to longer, more precise simulations, providing new insights into complex photochemical processes.

[1] Chakraborty, P., Liu, Y., Weinacht, T., & Matsika, S. (2021). Effect of dynamic correlation on the ultrafast relaxation of uracil in the gas phase. Faraday Discussions, 228, 266-285.

Poster A16

Modelling of CO Superrotor Collisions with Fitting Laws

Jonathan Stern,[a] Matthew Laskowski,[b] and Amy S. Mullin[a]

[a] *Dept. of Chemistry & Biochemistry, University of Maryland College Park. Email: jstern@umd.edu*
[b] *Current address:Department of Chemistry, University of Colorado, Boulder*

ABSTRACT

Superrotors are molecules that have rotational energies that surpass their average thermal energy and can surpass their bond energies. The optical centrifuge is an ultrafast laser-based technique that traps molecules in an optical field and drives them into extreme rotational states. Experiments in the Mullin group show that optically centrifuged molecules exhibit slow rotational relaxation and slow spatial reorientation, in contrast to the behavior of molecules at 300 K.[1] Previously, Michael et al[2] measured the collision dynamics of optically centrifuged CO with J up to 67, and Laskowski et al[3] used the SPEG model to simulate the CO relaxation kinetics. Here, the population decay of CO superrotors is modeled with master equation modelling using three different fitting laws, the SPEG, MEG, and ECS-EP models. State-to-state rate constants for rotationally inelastic collisions were extrapolated from experimental data[4] and quantum scattering calculations[5] on CO-CO collisions. The simulated population decay using the two sets of rate constants are compared for each fitting model and the results are compared to the experimental decay kinetics. Figure 1 shows the population decay for CO superrotors simulated using the MEG fit to experimental data.

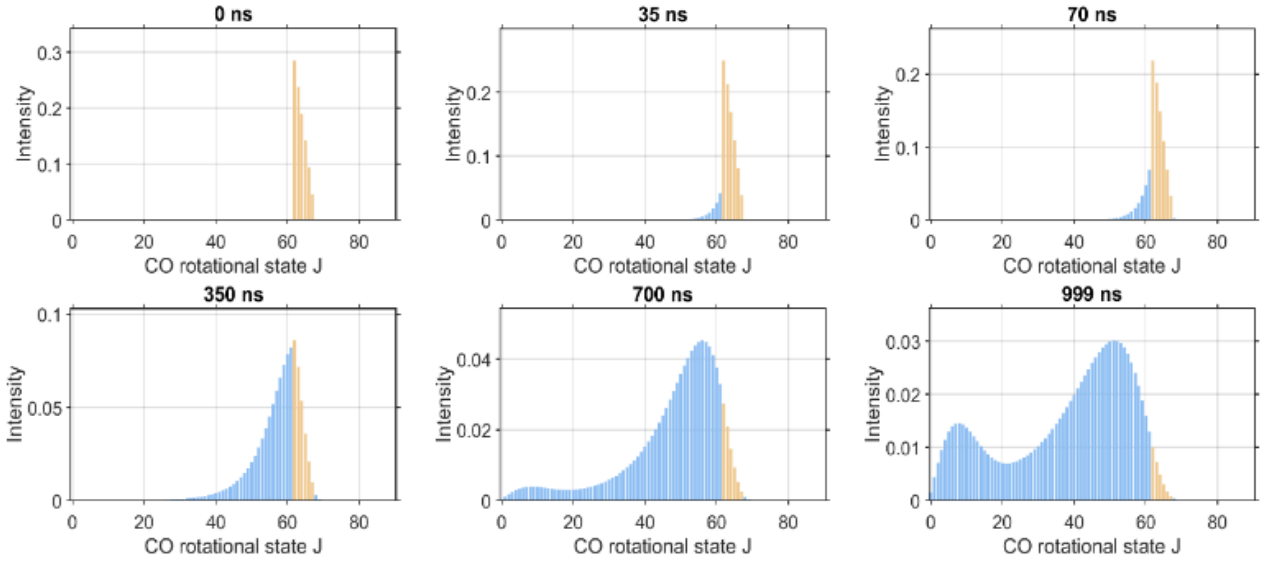


Figure 1. Simulated population decay of CO superrotors with J>60 based on experimental state-to-state rate

---

[1] Mullin, A. S. Generating superrotors and dynamics of molecules in extremely high rotational states. *Annu. Rev. Phys. Chem*. 76, 2025.
[2] Michael, T. J. et al. State-resolved rotational distributions and collision dynamics of CO molecules made in a tunable optical centrifuge. *J. Chem. Phys.,* 154(13), 2021.
[3] Laskowski, M. R. et al. Rotational energy transfer kinetics of optically centrifuged CO molecules investigated through transient IR spectroscopy and master equation simulations. *Faraday Discuss.,* 238, 87–112., 2022
[4] Phipps, S. P. et al. Investigation of the state-to-state rotational relaxation rate constants for carbon monoxide (CO) using infrared double resonance. *J. Chem. Phys*., 116(21), 2002.
[5] Żółtowski, M. et al. Collisional energy transfer in the CO-CO system. *Phys. Chem. Chem. Phys*., 24(19), 2022.

Poster B1

Maximizing the accuracy of measured and computed inelastic collision cross sections & rate constants

Denuwan Vithanage, Jacob Ruben, and Brian Stewart

Wesleyan University, Department of Physics, Middletown, CT 06459
Email: bstewart@wesleyan.edu

ABSTRACT

We are revisiting the computational and experimental study of collisions in the system

$$Li_2\,(A\ ^1\Sigma_u^+)(v_i,j_i) + X \rightarrow Li_2\,(A\ ^1\Sigma_u^+)(v_f,j_f) + X$$

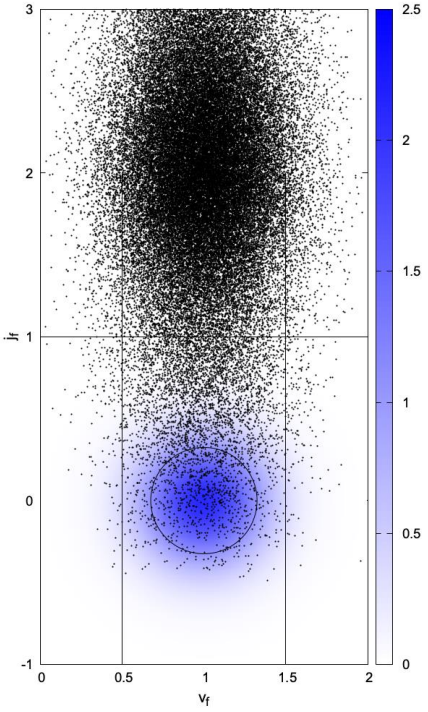
with X=Li or a rare gas. Collisions may be rotationally inelastic, rovibrationally inelastic, or reactive. The purpose of this work is to maximize the accuracy of measured and computed rate constants. Our twin goals are to

- secure the best possible measured rate constants for comparison with theory, and
- find the best way to handle classical trajectories to maximize agreement with fully quantum results.

In pursuit of these goals, we are

1. improving the kinetic model used to extract rate constants from spectroscopic data;
2. using time-reversal symmetry, in the form of microscopic reversibility and detailed balance, for quality control of both measured and quasiclassical cross sections and rate constants; and
3. revisiting initial-action selection and binning to optimize agreement with close-coupled quantum calculations.

When binning classical trajectories, finding the right bin width and shape is important if the distribution of trajectory final actions varies nonlinearly in the vicinity of the integer final action. While the truly classical binning distribution is a delta function, often approximated by a narrow Gaussian function[2], compatibility with the uncertainty principle requires that it have a standard deviation no smaller than $\sqrt{3}\hbar/2\pi$. Use of this width results in improved agreement between quasiclassical and quantum results for rotationally inelastic cross sections. When this "natural" bin width is combined with symmetrical binning (binning of initial as well as final actions), both forward and reverse cross sections are reproduced with equal fidelity and microreversibility is satisfied for rotationally inelastic collisions.



The image shows symmetrically-binned rotationally inelastic classical trajectory actions for v_i=1, j_i=2 and v_f=1, j_f=0 in Li_2-Xe using natural binning at collision energy 645 cm^{-1}. The heat map depicts the natural Gaussian distribution; the circle is one standard deviation.

---

[1] Peterson, K. A., unpublished potential energy function.
[2] See *e.g.* Bañares, L. *et al., J. Chem. Phys.* **118,** 565 (2003).

Poster A8

Ab Initio Characterization, PES development, and Mode-Specific Quasi-Classical Dynamics for the Cl + CH_3CN and O^- + CH_4/CD_4 Reactions

Petra Tóth, Tímea Szűcs and Gábor Czakó

MTA-SZTE Lendület "Momentum" Computational Reaction Dynamics Research Group, Interdisciplinary Excellence Centre and Department of Physical Chemistry and Materials Science, Institute of Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged H-6720, Hungary, Email: toth.petra.294@gmail.com

ABSTRACT

We present a comprehensive theoretical investigation of the Cl + CH_3CN[1,2] and O^- + CH_4/CD_4[3] reactions, employing benchmark electronic structure calculations, full-dimensional potential energy surface (PES) development, and quasi-classical trajectory (QCT) simulations with vibrational mode-specific analysis.

For both systems, multiple reactive pathways were explored by locating and characterizing stationary points on the PESs.[1,3] Based on these results, we constructed full-dimensional analytical PESs using permutationally invariant polynomial fits within the ROBOSURFER framework.[2] Extensive QCT simulations were then performed across a range of collision energies and impact parameters, including both ground-state and vibrationally excited reactants. Integral cross sections, opacity functions, scattering and attack angle distributions, and detailed product energy partitioning were determined. Mode-specific analyses using Gaussian binning were carried out to assess how vibrational excitation in the reactants influences the dynamics and final state distributions of the products.

For the Cl + CH_3CN system, we determined benchmark barrier heights and vibrationally adiabatic energies at the CCSD(T)-F12b/aug-cc-pVQZ level with additional corrections.[1] Among the possible channels, only the hydrogen-abstraction pathway shows significant reactivity.[2] The reaction mechanism shifts with collision energy and strongly favors methyl-end attack. Product energy distributions indicate dominant energy transfer into translation, with low vibrational and high rotational excitation. To explore vibrational effects, over 4.5 million trajectories were simulated by selectively exciting each of the eight CH_3CN normal modes across six collision energies and 17 impact parameters. These results enabled a systematic examination of how different modes influence key dynamical outcomes and mode-to-mode energy redistribution in the products.

For the O^- + CH_4 and O^- + CD_4 systems, we investigated five experimentally studied collision energies, allowing direct comparison with recent measurements that used CD_4. The hydrogen-abstraction channel again dominates, and the simulated scattering angle and internal energy distributions show good agreement with experiment. Mode-specific QCT simulations involving four CH_4 and CD_4 vibrational modes resulted in over 5.2 million trajectories and revealed clear trends in reactivity and product excitation patterns, highlighting the role of specific vibrational excitations in steering the reaction dynamics.

---

[1] P. Tóth, T. Szűcs, and G. Czakó. Benchmark Ab Initio Characterization of the Abstraction and Substitution Pathways of the Cl + CH_3CN Reaction. *J. Phys. Chem. A* 126, 2802-2810, 2022.

[2] P. Tóth, T. Szűcs, T. Győri, and G. Czakó. Dynamics of the Cl + CH_3CN Reaction on an Automatically-Developed Full-Dimensional Ab Initio Potential Energy Surface. *J. Chem. Phys.* 161, 084304, 2024.

[3] A. Ayasli, P. Tóth, *et al*. Imaging the Ion-Molecule Reaction Dynamics of O^- + CD_4. *J. Phys. Chem. A* 128, 3078-3085, 2024.

Poster B17

Tracking C–C Bond Formation Dynamics in Photoinduced and Photocatalytic Reactions on Reducible and Non-Reducible Oxide Surfaces

Keith Blackman[a], Aakash Gupta[a], Eric Segrest[a], Alejandro Rodriguez[a], and Mihai E. Vaida[a,b]

[a]*Department of Physics, University of Central Florida, Orlando, FL 32816, USA*
[b]*Renewable Energy and Chemical Transformations Cluster, University of Central Florida, Orlando, FL 32816, USA (mihai.vaida@ucf.edu)*

ABSTRACT

Carbon–carbon (C–C) bond formation is a key step in many catalytic processes central to the production of synthetic materials, including commodity chemicals, polymers, cosmetics, and pharmaceuticals. Despite its central role, the mechanisms of C–C bond formation at gas–solid interfaces remain only partially understood. Gaining a fundamental understanding of how C–C bonds form during heterogeneous reactions at gas-solid interfaces and how these processes depend on surface properties is critical for improving the efficiency of such reactions.

This study investigates the coupling of single-carbon species, specifically CH_3 radicals, into two-carbon compounds on different oxide surfaces. To monitor these reactions in real time, we employ a technique that integrates time-of-flight mass spectrometry with femtosecond pump-probe laser spectroscopy and rapid preparation of the surface with molecules.

On non-reducible oxide surfaces like silicon oxide, a 266 nm pump laser pulse excites the CH_3I precursor molecules into the dissociative A-band, producing CH_3 and I fragments. A subsequent ultraviolet probe pulse ionizes both intermediates and products, which are detected via mass spectrometry. Alongside bimolecular pathways such as I_2 formation and CH_3I reformation, we directly observe C_2H_6 formation with femtosecond resolution.

On reducible metal oxides such as TiO_2(110) and amorphous TiO_2, the reaction dynamics are more complex and occur on longer timescales. On TiO_2(110), CH_3 radicals formed via CH_3I photodissociation can couple to form C_2H_6, which then undergoes photocatalytic oxidative dehydrogenation, yielding products like C_2H_5, C_2H_4, and H_2O. An additional reaction channel is identified involving the dehydrogenation of adsorbed CH_3 radicals, leading to CH_2 species. In contrast, on amorphous TiO_2, C–C bond formation is primarily initiated by dissociative adsorption of CH_3I on the surface.

These results offer valuable mechanistic insight into carbon–carbon bond formation on oxide surfaces, revealing how the surface structure and compostion shape reaction pathways. Such studies open promising pathways for tailoring surface reactions relevant to industrial catalysis and materials synthesis.

Poster A11

Effect of Carbon Chain Length on Nascent Yields of Stabilized Criegee Intermediates in Ozonolysis of a Series of Terminal Alkenes

Lei Yang[a] and Jingsong Zhang[a,b]

[a] *Department of Chemistry, University of California, Riverside, CA 92521, USA*
[b] *Air Pollution Research Center, University of California, Riverside, CA 92521, USA*
Email: jingsong.zhang@ucr.edu

ABSTRACT

The yields of stabilized Criegee intermediates (sCIs), CH_2OO and RCHOO (C_2H_5CHOO, C_3H_7CHOO, C_4H_9CHOO, and $C_5H_{11}CHOO$), produced from ozonolysis of asymmetrical 1-alkenes (1-butene, 1-pentene, 1-hexene, and 1-heptene) were investigated at low pressures (5-16 Torr) using cavity ring-down spectroscopy (CRDS) and chemical titration with sulfur dioxide (SO_2). By extrapolating the low-pressure measurements to zero-pressure limit, nascent sCI yields were obtained. Combined with our previous studies on ethene and propene ozonolysis, the nascent sCI yields demonstrated an intriguing trend that increased with the addition of CH_2 groups and eventually reached a plateau at around 31% for longer chain 1-alkenes. In particular, the fraction of stabilized CH_2OO reached the plateau from propene, indicating that CH_2OO was produced with nearly the same internal energy distribution from propene to 1-heptene. The comparison between the experiments and RRKM calculations suggests that the dissociation of primary ozonide (POZ) of O_3 + ethene and propene can be treated by statistical theory, while that of O_3 + 1-butene to 1-heptene is non-statistical and intramolecular vibrational redistribution (IVR) of the initial energy on the 1,2,3-trioxolane of POZ throughout the entire molecule was incomplete on the dissociation time scale [1].

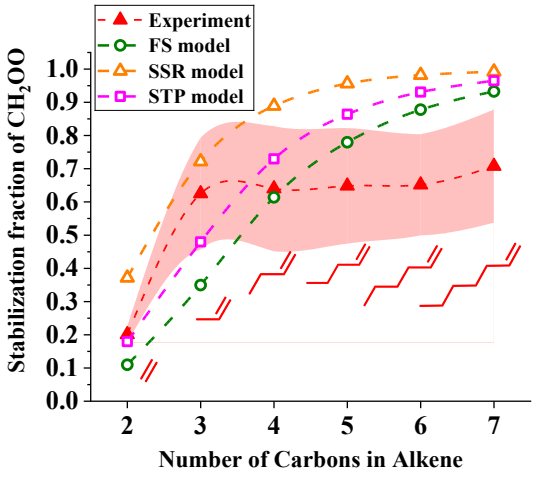


Figure 1 Nascent stabilization fractions of CH_2OO in ozonolysis of 1-alkenes compared to statistical models.

---

[1] Lei Yang and Jingsong Zhang, *Journal of the American Chemical Society,* **146**, 24591 (2024).

Poster B16

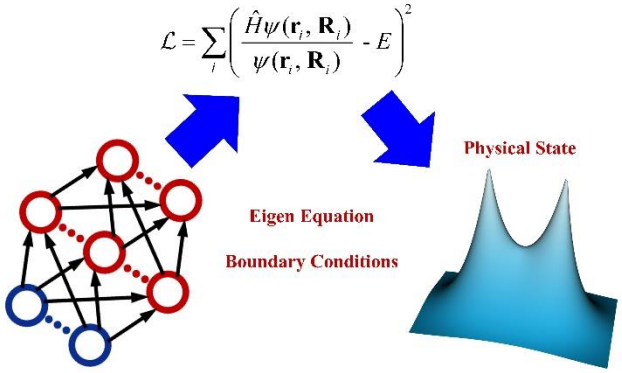
SchrödingerNet: A Universal Neural Network Solver for The Schrödinger Equation

Yaolong Zhang[a], Bin Jiang[b], and Hua Guo[a]

[a] Department of Chemistry and Chemical Biology, Center for Computational Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, USA Email: ylzhangch@unm.edu
[b] Key Laboratory of Precision and Intelligent Chemistry, Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

ABSTRACT

Recent advances in machine learning have enabled numerically accurate solutions of the electronic Schrödinger equation (SE) by integrating neural network (NN)-based wavefunction ansatzes with variational Monte Carlo (VMC) methods[1-2]. However, existing NN-based approaches typically rely on the Born–Oppenheimer approximation (BOA) and require separate, computationally intensive training for each nuclear configuration. In this work, we introduce SchrödingerNet, a novel NN wavefunction ansatz designed to solve the full electronic-nuclear SE by minimizing a loss function aiming to equalize local energies across the system[3]. Our approach proposes a new wavefunction ansatz inspired by quantum chemistry methods, incorporating multiple orbital types with configuration-dependent coefficients and an explicit electron–electron correlation term. This design combines physical interpretability with the expressive power of NNs, enabling the accurate description of multi-reference systems across a wide range of nuclear geometries using a few Slater determinants and significantly fewer parameters. Moreover, it naturally incorporates non-BOA effects. Benchmark results on molecular systems validate the accuracy and efficiency of SchrödingerNet.



---

[1] Hermann, J.; Schätzle, Z.; Noé, F., Deep-neural-network solution of the electronic Schrödinger equation. Nat. Chem. 12, 891-897, 2020.
[2] Pfau, D.; Spencer, J. S.; Matthews, A. G. D. G.; Foulkes, W. M. C., Ab initio solution of the many-electron Schrödinger equation with deep neural networks. Phys. Rev. Res. 2, 033429, 2020.
[3] Zhang, Y.; Jiang, B.; Guo, H., Schrödingernet: A universal neural network solver for the Schrödinger equation. J. Chem. Theory Comput. 21, 670-677, 2025.

Participants

First Name	Last Name	E-mail
Chris	**Avanessian**	cavanes1@jhu.edu
Benjamin	**Baldwin**	baldwbe@umd.edu
Adrian	**Batista-Planas**	albgzz@mst.edu
Erica	**Bocanegra**	erica.bocanegra@yale.edu
Ashley	**Borkowski**	aborkowski@anl.gov
Stephen	**Bradforth**	stephen.bradforth@usc.edu
Helen	**Chadwick**	h.j.chadwick@swansea.ac.uk
David	**Chandler**	chand@sandia.gov
Robert	**Continetti**	rcontinetti@ucsd.edu
Richard	**Dawes**	dawesr@mst.edu
Simone	**DeSouza**	sdesouz1@umd.edu
Michael	**Duncan**	maduncan@uga.edu
Chris	**Elles**	elles@ku.edu
Arkke	**Eskola**	arkke.eskola@helsinki.fi
Arden	**Floyd**	amfloyd@princeton.edu
Madison	**Foreman**	mmforeman@berkeley.edu
John	**Fourkas**	fourkas@umd.edu
Shane	**Goettl**	sgoettl@hawaii.edu
Hua	**Guo**	hguo@unm.edu
John	**Hack**	johnhack@berkeley.edu
Yarra	**Hassan**	yarramh@uw.edu
Chao	**He**	chao.he@unibas.ch
Rigoberto	**Hernandez**	r.hernandez@jhu.edu
Dmitry	**Ivanov**	di2224@columbia.edu
Greta	**Jacobson**	gretaja@uw.edu
Ahren	**Jasper**	ahrenjasper@gmail.com
Carolin Anna	**Joy**	carolin.joy@marquette.edu

Do Hyung	**Kang**	sonar112@berkeley.edu
Jai	**Khatri**	jaikhatri1997@gmail.com
Theofanis	**Kitsopoulos**	Theofanis.Kitsopoulos@usm.edu
Stephen	**Klippenstein**	sjk@anl.gov
Olivia	**Krohn**	okcarls@sandia.gov
Martin Chow Shing	**Lam**	chow-shing.lam@chem.ox.ac.uk
Rachel Mingxin	**Lei**	mingxin@terpmail.umd.edu
Marsha	**Lester**	milester@sas.upenn.edu
Benjamin	**Levine**	ben.levine@stonybrook.edu
Tucker	**Lewis**	tucker.wr.lewis@gmail.com
Yanan	**Liu**	ylmdw@missouri.edu
Yang	**Liu**	yliu218@unm.edu
Yu	**Liu**	yuliu@umd.edu
Bikramaditya	**Mandal**	bikramaditya.mandal@unlv.edu
Spiridoula	**Matsika**	smatsika@temple.edu
Anne	**McCoy**	abmccoy@uw.edu
Joseph	**McManus**	joseph.mcmanus@chem.ox.ac.uk
Qinghui	**Meng**	meng0260@umn.edu
Jennifer	**Meyer**	jennifer.meyer@chem.rptu.de
Mickey	**Moonkaen**	moonkp@uw.edu
Amy	**Mullin**	mullin@umd.edu
Steve	**Ndengue**	sndengue@haverford.edu
Jane	**Nelson**	janenelson@princeton.edu
David	**Nesbitt**	djn@jila.colorado.edu
Daniel	**Neumark**	dneumark@berkeley.edu
Barratt	**Park**	barratt.park@gmail.com
Andrew	**Petit**	apetit@fullerton.edu
Denisia	**Popolan-Vaida**	denisia.popolan-vaida@ucf.edu
Ernesto	**Quintas Sanchez**	quintassancheze@mst.edu

Kyle	**Renshaw**	ktr29p@missouri.edu
Brandon	**Rotavera**	rotavera@uga.edu
Mikhail	**Ryazanov**	mikhail.ryaznov@jila.colorado.edu
Madeeha	**Salik**	madeeha.salik@yale.edu
Juan Carlos	**San Vicente Veliz**	j.sanvicente@temple.edu
George	**Schatz**	g-schatz@northwestern.edu
Michael	**Schuurman**	Michael.Schuurman@uottawa.ca
Yinan	**Shu**	shuxx055@umn.edu
Brian	**Stewart**	bstewart@wesleyan.edu
Arthur	**Suits**	suitsa@missouri.edu
Petra	**Töth**	toth.petra.294@gmail.com
David	**Tannor**	david.tannor@weizmann.ac.il
Richard	**Thomas**	rdt@fysik.su.se
Ward	**Thompson**	wthompson@ku.edu
Katharine	**Tibbetts**	kmtibbetts@vcu.edu
Abraham	**Tillquist**	abraham.tillquist@utah.edu
Arthur	**Utz**	autz@tufts.edu
Juan Carlos	**San Vicente Veliz**	j.sanvicente@temple.edu
Marissa	**Weichman**	weichman@princeton.edu
Alec	**Wodtke**	alec.wodtke@mpinat.mpg.de
Graham	**Worth**	g.a.worth@ucl.ac.uk
Jingsong	**Zhang**	jingsong.zhang@ucr.edu
Yaolong	**Zhang**	ylzhangch@unm.edu

Sponsors

COLLEGE OF COMPUTER, MATHEMATICAL, & NATURAL SCIENCES

DEPARTMENT OF CHEMISTRY & BIOCHEMISTRY