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# RPPR Final Report

as of 12-Jun-2018

Agency Code:

Proposal Number: 69812CHCF

Agreement Number: W911NF-17-1-0096

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**Report Date:** 30-Apr-2018

Date Received: 09-Mar-2018

**Final Report** for Period Beginning 01-Feb-2017 and Ending 31-Jan-2018

**Title:** Funding Request for the 26th Dynamics of Molecular Collisions Conference

**Begin Performance Period:** 01-Feb-2017

**End Performance Period:** 31-Jan-2018

**Report Term:** 0-Other

Submitted By: David Yarkony

Email: yarkony@jhu.edu

Phone: (410) 516-7462

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:**

**STEM Participants:**

**Major Goals:** The principal goals included:

A. Allow graduate students, postdoctoral research associates, junior and senior faculty to describe and exchange ideas concerning state of the art work involving (i) cold chemistry, that is chemistry at a fraction of a K, (ii) chemistry at solid surfaces, (iii) nonadiabatic chemistry, and (iv) photodissociation and 'half' collisions in general.

B. Facilitate oral presentations by graduate students and postdoctoral research associates through hot topics and contributed talks

C. Provide financial support for participants

**Accomplishments:** The 26th Dynamics of Molecular Collisions (DMC) Conference, the premier meeting for scientists in the field of molecular dynamics, met as scheduled from the 9 – 14 July 2017 at the Granlibakken Conference Center,

in Tahoe City, California. A diverse group 116 scientists, from graduate students to emeritus professors, from the United States, Canada, China, Germany, Great Britain, Israel, The Netherlands, and Taiwan attended.

Using funds provided by Air Force Office of Scientific Research (AFOSR), Army Research Office (ARO) and Department of Energy, Basic Energy Science (DoE-BES) and collected from registrants we were able to assist over 90 participants with conference fees and meeting expenses (contributions to room and board) greatly facilitating participation.

Seventy-three posters were presented at four evening poster sessions with 5 winning poster awards: 3 \$150 awards provided by the American Chemical Society – to Ms. Jessalyn DeVine, UC Berkeley, Mr. Xinyou Ma, Texas Tech, and Ms. Vanessa Murray, Montana State University - and 2 \$50 book awards- to Dr Alexander Teplukhin, Marquette University, and Dr. Mark Pfeifle, Argonne National Laboratory, provided by the journal Physical Chemistry Chemical Physics better known as PCCP.

Talks by our keynote speaker William H. (Bill) Miller from UC Berkeley and Herschbach Awardees, Hanna Reisler from University of Southern California and John Tully from Yale University highlighted the program.

Nobel laureate Dudley Herschbach joined the meeting via SKYPE on the evening of the Herschbach Symposium. Participants heard talks from invited speakers and session chairs at 5 morning and 3 evening sessions. Seven 10 minute hot topics talks by graduate student and postdoctoral participants and 8 contributed talks rounded out the program.

The participants spend their free time hiking and enjoying nearby Lake Tahoe while discussing issues raised in the talks and poster presentations.

## **RPPR Final Report**

### **as of 12-Jun-2018**

**Training Opportunities:** The interaction between graduate students, postdoctoral research fellows and the attending faculty and senior scientists, in the relaxed and causal atmosphere at Granlibakken provided a unique opportunity for the next generation of scientists to learn from leaders in their fields

**Results Dissemination:** The proceedings are documented in a file (attached to this report) containing the program, abstracts, historical data, and lists of the participants and sponsors. This file was provided to the attendees on line and on a commemorative flash drive. We are grateful for the funding which made this meeting possible.

**Honors and Awards:** At each meeting the DMC board awards Herschbach Medals, to an experimentalist and theoretician “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.” At the DMC 2017 the Herschbach awardees were Hanna Reisler from University of Southern California and John Tully from Yale University.

**Protocol Activity Status:**

**Technology Transfer:** Nothing to Report

#### **PARTICIPANTS:**

**Participant Type:** Other (specify)

**Participant:** For all participants Please see the attached book

**Person Months Worked:** 1.00

**Funding Support:**

Project Contribution:

International Collaboration:

International Travel:

National Academy Member: Y

Other Collaborators:

# DYNAMICS OF MOLECULAR COLLISIONS XXVI

JULY 9 – 14, 2017

GRANLIBAKKEN CONFERENCE CENTER  
TAHOE CITY, CALIFORNIA



DAVID YARKONY, CHAIR

TIM MINTON, CO-CHAIR

# **2017 *Dynamics of Molecular Collisions* Conference**

Granlibakken Conference Center

July 9 – 14, 2017

## **History**

### *The History of the Conference on the Dynamics of Molecular Collisions*

- 1 – 1965 New Hampton, New Hampshire; *John Fenn*, Yale University
- 2 – 1968 Andover, New Hampshire; *John C. Polanyi*, University of Toronto
- 3 – 1970 Oak Ridge, Tennessee; *E. F. Green*, Brown University
- 4 – 1972 Plymouth, New Hampshire; *Sheldon Datz*, Oak Ridge National Laboratory
- 5 – 1974 Santa Cruz, California; *James L. Kinsey*, Massachusetts Institute of Technology
- 6 – 1976 Plymouth, New Hampshire; *Bruce E. Mahan*, University of California, Berkeley
- 7 – 1978 Pacific Grove, California; *Yuan T. Lee*, University of California, Berkeley
- 8 – 1981 Plymouth, New Hampshire; *R. James Cross*, Yale University
- 9 – 1983 Gull Lake, Minnesota; *W. Ronald Gentry*, University of Minnesota
- 10 – 1985 Snowbird, Utah; *Donald G. Truhlar*, University of Minnesota
- 11 – 1987 Wheeling, West Virginia; *Paul Dagdigian*, The Johns Hopkins University
- 12 – 1989 Pacific Grove, California; *William H. Miller*, University of California, Berkeley
- 13 – 1991 Lake George, New York; *James M. Farrar*, University of Rochester
- 14 – 1993 Helen, Georgia; *Joel M. Bowman*, Emory University
- 15 – 1995 Pacific Grove, California; *Daniel Neumark*, University of California, Berkeley
- 16 – 1997 Gull Lake, Minnesota; *George Schatz*, Northwestern University
- 17 – 1999 Lake Harmony, Pennsylvania; *James Valentini*, Columbia University
- 18 – 2001 Copper Mountain, Colorado; *James T. Muckerman*, Brookhaven National Laboratory
- 19 – 2003 Tahoe City, California; *Laurie J. Butler*, University of Chicago
- 20 – 2005 Pacific Grove, California; *Albert Wagner*, Argonne National Laboratory
- 21 – 2007 Sante Fe, New Mexico; *David Chandler*, Sandia National Laboratories
- 22 – 2009 Snowbird, Utah; *Anne McCoy*, Ohio State University
- 23 – 2011 Snowbird, Utah; *David Nesbitt*, JILA/University of Colorado
- 24 – 2013 Granlibakken, California; *Hua Guo*, University of New Mexico
- 25 – 2015 Pacific Grove, California; *Arthur Suits*, Wayne State University
- 26 – 2017 Tahoe City, California; *David Yarkony*, Johns Hopkins University

## Herschbach Medal

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. Herschbach



## Herschbach Medalists

- 2007: Richard N. Zare and William H. Miller
- 2009: Daniel Neumark and Donald Truhlar
- 2011: Yuan Lee and George Schatz
- 2013: Giacinto Scoles, J. Peter Toennies and Joel Bowman
- 2015: W. Carl Lineberger and Millard Alexander
- 2017: Hanna Reisler and John Tully

**Dynamics of Molecular Collisions XXVI**  
**Granlibakken Conference Center**  
**9-14 July 2017**  
**Tahoe City , California**

**Sunday**

4:00 Registration

6:00 *Dinner*

**Monday**

7:00 *Breakfast*

8:10 Welcome. David Yarkony

**Cold and Ultracold Collisions**

8:15 David Chandler, Sandia Combustion Research Facility, Session Chair

8:30 Heather Lewandowski, University of Colorado, "Quantum-state controlled radical-ion reactions"

9:10 Jeremy Hutson, University of Durham, "Ultracold collisions - sticky or not?"

9:50 Coffee

10:20 Stefan Willitsch, University of Basel, "Cold and controlled chemistry: From small molecules to complex systems"

11:00 Lorenzo S. Petralia, University of Oxford, "Cold ion-molecule reactive collisions in an ion trap"

11:20 Evardas Narevicius, Weizmann Institute, "Cold chemistry with cold molecules"

12:00 *Lunch*

1:30 Free Time

3:00 Refreshments

3:20 Keynote Introduction: Hua Guo

3:35 Keynote Address: William H. Miller, UC Berkeley, "Classical Molecular Dynamics Simulation of Electronically Non-Adiabatic Processes"

4:35 Hot Topics

*Stephen Cotton*, UC Berkeley " Classical Molecular Dynamics Simulation of Electronically Non-Adiabatic Processes via a Symmetrical Quasi-Classical Windowing Model"

*Dr. James F. Croft*, University of Nevada-Las Vegas, Symmetry and the Geometric Phase in Ultracold Hydrogen-Exchange Reactions

*Bin Jiang*, University of Science and Technology of China A Chemically Accurate Potential Energy Surface for Dissociative Chemisorption of Methane on Ni(111)

*Alicia O. Hernandez-Castillo*, Purdue University, Broadband Rotational Spectroscopy as a Tool to Detect & Characterize Pyrolysis Intermediates

*C. S. Hansen*, University of Bristol , Photochemistry of 2-bromothiophene following UV+VUV excitation: a multimasss velocity-map imaging study

*Nandini Mukherjee* Stanford University, "Quantum Control of Inelastic Scattering Near 1 K"

5:35 *Dinner*

**Bimolecular Collision Dynamics I**

7:00 Hua Guo, Univ of New Mexico, Session Chair

7:15 Floyd Davis, Cornell University, "Casting a New Light on Free Radical Photochemistry and Bimolecular Reaction Dynamics"

7:55 Kopin Liu, IAMS, "Mapping the angle-dependent barrier to reaction by polarized scattering experiment".

8:35 T. de Jongh, Radboud University "High Resolution Imaging of Partial Wave Resonances in Low-Energy Molecular Scattering"

8:55 Matthew Costen, Heriot-Watt University. "Imaging stereodynamics and state correlations in rotational energy transfer: NO(A) with rare gases and diatomics"

9:35 **Posters**

**Tuesday**

7:00 *Breakfast*

**Bimolecular Collision Dynamics II**

8:15 Ryan Steele, University of Utah, Session Chair

8:30 Arthur Suits, University of Missouri, "New probes for reaction dynamics"

9:10 Xueming Yang, Dalian Institute, "Probing Quantum Dynamics of Chemical Reactions using High Resolution H-atom Rydberg Tagging and Velocity Map Imaging"

9:50 Coffee

10:20 Anne McCoy, University of Washington, "Stories that are encoded in vibrational spectra: Investigating spectral signatures of large amplitude proton migration in ion/water complexes."

11:00 Amy S. Mullin, University of Maryland "Dynamics of Oriented Super-Rotors: Exploring the Behavior of Molecules in Extreme Rotational States with Transient Spectroscopy"

11:20 David Osborn, Sandia Combustion Research Facility, "Hunting for Intermediates in Complex-Forming Reactions: Better Hounds for an Elusive Quarry"

12:00 *Lunch*

1:30 Free Time

5:00 *Dinner*

**Nonadiabatic Dynamics I**

7:00 Session Chair: David Yarkony

7:05 Hot Topic: Bethan Nichols, UC Berkeley, "Investigation of the Two- and Three-Fragment Photodissociation of the tert-Butyl Peroxy Radical at 248nm"

7:15 Michael Ashfold, University of Bristol, "Molecular Photodissociation and Photoinduced Ring Opening"

7:55 Nandini Ananth, Cornell University, "Quantum coherences from classical trajectories"

8:35 Oleg Vasyutinskii, Ioffe Institute, "Femtosecond time-resolved vector-correlations in CH<sub>3</sub>I photolysis the role of nonadiabatic interactions and internal rotation

8:55 David Glowacki, University of Bristol, "Simulating non-adiabatic molecular dynamics and kinetics in atmospheric photochemistry"

**9:35 Posters**

**Wednesday**

**7:00 Breakfast**

**Interfaces, Clusters and Condensed Phase**

8:15 David Nesbitt, University of Colorado, Session Chair

8:30 Steven Sibener, University of Chicago. "Gas-Surface Scattering Encompassing Collisional Energy Exchange, Condensation, Embedding and Isotope Effects"

9:10 Alex Wodtke, University of Gottingen. "Imaging Transient Chemical Bond Formation by H-atom Scattering from Graphene"

9:50 Coffee

10:20 Svetlana Schauerman, Fritz-Haber Institute-Berlin: "Elementary Steps in Hydrogenation of Unsaturated Hydrocarbons over Pd Model Catalysts"

11:00 Eric J. Smoll, Montana State University, "Probing the Site-Resolved Structure and Function of a Liquid Interface by Reactive Atom Scattering"

11:20 Sharani Roy, University of Tennessee, "Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Exploring the Role of Subsurface Oxygen in Catalysis by Silver Surfaces."

12:00 Lunch

1:30 Free Time

5:00 Dinner

**Unimolecular/Photochemical Dynamics**

7:00 Curt Wittig, University of Southern California, Session Chair

7:15 Dan Neumark, UC Berkeley "Slow electron velocity-map imaging of cryogenically cooled anions: applications to bimolecular and unimolecular transition state spectroscopy"

7:55 Victoria Barber, University of Pennsylvania, "Tunneling Effects in the Unimolecular Decay of Criegee Intermediates"

8:15 Helen Fielding, University College London, "Tuning the electronic relaxation dynamics of molecules and protein chromophores"

8:55 Robert Continetti, UC San Diego, "Reaction Dynamics from Transition States to Nanoparticles"

**9:35 Posters**

**Thursday**

7:00 Breakfast

**Atmospheric, Astrochemistry and Combustion**

8:15 Anna Krylov, University of Southern California, Session Chair  
8:30 Ralf Kaiser, University of Hawaii "Unraveling the Formation of Interstellar Grains under Single Collision Conditions"  
9:10 Mitchio Okumura, Caltech, Frequency Comb Studies of the OD + CO Reaction"  
9:50 Coffee  
10:20 Miriam Freedman, Penn State University, "Liquid-Liquid Phase Separation in Submicron Aerosol Particles"  
11:00 Yanice Benitez, UC San Diego, "Dissociation Dynamics of the OH-CH<sub>4</sub> Complex Using Photoelectron Photofragment Coincidence Spectroscopy"  
11:20 Jim Lin, IAMS, "Structure-dependent Reactivity and Kinetics of Criegee Intermediates"

12:00 *Lunch*

1:30 Free Time

5:00 *Dinner*

### **HERSCHBACH PRIZE SESSION**

7:30 Introduction: Dudley Herschbach (via Skype)  
7:45 Introduction: Curt Wittig  
8:00 Hanna Reisler, University of Southern California, "Unimolecular Reaction Dynamics: From Isolated Molecules and Radicals to Networks"  
8:40 Introduction: David Yarkony  
8:55 John Tully, Yale University, "The Role of Electronic Excitations on Chemical Reaction Dynamics at Metal, Semiconductor and Nanoparticle Surfaces"

### **9:35 Posters**

### **Friday**

7:00 Breakfast

### **Nonadiabatic Dynamics II**

8:15 Marsha Lester, Univ of Pennsylvania, Session Chair  
8:30 Ben Levine, Michigan State University, "Painless Modeling of Dynamics near Conical Intersections"  
9:10 Jinsong Zhang, UC Riverside, "Competitive pathways in the photodissociation of polyatomic free radicals"  
9:50 Coffee  
10:30 Art Bragg, Johns Hopkins, "Structural control of nonadiabatic chemical dynamics in solution – from photoswitching to photochemical bond formation"  
11:00 Changjian Xie, University of New Mexico, "Geometric Phase Effects in Nonadiabatic Tunneling"  
11:20 Don Truhlar, University of Minnesota, "Photochemistry"

12:00 THANKS FOR ATTENDING: Tim Minton

12:05 Lunch

# Invited Talks Abstracts

# Quantum Coherences from Semiclassical Trajectories in Complex Systems

Nandini Ananth

*Department of Chemistry and Chemical Biology,  
Cornell University, Ithaca, NY 14853*

Simulating energy transfer pathways in reactions at metal surfaces requires methods that describe electronically nonadiabatic processes, capture quantum coherence effects, and remain computationally feasible for high dimensional systems. Quantum-limit semiclassical methods have proven remarkably effective in capturing quantum dynamic effects but are computationally expensive, limiting their applications to relatively low-dimensional systems. In this talk, we introduce the Mixed Quantum-Classical Initial Value Representation (MQC-IVR) [1], a semiclassical method for the calculation of real-time correlation functions that employs a uniform dynamic framework to describe a subset of system modes quantum mechanically while treating the rest classically without introducing uncontrolled approximations.

The MQC-IVR formulation is obtained using the Modified Filinov Filtration (MFF) method to smooth the oscillatory structure of the semiclassical integrand [2]. Previous work showed that the MFF method is ineffective in accelerating semiclassical simulations of wavepacket propagation [3]. By analyzing the phase and amplitude of the MQC-IVR integrand, we demonstrate here that the MFF is extremely effective in the context of correlation functions, improving numerical convergence properties significantly without loss of accuracy. [4] Having established the validity of the MFF technique, we then introduce a novel implementation that scales linearly with number of time steps and allows for highly parallel simulations. Finally, we introduce a protocol to quantify the error associated with the MQC-IVR implementation that will also help identify the ‘quantum’ modes of a system. [5]

We apply the MQC-IVR method to calculate correlation functions in a variety of model systems and we demonstrate its ability to systematically tune individual system modes between quantum-limit and classical-limit semiclassical behavior. [1, 4] We conclude with an MQC-IVR study of electronically nonadiabatic processes and a brief preview of our work modeling inelastic scattering at a metal surface.

## References

- [1] S. V. Antipov, Z. Ye, and N. Ananth, *J. Chem. Phys.* 142, 184102 (2015).
- [2] N. Makri and W. H. Miller, *Chem. Phys. Lett.* 139, 10 (1987).
- [3] M. Spanner, V. S. Batista, and P. Brumer, *J. Chem. Phys.* 122, 084111 (2005).
- [4] M. S. Church, S. V. Antipov, and N. Ananth, *J. Chem. Phys.* *Accepted* (2017).
- [5] R. L. Kenion, *Towards Simulating Complex Systems with Quantum Effects*, PhD Dissertation, Cornell University (2017).

# MOLECULAR PHOTODISSOCIATION AND PHOTOINDUCED RING OPENING

*Mike Ashfold*

*School of Chemistry, University of Bristol, Bristol, U.K. BS8 1TS*

Phenols and azoles are common chromophores in the nucleobases and the aromatic amino-acids that dominate the near UV absorption spectra of many biological molecules.  $\pi^* \leftarrow \pi$  excitations are responsible for these strong UV absorptions, but such molecules also possess excited states formed from  $\sigma^* \leftarrow \pi$  electron promotions. The  $\pi\sigma^*$  states typically have much smaller absorption cross-sections, but can be of profound photophysical importance. We have used photofragment translational spectroscopy (PTS) methods and complementary *ab initio* calculations to explore  $\pi\sigma^*$ -state mediated bond fission processes following UV excitation of many heteroaromatic molecules in the gas phase,<sup>1</sup> and ultrafast pump-probe studies to explore analogous processes in a range of solvents.<sup>2</sup> This presentation will:

- (i) summarize photophysical insights gained from PTS studies of thiophenols and thioanisole in the gas phase,
- (ii) illustrate the extent to which such knowledge can inform our interpretation of ultrafast pump-probe transient absorption (TA) studies of the UV photofragmentation of similar molecules in solution,
- (iii) show how such solution phase TA studies offer a route to exploring the possible role of  $\pi\sigma^*$ -states in the photoinduced ring-opening of heterocyclic molecules (e.g. 2-thiophenone and 2-furanone,<sup>3</sup>  $\alpha$ -pyrone,<sup>4</sup> etc), and
- (iv) describe our recent progress towards studying the dynamics of such photoinduced ring-opening processes in the gas phase.<sup>5</sup>

**Acknowledgements:** Funding from EPSRC through Programme Grant EP/L005913 is gratefully acknowledged.

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<sup>1</sup> M.N.R. Ashfold, G.A. King, D. Murdock, M.G.D. Nix, T.A.A. Oliver and A.G. Sage, *Phys. Chem. Chem. Phys.* **12** (2010) 1218.

<sup>2</sup> S.J. Harris, D. Murdock, Y. Zhang, T.A.A. Oliver, M.P. Grubb, A.J. Orr-Ewing, G.M. Greetham, I.P. Clark, M. Towrie, S.E. Bradforth and M.N.R. Ashfold, *Phys. Chem. Chem. Phys.* **15** (2013) 6567.

<sup>3</sup> D. Murdock, S.J. Harris, J. Luke, M.P. Grubb, A.J. Orr-Ewing and M.N.R. Ashfold, *Phys. Chem. Chem. Phys.* **16** (2014) 21271.

<sup>4</sup> D. Murdock, R.A. Ingle, I.V. Sazanovich, I.P. Clark, Y. Harabuchi, T. Taketsugu, S. Maeda, A.J. Orr-Ewing and M.N.R. Ashfold, *Phys. Chem. Chem. Phys.* **18** (2016) 2629.

<sup>5</sup> **R.A. Ingle, C.S. Hansen, E. Elsdon, M. Bain, S.J. King, J.W.L. Lee, M. Brouard, C. Vallance, R. Turchetta and M. N. R. Ashfold, *J. Chem. Phys.* **147** (2017) 013914.**

## Structural Control of Nonadiabatic Chemical Dynamics in Solution – from Photoswitching to Photochemical Bond Formation

Art Bragg

*Department of Chemistry, Johns Hopkins University*

*3400 N. Charles St., Baltimore, MD 21218*

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Elucidating how molecular structure impacts the nonadiabatic photochemistry of excited states is a key step towards controlling the action and efficiency of photochromic switches, mechanisms of aggregation-induced emission, and the synthesis of polyaromatic motifs via photocyclization. This talk will focus on recent ultrafast spectroscopic investigations by our group using wavelength-dependent pump-probe and pump-repump-probe spectroscopies to explore the photochemical pathways for motion in a recently identified class of E/Z photoswitch as well as the structure and solvent dependence of nonadiabatic photochemical bond formation of *ortho*-arenes.

Thienyl-ethene chromophores have had great success as pericyclic photoswitches through structural inhibition of a competing E/Z photoisomerization pathway. In contrast the photoresponsive behaviors of a recently discovered thienyl-ethene chromophore represented by the base structure 1,2-di(bisthienyl), 1,2-dicyanoethene (4TCE) exhibit exclusive E/Z photoisomerization following excitation with visible light. This switch differs from cyclizing switches according to alpha vs. beta linkage, respectively, between thiophene and ethene groups. Not only does this switch design offer an alternative to azobenzenes for E/Z photoswitching, it also presents the possibility of harnessing new photophysical pathways to drive material photoresponses. Time-resolved spectroscopic measurements reveal signatures of unusual multiplicity-specific isomerization pathways in 4TCE: whereas trans-to-cis isomerization occurs within the singlet manifold, cis-to-trans isomerization occurs via triplets populated by one of various ultrafast relaxation mechanisms. We focus on our work aimed at elucidating the various ultrafast mechanisms underlying reactive and nonreactive relaxation of photoexcited cis-4TCE.

We also describe the photochemical dynamics of a variety of *ortho*-arenes and related diarylethenes in solution that demonstrate how specific structural variations and chemical environment impact the feasibility for non-adiabatic chemical dynamics. *ortho*-terphenyl (OTP) and related molecules serve as useful probes of the solvent-dependence of low-barrier chemical reaction dynamics in solution: Photocyclization of this molecule is a direct process, the empirical barrier to cyclization is observed to be quite low, and cyclization rates are negligibly affected by electrostatic properties of the solvent. Solvent-dependent measurements reveal a highly significant correlation between non-adiabatic decay rate of OTP and solvent density regardless of the chemical nature of the solvent, offering new empirical insight about the general nature of mechanical solvent-solute interactions that impact chemical dynamics subject to low activation barriers.

# Reaction Dynamics from Transition States to Nanoparticles

Robert E. Continetti

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The study of the energetics and dynamics of transient species using negative ion precursors in conjunction with photoelectron-photofragment coincidence spectroscopy has been benefitted from the introduction of electrostatic ion beam traps and cryogenic RF accumulator traps in recent years. Recent progress in the examination of transient species, including the examination of hydroxyl radical reactions such as the  $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$  potential energy surface by photodetachment of  $\text{OH}^-(\text{CH}_4)$  will be reviewed.

The status of an instrument development project involving a single-particle dust accelerator/decelerator, the Aerosol Impact Spectrometer, will also be reviewed.<sup>1</sup> This apparatus makes use of electrospray ionization to produce charged nanoparticles, with the mass and charge of single nanoparticles measured using charge detection mass spectrometry techniques prior to acceleration or deceleration to desired final velocities for surface impact studies. Applications to measurements of the coefficient of restitution for polystyrene latex spheres and tin nanoparticles, as well as measurements of the durability of free-standing nanostructure with respect to particle impact, will be presented.

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# Imaging stereodynamics and state correlations in rotational energy transfer: NO(A) with rare gases and diatomics

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We have used crossed-molecular beam scattering with velocity-map imaging, combined with optical state-selection, to study the stereodynamics of rotational energy transfer of electronically excited NO( $A^2\Sigma^+$ ,  $v = 0$ ,  $N = 0$ ,  $j = 0.5$ ) with both rare gas and molecular colliders.<sup>1-4</sup> We extract state-to-state resolved differential cross sections (DCSs), and scattering angle-resolved rotational alignment moments. Comparison to the results of QS calculations enables us to provide high-quality tests of *ab initio* potentials for the rare gas colliders, and to make predictions about the hitherto unknown molecular collider potentials. The angular momentum polarization in these systems systematically deviates from the classical, hard-shell, behaviour observed in NO(X) collisions, in ways related to the differences in the respective potentials. RET with N<sub>2</sub> and O<sub>2</sub> results in rotational excitation of the unobserved collider, here we determine DCSs as a function collider internal energy, and uncover substantial differences depending on the collider, which respectively don't and do quench the NO(A) electronic state.

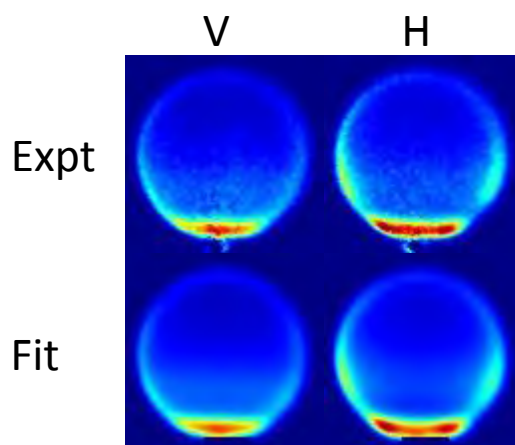


Figure: Example experimental and fit images for NO(A)+Ne scattering for product state  $N' = 7$ , acquired with probe polarization in-plane (H) or orthogonal (V).

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# **Casting a New Light on Free Radical Photochemistry and Bimolecular Reaction Dynamics**

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We are studying the photochemistry and bimolecular reaction dynamics of free radicals relevant to atmospheric chemistry and combustion chemistry. Our experimental approach employs a rotatable source crossed molecular beams apparatus combined with very high intensity pulsed tabletop vacuum ultraviolet (VUV) light sources in the 9-12 eV range for “soft” universal and resonant photoionization detection of products. In addition, conventional electron impact ionization detection provides a valuable cross calibration of branching ratios when multiple products are formed.

About 25 years ago, the competing photodissociation channels resulting from electronic excitation of gaseous chlorine dioxide (OCIO) were studied, revealing that in addition to simple bond fission forming  $\text{ClO} + \text{O}$ , a second minor channel ( $< 5\%$ ) produced  $\text{Cl} + \text{O}_2$  over a narrow wavelength range, with the branching ratios dependent upon the OCIO excited state vibrational mode. Subsequently, the much more elusive OBrO and OIO free radicals have been observed in the laboratory and atmosphere, and are thought to be relevant to atmospheric chemistry in coastal areas. Although photodissociation of OXO ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) producing  $\text{XO} + \text{O}$  leads to a net null cycle in the ozone balance, formation of  $\text{X} + \text{O}_2$ , if important, catalytically destroys atmospheric ozone. Despite considerable experimental effort over the past decade, the photochemistry of OIO has remained uncertain, with considerable disagreement between experimental interpretations from different groups. We will describe recent measurements in which the primary photochemistry of OIO via both pathways is determined unambiguously over a wide range of visible wavelengths.

Beginning with the classic photofragment spectroscopy experiments by Kent Wilson’s group more than 40 years ago, the photochemistry of alkyl iodides ( $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ ,  $\text{C}_3\text{H}_7\text{I}$ , etc.), has been studied extensively, and now represents a benchmark in the field of polyatomic photodissociation dynamics. During the course of developing photolytic sources of alkyl radicals for studies of photochemistry and bimolecular reaction dynamics, we have found that the photochemistry of secondary and tertiary alkyl iodides is more complex than previously thought.

The 1- and 2- propyl radicals ( $\text{C}_3\text{H}_7$ ), while structurally fairly simple, undergo photochemical and bimolecular oxidation reactions via multiple pathways leading to multiple chemically distinct product channels. Some of our recent experimental studies in these areas will be discussed.

# Tuning the electronic relaxation dynamics of molecules and protein chromophores

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Light-induced processes are ubiquitous in nature. Isolated biological chromophores are ideal starting points for studying the key elementary processes following light-absorption, free from the complications of interactions with aqueous or protein environments. Here, we describe our recent time-resolved photoelectron spectroscopy studies of the non-radiative relaxation dynamics of isolated pyrrole molecules and show how the introduction of an N–H $\cdots\pi$  interaction, in pyrrole dimers, opens up a low-energy, electron-transfer relaxation pathway.<sup>1,2</sup> We also describe our recent photoelectron spectroscopy studies of isolated green fluorescent protein chromophore anions and show how chemical substitution allows us to tune the competition between electron emission and internal conversion.<sup>3,4</sup>

**Acknowledgments:** This work was supported by EPSRC grants EP/L005646 and EP/L005697.

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## Liquid-Liquid Phase Separation in Submicron Aerosol Particles

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The chemical and physical properties of aerosol particles that determine their impact on climate are determined in part by their composition, size, shape, and morphology. We have characterized the morphology of submicron aerosol particles composed of organic compounds mixed with ammonium sulfate using cryo-transmission electron microscopy. Particles are made under ambient conditions without the influence of a substrate. Our results are consistent with previous results on supermicron particles for particle sizes  $> 300$  nm in diameter [1]. Surprisingly, however, the morphology of some systems is dependent on their size, where small particles are homogeneous and large particles are phase separated [2]. The size at which particles transition from homogeneous to phase separated depends on the drying rate. Even at the slowest drying rates, however, the size dependence is observed, where particles  $< 40$  nm in diameter are homogeneous. The dependence of the diameter at which the change in morphology is observed on drying rate suggests that the size dependence should occur at infinitely slow drying rates. As a result, this phenomenon is a consequence of a finite size effect in atmospheric particles, rather than due purely to kinetics. In addition, we unexpectedly observed that the size dependence is a function of the organic to sulfate ratio, where for some compositions, phase separation occurs at all sizes, and at others, phase separation only occurs for larger particles. This result is explained by the mechanism of forming a two-phase system. The size dependence is present for systems that separate through the activated process of nucleation and growth, and absent for systems that separate spontaneously through spinodal decomposition [3]. Finally, we have demonstrated that cloud condensation nucleus activity is dependent on the particle morphology. Phase separated particles with partially engulfed morphologies have the same activation diameter as ammonium sulfate, whereas homogeneous particles have an activation diameter between that of the salt and organic compound. This result indicates that morphology of particles can impact their ability to form cloud nuclei, and therefore affect climate.

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# Non-adiabatic molecular dynamics simulations of photochemical isoprene oxidation intermediates

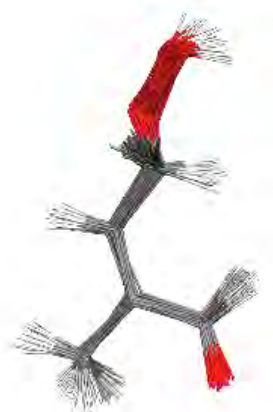
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Isoprene is amongst the most abundant volatile organic hydrocarbons in the atmosphere, with annual biogenic emissions comparable to methane. Nevertheless, our understanding of its atmospheric oxidation sequence is not complete. [1] Assorted pieces of indirect evidence suggest that intermediates produced during isoprene oxidation photochemically produce OH. [2] In this talk, I will describe new work designed to investigate the photochemical molecular dynamics (MD) of hydroperoxy-aldehydes (HPALDs), which are isoprene oxidation intermediates hypothesized to photolytically produce OH. [3]

Using a range of excited state quantum chemistry methods, we have been able to characterize the excited electronic states of both C5 and C6 HPALD variants, and calculated their corresponding excited state absorption cross sections. Our results quantitatively reproduce experimentally measured photolysis rate coefficients, [3] and indicate that a weak  $S_1$   $n \rightarrow \pi^*$  absorption feature is largely responsible for the photolysis rate coefficient observed under ambient atmospheric conditions. Exploiting a fast GPU-accelerated TDDFT framework, we ran *ab initio* multiple spawning non-adiabatic MD simulations initialized in the C5 HPALD  $S_1$  state. The results highlight an avoided crossing which facilitates fast internal conversion, and transfers population from one side of the molecular to the other – i.e., from a bound  $C=O$   $\pi^*$  state on one side to a dissociative  $O-OH$   $\sigma^*$  state on the opposite side. In order to understand how the *in vacuo* MD kinetics extrapolate to atmospheric temperatures and pressures, we have implemented Zhu-Nakamura theory into the MESMER non-equilibrium statistical mechanics package to construct a non-adiabatic variant of microcanonical transition state theory. Formulating and solving a non-adiabatic energy-grained master equation (EGME) allows us to investigate the photochemical kinetics of HPALD photochemistry under typical atmospheric temperatures and pressures, and provides direct evidence for OH production in near unity quantum yield.



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# Ultracold molecular collisions: sticky or not?

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We can now make trapped samples of ultracold polar  $^{87}\text{RbCs}$  molecules at temperatures around  $1\text{ }\mu\text{K}$ . The molecules are formed by magnetoassociation at a zero-energy Feshbach resonance [1] and then transferred to their absolute ground state by STIRAP (Stimulated Raman adiabatic passage) [2, 3]. We have used the molecules to measure the RbCs dissociation energy more accurately than for any other molecule [4], characterise its microwave spectrum [5] and uncover complex patterns of avoided crossings due to the AC Stark effect of the trapping lasers [6]. We are now in a position to study collision properties. Ultracold RbCs molecules are bosonic, and non-reactive [7].

A key question is whether ultracold molecular collisions are *sticky*. If every collision produces a long-lived collision complex, and the lifetime is long enough that a third molecule collides with the complex before the partners separate, then 3-body processes (with effectively 2nd-order kinetics) are likely to destroy the molecules.

Mayle *et al.* [8, 9] have proposed a model of sticky collisions based on the density of states at the collision energy. The model makes key assumptions that can be justified on the basis of random matrix theory (RMT). The assumptions are related to ideas of *quantum chaos* and essentially amount to assuming that all available energy is randomised among all available degrees of freedom during a collision.

My view is that this model is very much a limiting case, and may not describe collisions between real molecules. Real collision systems have Hamiltonians with far more structure than RMT, often with hierarchies of couplings of distinct magnitudes. Quantum numbers (or nearly conserved quantities) tend to persist (or emerge) in molecules, even when the density of states is very large. If this happens in the collision complexes formed in ultracold molecular collisions, the *effective* densities of states may be far smaller than the *actual* density of states, and the collision complexes may be much shorter-lived.

My talk will ask more questions than it answers about sticky collisions, but I will describe some initial studies in which we have explored signatures of quantum chaos in molecular collision systems such as  $\text{Li}+\text{CaH}$  and  $\text{Li}+\text{CaF}$  and found unexpected dependence on coupling strength [10].

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## **One Step at a Time - Unraveling the Formation of Interstellar Grains under Single Collision Conditions**

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During the last years, the energetics and dynamics of elementary reactions of the simplest silicon-bearing radical, silylidyne (SiH), with hydrocarbons and with molecular oxygen under single collision conditions and the inherent formation of small silicon-bearing molecules have received considerable attention both from the experimental and theoretical viewpoints spanning astrochemistry, physical organic chemistry, and chemical bonding. An understanding of these dynamics is vital to explore the underlying molecular processes involved in the formation of (organo)silicon-bearing molecules in cold molecular clouds and in outflows of circumstellar envelopes of Asymptotic Giant Branch (AGB) stars as these species can act as molecular building blocks of interstellar silicates and silicon-carbide based grains.

By merging crossed molecular beams with electronic structure calculations, we present new data on the formation of small (organo)silicon molecules in extraterrestrial environments. These studies yield a unified picture of the energetics and dynamics of ground state silylidyne radical reactions with prototype hydrocarbon molecules as well as with molecular oxygen and aid in a better understanding how molecular building blocks to interstellar grains are formed from the bottom up in extreme environments.

## Painless Modeling of Dynamics near Conical Intersections

Prof. Benjamin G. Levine, Dept. of Chemistry, Michigan State University

### Abstract:

It is now well established that conical intersections play an important role in facilitating non-radiative transitions in electronically excited molecules and materials, but modeling nonadiabatic dynamics in their vicinity is extremely challenging. In the adiabatic representation, singular first- and second-derivative coupling matrix elements arise due to discontinuities in the electronic wave functions at such intersections. Second-derivative coupling terms are particularly troubling, because they are non-integrable. Transformation into a quasidiabatic basis eliminates these singularities, but defining a globally well-behaved quasidiabatic basis is a system specific challenge. We present a new fully quantum mechanical nonadiabatic molecular dynamics ansatz that directly addresses these challenges: diabaticized Gaussians on adiabatic surfaces (DGAS). DGAS employs a basis of vibronic functions that follow the adiabatic potential energy surfaces, but that are continuous at conical intersection points. This eliminates singularities in the first- and second-derivative coupling matrix elements arising from the Hamiltonian. Instead, our vibronic basis may change discontinuously in time, leading to singular time-derivative matrix elements. Fortunately, these new singularities are integrable and can be gracefully handled in practice by interpolating the electronic wave function in time. The result is a nonadiabatic molecular dynamics ansatz that shares the advantages of the adiabatic and quasidiabatic representations while avoiding their respective pitfalls.

## Quantum-state controlled radical-ion reactions

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Radicals and ions frequently play an important role in gaseous media such as the Interstellar Medium (ISM) and the upper atmosphere. Although collisions in the ISM between ions and radicals are very rare events, the long timescales involved mean such reactions make important contributions to the pathways for assembly and destruction of complex chemical species. Unfortunately, experimental measurements of the rates and particularly the dynamics of reactions between ions and radicals are very few and far between. Our system overcomes some of the experimental challenges by using trapped molecular ions and Stark decelerated neutral radicals. Here, we can study reactions between molecules in single quantum states down to millikelvin temperatures. Our very high sensitivity allows us to study reactions where the reaction rate can be as low as one reaction per minute. We present first results from two systems (1)  $\text{Ca}^+ + \text{NO}$  and (2)  $\text{C}_2\text{H}_2^+ + \text{propyne}$  and allene.

# Structure-dependent Reactivity and Kinetics of Criegee Intermediates

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Ozonolysis of alkenes produces Criegee intermediates, which are highly reactive carbonyl oxides and may oxidize atmospheric trace gases, like SO<sub>2</sub> (to form SO<sub>3</sub> and subsequently H<sub>2</sub>SO<sub>4</sub>), NO<sub>2</sub>, organic and inorganic acids, etc. After the discovery of an efficient preparation method [1], Criegee intermediates have gained considerable attentions. Welz et al. [1] found that the reactions of CH<sub>2</sub>OO with SO<sub>2</sub> and NO<sub>2</sub> are much faster than previously thought, suggesting that Criegee intermediates may play a more significant role in atmospheric chemistry, including acid rain and aerosol formation. However, our study demonstrated that most of the atmospheric CH<sub>2</sub>OO would be consumed very quickly by its reaction with water dimer under typical tropospheric conditions [2]. Interestingly, the rate of this reaction exhibits strong negative temperature dependence. On the other hand, the reactions with water vapour were found to be slow for dialkyl substituted Criegee intermediates, like (CH<sub>3</sub>)<sub>2</sub>COO, opening an opportunity for them to react with atmospheric trace gases, like SO<sub>2</sub> [3]. However, the thermal decomposition of such type of Criegee intermediates is measured to be fast, fast enough to reduce their atmospheric concentrations. Other studies also show that the reactivity of a Criegee intermediate toward reaction with water vapour and its thermal decomposition depends very strongly on its structure. Thus, its atmospheric fate also depends on structure. Furthermore, new unpublished kinetic results of Criegee intermediates will be discussed.

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## **Direct Mapping of the Angle-Dependent Barrier to Reaction by Polarized Scattering Experiment**

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The transition state, which gates and modulates the reactive flux, serves as the central concept in our understanding of chemical reactivity of an activated reaction. While the barrier height of the transition state can be estimated from the activation energy in thermal kinetics data or from the energetic threshold of the reactive excitation function, another critical and equally important property—the angle-dependent barrier to reaction—has not yet been amenable to experimental determination till now. In this talk, using the benchmark reaction of  $\text{Cl} + \text{CHD}_3(v_1 = 1)$  as an example, we will show how to map such anisotropic property of the transition state from the preferred reactant bond-axis alignment of the backward-scattered products in a polarized scattering experiment. The deduced bend potential of the Cl–H–C configuration at the transition state agrees with *ab initio* calculated ones [1]. We expect that the method should be applicable to many other direct reactions with a collinear barrier.

If time permits, we will present a different set of experiments on the ground-state reaction of  $\text{F} + \text{CH}_3\text{D}$ , which suggests the possibility of inferring the well depth of the vibrationally adiabatic well—one of the key features of the potential energy surface in characterizing the quantum dynamical resonances—from the experimentally sighted ‘reactive rainbow’ [2].

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# **Stories that are encoded in vibrational spectra: Investigating spectral signatures of large amplitude proton migration in ion/water complexes**

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In this talk, I will discuss recent work in our group in which we made connections between proton transfer processes and hydrogen bonding and vibrational frequencies and intensities. Due to the large amplitude motions associated with proton transfer along a hydrogen bond, the vibrational spectra of these systems contain features that cannot be understood by the usual harmonic description of molecular vibrations. The breakdown reflects both the anharmonicity along this coordinate and coupling between this mode and other low frequency modes in these systems. It also reflects changes in the electronic structure as molecules vibrate. The presentation will draw from reported vibrational spectra for systems either containing intra- or intermolecular hydrogen bonds. Both the theoretical approaches used to study these systems and the insights gained from the studies will be described. The theoretical approaches range from the introduction of higher order terms to the harmonic analysis to adiabatic treatments in which the high- and low-frequency modes are treated at different levels of approximation and diffusion Monte Carlo studies in the full dimensionality of the system of interest.

# Symmetrical Quasi-Classical Model for Classical Molecular Dynamics Simulations of Electronically Non-Adiabatic Processes

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## Abstract

A recently described symmetrical windowing methodology [*J. Phys. Chem. A* **117**, 7190 (2013)] for quasi-classical (SQC) trajectory simulations has been applied to the Meyer-Miller (MM) [*J. Chem. Phys.* **70**, 3214 (1979)] model for the electronic degrees of freedom in electronically non-adiabatic dynamics. The approach treats nuclear and electronic degrees of freedom (DOF) equivalently (i.e., by classical mechanics, thereby retaining the simplicity of standard molecular dynamics), and provides "quantization" of the electronic states through the symmetrical quasi-classical (SQC) windowing model. The approach is seen to be capable of treating extreme regimes of strong and weak coupling between the electronic states, as well as accurately describing coherence effects in the electronic DOF (including the decoherence of such effects caused by coupling to the nuclear DOF). A survey of recent applications to a variety of problems is presented to illustrate the performance of the approach. Also described is a newly developed variation on the original SQC model (found universally superior to the original) and a general extension of it to obtain the full electronic density matrix (at no additional cost/complexity). It has also been pointed out that even though the MM classical vibronic Hamiltonian generates 'Ehrenfest dynamics', when this is processed via the SQC windowing methodology detailed balance is described correctly.

## Cold chemistry with cold molecules

Evardas Narevicius, Weizmann Institute of Science

We will discuss our efforts towards reaching ultra-cold temperatures with trapped molecules where molecular beams carrying both cold molecules and atoms have been decelerated and trapped in a permanent magnetic trap. I will present our plans and prospects of further cooling via evaporation or collisions with laser cooled atoms. In the second part of my talk we will focus on cold collisions with cold molecular partners that have been magnetically merged in order to reach collisions temperatures of  $\sim 10$  mK. I will show that quantum phenomena dominates collisions in this cold regime and discuss the importance of molecular degrees of freedom on cold reactions. I will present our latest results where Penning ionization reaction products have been detected using the Velocity Map Imaging technique allowing us to observe inelastic collisions between vibrationally excited cold molecular  $\text{H}_2^+$  ions and neutral helium atoms. The high resolution of VMI at low collision energies enables us to resolve the final quantum rotational states of collision products with sharp differences in statistics for the case of ortho and para  $\text{H}_2^+$ .

**Slow electron velocity-map imaging of cryogenically cooled anions: applications to bimolecular and unimolecular transition state spectroscopy**

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The spectroscopy and dynamics of complex free radicals, transition metal oxide clusters, and bimolecular/unimolecular transition states are being investigated with slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI). In cryo-SEVI, mass-selected anions are trapped and cooled to  $\sim 10\text{K}$ . Their photoelectron spectra are then measured at high resolution, as good as  $1\text{-}2\text{ cm}^{-1}$ , using a variant of photoelectron imaging. The method is versatile, and yields well-resolved spectra for many types of transient neutral species accessible by photodetachment. Results will be presented for polycyclic aromatic hydrocarbon radicals, hydrated metal oxide clusters, and reactive transition states with particular focus on new results for vinylidene  $\rightarrow$  acetylene isomerization.

# Frequency Comb Spectroscopy of the OD + CO Reaction

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Frequency comb lasers are a promising approach for broad-band transient absorption spectroscopy with high spectral and temporal resolution. The high spectral purity of the comb teeth makes the technique especially sensitive for time-resolved detection of gas phase transient intermediates. We have applied mid-infrared Transient Frequency Comb Spectroscopy (TrFCS) to study the deuterated analog of the OH + CO reaction, detecting OD( $\nu$ ), DOCO and product CO<sub>2</sub>.

The OH + CO  $\rightarrow$  H + CO<sub>2</sub> reaction has been investigated extensively due to its importance in the chemistry of combustion and the atmosphere; it has served as a benchmark system in reaction dynamics and kinetics. The reaction proceeds through the bound HOCO intermediate and over a small barrier to form products. The effective bimolecular rate coefficient is pressure dependent and exhibits an anomalous Arrhenius behavior, the result of competition between product formation and association to form HOCO, in both its ground state *trans* isomer and the higher energy *cis* isomer.

In the JILA TrFCS experiment, a mid-infrared femtosecond frequency comb is coupled to an external optical cavity combined with a spatially dispersed detection system. Cavity enhanced absorption (CEAS) spectra can be acquired with 10  $\mu$ s time resolution, with significant improvements in sensitivity over incoherent broadband CEAS due to locking of the comb to cavity resonances. Reactions of OD + CO at room temperature and 100 Torr are initiated by pulsed laser photolysis of precursors within the optical cavity. Observation of the time-dependent concentrations of OD( $\nu$ ), DOCO and CO<sub>2</sub> allows us to characterize the kinetics and dynamics of this reaction, including DOCO formation, isomerization, and product yields.

## Hunting for Intermediates in Complex-Forming Reactions: Better Hounds for an Elusive Quarry

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Complex-forming reactions have at least one deep well on their potential energy surface, where the well represents a reactive intermediate on the pathway to products. Just as in direct reactions, where the observation of a transition state complex provides important clues to the reaction mechanism, the characterization of reactive intermediates is enormously useful in discovering the mechanism of complex-forming reactions. Most reactive intermediates are short-lived, elusive molecules that are difficult to catch and challenging to detect. In this presentation, I'll discuss the first observation of one of these key species: a hydroperoxyalkyl radical (denoted •QOOH) that plays an important role in autoignition and autooxidation. As reaction complexity increases, many more intermediates may be energetically and entropically feasible, making the hunt for reactive intermediates increasingly difficult. To address these challenges, I'll present a new breakthrough in an old technique: photoelectron photoion coincidence spectroscopy (PEPICO). By teaching PEPICO a new trick, the ability to identify and reject false coincidences, we have extended its dynamic range by a factor of 100, promising a potent new method to unravel chemical reaction mechanisms.

## Unimolecular Reaction Dynamics: From Isolated Molecules and Radicals to Networks

Dr. Hanna Reisler

A detailed description of unimolecular dynamics on the ground and excited electronic states has been an ongoing goal of experiment and theory in the past several decades, striving to provide a state-to-state description of the decomposition process. Recently, such detailed examination has been extended to include small hydrogen-bonded networks. In this talk I will emphasize the close collaboration between theory and experiment that was essential to advancing our understanding of the dissociation of small molecules and radicals, such as NCNO and CH<sub>2</sub>OH, to the vibrational predissociation of molecular dimers and hydrogen bonded networks in cyclic trimers and tetramers.

## **Interaction of Atomic Oxygen with Ag(111) and Ag(110) Surfaces: Oxygen Adsorption and Kinetics at Surface versus Subsurface**

Dr. Sharani Roy, University of Tennessee

Transition metals are commonly used to catalyze transformations of small organic compounds, but the mechanisms of these catalytic reactions are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. Does subsurface oxygen affect catalysis by changing the electronic and geometric properties of silver, or does it emerge to the surface to directly interact with reactants? Does it initiate or promote surface reconstructions of silver? Does the participation of subsurface oxygen change with reaction conditions, such as surface structure, surface temperature, and oxygen coverage? Answers to such questions will promote a deeper mechanistic understanding of heterogeneous catalysis by silver, and help to design more effective industrial catalysts. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate the adsorption and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces, and examine their effects on the structural and catalytic properties of silver. On the Ag(111) surface, it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption, resulting in oxygen binding more strongly to the subsurface than to the surface at coverages above 0.5 ML. In contrast, surface adsorption remained stronger than subsurface adsorption at higher coverages on the Ag(110) surface. Calculations also show that kinetic barriers for formation of subsurface oxygen or its emergence into the surface are strongly dependent on coverage, indicating that the direct participation of subsurface oxygen in catalysis might strongly depend on coverage. Overall, our results provide valuable insight into the competition between adsorption and kinetics of oxygen on different facets of the silver surface, the importance of charge transfer in the binding and motion of atomic oxygen on silver, and the role of subsurface oxygen in catalysis by silver.

# Elementary Steps in Hydrogenation of Unsaturated Hydrocarbons over Pd Model Catalysts

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Atomistic-level understanding of surface processes is a key prerequisite for rational design of new catalytic and functional materials. In our studies, we investigate mechanisms, kinetics, thermodynamics and dynamics of heterogeneously catalyzed reactions and adsorption processes on nanostructured model supported catalysts by combination of multi-molecular beam techniques, infrared reflection-absorption spectroscopy and single crystal adsorption calorimetry. By employing these methods under well-defined ultra high vacuum conditions, we study the mechanistic details of complex multi-pathway surface reactions, such as hydrocarbon transformations in presence of hydrogen or selective hydrogenation of multi-unsaturated hydrocarbons.

Specifically, I will present a mechanistic study on selective partial hydrogenation of acrolein containing the conjugated C=C and C=O double bonds. It was found that the selective hydrogenation of the C=O bond in this molecule to form an unsaturated alcohol can occur with 100% selectivity over Pd(111), but not on Pd nanoparticles. We show that Pd(111) surface turns highly selective only after a very distinct modification with an overlayer of oxopropyl spectator species, which are formed from acrolein during the initial stages of reaction. The origin of the missing hydrogenation activity on Pd nanoparticles will be discussed.

In the second part, I will address hydrogen diffusion process into the subsurface region of model Pd nanoparticles and Pd(111). Particular emphasis will be placed on understanding the role of atomically flexible low-coordinated surface sites, such as edges and corners that are present on the nanoparticles, on the diffusion process and on exploring how modification of these surface sites with carbon affects the subsurface diffusion rate. To probe hydrogen subsurface diffusion, the  $\text{H}_2 + \text{D}_2 \rightarrow \text{HD}$  exchange reaction was conducted in the temperature range where this reaction is limited by the formation rate of subsurface H(D) species. We provide direct experimental evidence that – in line with the theoretical predictions – the atomically flexible low-coordinated surface sites on Pd particles play a crucial role in the diffusion process and that their selective modification with carbon results in marked facilitation of subsurface hydrogen diffusion.

## Gas-Surface Scattering Encompassing Collisional Energy Exchange, Condensation, Embedding, and Isotope Effects

Grant Langlois, Becca Thompson, Kevin Nihill, Jacob Graham, Wenxin Li, Kevin Gibson, Daniel Killelea, Hanqiu Yuan, Alison McMillan and Steven J. Sibener

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The interaction of energetic atomic and molecular species with ice is of fundamental importance for both terrestrial and astrophysical chemistry. This presentation will examine our recent discovery of a new mechanism by which atomic and molecular species can enter ice, energetic ballistic embedding. This mechanism can lead to the direct absorption of species into the subsurface/selvedge region of ice formations, allowing for the laboratory investigation of fundamental kinetic and thermodynamic processes associated with gas capture. Our initial efforts in ice chemistry demonstrated that translational energy activates the embedding of Xe and Kr atoms in the near surface region of ice surfaces [1-3]. We have also explored the sticking of water on ice as well as the sputtering of ice using high kinetic energy neutral atom bombardment. These studies revealed a rich palette of dynamics that are dependent upon the kinetic energy and momentum of the gas-surface encounter, the size and mass of the incident specie, as well as the nature of the ice itself; differing dynamics are seen for crystalline ice in comparison to amorphous solid water. We have expanded these studies to include the energetic embedding dynamics of molecular systems, first CF<sub>4</sub> [4] and most recently CO<sub>2</sub> [5], with ice interfaces using a combination of *in situ* FTIR, scattering, and desorption measurements. The CO<sub>2</sub>/ice system is of particular interest because of its fundamental role in the Earth's aqueous, atmospheric, permafrost, and seabed geosciences, as well as in the interstellar and circumstellar regions. These results show that energetic ballistic embedding in ice is a general phenomenon, and represents a significant new channel by which incident species can be trapped under conditions where they would otherwise not be bound stably as surface adsorbates. These studies have direct implications for environmental science including global warming, molecule storage and release from permafrost, glacial ice, clathrates, trace gas collection/release, and the composition of astrophysical icy bodies in space. This talk will conclude with very recent developments from our group in which we will demonstrate that a quantitative understanding of isotope-dependent scattering can lead to new, efficacious routes for isotopic enrichment and separation [6].

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4. Molecular Interactions with Ice: Molecular Embedding, Adsorption, Detection and Release, K. D. Gibson, Grant G. Langlois, Wenxin Li, Daniel R. Killelea, and S. J. Sibener, J. Chem. Phys. **141**, 18C514/1-10 (2014).
5. Capture of Hyperthermal CO<sub>2</sub> by Amorphous Water Ice *via* Molecular Embedding, Grant G. Langlois, Wenxin Li, K.D. Gibson, & S.J. Sibener, J. Phys. Chem. A **119**, 12238-12244 (2015).
6. Separation of Isotopes in Space and Time by Gas-Surface Atomic Diffraction, Kevin J. Nihill, Jacob D. Graham, and S. J. Sibener, to be submitted (2017).

## **New Probes of Reaction Dynamics and Spectroscopy**

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We are pursuing a number of new directions in the study of chemical reaction dynamics and will present highlights from several of these. We have recently developed a chirped-pulse microwave spectrometer coupled to a uniform supersonic flow. We will show its application to propargyl radical photodissociation and to bimolecular reactions, and discuss the unique capabilities and challenges of this instrument for reaction dynamics, kinetics, and spectroscopy. The high-performance supersonic flow we developed also represents an ideal environment in which to apply highly sensitive cw-cavity ring-down spectroscopy for detection of reaction intermediates and to study their kinetics. We will describe a new instrument taking advantage of this unique combination. Finally, we will describe new directions in DC slice and 3D velocity map and multimass imaging, and our new Finite slice Analysis (FinA) image reconstruction method.

Photochemistry

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This talk will be concerned with our current quantum mechanical and semiclassical calculations of photochemistry. Our techniques will be illustrated by our recent work on the photodissociation of thioanisole ( $\text{C}_6\text{H}_5\text{SCH}_3$ ). The photodissociation of thioanisole, as well as that of similar molecules such as phenol, thiophenol, and anisole, is a prototype of the photo-induced hydrogen/methyl detachment and proton transfer reactions mediated by conical intersections between a bound  $^1\pi\pi^*$  state and a repulsive  $^1\pi\sigma^*$  or  $^1n\sigma^*$  state. Analytic potential energy surfaces (PESs) and state couplings of the ground and two lowest singlet excited states of thioanisole were constructed in a diabatic representation based on electronic structure calculations including dynamic correlation by the XMC-QDPT method. They cover all 42 internal degrees of freedom and a wide range of geometries including the Franck-Condon region and the reaction valley along the breaking S-CH<sub>3</sub> bond with the full ranges of the torsion angles. The parameters in the PESs and couplings were fitted to the results of diabatic electronic structure calculations diabaticized by the fourfold way. The fit was accomplished by the anchor points reactive potential method with two reactive coordinates and 40 nonreactive coordinates, where the anchor-point force fields are obtained with a locally modified version of the QuickFF package. We used the PESs and couplings for 78011 full-dimensional semiclassical multi-state trajectories of the photodissociation process using the coherent switching with decay of mixing dynamics method. The photodissociation of thioanisole is very interesting because the experiments of Lim and Kim provide evidence for mode-specific effects on the product distribution. They showed that, with a specific S-CH<sub>3</sub> stretching mode being excited as the reagent is excited to the S<sub>1</sub> electronic state, there is a sharp increase in the proportion of the ground-state product to the excited-state product. We made calculations for four sets of initial conditions, one corresponding roughly to 0-0 excitation and three corresponding to exciting one vibrational mode, to look for mode-specific effects. The simulations show no significant mode-specific effect on the product energy distributions, but they do show an effect on the distribution of minimum-energy gaps in the trajectories and on the induction time for dissociation. We found that excitation of the S-CH<sub>3</sub> stretching mode leads to trajectories passing closer to the S<sub>0</sub>-S<sub>1</sub> conical intersection and to shorter lifetimes. This provides a possible explanation of why experimental results are different for excitation of this vibration.

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The Role of Electronic Transitions on Chemical Reaction Dynamics at Metal Surfaces  
John Tully, Yale University

The adiabatic (Born-Oppenheimer) approximation that underlies most of our understanding of chemical reaction dynamics is justified, in part, by the fact that energy spacings between electronic states are generally large compared with rotational and vibrational spacings. This is not the case at metal surfaces, however, for which conduction electrons exhibit infinitesimal energy spacings. As a result, for reactions at metal surfaces, even at thermal energies, nonadiabatic behavior is the rule rather than the exception. Electron-hole pair transitions, charge transfer and hot-electron-induced motion can be dominant pathways for energy flow and can drastically alter reaction pathways. This talk will describe progress towards developing practical computational tools for simulating nonadiabatic dynamics at metal surfaces, with applications to energy transfer in molecule-surface scattering.

# Cold and controlled chemistry: From small molecules to complex systems

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The recent progress in the cooling and control of neutral molecules and ions in the gas phase has enabled new approaches to the study of the mechanisms and dynamics of chemical reactions. In this context, ensembles of cold, spatially localized ions in traps, often referred to as Coulomb crystals, are attractive systems in which it is possible to observe, manipulate and control single isolated particles under precisely controlled conditions [1].

In our presentation, we will give an overview of recent experiments in which Coulomb crystal experiments are combined with molecular beams or trapped cold atoms and molecules in order to study the mechanisms and dynamics of chemical reactions in the gas phase. First, we will discuss a new type of dynamic trapping experiment in which clouds of ultracold atoms are shuttled through Coulomb crystals using precisely defined radiation-pressure forces in order to study the energy dependence of ion-atom reactions in an energy range corresponding to  $\approx 10$ -1000 mK [2]. An application of this technique is the precise characterization of the effects of long-range intermolecular interactions, as will be exemplified in reactions of Coulomb-crystallized  $\text{N}_2^+$  and  $\text{O}_2^+$  ions with velocity-controlled Rb atoms.

Second, we will present recent progress in the study of chemical reactions of polyatomic molecules which have either been conformationally or quantum-state selected using an electrostatic deflector [3]. Specifically, we focus on the characterization of conformational effects in polar cycloadditions (ionic Diels-Alder-type reactions) in which the diene has been conformationally selected and on the reactivity of the ortho and para nuclear spin isomers of  $\text{H}_2\text{O}$  towards cold ions.

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# Imaging Transient Chemical Bond Formation by H-atom Scattering from Graphene

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In this talk, I will describe how a fruitful interplay between experiment and theory can lead to accurate atomic-scale simulations of simple reactions at metal surfaces. I will emphasize the significant challenges surface chemistry presents to obtaining a dynamical understanding including the problems of high dimensionality and the common failure of the Born Oppenheimer approximation. I will present two concrete examples. In the first, results of a full dimensional experimentally validated theoretical approach to hydrogen atom adsorption at a metal surface that includes the effects of Born-Oppenheimer failure leads to an atomic scale view of H-atom adsorption at a noble metal as well as a dynamical explanation for chemicurrents. In the second, energy loss dynamics occurring on a 25-fs time scale are deduced from joint experimental and theoretical studies of the scattering of hydrogen atoms from a graphene surface. The dynamics are dominated by formation of a transient C-H chemical bond. The rate of energy flow out of the transient chemical bond into the solid is remarkably efficient and accounts for the large sticking probability of H to graphene measured experimentally. The experimental results also allow us to accurately obtain the barrier height to adsorption. H interactions on graphene are strongly influenced by the choice of metal substrate upon which the graphene is grown.

# Probing Quantum Dynamics of Chemical Reactions using High Resolution H-atom Rydberg Tagging and Velocity Map Imaging

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## Abstract

Quantized transition states and reaction resonances in chemical reactions are interesting topics in chemical reaction dynamics. In the recent years, we have made significant progresses in the study of the dynamics of a few triatomic benchmark reactions using quantum-state resolved crossed molecular beams scattering method, in combination with accurate quantum dynamics theory. Experimentally, we have developed state-of-art crossed molecular beam techniques that allow us to probe resonance structures in the triatomic reactions through H-atom Rydberg tagging and velocity map imaging. Theoretically, we have developed the most accurate potential energy surfaces for accurate quantum dynamics studies to provide deep dynamics insights of these chemical reactions at the most fundamental level. In this talk, I will provide an overview of the experimental and theoretical results on the three benchmark reaction systems:  $\text{H}+\text{H}_2$ ,  $\text{F}+\text{H}_2$ , and  $\text{Cl}+\text{H}_2$ . Through the combined experimental and theoretical efforts, we have shown that energy dependent backward scattering differential cross section measurement can provide clear spectroscopic information on the quantum structures in the transition state region. The nature of the resonances observed in the  $\text{F}+\text{H}_2$  and  $\text{Cl}+\text{H}_2$  will be also discussed in this talk. Through the studies of reaction resonances in these systems, we found that resonances can exist in many chemical reactions, especially in the reactions of vibrationally excited species. In addition, through high angular resolution velocity map imaging studies, we can now provide detailed understanding of the quantum dynamics of chemical reactions.

## Competitive pathways in the photodissociation of polyatomic free radicals

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The UV photodissociation dynamics of a series of alkyl radicals are investigated. The H-atom channels in the photodissociation of jet-cooled ethyl radical ( $\text{C}_2\text{H}_5$ ) via the  $\tilde{\text{A}}^2\text{A}'(3\text{s})$  Rydberg state are studied with more details. The dissociation of the ethyl  $\tilde{\text{A}}^2\text{A}'(3\text{s})$  state is mediated by a conical intersection. A non-statistical, repulsive  $\text{H} + \text{C}_2\text{H}_4(\tilde{\text{X}}^1\text{A}_\text{g})$  product channel is observed with the  $\text{C}_2\text{H}_4$  product vibrational state distribution partially resolved, giving some geometry information about this direct dissociation pathway. A statistical  $\text{H} + \text{C}_2\text{H}_4(\tilde{\text{X}}^1\text{A}_\text{g})$  product channel via unimolecular dissociation from the hot ground-state ethyl after internal conversion from the Rydberg state is studied, with its dissociation time further evaluated by energy-dependent angular distribution and pump-probe delay measurements. A slow  $\text{H} +$  triplet  $\text{C}_2\text{H}_4(\tilde{\text{a}}^3\text{B}_{1\text{u}})$  pathway is also identified.

The photodissociation of *n*-propyl radical via the  $3\text{s}$  Rydberg state and *i*-propyl radical via the  $3\text{p}$  Rydberg states also show a non-statistical and a statistical dissociation channel. The  $\text{H} +$  propene product  $P(E_\text{T})$ 's of both radicals are bimodal. The product angular distributions of the slow components of *n*- and *i*-propyl are isotropic, while that of the fast component of *n*-propyl is anisotropic and that of *i*-propyl is isotropic.  $\beta$  H atom loss is confirmed using partially-deuterated radicals. The photodissociation of *n*-butyl, 2-butyl, and *t*-butyl radical via the Rydberg states also show a non-statistical and a statistical dissociation channel. The photodissociation of cyclohexyl radical via its Rydberg state has a predominant non-statistical channel, and cyclohexyl is the largest alkyl radical so far showing the direct dissociation mechanism. Non-statistical dissociation mechanism is also identified in several unsaturated hydrocarbon radicals and will be briefly discussed.

# Poster Presentations Abstracts

**A versatile new apparatus for imaging and high-resolution time-of-flight:  
Intrabeam scattering near the ultracold limit**

Chandika Amarasinghe and Arthur G. Suits

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Ultra-cold environments have provided a unique experimental medium to study quantum mechanical effects. While cold experiments reveal interesting non-classical phenomena, capturing these underlying chemistries state specifically at sufficiently low temperatures is challenging. In scattering experiments to reach low collision energies the two colliding beams should possess similar velocities with low velocity spreads with intersecting angles close to zero. Merged beams have proved to be a useful way to achieve these conditions as many pioneering studies have recently demonstrated.

A versatile new apparatus for merged-beam and intrabeam scattering has been introduced. In the present study, achieving short pulse, high speed ratio supersonic beams from a home built valve and a high-speed chopper has been demonstrated. Instead of merging two beams to reduce the intersecting angle, the possibility of intrabeam collisions has been investigated. This method relies on the slippage of high mass species (Xe) from low mass molecules (Ar) in the same molecular beam to facilitate collisions. Production of Xenon (Xe) ions from collisions with Argon (Ar) Rydberg atoms has been observed in a single molecular beam. Given that the both collisional partners reside in the same beam the expected collisional temperatures for the penning ionization reaction estimated to be between 200 mK and 2 K. Latest results and future directions will be presented.

## The role of OH torsion in the photodissociation dynamics of nitrous acid (HONO)

Chandika Amarasinghe, Alexander Kamasah, Casey D. Foley, James O. F. Thompson, and Arthur G. Suits

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Nitrous acid (HONO) is one of the key molecules present in the atmosphere which serves as a major source of OH radicals. Owing to the fact that both photodissociation products can be detected state specifically, this molecule has been in the center of many experimental and theoretical investigations. The UV absorption spectrum of HONO between 300 – 400 nm is dominated by the transition to excited state via metastable levels of varying excitation in the  $\nu_2$  (N=O stretch) vibrational mode. There have been many experimental studies of HONO mostly led by Vasudev and coworkers where they achieved complete characterization of the OH photofragment and NO photofragment produced from *trans*-HONO  $S_1$  state dissociation. They saw limiting anisotropy for a perpendicular transition for the  $0_0^0$  band but it deviated from the limiting value for  $2_0^1$  and  $2_0^2$ . They ascribed this to rotation-induced deviation from axial recoil coupled with the longer lifetime for vibrational predissociation from excited levels in  $S_1$ .

In the present study, both the *trans*-HONO and *cis*-HONO were photodissociated through the  $2_0^2$  band and  $2_0^1$  of the  $S_1$ - $S_0$  transition. The resulting NO photofragment was subjected to (1+1) REMPI and studied using the DC slice imaging technique. The recoil anisotropy parameter for all the images show values between (-0.6) – (-0.8) and *cis*-HONO was more anisotropic than the *trans*-HONO. Analysis of the images with our new FinA slice imaging reconstruction method also show rotational state-correlations in the OH cofragment. The anisotropy values we obtain are very similar to those reported earlier despite the fact that in the present case the results are obtained in a cold molecular beam rather than at room temperature. Therefore, the deviation from the limiting value cannot simply be attributed to parent rotation and must involve OH torsion. Possible mechanisms for this effect will be discussed.

## Probing Water Splitting by Group-IV Metal Oxides with Slow Electron Velocity-Map Imaging

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Slow electron velocity-map imaging of cryogenically-cooled anions (cryo-SEVI) is a high resolution photoelectron spectroscopic technique capable of providing vibronic information of elusive neutral species via photodetachment of the corresponding anion. Previously, cryo-SEVI has successfully characterized geometric and electronic structures of numerous gas-phase metal oxide clusters, which serve as model systems for reaction centers on bulk catalytic surfaces. Recent modifications to our laser ablation source used to generate gas-phase  $M_xO_y$  anions permit addition of a reactant gas during cluster formation, providing access to reacted  $M_xO_y$  neutral clusters. To demonstrate the success of this improvement, we present cryo-SEVI spectra for  $(MO_2)_x(H_2O)_y$  clusters, where M is Ti or Zr and  $x,y = 1$  or 2. Comparison to theory allows assignment of cluster geometries and shows these species are capable of splitting at least two water molecules.

# Tunneling Effects in the Unimolecular Decay of Criegee Intermediates

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In the atmosphere, unimolecular decay of Criegee intermediates produced in alkene ozonolysis is known to be a major source of tropospheric hydroxyl (OH) radical. In this work, unimolecular decay of two prototypical Criegee intermediates, *syn*-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO, is shown to occur at energies significantly below the transition state barriers for 1,4-hydrogen transfer that produce OH, indicating that the reaction proceeds by quantum mechanical tunneling. The rate of appearance of OH products is obtained via direct, time-domain measurements following vibrational activation of the Criegee intermediates. Vibrational activation at energies nearly 2000 cm<sup>-1</sup> below the barrier is achieved via IR excitation of combination bands involving CH stretch and another lower frequency mode. The resulting OH products are detected by UV laser-induced fluorescence. OH appearance times in this deep-tunneling region are about 100 times slower than those observed in the vicinity of the TS barrier for both systems. Experimentally measured rates are in good agreement with RRKM calculated microcanonical dissociation rates of both *syn*-CH<sub>3</sub>CHOO and (CH<sub>3</sub>)<sub>2</sub>COO. Based on the calculated microcanonical rates, master equation modeling is used to predict the thermal decay rates under atmospheric conditions. Thermal unimolecular decay is shown to have significant contributions from tunneling at energies much below the barrier to H-atom transfer. The effect of tunneling on the unimolecular decay of Criegee intermediates is further investigated in experiments on a deuterated analogue of the *syn*-CH<sub>3</sub>CHOO Criegee intermediate.

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## Angular Dependent Ionization and Dissociative Double Ionization of Nitrosobenzene ( $\text{C}_6\text{H}_5\text{NO}$ )

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The double ionization and the angular dependent ionization of Nitrosobenzene ( $\text{C}_6\text{H}_5\text{NO}$ ) by 800 nm laser, was studied using a Photoion-Photoelectron coincidence imaging apparatus. The apparatus can detect both the single ions and the two electrons resulting from the dissociative double ionization and from quadruple coincidence (cation-cation-electron-electron), the three-dimensional electron-electron momentum correlation can be characterized. Double ionization of Nitrosobenzene resulted three dissociation pathways. A theoretical investigation of the dissociation pathways is being studied.

# Dissociation Dynamics of the OH-CH<sub>4</sub> Complex Using Photoelectron-Photofragment Coincidence Spectroscopy

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Radical-molecule reactions play an essential role in understanding both atmospheric and combustion chemistry. The reaction involving the hydroxyl radical with the simplest hydrocarbon, methane, involves a hydrogen abstraction mechanism which yields a methyl radical and water. This process is atmospherically relevant since methane is the most abundant hydrocarbon in the troposphere where it helps modulate the concentration of hydroxyl radicals, providing a chemical sink for both CH<sub>4</sub> and OH. To probe the dynamics of this system, we carried out experiments using our photoelectron-photofragment coincidence (PPC) spectrometer. PPC helps characterize transient gas phase species by measuring energy partitioning of reaction pathways. A dual pulsed valve setup (Lu et al. 2015) was used to synthesize the OH(CH<sub>4</sub>)<sup>-</sup> anion complex needed to study the dynamics of the OH + CH<sub>4</sub> → H<sub>2</sub>O + CH<sub>3</sub> neutral reaction. The dual pulsed valve setup operates by entrainment of a plasma generated in a side discharge into the high density region of the primary supersonic expansion which allows for the creation of cold anions and provides a rational approach to synthesizing anions of interest. PPC measurements were carried out on OH(CH<sub>4</sub>)<sup>-</sup> at a photon energy of 3.20 eV and evidence for stable (1 e<sup>-</sup> + 1 particle) and dissociative (1 e<sup>-</sup> + 2 momentum-matched particles) complexes were observed. Based on calculations of the AEA for OH(CH<sub>4</sub>)<sup>-</sup> performed at MP2/6-311++G(3df, 2p) level of theory, the entrance channel complex is being formed (H atom of OH weakly bonding to center of tetrahedral face of methane). Calculations of the kinetic energy (KE) maximum thresholds suggest that the prominent dissociative channel are the reactants in the entrance channel, OH + CH<sub>4</sub> with some evidence of accessing the H<sub>2</sub>O + CH<sub>3</sub> product channel. In addition, there is evidence of excitation of an asymmetric stretch of methane in the OH + CH<sub>4</sub> reactant channel. This high dimensionality seven-atom system should serve as an ideal benchmark system for hydroxyl radical reactions with simple alkanes.

This work was funded by the United States Department of Energy, Basic Energy Sciences under grant number DE-FG03-98ER14879.

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# IR Spectroscopy on a Series of Imidazolium- and Pyridinium-Based Ionic Liquids with the [tf<sub>2</sub>n] Anion

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Ionic liquids (ILs) have been shown to be extremely useful in areas ranging from chemical synthesis to energetic materials. While ILs are useful for a large number of applications, there is a lack of understanding of the microscopic origins of their macroscopic properties and bulk structure. A useful starting point for understanding the bulk structures of ILs is to investigate the structure of the cation-anion ion pair. To this end, we have used IR/UV action spectroscopy to investigate a number of ILs using two different cations, imidazolium and pyridinium, and one anion, bis(trifluoromethylsulfonyl)imide ([tf<sub>2</sub>n]).

Comparison of IR spectra for three imidazolium-based ILs of varying alkyl side chain length (methyl, ethyl, and butyl) along with their mono-deuterated analogs show the same three distinct families of conformers in each. These conformers are differentiated *via* the strength of their hydrogen bond between the cation and anion through the C2-H group, leading to a characteristic stretching frequency for each family of conformers. The similarities in these spectra demonstrate that the conformers of the ion pair are not affected by the length of the alkyl side chain. Additionally, we have acquired the IR spectra of a series of three pyridinium-based ILs with the [tf<sub>2</sub>n] anion (N-ethylpyridinium, N-ethyl-3-methylpyridinium, N-butyl-4-methylpyridinium) in an effort to determine structural effects of N-alkyl chain length and methyl substituent position on the aromatic ring. The IR spectra of the pyridinium-based ILs seem to exhibit fewer anharmonic effects than the imidazolium-based ILs, as evidenced by the lack of frequency and intensity changes across the series of ILs.

Synthesis of Titanium Boride Nanoparticles by Reactive Collisions in RF Thermal Plasma

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Abstract

Titanium boride nanoparticles were synthesized by a RF thermal plasma system. In order to understand the synthesis mechanism, numerical simulation on thermal plasma has been carried out. Optimal design and operating variable of the plasma system for nanoparticle synthesis were predicted by the numerical analysis. An extremely high temperature of 9,000 K which is enough for the evaporation of micro-sized boron and titanium raw powders was predicted in a thermal plasma generator. In a quenching reactor, a high quenching rate of  $10^4$  K/s was achieved according to the numerical simulation. The reaction mechanism between evaporated boron and titanium molecules has been studied by Gibb's free energy and homogeneous nucleation model based on the vapor saturation. The temperature in the tail region of thermal plasma flame is sufficiently high for the chemical reactions between boron and titanium molecules producing titanium borides. In addition, the nucleation temperature of boron and titanium were estimated at 2,600 K and 2,150 K, respectively. Therefore, the synthesis mechanism of titanium boride nanoparticles is expected as the co-condensation of boron and titanium vapors on boron nuclei in a rapid quenching of thermal plasma flame. In experiment, 15 kW of RF plate power was used for synthesizing nanoparticles. Titanium boride nanoparticles with 42 nm in average diameter were found in a powder collector. Produced nanoparticles were embedded in a hydrogel for the purpose of a soft functional material for nuclear radiation shielding. The attenuation coefficient of prepared titanium boride nanoparticles embedded hydrogel was  $0.238\text{ cm}^{-1}$  for 0.662 MeV  $\gamma$ -ray from  $^{137}\text{Cs}$  source.

Classical Molecular Dynamics Simulation of Electronically Non-Adiabatic  
Processes via a Symmetrical Quasi-Classical Windowing Model

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ABSTRACT

A symmetrical quasiclassical (SQC) windowing model for “quantizing” the electronic harmonic oscillator degrees of freedom (DOF) in the Meyer-Miller (MM) classical vibronic (nuclear + electronic) Hamiltonian has been shown to be a simple approach for extending classical molecular dynamics (MD) simulation to the treatment of electronically non-adiabatic processes. The SQC/MM approach treats the electronic DOF in non-adiabatic dynamics fully classically, thereby maintaining dynamic consistency with the standard classical MD treatment of the nuclear DOF and potentially scaling well to the treatment of complex chemical systems. The accuracy of the approach has been demonstrated (via benchmarking against exact quantum results) for a number of applications (particularly in the context of popular spin-boson-type models of condensed-phase electronic dynamics) where the methodology is seen capable of treating quantum coherence effects in extreme regimes of strong to weak coupling between the electronic states, and of accurately simulating the decoherence of such effects as caused by coupling to the nuclear DOF. Here we present further recent developments in the SQC/MM approach including: (i) the development of a new SQC windowing model which elegantly handles the weak-electronic coupling limit (and is universally superior to the original model), (ii) an extension of the SQC model for extraction of the full electronic density matrix from a standard SQC calculation (arising through viewing the SQC window functions as pre-limit Wigner functions in action-angle variables), and (iii) a “kinematic” adiabatic representation of MM vibronic dynamics which totally eliminates the need to calculate second-derivative couplings (as appear in the adiabatic multi-state/channel Schrödinger Eq.) when it is desirable to use standard Born-Oppenheimer electronic states and energy surfaces (e.g., calculated via *ab initio* quantum chemistry) in realistic simulations.

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# Symmetry and the Geometric Phase in Ultracold Hydrogen-Exchange Reactions

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We present results of quantum reactive scattering calculations for the ultracold hydrogen-exchange reaction and its non-reactive atom-exchange isotopic counterparts, proceeding from excited rotational states. We show that while the geometric phase (GP) does not necessarily control the reaction to all final states one can always find final states where it does. For the isotopic counterpart reactions these states can be used to make a measurement of the GP effect by separately measuring the even and odd symmetry contributions, which experimentally requires nuclear-spin final-state resolution. This follows from symmetry considerations that make the even and odd identical-particle exchange symmetry wavefunctions which include the GP locally equivalent to the opposite symmetry wavefunctions which do not. This equivalence reflects the important role discrete symmetries play in ultracold chemistry generally and highlights the important role ultracold reactions can play in understanding fundamental aspects of chemical reactivity.

# Universality and Chaoticity in Ultracold Chemical Reactions

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We present results of explicit quantum reactive-scattering calculations for ultracold reactions of K with KRb. We show the total rate is universal in character - validating the use of simple universal models for other similar reactions. On the other hand, the product rotational distribution is shown to be statistical in character, which we attribute to the chaotic nature of the reaction complex. The statistical character stems from quite general considerations and, as such, our results have implications for a broad class of ultracold atom-dimer and dimer-dimer reactions currently under investigation.

# Isomer-specific detection in the UV photodissociation of the propargyl radical by Chirped-Pulse mm-Wave spectroscopy in a Pulsed Quasi-Uniform Flow

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The UV photodissociation of the propargyl radical has been investigated by Chirped-Pulse mm-wave spectroscopy in a pulsed quasi-uniform flow (CPUF). This approach utilizes broadband microwave spectroscopy to extract isomer-specific information with MHz resolution and near-universal detection, coupled with the well-defined, low-temperature and high number densities afforded by a hybrid flow that we have identified as an ideal environment in which to make spectroscopic measurements. The propargyl radical ( $C_3H_3$ ) is produced by the 193nm photodissociation of 1,2-butadiene and other precursors. Upon absorption of a second photon at this same wavelength, H atom loss gives rise to three  $C_3H_2$  isomers: *c*- $C_3H_2$  (cyclopropenylidene),  $^1l$ - $C_3H_2$  (propadienylidene), and  $^3HCCCH$  (propargylene). In this work, the branching between these three channels is determined by direct measurement of *c*- $C_3H_2$  and  $^1l$ - $C_3H_2$ . In addition to their respective low-temperature branching fractions, their unique time-dependent behavior is also captured by the CUPF approach.

## High Resolution Imaging of Partial Wave Resonances in Low-Energy Molecular Scattering

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At specific energies in molecular scattering, particles can form a quasi-bound complex for a short period of time. These so-called scattering resonances are a result of temporary capture in the well of the interaction potential. They manifest themselves as rapid variations in the scattering cross sections as a function of the collision energy. Furthermore, they have a profound influence on the angular distribution of the scattering products. Scattering resonances provide great insight into molecular interactions as their nature depends on the full range of the interaction potential. Moreover, at low energies they are dominated by single quantum-scattering states, or partial waves. Observation of resonances therefore allows for a full understanding of the state evolution during a molecular collision.

However, the effects of resonances on the angular distribution of the scattering products have proven to be extremely challenging to observe experimentally due to the requirement of low collision energies and high resolution detection techniques. We present a setup that combines the Stark deceleration and Velocity Map Imaging techniques. In the apparatus the particles scatter at an angle of  $10^\circ$ , allowing for collision energies below 1 K. We report recent measurements of resonances in NO-He and NO-H<sub>2</sub> collisions and compare the results with state of the art quantum-scattering calculations.

## Slow Electron Velocity-Map Imaging of Cryogenically Cooled Vinylidene

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Slow electron velocity-map imaging of cryogenically-cooled anions (cryo-SEVI) is a high-resolution variation of traditional photoelectron spectroscopy that selectively detects slow electrons with sub-meV resolution. We present cryo-SEVI spectra of vinylidene ( $\text{H}_2\text{CC}^-$  and  $\text{D}_2\text{CC}^-$ ) showing detachment to a number of electronic states, providing comprehensive photoelectron spectra for both isotopologues. Detachment to the electronic ground state directly probes the benchmark unimolecular isomerization between vinylidene and acetylene, and these spectra resolve discrepancies regarding the stability of neutral vinylidene, the extent to which it couples to acetylene, and the manifestation of this coupling in its photoelectron spectrum. In contrast to the previous photoelectron spectra, we find no evidence for lifetime broadening, indicating detachment to a neutral species that does not undergo subsequent dynamics. Regardless, there are several clear indications of acetylenic influence, such as regions of unresolved structure and autodetachment to delocalized intermediate-well states. The excited states, though fully decoupled from acetylene, prove to be interesting in their own right, with a region of sharp, irregular structure reflecting a conical intersection between triplet states. In addition to these spectral complexities, several electronic states are observed experimentally for the first time, further demonstrating the success of theoretical treatments of this fundamental tetratomic system.

## O<sub>2</sub> Photodissociation: Transient Detection of the SO Radical Photofragments

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The early earth rock record shows significant isotopic variation in sulfur concentration in an era when the atmosphere was transparent to UV light. UV photodissociation of gas-phase SO<sub>2</sub> has been implicated as the source of this phenomenon. We investigate the dynamics of SO<sub>2</sub> photodissociation from an electronically excited state using tunable, pulsed UV light (200-220 nm) and high-resolution state-resolved transient IR spectroscopy to measure the energy partitioning in the SO radical photofragments. State-resolved techniques are used to measure the appearance of individual ro-vibrational states of the SO products. Doppler-broadened line profiles are measured to get nascent translational energy distributions and branching ratios are determined from rate measurements. In this work, photons with  $\lambda = 200$  to 220 nm electronically excite SO<sub>2</sub> from the ground state to an excited state, where avoided crossings on the excited potential energy surface create metastable bound states. UV-wavelength-dependent studies of the product energy partitioning are designed to identify the dissociation dynamics of the predissociative states.

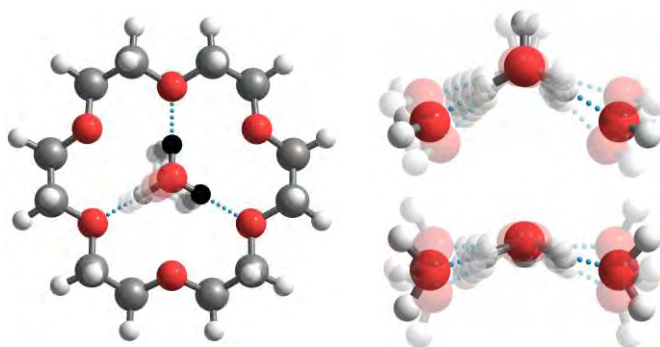
## Cryogenic Hydronium Nested in the 18-Crown-6 Ether Ionophore and Protonated Water Trimer: Tracking Photo-induced Intermolecular Proton Transfer

Chinh H. Duong,<sup>a</sup> Nan Yang,<sup>a</sup> Olga Gorlova,<sup>a</sup> Stephanie M. Craig,<sup>a</sup> Fabian S. Menges<sup>a</sup>, Patrick Kelleher,<sup>a</sup> Qi Yu,<sup>b</sup> Joel M. Bowman,<sup>b</sup> Anne B. McCoy,<sup>c</sup> and Mark A. Johnson<sup>a</sup>

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Cryogenic “messenger tagging” vibrational spectroscopy provides a microscopic picture into the dynamics of molecular clusters near their zero-point energy. We present predissociation spectra of the hydronium and methyl ammonium ions embedded within the  $C_{3v}$  pocket of an 18-crown-6 ether ionophore. The NH stretching bands of the  $\text{CH}_3\text{NH}_3^+$  ion are sharp and comparable with harmonic predictions, but the OH stretching bands of the  $\text{H}_3\text{O}^+$  display broad, diffuse signatures spanning a range of  $800\text{ cm}^{-1}$  that do not align with harmonic calculations. These features persist even with partial deuteration where only a single OH group remains in the  $\text{HD}_2\text{O}^+$  isotopologue. This broadening disappears in the OD stretching region, which instead displays a regular progression involving soft breathing modes of the crown ether at  $\sim 85\text{ cm}^{-1}$ . A vibrationally adiabatic model was employed to rationalize the broad OH stretching region. This model indicates that the displacement of the  $\text{H}_3\text{O}^+$  ion in the crown’s tri-coordinated H-bonding environment greatly impacts the OH stretching frequency due to the onset of frustrated intermolecular proton transfer. The broad bands are thus traced to the relatively low barriers for proton transfer within the complex.

The effect of lowering the symmetry in the tri-coordinated environment around hydronium can be addressed with the protonated water trimer (**3H**). Indeed, the availability of intra-cluster proton transfer processes upon excitation in OH stretching region results in extremely complex band patterns. Perturbation of these patterns due to messenger tagging were found to be negligible using two color IRMPD experiments on the cold, bare ion. These measurements were taken using a new background free, dual laser, cryogenic ion custom mass spectrometer that obtained the linear spectra of bare **3H** to eliminate tag perturbations. The major bands associated with the intra-water hydrogen bond indicate strong mixing and are not assignable by harmonic or perturbative theories, but instead require a new model developed by Joel Bowman’s group based on extensive (18) mode-couplings on a realistic potential energy surface.

# Collisionally induced rotational energy transfer in the $E(3)^1\Sigma_g^+$ and $F(4)^1\Sigma_g^+$ states of the lithium dimer

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We have investigated collision induced rotational energy transfer in the  $\text{Li}_2 - \text{Ne}$  system for the highly electronically excited  $E(3)^1\Sigma_g^+(v_i = 4, j_i = 31)$  and  $F(4)^1\Sigma_g^+(v_i = 10, j_i = 31)$  states of the lithium dimer under single-collision conditions at an experimental temperature of 923 K. Level-to-level rotationally inelastic rate constants for both of these states were found to be significantly more narrowly distributed around their respective initial levels than analogous rate constants derived for the  $A(1)^1\Sigma_u^+(v_i = 12, j_i = 30)$  state of the same molecule. This difference was investigated in detail through the use of classical trajectory calculations in conjunction with Reverse Monte-Carlo methodology to fit molecular interaction potentials for the E, F, and A states. A model potential of the form  $V(r, \gamma) = Ae^{-\alpha R}(1 + \beta \cos^6 \gamma)$  with adjustable anisotropy parameter  $\beta$  was used for all three states. Interaction potentials for the E and F states were found to be much more isotropic than that of the A state.

## **Infrared Multiphoton Excitation and Dissociation of Propargyl Chloride:**

### **Dynamics of Cl and HCl Elimination**

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Alkyl halides have been widely studied by photofragment imaging due to their prevalence in the atmosphere, accessible excited electronic states, and ease of detecting their photoproducts. UV photodissociation of propargyl chloride has been well characterized at 193nm with high and low recoil translational energy distributions of Cl from C-Cl bond fission observed. Approximately 95% of Cl products were at high translational energy and those at relatively low translational energy were only in the ground spin-orbit state.<sup>1</sup> Dynamics of HCl formation is a more complicated process and has not been studied in detail. Few IRMPD experiments of alkyl chlorides have been performed. Recently, HCl formation from IRMPD of vinyl chloride was seen by REMPI detection with DC slice imaging, suggesting formation of cold vinylidene.<sup>2</sup>

Here, we perform infrared multiphoton dissociation (IRMPD) of propargyl chloride to further understand the dynamics of dissociation by fragmenting near threshold. Translational energy distributions of Cl, Cl\*, and HCl all show significant differences when propargyl chloride is dissociated by IR compared to one-color UV (probe) photons. The fast dissociation channel peaking at 14 kcal/mol for UV dissociation giving Cl and Cl\* both are shifted to higher translational energies when pre-excited by infrared radiation while an additional slow component peaking at ~3.75 kcal/mol is also produced. The shift to higher translational energies and the anisotropy of fast fragments, however, suggests an IR-enhanced UV photodissociation process is playing a role. Low translational energy (0 to 1 kcal/mol), isotropic HCl molecules are formed at low IR power. At increasing IR laser power, the slow translational energy component proportionally increases. REMPI detection via the  $F^1\Delta_2 \leftarrow X^1\Sigma^+(0,0)$  band showed a cold HCl rotational distribution consistent with IRMPD for this process.

[1] L.R. McCunn, D.I.G. Bennett, L.J. Butler, H. Fan, F. Aguirre, S.T. Pratt. *J. Phys. Chem. A*. 2006, 110, 843 – 850.

[2] R. Fernando, C. Qu, J.M. Bowman, R.W. Field, A.G. Suits. *J. Phys. Chem. Lett.* 2015, 6, 2457 – 2462.

## **Building a photoelectron-photofragment coincidence spectrometer for multiply charged anions**

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Multiply charged anions, such as the dicarboxylate anions, have been the focus of much recent theoretical and experimental work. By measuring the energy of the photofragments produced during dissociative photodetachment, at the same time as measuring the photoelectrons, recent photodetachment studies can be extended to give a more complete understanding of the low energy decomposition pathways available to an anion. In our new experiment an electrospray ionisation source is coupled with a radio frequency accumulation trap to create high density packets of cold anions. After ejection the ions are accelerated to beam energies in the tens of keVs using a linear accelerator, before being crossed by a laser. Subsequent measurement, in coincidence, of the photoelectron and the photoneutral fragments gives a kinematically complete picture of the dissociation dynamics of the multiply charged anions. Here we present the outline of our experimental setup and the results of our characterisation studies to date.

This work is supported by the NSF Division of Chemistry under grant CHE-1464548.

## The photochemistry of 2-bromothiophene following UV+VUV excitation: a multi-mass velocity-map imaging study.

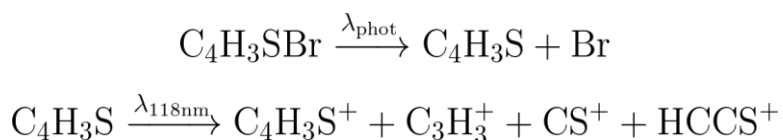
C. S. Hansen,<sup>1</sup> R. A. Ingle,<sup>1</sup> E. Elsdon,<sup>1</sup> M. Bain,<sup>1</sup> S. J. King,<sup>2</sup> J. W. L. Lee,<sup>2</sup> M. Brouard,<sup>2</sup> C. Vallance<sup>2</sup> and M. N. R. Ashfold<sup>1</sup>

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The velocity-map imaging (VMI) apparatus at Bristol has been recently extended to incorporate a PImMS2 camera<sup>1</sup> for multi-mass imaging and a vacuum ultraviolet (VUV) laser source for 'universal' detection, allowing more holistic insight into rich photochemistry. This talk will provide a brief overview of these experimental enhancements before discussing the results of a study into the ultraviolet (UV) photochemistry of 2-bromothiophene (C<sub>4</sub>H<sub>3</sub>SBr).<sup>2</sup> This molecule has been studied previously by velocity-map imaging the Br fragment, revealing striking wavelength-dependent photophysical behaviour and providing some evidence for gas-phase photochemical ring-opening.<sup>3</sup> In this work, multi-mass imaging and universal detection were used to simultaneously observe the thiophenyl fragment and the other lighter masses formed.

The UV photodissociation of 2-bromothiophene was investigated across the photolysis wavelength range  $265 \geq \lambda_{\text{phot}} \geq 245$  nm with ionic fragments detected following VUV ionisation with 118 nm light:



At all wavelengths, the Br-loss photoproduct (C<sub>4</sub>H<sub>3</sub>S) was found to exhibit recoil velocities and anisotropies consistent with those reported elsewhere for the Br fragment.<sup>3</sup> Velocity-map images for all lighter ions were also acquired simultaneously and include a C<sub>3</sub>H<sub>3</sub><sup>+</sup> channel that dominates the ion yield spectrum at  $\lambda_{\text{phot}} \leq 255$  nm. Anisotropy and velocity information from these images, alongside those from the REMPI-ionised Br fragment, reveal that these lighter ions arise from dissociative ionisation (from the VUV probe laser) of the most internally excited C<sub>4</sub>H<sub>3</sub>S fragments.

<sup>1</sup> <http://pimms.chem.ox.ac.uk/pimms2.php>

<sup>2</sup> *J. Chem. Phys.* **147**, 013923 (2017)

<sup>3</sup> *J. Chem. Phys.* **142**, 224303 (2015)

## Toward a Fundamental Understanding of Ionic Liquids for Space Applications: Collision-Induced Dissociation of Small Ionic Clusters

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Ionic liquids (ILs) are highly suited for space applications due to their low vapor pressure—and thus inherent vacuum compatibility—and task-specific tunability. Due to the wide range of potential cations, anions, and combinations thereof, tunability is mainly hindered by a lack of predictive structure/function correlation models. Insight into the thermochemical properties of ion clusters is needed for future modeling of thruster operation, as upcoming systems make use of these ILs. Previous experiments using tungsten needle surfaces found that droplets mainly emitted on-axis and small ionic clusters dominated the off-axis emissions. The presence or absence of specific ionic clusters from the plume of laboratory electrospray thrusters operating at low volumetric flow rates has been directly linked to the magnitude of the binding energies of specific ionic clusters, at least theoretically. As a result, it is necessary to determine the binding energies of these clusters and droplets experimentally. To buttress these experiments, molecular dynamics (MD) and quantum mechanical (QM) calculations can help to not only confirm binding energies measured, but are needed tools to determine the wide range of cation ion pairs available. The experimental measurements can provide benchmark gas-phase measurements to help evaluate theoretical approaches and move toward *in silico* evaluations in the early phases of research and development. Collision induced dissociation (CID) is well suited to gain information of 0 K binding energies. More generally, guided ion beams (GIB) can be used to study the interactions of ions upon collision with a neutral partner, often an atomic gas, which can be a reactant to form a new product or purely dissociation of the parent ion.

In the present work, we focus on determining the binding energies of IL clusters generated from electrospray ionization (ESI), as well as their dissociation pathways upon collisional activation and binding energies. Clusters of the form  $[C_{n+1}A_n]^+$  ( $n=1-2$ ) are our current focus. Cations of interest include 1-ethyl-3-methylimidazolium (EMIM), 1-butyl-3-methylimidazolium (BMIM). Anions of interest include dicyanamide (DCA) and bis(trifluoromethylsulfonyl)imide ( $Tf_2N$ ).

Preliminary experiments show that clusters of various C, A, and n can be readily produced by ESI and that they typically undergo loss of a neutral pair (CA) upon CID. For larger cluster sizes of  $n=2$ , the products are first dominated by loss of a neutral pair and the daughter  $n=1$  cluster. Upon increased collision energy, the  $n=1$  product decreases and the bare cation increases. Breakdown curves have been measured and comparisons to theoretical models are currently underway. It is noteworthy that the IL clusters' internal energies, as determined by theory, tend to exceed the theoretical binding energies; though, without additional activation, their lifetimes are calculated to be considerably longer than the mass spectrometric timescale. Thus far, we have determined the binding energy of the  $n=1$  clusters of  $[EMIM][DCA]$  and  $[BMIM][DCA]$  to be  $1.9 \pm 0.04$  eV and  $1.20 \pm 0.03$  eV, respectively. Both within fair agreement with initial MD and QM calculations. In the case of  $EMIM^+([EMIM][DCA])_2$  cluster, the binding energy measured is  $1.29 \pm 0.1$  eV closed to an MD simulation value of 1.32 eV. For  $BMIM^+([BMIM][DCA])_2$ , the measured binding energy of  $1.53 \pm 0.01$  eV is between the MD and QM values of 1.3 eV and 1.71 eV, respectively.

# Inelastic Collisions of State-selected NO with Ar in the Side-on Geometry

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Our crossed-molecular beam experiments combine hexapole state-selection with a static electric field to orient NO molecules prior to collision with Ar atoms. While a substantial amount of previous work has focused on end-on collisions (in which the rare gas atoms approach the NO molecules either on the N- or the O-end), our latest studies explore the dynamics ensuing when the Ar atoms collide with the NO molecules on the side. In this geometry, the symmetry around the relative velocity vector,  $\mathbf{k}$ , is broken, leading to distinct scattering characteristics in the two hemispheres to either side of  $\mathbf{k}$  ( $\mathbf{k}$  defines the z-axis in the scattering frame).

We employ a (1+1') REMPI scheme to ionize the scattered NO molecules in a specific final rotational state,  $j'$ , and velocity-map imaging to obtain angle-resolved cross sections for collisions on either side of the diatomic. Comparison of the differential cross sections for the two sides reveals distinct patterns arising from attractive and repulsive collisions of the Ar closer to the N-end or closer to the O-end. Most significantly, the integral steric asymmetry, which quantifies the overall preference of the NO to be scattered into the “left” or the “right” hemisphere, exhibits a pronounced change in sign as a function of final  $j'$  state. This propensity is similar to what has been observed in the end-on geometry case, however, the dynamics appear to be more complex and more sensitive to subtle features on the potential energy surface than for end-on collisions. A newly developed quantum-mechanical treatment, which may be applied to any arbitrary orientation of a diatom-atom collision system, is able to capture these subtleties and model the experimental results well.

## **Broadband Rotational Spectroscopy as a Tool to Detect & Characterize Pyrolysis Intermediates**

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The chemical complexity of hydrocarbon fuels and the fast-expanding list of potential plant-derived biofuels pose a challenge to the scientific community seeking to provide a molecular-scale understanding of their combustion. More refined spectroscopic tools and methodologies must be developed to selectively detect and characterize the widening array of fuel components and combustion reactive intermediates. The direct relationship between molecular structure and rotational frequencies makes rotational spectroscopy highly structural specific, therefore, it offers a powerful means of characterizing pyrolysis intermediates. However, the observed spectra contain contributions from many distinct species, creating a complicated spectrum with interleaved transitions that make spectral assignment challenging. To assist with this process, we have developed a protocol we call ‘strong-field coherence breaking’ (SFCB) that exploits multi-resonance effects that accompany sweeping the microwave radiation under strong-field conditions to output a set of transitions that can confidently be assigned to a single component in a mixture, thereby reducing the spectral assignment time.

The pyrolysis of 2-methoxy furan and guaiacol were carried over the 300-1200 K temperature range, with microwave detection in the 8-18 GHz frequency range, using a high-temperature flash pyrolysis micro-reactor coupled with a supersonic expansion. The SFCB technique was used to analyze and speed up the line assignments. The 2-furanyloxy radical, a primary, resonance-stabilized radical formed by loss of a methyl group in the pyrolysis of 2-methoxy furan, was detected and structurally characterized. Likewise, we observed radical intermediates from the thermal decomposition of guaiacol. The new structural insights derived from analysis of the observed radicals, the new broadband rotational technique, and the pyrolysis setup will be discussed.

# Identifying the First Folded Alkylbenzene via Ultraviolet, Infrared, and Raman Spectroscopy of Pentylbenzene through Decylbenzene

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## Abstract

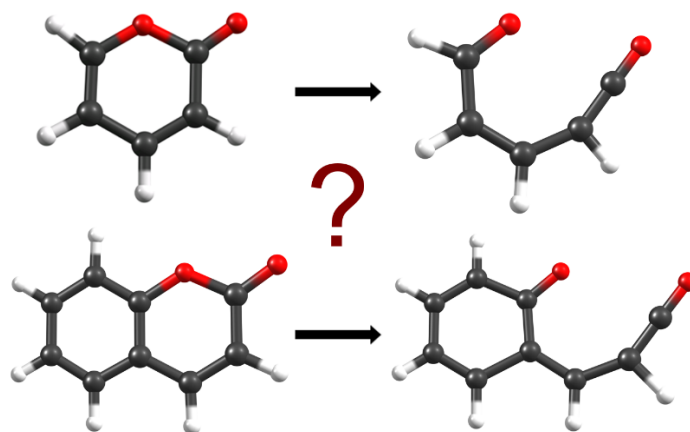
The conformational preferences of pentyl- through decylbenzene are studied under jet-cooled conditions in the gas phase. Laser-induced fluorescence excitation spectra, fluorescence-dip infrared spectra in the alkyl CH stretch region, and Raman spectra are combined to provide assignments for the observed conformers. Density functional theory calculations at the B3LYP-D3BJ/def2TZVP level of theory provide relative energies and normal mode vibrations that serve as inputs for an anharmonic local mode theory introduced in earlier work on alkylbenzenes with  $n=2-4$ . This model explicitly includes anharmonic mixing of the CH stretch modes with the overtones of scissors/bend modes of the  $\text{CH}_2$  and  $\text{CH}_3$  groups in the alkyl chain, and is used to assign and interpret the single-conformation IR spectra. In octylbenzene, a pair of LIF transitions shifted  $-92$  and  $-78\text{ cm}^{-1}$  from the all-*trans* electronic origin have unique alkyl CH stretch transitions that are fit by the local model to a g1g3g4 conformation in which the alkyl chain folds back over the aromatic ring  $\pi$  cloud. Its calculated energy is only  $1.0\text{ kJ/mol}$  above the all-*trans* global minimum. This fold is at an alkyl chain length less than half that of the pure alkanes ( $n=18$ ), consistent with a smaller energy cost for the g1 dihedral and the increased dispersive interaction of the chain with the  $\pi$  cloud. Local site frequencies for the entire set of conformers from the local mode model show ‘edge effects’ that raise the site frequencies of  $\text{CH}_2(1)$  and  $\text{CH}_2(2)$  due to the phenyl ring and  $\text{CH}_2(n-1)$  due to the methyl group. The g1g3g4 conformer also shows local sites shifted up in frequency at  $\text{CH}_2(3)$  and  $\text{CH}_2(6)$  due to interaction with the  $\pi$  cloud.

## Beyond a Static View on Conical Intersections: Understanding Photoproduct Branching Ratios

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Photoinduced ring-opening is an important energetic deactivation pathway in heterocyclic molecules. In previous work, we have investigated the solution phase dynamics of two structurally related heterocycles,  $\alpha$ -pyrone and coumarin (benzo- $\alpha$ -pyrone) using time-resolved vibrational absorption spectroscopy (TVAS). This revealed the formation of a ring-opened ketene isomer to be a significant photoinduced reaction pathway for  $\alpha$ -pyrone whereas in coumarin, photoexcitation results entirely in reformation of the ring-closed parent molecule.<sup>1</sup>



Use of a novel, automated search algorithm for the location of conical intersections<sup>2</sup> revealed that the two lowest energy conical intersections for both  $\alpha$ -pyrone and coumarin were remarkably similar in structure, despite the differences in the observed photochemistry. Complementary adiabatic and nonadiabatic *ab initio* molecular dynamics (AIMD) simulations have provided some important insights into how the dynamics around these critical regions of the potential energy surface ultimately determine the observed product branching.

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# A Chemically Accurate Potential Energy Surface for Dissociative Chemisorption of Methane on Ni(111)

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The dissociation of methane on metal surface has become one of the most studied gas-surface reactions due to not only its industrial significance but also the newly observed vibrational mode specificity. In the present work, we report a chemically accurate fifteen-dimensional potential energy surface (PES) for CH<sub>4</sub> on rigid Ni(111) surface with the (permutation invariant polynomial-neural network (PIP-NN) approach<sup>[1]</sup> based on the recently proposed SRP functional.<sup>[2]</sup> Starting from 1000 AIMD trajectories, overall 188188 points were sampled with additional quasi-classical trajectory (QCT) calculations, which were fit to a 323-12-40-1 NN with 323 PIPs in the input layer, yielding an RMSE of 15.76 meV. After applying the lattice relaxed sudden (LRS) model of Jackson,<sup>[3]</sup> the realistic dissociative sticking coefficients agreed with AIMD data on movable surface and the experiment very well, validating the chemical accuracy of this new PES. This new PES will offer us a new opportunity to quantitatively investigate the mode specificity and bond selectivity of this prototypical system.

**Keywords:** Methane; reaction dynamics; Dissociative chemisorption; potential energy surface

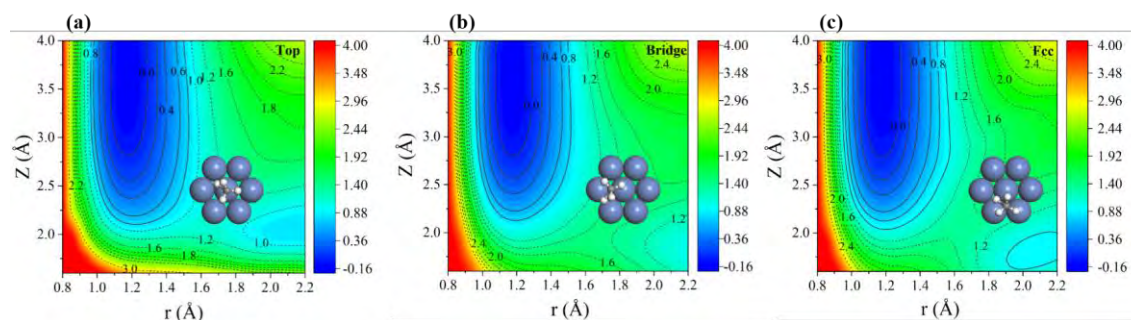


Fig.1 CH<sub>4</sub>+Ni(111) PES on the top (a), bridge (b), and fcc (c) sites.

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## **Imaging the inelastic scattering of vibrationally excited NO ( $v = 1$ ) with Ar**

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The inelastic scattering of a vibrationally excited NO ( $v = 1$ ) with Ar at a collision energy of  $3.0 \text{ kcal mol}^{-1}$  was investigated with our cross-molecular beam DC slice ion imaging apparatus. The vibrationally excited NO at  $v = 1$  was generated from flash pyrolysis and rotationally cooled by the supersonic expansion. The final product rotational states of NO from the scattered NO ( $v = 1$ ) with Ar was compared to the vibrational ground state NO ( $v = 0$ ) with Ar. The results show a strong  $J$  dependence of the rotational rainbow maxima from the inelastic scattering for both  $v = 0$  and  $v = 1$ . Our findings do not reveal significant scattering differences between NO  $v = 0$  and  $v = 1$  in terms of the location of the rotational rainbow maxima.

**Title:** The Vibrational Predissociation of the HCl-(H<sub>2</sub>O)<sub>3</sub> Tetramer: HCl and H<sub>2</sub>O products

**Authors:** Kwasniewski, Daniel; Zuraski, Kristen; Reisler, Hanna

**Institution:** Department of Chemistry, University of Southern California, Los Angeles, CA

**Abstract:** The vibrational predissociation of the HCl-(H<sub>2</sub>O)<sub>3</sub> tetramer, the largest HCl-(H<sub>2</sub>O)<sub>n</sub> cluster for which HCl is predicted to maintain its neutrality, is reported. Following IR laser excitation of the hydrogen bonded OH stretch fundamental, two pathways were observed: (i) HCl + (H<sub>2</sub>O)<sub>3</sub> and (ii) H<sub>2</sub>O + HCl (H<sub>2</sub>O)<sub>3</sub>. HCl and H<sub>2</sub>O fragments were monitored state-selectively using 2+1 resonance enhanced multiphoton ionization (REMPI) combined with time-of-flight mass spectrometry (TOF-MS). Velocity map images (VMI) of HCl and H<sub>2</sub>O in selected rotational levels were used to observe internal energy distributions of the pair-correlated co-fragments. The energy distributions in the fragments are broad, encompassing the entire range of allowed states for each pathway. From the maximum translational energy release, the bond dissociation energies,  $D_0$ , were measured to be (I)  $2000 \pm 100 \text{ cm}^{-1}$  and (II)  $2400 \pm 100 \text{ cm}^{-1}$  for the investigated channels. The global rotational state distribution of the HCl fragment was determined by using 2+1 REMPI via several electronic states.

# State-to-state rotational energy transfer of CO in collision with H<sub>2</sub> and Ar at very low temperatures

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The study of rotational energy transfer (RET) is vital to understand and describe a wide variety of astrophysical media via radiative transfer calculations [1]. RET at the state-to-state level provides information which is very important for the understanding of many gas-phase processes, especially at very low temperatures where molecular collisions are governed by resonance phenomena and long-range forces [2][3].

Using an Infrared Vacuum Ultraviolet Double Resonance (IRVUVDR) technique, implemented with the CRESU technique (a French acronym for reaction kinetics in uniform supersonic flow), we present experimental state-to-state rate coefficients and thermally averaged cross sections for RET of CO ( $v = 2, j = 0, 1, 4, 6$ ) in collision with the most abundant partner in the interstellar medium, H<sub>2</sub>, from 293 K down to 5.5 K, and in collision with Ar from 293 K to 30 K.

The experimental results for CO – H<sub>2</sub> are compared with inelastic scattering calculations using the new high quality diatomic-diatom six-dimensional potential energy surface PES of Faure et al [4]. The CO – Ar experimental results are compared with inelastic scattering calculations employing the new three-dimensional PES for the CO – Ar complex of Sumiyoshi and Endo [3][4].

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## Scattering Dynamics at the Gas-Liquid Interface

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The gas-liquid (G-L) interface is ubiquitous in nature, and important in industrial processes and atmospheric chemistry.<sup>1</sup> In recent years, new experimental methodologies have led to an increasing knowledgebase of inelastic and reactive dynamics at the G-L interface. One intriguing possibility is to use the G-L interface as a partially solvated environment, and thereby gain information on dynamics in solution. We are developing a new apparatus to study the dynamics of inelastic and reactive scattering of CN radicals at the surfaces of hydrocarbon liquids. We generate a molecular beam of CN radicals from BrCN seeded in He *via* an electric discharge. The resulting rotationally and translationally cold beam of CN radicals is scattered from a continually refreshed liquid surface. Elastically scattered CN radicals are probed with frequency-modulated (FM) absorption spectroscopy in the near infrared, using a multi-pass optical cell.<sup>2</sup> Reactive scattering, in which the CN radicals abstract a hydrogen, results in the production of HCN. To probe these a FM mid-infrared (MIR) source is being developed. We will report the progress made characterizing the CN radical molecular beam, as well as the development of the FM MIR source.

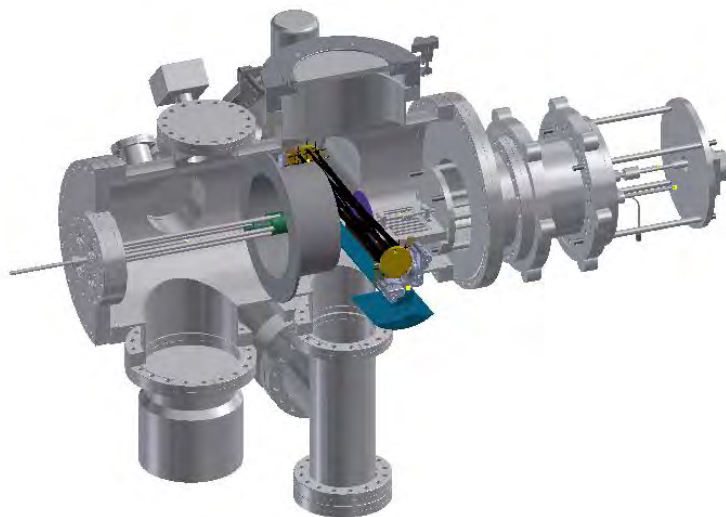


Figure 1: A cross-section of the experimental apparatus.

**Acknowledgments:** This work is funded by the U.K. EPSRC (EP/M021823/1).

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## Dynamics of Complex-Forming Bimolecular Reactions

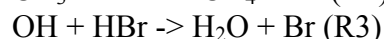
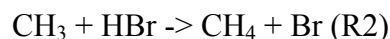
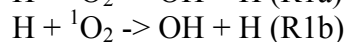
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<sup>1</sup> Institute of Chemistry, University of Pannonia, P.O.B. 158, Veszprém, H-8201 Hungary

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Reactions in which two reactants form a strongly or weakly bound complex are ubiquitous in atmospheric and combustion chemistry. Theoretical description of such reactions is generally based on some version of statistical rate theories. However, dynamical methods are essential in finding out what actually happens in the reacting system and can help us establish the connection between the shape of the potential energy surface and the dynamics of the reaction.

We present result on quasiclassical trajectory calculations on reactions



In reactions R1a and R1b a strongly bound complex is formed. The trajectory calculations [1,2] showed numerous common dynamical features even though the topography of the potential surfaces is different except the presence of the deep potential well. This is found to occur partly because of the common features of the two potential surfaces, partly due to mechanical conservation rules, partly incomplete loss of memory in the complex. In reaction R1b a dominant fraction of trajectories tends to return to reactants after passing the barrier in the entrance channel and getting deeply immersed into the deep potential well of the HO<sub>2</sub> complex.

In reactions R2 and R3 weakly bound complexes are formed by the reactants and in both cases the barrier separating the potential well corresponding to the complex from the products is submerged below the bimolecular reactant level. Not all complexes form immediately products. There is a large fraction of collisions in which the partners linger around one another for a long time without entering the potential well which turns out to be prevented by the centrifugal barrier arising because of angular momentum conservation. excitation of reactant rotation and vibration reduces the rate. A significant fraction of trajectories return to reactants after passing the potential barrier and going halfway down on the slope of the potential surface on the product side of the potential surface. Reasons for these dynamical features will be discussed.

We acknowledge financial support via OTKA grant No. K108966.

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# Testing a Reduced Dimensionality Reactive Scattering Model Using Classical Mechanics

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Application of exact quantum scattering methods in theoretical reaction dynamics of bimolecular reactions is limited by the complexity of the equations of nuclear motion to be solved. Simplification is often achieved by reducing the number of degrees of freedom to be explicitly handled by freezing the less important spectator ones. The reaction cross sections obtained in reduced-dimensionality (RD) quantum scattering methods can be used in the calculation of rate coefficients, but their physical meaning is limited. The accurate test of the performance of a reduced-dimensionality method would be a comparison of the RD cross sections with those obtained in accurate full-dimensional (FD) calculations, which is not feasible due to the lack of complete full-dimensional results. However, classical mechanics allows one to perform reaction dynamics calculations using both the RD and the FD model.

In this paper an RD vs. FD comparison is made for the 8-dimensional Palma-Clary model on the example of four isotopologs of the  $\text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2$  reaction, which has 12 internal dimensions. In the Palma-Clary model the only restriction is that the methyl group is confined to maintain  $\text{C}_{3v}$  symmetry. Both RD and FD opacity and excitation functions as well as differential cross sections were calculated using the quasiclassical trajectory method. The initial reactant separation can be handled according to our one-period averaging, 1PA method<sup>1</sup> or by an adaptation of the adiabatic switching method.<sup>2</sup> The RD and FD excitation functions were found to be close to each other for some isotopologs but in general, the RD reactivity parameters are lower than the FD ones beyond statistical error and for one of the isotopologs the deviation is significant. This indicates that the goodness of RD cross sections cannot be taken for granted.<sup>3</sup>

The quasiclassical trajectory calculations necessitated generation of semiclassically quantized initial conditions. We used two different methods. In normal mode sampling in reduced dimensionality, for which we derived equations of motion that properly assign masses to a reduced set of internal coordinates without rotational contamination. We present the formulation that will be generally applicable.<sup>4</sup>

For the generation of semiclassical initial states both in reduced and full dimensionality, we formulated adiabatic switching using a black-box type Hamiltonian appropriate for polyatomic molecules, using equations of motion of the type mentioned above. The adiabatic switching method has also been extended to prepare semiclassically quantized rotationally excited states.<sup>2</sup> Results on methane will be presented.

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## Crossed-Beam Slice Imaging of Atomic Oxygen Reaction Dynamics with Dimethylamine

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The dynamics of bimolecular reaction of oxygen atom  $O(^3P)$  with  $(CH_3)_2NH$  is studied by means of crossed beam scattering combined with universal DC slice imaging. Single-photon ionization at 157 nm (7.9 eV) is employed to measure the velocity-flux contour maps of the  $CH_3NHCH_2$  radical products at collision energies around 8 kcal mol<sup>-1</sup> in single-collision conditions. The product translational energy release is found to peak at very low energy and the angular distribution is found to be isotropic following this bimolecular reaction. These experimental results indicate that this reaction undergoes complex formation first and then eliminates OH to produce  $CH_3NHCH_2$  radicals. A channel producing  $(CH_3)_2N$  is also possible but not likely detected by our 7.9 eV probe. The reaction of  $O(^3P)$  with the partially deuterated isotopologue  $(CD_3)_2NH$  is also studied to verify the H/D removal by O occurring at the methyl site rather than the amine site for the product we detect at 157nm, which is consistent with *ab initio* ionization energy calculations. Further details about the nature of this complex-elimination mechanism for this bimolecular reaction are very intriguing to explore from the theoretical perspective. The results suggest either intersystem crossing to the singlet surface, or a roaming mechanism on the triplet surface, widely recognized in unimolecular reactions and observed recently in bimolecular reaction from our lab.

“Carbon Monoxide Gas-Liquid Scattering: Energy Dependence and Sub-Thermal Thermal Desorption”

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**Abstract**

With a strong IR absorption cross section and a reasonable density of rotational states, CO can be used with direct IR absorption methods to probe scattering processes more sensitively than previously measured. In this work, supersonically cooled CO is scattered off multiple liquids at multiple beam energies. The lowest beam energy (1 Kcal/mol) is measured at multiple different surface temperatures. Scattering performed at low collision energies, which normally isolates the trapping desorption (TD) component, has shown that CO does not desorb at the temperature of the surface, but rather with a sub-thermal temperature distribution in both the rotational and translational degree of freedom perpendicular to the scattering plane. Measured as a function of beam energies ( $E_{\text{inc}} = 1$  to 17 Kcal/mol), the average energy in each degree of freedom increases linearly with the beam energy. The branching ratio between the sub-thermal TD component and the IS component shows a negligible dependence on incident energy above 4 Kcal/mol ( $\sim 6$  kT). These measurements inform on both non-traditional TD scattering and the onset of the IS scattering component with increasing incident beam energy.

## Multi-mass Capabilities of Photoelectron-Photofragment Coincidence Spectroscopy

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Photoelectron-photofragment coincidence (PPC) spectroscopy creates a kinematically complete picture of reaction dynamics of simple systems that can be obtained by measuring the momenta of ejected electrons and the resulting neutrals from anion precursors. Because each of these particles is measured in coincidence, multiple anions with small mass variations can be collected simultaneously and the electrons disentangled based on neutral particle time of arrival. Using this technique, seven different masses were collected and analyzed, most notably, N<sub>2</sub>O<sub>2</sub>. Nitrogen oxides have an important role in both combustion and atmospheric chemistry (1,2). N<sub>2</sub>O<sub>2</sub> has been seen experimentally to have multiple anion isomers which result in different reaction pathways (2,3). The addition of a cryogenic octopole accumulation trap (COAT) has allowed greater control over the internal temperature of the precursor anions, as well as stabilization of different anion states that are produced. Using this approach, we have produced different isomeric states of the N<sub>2</sub>O<sub>2</sub> anion, revealing a diversity of dissociative photodetachment and ionic photodissociation pathways in experiments at 3.20 eV (388 nm). The implications of these results for the structure, energetics and dynamics of these anions and corresponding neutrals will be presented.

This work was funded by the United States Department of Energy, Basic Energy Science under grant number DE-FG03-98ER14879.

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# Effects of Vibrational and Rotational Energies on the Lifetime of the Pre-Reaction Complex for the $F^- + CH_3I$ $S_N2$ Reaction

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Unimolecular dynamics of the pre-reaction molecular complex  $F^- \cdots HCH_2I$  for the  $F^- + CH_3I$   $S_N2$  reaction were investigated with direct dynamics simulation. The total energy available in the pre-reaction complex is in consistence with the previous experimental and theoretical study of  $F^- + CH_3I$   $S_N2$  reaction with 0.32 eV collision energy. The unimolecular dynamics behaviors were investigated with the excitation energy partitioned in two different ways: 1) primarily excited in vibration, and 2) primarily excited in rotation. In the former simulation, almost all trajectories dissociated to the  $S_N2$  product  $CH_3F + I^-$ , crossing the  $S_N2$  transition state barrier of 2.4 kcal/mol, and dissociation to the  $S_N2$  reactant  $F^- + CH_3I$  is negligible with a barrier of 20.2 kcal/mol. This gives unimolecular dissociation rate constant of  $2.2 \text{ ps}^{-1}$  which is in good agreement with the RRKM theory. In the latter simulation, rotational energies were equally added to the three external rotational axes of the molecular complex, and the correspondent rotational quantum number  $J$  and  $K$  are 357 and 66. The dynamics are essentially different from the former simulation and the trajectories reveals non-RRKM dynamics behavior. Nearly 3/4 of trajectories dissociates to  $F^- + CH_3I$  pathway and this is due to the higher rotational barrier at the  $S_N2$  transition state than the  $S_N2$  reactants. The  $F^- \cdots HCH_2I$  decomposition instantaneous unimolecular rate constant increases with time, and the rate constant is much smaller than that in the vibrational excitation simulation, showing that the  $K$ -mixing and vibrational/rotational energy redistribution is a long process in this simulation. At the end of 20 ps simulation, the instantaneous rate constant is much smaller than the harmonic RRKM rate constant by treating the  $K$  rotational quantum number as an active degree of freedom, indicating that the vibrational/rotational energy redistribution is not complete in the simulated time scale.

# Modeling Anharmonic Behavior of the Protonated Water Dimer using Diffusion Monte Carlo

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## ABSTRACT

Water clusters have highly coupled vibrations. This is particularly true for vibrations involving shared, hydrogen-bonded protons where the customary harmonic approximations fail to provide an appropriate zero-order description. Diffusion Monte Carlo, a stochastic method for solving the time independent Schrödinger equation, has been used to study the vibrations of protonated ( $\text{H}_5\text{O}_2^+$ ) and deprotonated ( $\text{H}_3\text{O}_2^-$ ) water dimer systems. The wave function for systems of interest is propagated on potential energy surfaces developed by Bowman, et al. [1, 2] Previously, the exact ground state vibrational wave function was used in combination with excitation operators based on the harmonic oscillator description of molecular vibrations in order to predict the frequencies and infrared absorption intensities of these water clusters. [3, 4] Presently, these water dimers are used as a testing ground to explore the choices made when selecting coordinates to define the vibrational modes. Insights from these choices are carried forward to investigate notoriously challenging modes using the fixed node approximation. New approaches for determining the IR absorption intensity between the ground and first excited state defined on the fixed node surface will also be discussed.

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# Chemical Dynamics Simulation of N<sub>2</sub> Collision with Graphite

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Understanding energy transfer processes at the gas-surface interface provides the fundamental information concerning the gas – surface chemical dynamics. The greater interest in the gas-surface scattering phenomena associated with the interpretation of the microscopic details of the aerodynamic drag of an object moving through atmosphere. In that case, N<sub>2</sub> + Graphite serves as prototype model for understanding the highly energetic collisions of closed-shell molecules with the surface of the spacecraft in the low Earth orbit (i.e., at 200-700 km altitude). Collisions of N<sub>2</sub> with a graphite surface were simulated to study attributes of energy transfer in ablation. The simulations were performed as a function of collision energy, incident polar angle, and surface temperature. The following properties are analyzed for the N<sub>2</sub> + graphite collisions: (1) the translational and rotational energy distributions of the scattered N<sub>2</sub> molecules; (2) the distribution of the final polar angle for the scattered N<sub>2</sub> molecules; and (3) the number of bounces of the N<sub>2</sub> molecules on the surface before scattering. Direct scattering with only a single bounce is dominant for all incident angles. Scattering with multiple bounces becomes important for incident angles far from the surface normal (incident polar angle of 70°).

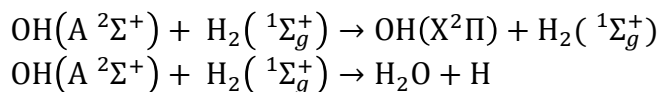
**Application of fitted, coupled potential energy surfaces via a *quasi*-diabatic Hamiltonian to the bimolecular reaction of OH+H<sub>2</sub>.**

Christopher Malbon and David Yarkony,  
Department of Chemistry, Johns Hopkins University

Nonadiabatic dynamics on fit representations of coupled adiabatic potential energy surfaces offers the most lucid description of nonadiabatic chemistry. Based upon high-level ab initio electronic structure, fit surfaces yield accuracy not accessible via on-the-fly methods. A recently introduced method [1] for fitting coupled adiabatic potential energy surfaces has been successfully applied to single-channel [2] [3] and multi-channel [4] multi-state photodissociation problems. Additionally, the procedure has been used in single-surface adiabatic dynamics to correctly account for the geometric phase resulting from energetically inaccessible conical intersections. [5]

Here we apply the aforementioned procedure to the bimolecular reaction of OH+H<sub>2</sub>, a classic problem in nonadiabatic chemistry it presents two obstacles the SURFGEN program is well suited to overcome: multiple reaction pathways and dramatically changing electronic structure. CNPI group symmetry allows for a global description of the coupled states. The fitting of the representation via least-squares “smoothens” otherwise discontinuous ab-initio data, providing at times a better description of the physics than the underlying ab initio.

We present our current, preliminary four-state quasi-diabatic representation for the OH+H<sub>2</sub> system based upon a multireference configuration interaction single and double excitation expansion, describing the relevant pathways:



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## State-specific Dissociation Rate Coefficients for $\text{H}_2(v, j) + \text{H}_2(v', j')$

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Dissociation of molecular hydrogen is an important cooling mechanism in regions of the interstellar medium associated with star formation. Full dimensional quasiclassical trajectories were calculated for all combinations of  $(v, j)$  with internal energy below 1 eV. Using the chemically accurate BMKP2 interaction potential with a minimum of 80000 trajectories at each translational energy, cross sections were calculated. Since the values of rate coefficients can exhibit high sensitivity to the values of the cross sections near threshold, additional large batches of trajectories were calculated to achieve the desired precision. State-specific rate coefficients were calculated at temperatures between 100 K and 100000 K using a piecewise linear excitation function. The resulting state-specific rate coefficients,  $\gamma$ , are parametrized as a function of temperature over the range 600 - 10000 K using:

$$\log_{10} \gamma(t) = a + bz + cz^2 - d \left( \frac{1}{t} - 1 \right)$$

where  $t = T/4500$  K and  $z = \log_{10} t$ .

It was found that the values of the resulting rate coefficients were sensitive to the internal energy of both molecules with initial vibrational energy having a slightly greater effect than rotational energy. This effect diminished as temperature increased.

## Quantum Control of Inelastic Scattering Near 1 K

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A 1:5.5 mixture of HD and D<sub>2</sub> is supersonically co-expanded and HD ( $v=1$ ,  $J=2$ ,  $M$ ) molecules are prepared using Stark-induced adiabatic Raman passage (SARP). Inelastic collisions of HD with D<sub>2</sub> are detected by (2+1) resonance enhanced multiphoton ionization of scattered HD ( $v=1$ ,  $J=0,1$ ) and the scattered angular distribution is deduced from time-of-flight measurements. Because the collisions take place in a single molecular beam, the collision energy is near 1 Kelvin, and the direction of the relative velocity of the two collision partners is restricted to lie along the beam axis ( $< 20$  m/s transverse velocity component). The selection of specific  $M$ -states aligns the HD molecular axis. Using appropriate pump and Stokes polarizations, SARP prepares molecular axes preferentially distributed parallel or perpendicular to the relative velocity of the colliding partners, thus allowing us to control collision geometry at the quantum level. By fitting the angular distribution using a partial wave analysis, we are able to measure the four-vector correlation, namely,  $\mathbf{k}$ ,  $\mathbf{J}$ ,  $\mathbf{k}'$ ,  $\mathbf{J}'$ , where  $\mathbf{k}$  and  $\mathbf{k}'$  are the initial and final velocities in the center of mass frame and  $\mathbf{J}$  and  $\mathbf{J}'$  are the initial and final rotational angular momenta of HD.

Figure 1 shows the fitted time-of-flight data of collisionally relaxed HD ( $v=1$ ,  $J=1$ ) for the initial HD ( $v=1$ ,  $J=2$ ) axis prepared (a) perpendicular and (b) parallel to  $\mathbf{k}$ . Dramatic stereodynamic effects are observed in both the integral and differential scattering cross-sections. The partial wave analysis allows us to correlate the peaks in the scattered distribution to specific angular momentum polarizations ( $M=0, \pm 1$ ) of the scattered HD ( $v=1$ ,  $J=1$ ).

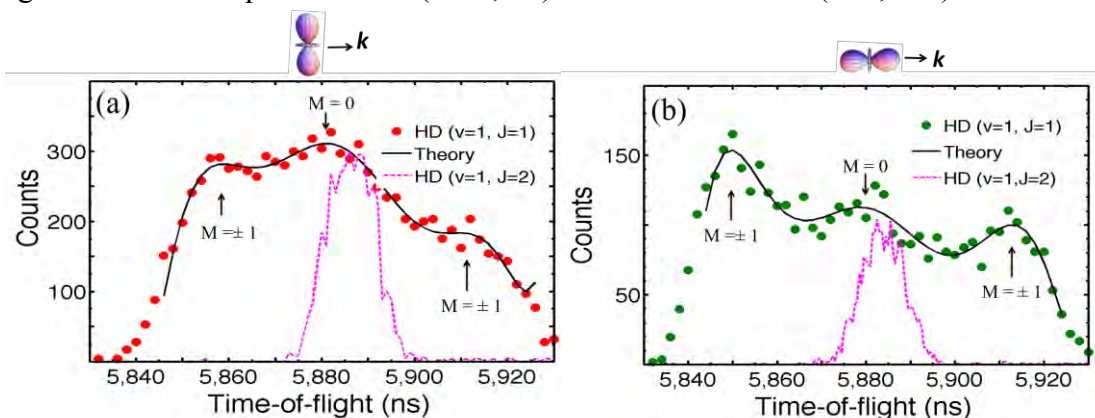


**Figure 1.** Time-of-flight distribution of HD ( $v=1$ ,  $J=1$ ) generated by inelastic scattering of HD ( $v=1$ ,  $J=2$ ) with D<sub>2</sub> when the former is aligned (a) perpendicular and (b) parallel to the relative velocity  $\mathbf{k}$ . The center of the time-of-flight distribution for the unscattered HD ( $v=1$ ,  $J=2$ ) molecular beam (purple dashed) corresponds to a scattering angle of 90 degrees for the scattered HD ( $v=1$ ,  $J=1$ ).

This experimental demonstration of collisions near 1 Kelvin using vibrationally excited, state-prepared molecules opens new possibilities for coherent control of molecular scattering.

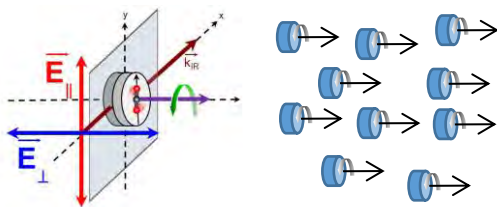
This work is supported by the Army Research Office under ARO Grant No. W911NF-16-1-0161.

## Dynamics of Oriented Super-Rotors: Exploring the Behavior of Molecules in Extreme Rotational States with Transient Spectroscopy

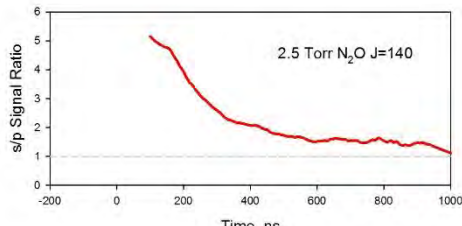
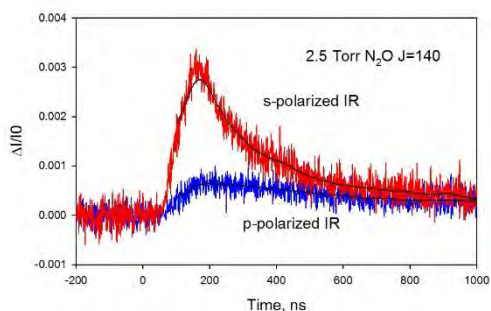
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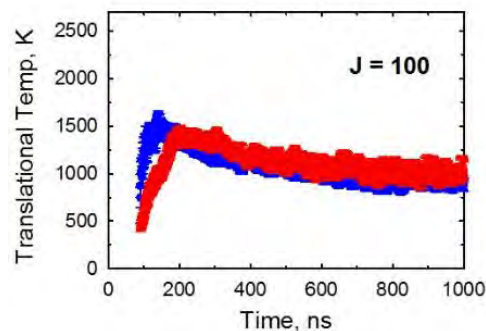
Molecules in extreme rotational states with oriented angular momenta are prepared in an optical centrifuge and their collision dynamics are investigated with high-resolution transient IR absorption spectroscopy. Polarization-dependent, time-resolved experiments investigate the J-dependence for lifetimes of orientational anisotropy of CO<sub>2</sub> and N<sub>2</sub>O. Doppler-broadened transient line profiles for individual rotational states (up to J=180) show that collisions of centrifuged molecules occur with small  $\Delta J$  values and have product translational energies that decrease with increasing J. Buffer gas studies highlight the role of rotational adiabaticity in super-rotor collisions.



The optical centrifuge is made by combining oppositely chirped pulses of light near 800 nm. The optical centrifuge pulse prepares an ensemble of molecules in high J states with oriented angular momentum and unidirectional spin.



Polarization-dependent transients for N<sub>2</sub>O J=140 caused by orientational anisotropy of the centrifuged molecules. At 2.5 Torr, the collision time is  $t_{\text{col}}=40$  ns.



Polarization-dependent translational temperatures for CO<sub>2</sub> J=100 at 10 Torr ( $t_{\text{col}}=10$  ns). At early times, in-plane rotors have lower translational energy indicating near-resonant rotational energy transfer between super-rotors.

## DYNAMICS OF GRAPHITE OXIDATION AT HIGH TEMPERATURES

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Gas-surface interactions at high temperatures are of great importance to atmospheric re-entry of spacecraft. Hypersonic flows generate the most extreme thermal conditions experienced by any flight vehicle. For a flight vehicle to survive in this environment, it requires a thermal protection system (TPS) composed of materials that can function at extreme temperatures under harsh oxidizing conditions. Most TPS materials are based on carbon, either in pure form or in a composite. During atmospheric re-entry, these materials are exposed to partially oxidized air at temperatures that can exceed 2000 K. The fundamental reactive and non-reactive dynamics between carbon and atomic or molecular oxygen strongly impact the thermal load on these TPS materials, but they have not been studied in extreme environments such as re-entry.

Hyperthermal interactions of ground-state atomic and molecular oxygen,  $O(^3P)$  and  $O_2(^3\Sigma_g^-)$ , from a highly oriented pyrolytic carbon (HOPG) surface were investigated with a broad range of surface temperatures from 1100 K to approximately 2300 K. A molecular beam composed of 93% O atoms and 7%  $O_2$ , with average translational energies of 5 eV and 10 eV, respectively, was directed at the surface. Translational energy and angular distributions for an incidence angle of  $\theta_i = 45^\circ$  were obtained for inelastically and reactively scattered products using a rotatable mass spectrometer detector. Four scattered products were observed:  $O_2$ , O, CO and  $CO_2$ . The  $O_2$  was attributed to inelastic scattering of  $O_2$  present in the incident molecular beam. Inelastically scattered O atoms exhibited both direct (non-thermal) and indirect (thermal) components. The primary reaction product observed was carbon monoxide (CO); carbon dioxide ( $CO_2$ ) was observed only with relatively low temperatures. Both reaction products were formed through non-thermal and thermal mechanisms. While there is evidence for direct Eley-Rideal reactions, CO and  $CO_2$  were formed predominantly through thermal reaction mechanisms. The angular flux distributions were peaked about the surface normal and were significantly narrower than a cosine distribution. Additionally, the energies of the desorbing products were much higher than  $2RT$  at final angles close to the surface normal and decreased at grazing final angles. Both of these observations indicate that CO and  $CO_2$  are desorbing over a barrier. The components of the non-thermal and thermal  $CO_2$  reactions could not be easily separated in the TOF and angular flux distributions, and a desorption barrier could not be determined for the thermal reaction. The desorption barrier of CO was determined by using the principle of detailed balance. As the surface temperature increased, the amount of CO and  $CO_2$  produced via a thermal mechanism decreased and the calculated desorption barrier for CO increased. Simultaneously, the number of O atoms that scattered via thermal desorption increased, which reduced the number of O atoms available for reaction at higher temperatures. The thermal O atoms were also found to desorb over a barrier which decreased with increasing surface temperature. It is likely that reducing the surface coverage of O atoms caused the desorption barriers for CO and  $CO_2$  to increase. The combined effect of reduced surface coverage and increased desorption barriers apparently limits the reactivity of the surface at extreme temperatures.

## Investigation of the Two- and Three-Fragment Photodissociation of the *tert*-Butyl Peroxy Radical at 248nm

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Alkyl peroxy (RO<sub>2</sub>) radicals have long been understood to be important species in both atmospheric and combustion chemistry.<sup>1-2</sup> In atmospheric chemistry, these species are crucial intermediates in formation of tropospheric ozone from hydrocarbons and oxygen.<sup>3</sup> Examining the unimolecular dissociation dynamics of these species can provide valuable insight into the energetics and reactivity of these radicals.

The photodissociation dynamics of the *tert*-butyl peroxy (*t*-BuOO) radical were studied by means of fast radical beam coincidence translational spectroscopy. The neutral *t*-BuOO radical was formed by photodetachment of the corresponding *t*-BuOO<sup>-</sup> anion at 700 nm, followed by dissociation at 248 nm (5.00 eV). Mass distributions and photofragment translational energy distributions were obtained.

The major channel is found to be three-body fragmentation to form O, CH<sub>3</sub> and acetone (83%), with minor two-body fragmentation channels leading to the formation of O<sub>2</sub> + *tert*-butyl radical (10%) and HO<sub>2</sub> + isobutene (7%). Experimental results show that the translational energy distribution for two-body dissociation peaks close to zero kinetic energy, with an isotropic angular distribution of fragments. These results indicate that two-body fragmentation proceeds via internal conversion to the ground electronic state followed by statistical dissociation. For three-body dissociation, the translational energy distribution peaks closer to the maximum allowed kinetic energy and shows an anisotropic distribution of the plane of the dissociating fragments, implying rapid dissociation on an excited state surface. A small shoulder in the three-body translational energy distribution suggests that some three-fragment dissociation events proceed by a different mechanism, involving internal conversion to the ground electronic state followed by sequential dissociation.

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Kevin Nihill

Dynamics of Molecular Collisions 2017 – Abstract for poster presentation

Experimental and Theoretical Study of Rotationally Inelastic Diffraction of H<sub>2</sub>(D<sub>2</sub>) from Methyl-Terminated Si(111)

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Fundamental details concerning the interaction between H<sub>2</sub> and CH<sub>3</sub>-Si(111) have been elucidated by the combination of diffractive scattering experiments and electronic structure and scattering calculations. Rotationally inelastic diffraction (RID) of H<sub>2</sub> and D<sub>2</sub> from this model hydrocarbon-decorated semiconductor interface has been confirmed for the first time *via* both time-of-flight and diffraction measurements, with modest  $j = 0 \rightarrow 2$  RID intensities for H<sub>2</sub> compared to the strong RID features observed for D<sub>2</sub> over a large range of kinematic scattering conditions along two high-symmetry azimuthal directions. The Debye-Waller model was applied to the thermal attenuation of diffraction peaks, allowing for precise determination of the RID probabilities by accounting for incoherent motion of the CH<sub>3</sub>-Si(111) surface atoms. The probabilities of rotationally inelastic diffraction of H<sub>2</sub> and D<sub>2</sub> have been quantitatively evaluated as a function of beam energy and scattering angle, and have been compared with complementary electronic structure and scattering calculations to provide insight into the interaction potential between H<sub>2</sub> (D<sub>2</sub>) and hence the surface charge density distribution. Specifically, a six-dimensional potential energy surface (PES), describing the electronic structure of the H<sub>2</sub>(D<sub>2</sub>)/CH<sub>3</sub>-Si(111) system, has been computed based on interpolation of density functional theory (DFT) energies. Quantum and classical dynamics simulations have allowed for an assessment of the accuracy of the PES, and subsequently for identification of the features of the PES that serve as classical turning points. A close scrutiny of the PES reveals the highly anisotropic character of the interaction potential at these turning points. This combination of experiment and theory provides new and important details about the interaction of H<sub>2</sub> with a hybrid organic-semiconductor interface, which can be used to further investigate energy flow in technologically relevant systems.

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# The Cryptic Saddle Points in Combustion Reactions of CH<sub>4</sub>

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Concentrating on the saddle points (SPs) of potential energy surfaces, this paper represents an attempt to extend the mechanisms of combustion reactions. Three SPs are identified in the combustion reaction CH<sub>4</sub> + O(<sup>3</sup>P) using CASSCF and *ic*MRCI methods with a kind of optimized CVDZ basis sets. Our calculations give a fairly accurate description of the regions around the twin SPs in the O(<sup>3</sup>P) attacking a near-collinear H-CH<sub>3</sub> direction. One second-order saddle point between the above twin saddle points is the result of the *C*<sub>3h</sub> symmetry *Jahn-Teller* coupling within the branching space. Subsequently, thermal rate constants for this hydrogen-abstraction are calculated using the canonical unified statistical theory method with the temperature ranging from 298 to 1000 K. The present work reveals the reaction mechanism of hydrogen-abstraction by the O(<sup>3</sup>P) from methane, and develops a better understanding for the role of SPs. The behavior of re-crossing dynamics of the title reaction shows a characteristic of complex-formation reaction.

## Cold targets for slow bullets: Cold ion-molecule reactive collisions in an ion trap

Lorenzo S. Petralia<sup>1</sup>, Tim P. Softley<sup>2</sup> and Brianna R. Heazlewood<sup>1</sup>

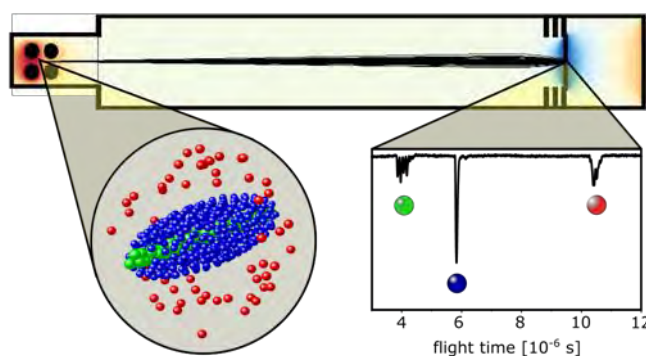
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With the ultimate goal of exploring the quantum dynamics of ion-neutral reactions in cold conditions, we employ two sources of cold neutral molecules in combination with ions held in a linear ion trap and cooled by lasers. The two sources of cold neutral molecules we adopt are a Stark decelerator and a quadrupole guide velocity selector combined with a buffer gas cooling system [1]. Laser-cooled atomic ions within the trap undergo a phase transition, adopting an ordered structure called a Coulomb crystal [2]. Other non-laser cooled species can be sympathetically cooled into the Coulomb crystal, enabling a range of ionic targets to be prepared. Reactions are investigated by monitoring the change in the morphology of Coulomb crystals over time and by performing time-of-flight mass spectrometry measurements [3,4]. In this way, we can examine the progress of ion-molecule reactions within Coulomb crystals.

We also report on the extent to which the spatial orientation of cold polar molecules can be controlled as molecules pass through various electric field regions of the experimental apparatus involving the quadrupole guide velocity filter [5].



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# Theoretical Study of Intersystem Crossing in the Cyanonitrene Diradical, $^1\text{NCN} \rightarrow ^3\text{NCN}$

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The cyanonitrene diradical (NCN) is an important intermediate of prompt nitric oxide formation in combustion chemistry [1]. Hence, its kinetics are of considerable interest for flame modelling. In laboratory studies, NCN is often generated by thermal or photochemical decomposition of cyanogen azide ( $\text{NCN}_3$ ). This predominantly produces  $^1\text{NCN}$  at first, which is converted to ground state  $^3\text{NCN}$  via intersystem crossing (ISC). Such delayed  $^3\text{NCN}$  formation can complicate the analysis of kinetic experiments involving NCN. Recent laboratory studies have revealed a complex dependence of the relaxation dynamics on temperature, pressure and bath gas [2,3]. Details of the mechanism, consisting of electronic, vibrational and rotational relaxation, are unclear to date.

The goal of this contribution is to gain insight into this mechanism from a theoretical point of view. In the first part, dissociation pathways of  $\text{NCN}_3$  were examined in detail by means of multi-reference configuration interaction (MRCI) calculations. This analysis helps to constrain the electronic states of NCN that are initially populated after precursor fragmentation (Fig. 1).

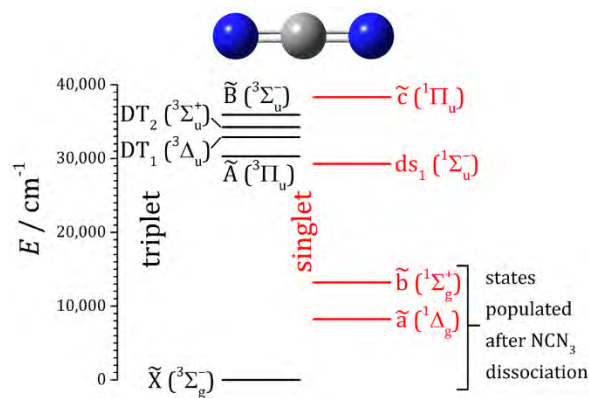


**Fig. 1.** Lowest electronic states of NCN.

The second part is focused on NCN ISC pathways via crossings of the singlet and triplet potential energy surfaces (PESs). To this end, MRCI calculations for a wide range of internal coordinates were performed. A crossing between the  $1^3\text{B}_1$  and  $1^1\text{A}_1$  PESs—corresponding to the lowest triplet and singlet states—was found at a strongly bent configuration ( $\theta \approx 107^\circ$ ). Its minimum on the seam of crossing (MSX) was characterized for estimating ISC rate coefficients with non-adiabatic statistical rate theory. An analogous

analysis was performed for  $\text{NCN} + \text{He}$  ( $\text{Ne}$ ) to assess the effect of an inert collider gas on ISC rates.

In a complementary study, the possibility of collision-induced ISC via a gateway-state mechanism [4] was explored. This involves the search for rovibrational states with mixed singlet/triplet character that can act as gateways for the spin-forbidden transition. A rigid-bender molecular model taking into account the Renner-Teller vibronic interaction of the degenerate  $^1\Delta_g$  state was set up. From its solution, spin-orbit coupling matrix elements between  $^1\text{NCN}$  and  $^3\text{NCN}$  rovibrational states were calculated and used in a screening process to identify potential gateway states.

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# Inelastic Scattering and Reactive Dynamics of O(<sup>3</sup>P) on Hot Carbon Preform

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## Abstract

Oxidation of a commercial grade carbon preform (carbon composite without the matrix) called FiberForm was studied using a hyperthermal beam of O/O<sub>2</sub> with a mole ratio of O: O<sub>2</sub> = 0.92:0.08. FiberForm is used as a precursor material in PICA, a heat shield material used by NASA for hypersonic entry/re-entry. This work is part of a continued effort in our lab to study the oxidation of carbon surfaces where the oxidation of vitreous carbon was studied previously. It was observed that the reactive dynamics of FiberForm was qualitatively analogous to vitreous carbon where the dominant reactive product was CO, and CO<sub>2</sub> was a minor product of reaction. In addition to time-of-flight (TOF) signal that could be fit with a Maxwell-Boltzmann distribution, long tails were observed for the CO TOF distribution (slow-CO) which were attributed to reactions occurring over long times (>200 μs). The slow-CO was modeled as a pseudo first-order process and two first order processes with distinct lifetimes were required to fit the CO TOF distribution. Temperature hysteresis was also observed in FiberForm like vitreous carbon where a decrease in CO flux was observed at the same surface temperature when the surface temperature was reduced from high to low. The decrease in CO flux due to hysteresis corresponded to an increase in the thermal O-atom flux analogous to the case of vitreous carbon. The results from FiberForm study suggests that similar reaction mechanisms are occurring on both FiberForm and vitreous carbon and the differences observed in the TOF distributions arise from the three-dimensional porous nature of FiberForm microstructure and not chemical reactivity.

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# Post Transition State Reaction Dynamics of H atom-Abstraction from CH<sub>3</sub>CN by F Atom: Non-IRC Dynamics and Product Energy Partitioning

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## Abstract

Born-Oppenheimer direct dynamics as implemented in VENUS/NWChem [1] program was applied to study the atomistic details of gas phase H-abstraction reaction  $F + CH_3CN \rightarrow HF + CH_2CN$ . Post transition state reaction dynamics were initiated at the H atom-abstraction transition state (TS), H--HCH<sub>2</sub>CN, with a Boltzmann distribution of energy at 300 K, as assumed by transition state theory (TST) [2]. Each trajectory was initiated with M06-2X/6-311++g\*\* level of theory. The product formation was rapid, first signature of HF formation was observed within 0.014ps of trajectory initiation. Five different types of exit channel trajectories were observed. Only a small number of trajectories, 11% approximately followed the intrinsic reaction coordinate (IRC), giving a predominantly non-IRC type reaction dynamics. A very few trajectories, 3%, led to a CH<sub>2</sub>CN---HF complex formation. As the trajectories evolve from TS to fully separated products, a large amount of potential energy is released and this energy gets partitioned between the relative translation, rotation, and vibrational energies of the products. The fractions of the available energy partitioned to HF rotation and vibration are 11% and 60%, respectively, for the approximate anharmonic zero point energy (ZPE) constraint analysis, and vibrational population inversion of product HF was observed. Only 23% of the available product energy is partitioned to CH<sub>2</sub>CN rotation and vibration, and CH<sub>2</sub>CN behaved very much as a spectator. HF + CH<sub>2</sub>CN product energy partitioning, showed qualitative agreement with experiments [3] by Setser and co-workers.

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## Generalized Tolman Activation Energy with Application to Molecular Dynamics Simulations\*

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We present a method based on Tolman's interpretation of activation energy that can be applied to thermal and non-thermal chemical reactions in molecular dynamics simulations of bulk gases. We use Boyd's assumption of local equilibrium thermodynamics to generalize Tolman's concept for application to individual reaction clusters, which include all chemical species that participate in an isolated reaction, for which we define the *reaction cluster local energy* (RCLE). The RLCE is shown to be conserved during the course of a reaction. We identify the *transition configuration* (TC), which is the point where the local energy of the reactants becomes equal to that of the products. The TC is a unique point that separates reactants and products. We have demonstrated application of the method by computing activation energies of the reactions  $\text{O}_2 + \text{H}_2 \rightarrow \text{H} + \text{HO}_2$  and  $2\text{O}_2 + \text{H}_2 \rightarrow 2\text{HO}_2$  in molecular dynamics simulations of equivalent mixtures of  $\text{H}_2:\text{O}_2$  with the ReaxFF reactive force field.

\* This work was supported by the U. S. Army Research Laboratory and the U. S. Army Research Office under grant number W911NF-14-1-0359.

## Cyclopentadienyl Photodissociation Dynamics at 248 nm

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The cyclopentadienyl radical plays an integral role in understanding both the thermal decomposition and the molecular growth of aromatic hydrocarbons during combustion reactions. Experimental characterization of the photodissociation dynamics of cyclopentadienyl at 248 nm provides a means of studying the important unimolecular chemistry of this radical species. In addition to the commonly discussed propargyl + acetylene channel, we provide evidence for the  $C_5H_4 + H$  dissociation pathway. The photoproduct translational energy distributions for these two channels are determined, and suggest that each process occurs *via* a statistical ground state mechanism that begins with the opening of the  $C_5H_5$  ring. Experimental and RRKM branching ratios overwhelmingly favour the propargyl + acetylene channel, with a small contribution of H-loss.

## **Photodissociation of vibrationally excited CO<sub>2</sub> at 205-230 nm: Boltzmann vs. Franck-Condon effects**

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University of Southern California, Los Angeles, CA

Photodissociation dynamics of hot CO<sub>2</sub> plays a key role in combustion, atmospheric processes, and in Venus and other exo-planets. Vibrationally excited CO<sub>2</sub> at temperatures up to 1800 K was studied using Resonance Enhanced Multiphoton Ionization (REMPI). Detection of hot CO<sub>2</sub> was achieved by 3+1 REMPI via the  $3p^1\Pi_u$  state at 325 nm to confirm the extent of vibrational excitation in the CO<sub>2</sub> molecule. The increasing absorption cross section to excited electronic states compensates for the decreasing Boltzmann population of excited vibrational levels in the heated CO<sub>2</sub> pyrolysis pulsed nozzle. The CO and O dissociation products have been studied in a separate experiment. The highly vibrationally excited CO<sub>2</sub> absorbs radiation even up to 300 nm making it possible to directly access several close-lying excited states whose interactions and dissociation mechanism(s) are not yet fully understood.

Photodissociation of  $\text{C}_2\text{H}_4\text{BrCl}$  as a Precursor to  $\text{C}_2\text{H}_4\text{X}$ : Several Excited-State Pathways and Radical Dissociation Channels

Preston G. Scrape, Jonathan D. Adams, and Laurie J. Butler

The James Franck Institute and Department of Chemistry, The University of Chicago,  
Chicago, Illinois 60637, United States

We photodissociate  $\text{CH}_2\text{BrCH}_2\text{Cl}$  and  $\text{CHBrClCH}_3$  at 193 nm as photolytic precursors to four haloethyl radicals in a crossed laser-molecular beam scattering apparatus. The photoproduct time-of-flight distributions provide evidence for several competing excited-state channels, which can produce Br, Cl, HBr, and HCl. Some of the haloethyl radicals are also formed in an electronic excited state; TD-DFT calculations suggest that this excited state is weakly bound, with a relatively large C-X bond length. The data further allow us to characterize the dissociation behavior of vibrationally hot haloethyl radicals. The radicals  $\text{CH}_2\text{BrCH}_2$  and  $\text{CH}_2\text{ClCH}_2$  overwhelmingly dissociate to X + ethene, providing evidence against a hypothetical  $\text{HX}$  + vinyl channel. Interestingly, the radicals  $\text{CHBrCH}_3$  and  $\text{CHClCH}_3$  are found to dissociate to  $\text{HX}$  or to atomic halogen, despite the very large energetic barriers to these processes.

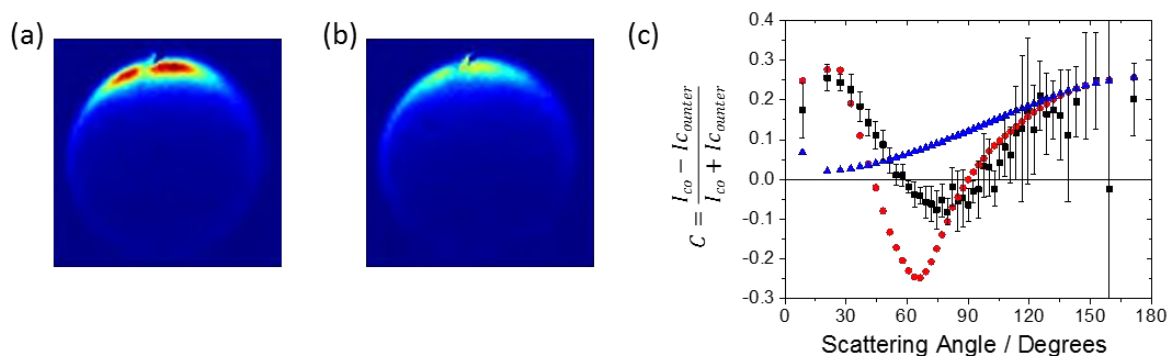
## Scattering-angle dependent orientation transfer: the $\mathbf{k}\text{-}\mathbf{j}\text{-}\mathbf{k}'\text{-}\mathbf{j}'$ correlation in $\text{NO}(\text{A}^2\Sigma^+) + \text{Ne}$ Rotational Energy Transfer

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We present the measurement of a four-vector correlation in rotational energy transfer (RET) in  $\text{NO}(\text{A}^2\Sigma^+) + \text{Ne}$  collisions, and compare our experimental measurements to quantum scattering calculations using a recently-calculated potential energy surface (PES) for this system. We spectroscopically prepare an oriented sample of  $\text{NO}(\text{A}; v = 0, N = 2, j = 1.5)$  in the crossing region of a crossed molecular beam velocity map imaging (CMB-VMI) apparatus, and measure the scattering angle dependence of the orientation of the scattered products. These measurements reveal the angular correlation between the initial angular momentum ( $\mathbf{j}$ ) and final angular momentum ( $\mathbf{j}'$ ) of the  $\text{NO}(\text{A})$  and, uniquely, the dependence of this correlation on the angle between the initial relative velocity ( $\mathbf{k}$ ) and final relative velocity ( $\mathbf{k}'$ ) of the collision partners. The measurement of such a  $\mathbf{k}\text{-}\mathbf{k}'\text{-}\mathbf{j}\text{-}\mathbf{j}'$  has long been a goal in the study of the dynamics of RET processes, and provides novel insights into the collision stereodynamics.



(a) and (b): Velocity map images of  $\text{NO}(\text{A}; v = 0; N' = 5)$  recorded with the pump and probe light in co- (a) and counter- (b) rotating geometries. (c): Experimentally measured sum-normalized difference in intensity between co- and counter- rotating geometries as a function of scattering angle (black squares) compared to quantum scattering calculations (red circles) and the kinematic apse model (blue triangles).

The above figure shows velocity map images of  $\text{NO}(\text{A}; v = 0; N' = 5)$  generated through scattering with Ne at a mean collision energy of  $683 \text{ cm}^{-1}$ . The two images are recorded with circularly polarised probe light of opposite handedness, and the differences between them result from the orientation of the molecules following collision. We compare the scattering angle dependence of the measured orientation for  $\text{NO}(\text{A}; v = 0; N' = 4 - 9)$  to the predictions of quantum scattering calculations on the RCCSD(T) PES of Cybulski and Fernández<sup>1</sup> and to a classical hard-shell (kinematic apse) model of the scattering. The quantum scattering calculations reproduce the qualitative features of this scattering angle dependence, which are in marked disagreement with hard shell predictions. We discuss our observations in the context of our recently-published measurements of strong deviations from hard-shell behaviour in the alignment generated in  $\text{NO}(\text{A}) + \text{Rg}$  collisions.

<sup>1</sup>Cybulski and Fernández, *J. Phys. Chem. A* **116**, 7319 (2012).

## PROBING THE SITE-RESOLVED STRUCTURE AND FUNCTION OF A LIQUID INTERFACE BY REACTIVE ATOM SCATTERING

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Descriptions of solid interfaces, including metals and oxides, are well developed and provide an understanding of their chemical and physical activities in exquisite detail down to the atomic level. However, a similar description of a liquid interface in terms of sites with varying structure and function has yet to be developed. The description of a relatively disordered and fluctuating liquid interface has been limited by existing experimental techniques, which provide information on highly averaged characteristics of the interface but do not allow detection of specific molecular conformations and therefore an understanding of site-specific activity. We have moved toward a detailed description of a model vacuum-liquid interface by studying the F-atom scattering dynamics on a common ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. Our data demonstrate that the dynamical behavior and yield of reactively scattered hydrogen fluoride can resolve distinct signatures of the cation methyl, imidazolium-ring, and butyl groups when given contrast by isotopic labeling. These experimental signatures reveal the dominant conformational ordering of the cation at the interface and the identity and abundance of a cation conformational defect. Additional information on the site-dependent reactivity of the incident atoms and the site-dependent solvation of the reactive products is also contained in these signatures.

# Accelerating *Ab Initio* Simulations of Molecular Dynamics

Prof. Ryan P. Steele

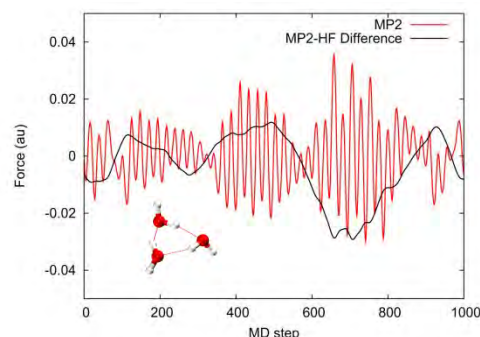
Henry Eyring Center for Theoretical Chemistry

University of Utah

Molecular dynamics simulations, based on an underlying potential from quantum chemistry methods, offer the possibility of determining real-time chemical dynamics in cases of strong polarization, charge transfer, bond-making/breaking, and even non-adiabatic effects. This presentation will cover new developments in the acceleration of these simulations for dynamics and spectroscopy.

The methods developed in this work fall under the heading of “multiple-timestep” methods, in which separable pieces of potential energies (or forces) are updated on different timescales throughout an MD trajectory. Such approaches have been used extensively in force field-based simulations, but they are (superficially) not transferable to electronic structure theory. We have discovered several avenues to remove this restriction and thereby extend the range of applicability of AIMD toward multiple-timestep methods. The field of EST employs several common approximations, all of which are amenable to these splittings, including the  $n$ -electron expansion (electron correlation), the 1-electron expansion (basis sets), many-body decompositions, and even the evaluation of electron-repulsion integrals. Recent extensions to including nuclear quantum effects will also be discussed.

Finally, application of these methods to chemical systems with challenging electronic structures will be discussed. Namely, oxidized water clusters,  $(H_2O)_n^+$ , and water in the presence of strong (but simple) oxidants will be presented.



## Relevant Publications

### Signatures of Size-Dependent Structural Patterns in Hydrated Copper(I) Clusters, $Cu^+(H_2O)_n$

J.D. Herr and R. P. Steele, *J. Phys. Chem. A*, **120**, 10252-10263 (2016)

### Quantum Molecular Motion in the Mixed Ion-Radical Complex, $[(H_2O)(H_2S)]^+$

S. D. Floris, J. J. Talbot, M. J. Wilkinson, J. D. Herr and R. P. Steele, *Phys. Chem. Chem. Phys.* **18**,

### Accelerating *Ab Initio* Molecular Dynamics Simulations by Linear Prediction Methods

J. D. Herr and R. P. Steele, *Chem. Phys. Lett.* **661**, 42-47 (2016) “Editor’s Choice” Article

### Ion-Radical Pair Separation in Larger Ionized Water Clusters, $(H_2O)_n^+$ , $n=6-21$

J. D. Herr and R. P. Steele, *J. Phys. Chem. A* **120**, 7225-7239 (2016)

### Accelerating *ab initio* path integral simulations via imaginary multiple-timestepping

X. Cheng,\* J.D. Herr,\* and R. P. Steele, *J. Chem. Theor. Comput.* **12** 1627-1638 (2016)

### Multiple-timestep *ab initio* molecular dynamics using an atomic basis set partitioning

R. P. Steele, *J. Phys. Chem. A* **119** 12119 (2015)

\*Invited Article for “Dynamics of Molecular Collisions XXV: Fifty years of chemical reaction dynamics” Issue

### Multiple-timestep *ab initio* molecular dynamics based on two-electron integral screening

S. Fatehi and R. P. Steele, *J. Chem. Theor. Comput.* **11** 884-898 (2015)

### Nuclear Motion in the $\sigma$ -Bound Limit of Metal- $H_2$ Complexes: $[Mg(H_2)_{n=1-6}]^{2+}$

B. Mitchell and R. P. Steele, *J. Phys. Chem. A* **118** 10057-10066 (2014)

### Communication: Multiple-timestep *ab initio* molecular dynamics with electron correlation

R. P. Steele, *J. Chem. Phys.* **139**, 011102 (2013).

**Poster Title:****Oxidation Dynamics of 8-Oxoguanine by Singlet Molecular Oxygen Using Guided-Ion Beam Scattering and Density Functional Theory**

Yan Sun (presenter),<sup>a,b</sup> Wenchao Lu,<sup>a,b</sup> and Jianbo Liu<sup>a,b</sup>

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**Abstract:**

8-Oxo-7,8-dihydro-2'-deoxyguanosine (8-oxodGuo) is one of the most common DNA lesions resulting from reactive oxygen species and ionizing radiation, and is involved in mutagenesis, carcinogenesis, and cell death. Notably, 8-oxodGuo is more reactive toward singlet ( $a^1\Delta_g$ )  $O_2$  than the undamaged guanosine, and the lesions arising from the secondary oxidation of 8-oxodGuo are more mutagenic. In this poster the  $^1O_2$  oxidation dynamics of free base 8-oxoguanine (8-oxoG) was presented at different initial conditions including protonated  $[8\text{-oxoG} + H]^+$ , deprotonated  $[8\text{-oxoG} - H]^-$ , and their monohydrates. Experiment was carried out on a guided-ion beam scattering tandem mass spectrometer coupled with electrospray ionization source. Measurements include the effects of collision energy ( $E_{col}$ ) on reaction cross sections over a center-of-mass  $E_{col}$  range from 0.1 to 0.5 eV. The aim of this study is to quantitatively probe the sensitivity of the early stage of 8-oxoG oxidation to ionization and hydration states. Density functional theory and Rice–Ramsperger–Kassel–Marcus calculations were performed to identify the intermediates and the products along reaction pathways and locate accessible reaction potential energy surfaces, and to rationalize reaction outcomes from energetic and kinetic points of view. No product was observed for the reaction of  $[8\text{-oxoG} + H]^+ \cdot (H_2O)_{0,1} + ^1O_2$  because insurmountable barriers block the addition of  $^1O_2$  to reactant ions. Neither was  $[8\text{-oxoG} - H]^-$  reactive with  $^1O_2$ , in this case due to the rapid decay of transient intermediates to starting reactants. However, the nonreactivity of  $[8\text{-oxoG} - H]^-$  toward  $^1O_2$  was inverted by hydration of the reactant ions; as a result, 4,5-dioxetane of  $[8\text{-oxoG} - H]^-$  was captured as the main oxidation product. Reaction cross section for  $[8\text{-oxoG} - H]^- \cdot H_2O + ^1O_2$  decreases with increasing  $E_{col}$  and becomes negligible above 0.3 eV, indicating that the reaction is exothermic and has no barriers above reactants. The contrasting oxidation behaviors of  $[8\text{-oxoG} + H]^+ \cdot (H_2O)_{0,1}$  and  $[8\text{-oxoG} - H]^- \cdot (H_2O)_{0,1}$ , which are closely relevant to the pH dependence of 8-oxoG oxidation in aqueous solution, are interpreted in terms of different  $^1O_2$  addition pathways.

Photodissociation of hot CO<sub>2</sub> in 205-230 nm: Imaging studies of CO(X<sup>1</sup>Σ<sup>+</sup>) and O(<sup>3</sup>P, <sup>1</sup>D) products.

Subhasish Sutradhar, Bibek R. Samanta, Amit K. Samanta, Hanna Reisler.

Department of Chemistry

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### **Abstract**

Vibrationally hot CO<sub>2</sub> plays an important role in combustion and hydrocarbon flames. Vibrationally excited CO<sub>2</sub> is found to be a major element in the environment of hot planets (400-2500 K) like Mars and Venus. Studies of the UV photodissociation and product state distributions of thermally activated CO<sub>2</sub> are important to model hydrocarbon flame dynamics and the atmospheres of hot planets. Photodissociation of carbon dioxide is negligible at energies below 6 eV ( $\lambda > 200$  nm) due to small absorption cross sections. The absorption cross section at  $\lambda > 200$  nm increases rapidly with temperature. Elevated temperatures can give access to different product channels even at  $\lambda > 200$  nm. In this work photodissociation of hot CO<sub>2</sub> is studied at  $\lambda > 200$  nm using time-sliced Velocity Map Imaging. CO(X<sup>1</sup>Σ<sup>+</sup>, v=0) produced from photodissociation of hot CO<sub>2</sub> at  $\lambda > 230.1$  nm has been identified using 2+1 REMPI in a one-color experiment. O(<sup>3</sup>P) and O(<sup>1</sup>D) cofragments associated with CO(X<sup>1</sup>Σ<sup>+</sup>) are detected using 2+1 REMPI around 225.6 nm and at 205.47 nm, respectively. The kinetic energy distributions of CO (X<sup>1</sup>Σ<sup>+</sup>, v=0) products show considerable vibrational excitation in the parent CO<sub>2</sub> molecule. The kinetic energy distributions obtained by monitoring O(<sup>3</sup>P) and O(<sup>1</sup>D) products indicate the formation of rovibrationally hot CO (X<sup>1</sup>Σ<sup>+</sup>) cofragments.

## Accurate calculation of vibrational states of substituted ozone in full configuration space

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In this work we present calculations of bound and resonances states of substituted ozone in the full configuration space that has three covalent minima, three dissociation channels and six transition states. The necessity to include all molecular configurations is justified by the fact that as soon as at least one atom is substituted for a heavier isotope, the threefold permutation symmetry of the system is lost and one-well calculation is not sufficient to obtain complete vibrational states. An accurate calculation of those states and their lifetimes for different rotational excitations will allow to compute rate coefficient of ozone forming recombination reaction for different isotopologues and study puzzling anomalous isotope effect in ozone. The isotopologues examined in this study are singly and double substituted molecules  $^{50}\text{O}_3$  and  $^{52}\text{O}_3$ . The method for calculation of vibrational states is based on hyperspherical coordinates, sequential diagonalization-truncation approach, generation of optimal grid for dissociative coordinate, symmetric top approximation for rotation and complex absorbing potential technique to extract resonance widths.<sup>1</sup> Recently, we applied our method to unsubstituted ozone molecule  $^{48}\text{O}_3$ , where only one covalent minima was included, and found it to closely reproduce an absolute value of recombination rate coefficient as well as its pressure and temperature dependences.<sup>2</sup>

The figure on the right demonstrates examples of three-well resonance states for  $^{50}\text{O}_3$ . The rovibrational state belongs either to symmetric molecule with  $^{18}\text{O}$  as a central atom (top panel), or to asymmetric molecule with  $^{18}\text{O}$  as a terminal atom (two other panels). The resonance states exhibit complex nodal structure and large-amplitude motion.

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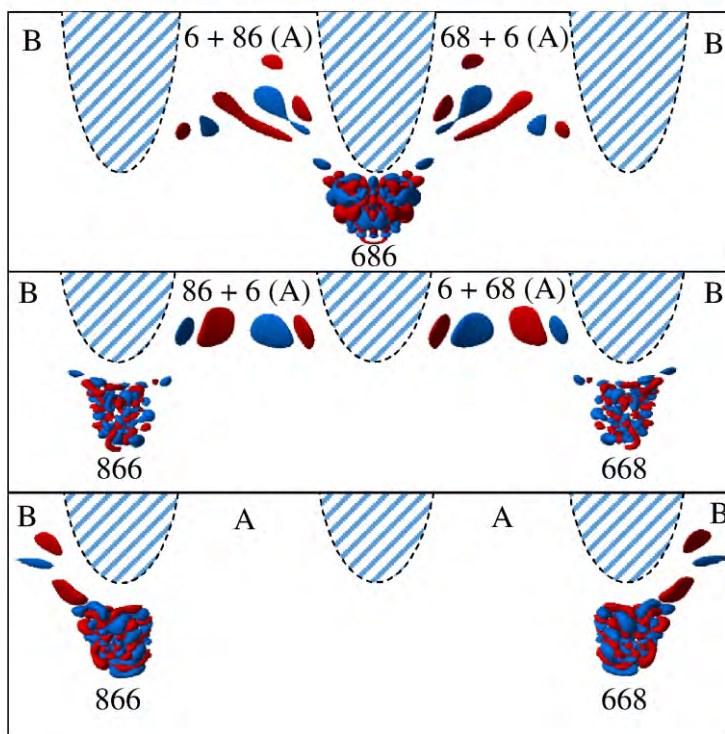


Fig. 1. Types of three-well resonance states of  $^{50}\text{O}_3$  isotopologue: single-well state of symmetric molecule (top panel) and double-well state of asymmetric molecule decaying into channel A, where  $\text{O}_2$  is heteronuclear (middle panel), or into channel B, where  $\text{O}_2$  is homonuclear (bottom panel). The molecule is in a typical rotational state  $J = 24$   $K = 2$ .

## Cold state-selected radicals for the study of low temperature chemistry

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In Zeeman deceleration, time-varying spatially-inhomogeneous magnetic fields are used to create packets of translationally cold, quantum-state-selected paramagnetic particles with a tuneable forward velocity, which are ideal for cold reaction dynamics studies.

Here, the covariance matrix adaptation evolutionary strategy (CMA-ES) is adopted in order to optimise deceleration switching sequences for the operation of a Zeeman decelerator. Using the optimised sequences, a 40% increase in the number of decelerated particles is observed compared to standard sequences for the same final velocity, imposing the same experimental boundary conditions. Furthermore, we demonstrate that it is possible to remove up to 98% of the initial kinetic energy of particles in the incoming beam, compared to the removal of a maximum of 83% of kinetic energy with standard sequences. Three-dimensional particle trajectory simulations are employed to reproduce the experimental results and to investigate differences in the deceleration mechanism adopted by standard and optimised sequences. It is experimentally verified that the optimal solution uncovered by the evolutionary algorithm is not merely a local optimisation of the experimental parameters – it is a novel mode of operation that goes beyond the standard periodic phase stability approach typically adopted.

Ultimately, we seek to combine the decelerator with an ion trap to undertake collision studies between paramagnetic species and trapped ions. The design of a new magnetic guide to select decelerated particles travelling at a specific velocity whilst filtering out the rest of the beam is presented. The guide, made of a series of permanent hexapole magnets, is predicted by numerical particles trajectory simulations to yield a pure beam of state-selected particles.

Prompt release of O <sup>1</sup>D products  
upon UV excitation of CH<sub>2</sub>OO Criegee intermediates\*

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The photodissociation dynamics of the simplest Criegee intermediate CH<sub>2</sub>OO in the long wavelength tail region (364 to 417 nm) of the B<sup>1</sup>A' – X<sup>1</sup>A' spectrum was investigated using velocity map imaging (VMI).<sup>1</sup> Following UV excitation, the O <sup>1</sup>D products associated with the primary H<sub>2</sub>CO X<sup>1</sup>A<sub>1</sub> + O <sup>1</sup>D product channel are detected by 2+1 REMPI. The anisotropic angular distributions of the O <sup>1</sup>D images indicate that dissociation occurs faster than the rotational period of CH<sub>2</sub>OO (ps). The anisotropy implies that the broad oscillatory structure in the long wavelength region of the UV spectrum is due to short-lived resonances associated with the excited B<sup>1</sup>A' state that decay by nonadiabatic coupling to repulsive singlet states. The total kinetic energy release distributions show that the available energy is nearly equally partitioned, on average, between product translational energy and internal excitation of the H<sub>2</sub>CO co-fragments. The anisotropy and energy partitioning are unchanged with excitation wavelength, and consistent with previously reported experimental and theoretical findings of the CH<sub>2</sub>OO B-X transition moment and dissociation energy to H<sub>2</sub>CO X<sup>1</sup>A<sub>1</sub> + O <sup>1</sup>D products.<sup>2,3</sup>

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# Femtosecond time-resolved vector-correlations in CH<sub>3</sub>I photolysis: the role of nonadiabatic interactions and internal rotation

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As was realized many years ago, angular momentum correlations play a significant role in molecular photodissociation. Molecular interactions always occur through anisotropic forces and give rise to anisotropic angular momentum distributions which may have relation to approach direction, scattering direction, photon polarization, etc [1].

We report the results of experimental and theoretical study of time-resolved vector correlations in the femtosecond photolysis of polyatomic molecules by predissociation and direct dissociation mechanisms [2]. Experimentally, the photolysis of methyl iodide (CH<sub>3</sub>I) via the B-band at 201.2 nm has been studied [3]. Time-dependent anisotropy parameters  $\beta_i$  has been determined from fragment angular distributions using the pump-probe technique coupled with the velocity map imaging detection of the dissociation products CH<sub>3</sub>(v=0) and I\*(<sup>2</sup>P<sub>1/2</sub>). The results obtained were theoretically interpreted with a quantum mechanical quasiclassical theory which took into account the alignment of CH<sub>3</sub> photofragments orbital momentum, nonadiabatic interaction between the <sup>3</sup>R<sub>1</sub> and <sup>3</sup>A<sub>1</sub>(E) excited states, excited state symmetries, the parent molecule rotation during dissociation, and the CH<sub>3</sub> fragment rotation after the bond break. The time-dependent vector correlations were described by a set of the anisotropy transforming coefficients  $c_{K,q}^K$  [4,5].

The results obtained demonstrate an important role of the molecular orbital angular momentum alignment and molecular rotation on the time-dependent photolysis. Comparison between the photolysis via the predissociative <sup>3</sup>R<sub>1</sub> and direct dissociative <sup>3</sup>A<sub>1</sub>(E) excited states showed the profound role of the predissociation mechanism. The <sup>3</sup>R<sub>1</sub> and <sup>3</sup>A<sub>1</sub>(E) excited state lifetimes, anisotropy transforming coefficients, parent molecule beam temperature, and molecular rotation angles were determined from the experimental data.

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# Interfacial Solvation and Surface pH of Phenolic Aqueous Nanoaerosols Probed via Aerosol VUV Photoelectron Spectroscopy

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## Abstract

While water is the primary species constituting clouds, presence of organic species- either of anthropogenic- or biogenic- origins may drastically alter the cloud formation microphysics as well as the compositions and nature of the clouds. As the atmospheric and/or sea spray aqueous aerosols begin to exert their chemical activities from their liquid/air interfaces, the valence electronic structures and interfacial solvation properties of organic-containing aqueous aerosols are of crucial importance in assessing their impacts in the atmospheric processes. Among numerous organic species, phenol and phenolic compounds represent a major resource of secondary organic aerosols (SOA) in the atmosphere. Here, we applied the recently built aerosol VUV photoelectron spectroscopy [1,2] to investigate for the first time the valence photoelectron spectroscopy of phenol and three dihydroxybenzene (DHB) isomers including catechol, resorcinol and hydroquinone in the aqueous nanoaerosol form, using the undulator-based VUV radiation as the ionization source (BL21B2, NSRRC) [3]. By evaluating two photoelectron features of the lowest vertical ionization energies (VIE) originated from the  $b_1(\pi)$  and  $a_2(\pi)$  orbitals for phenolic aqueous nanoaerosols, their pH-dependent valence electronic structures and interfacial solvation characteristics are unraveled. Both phenol and phenolate are highly surface-active. On the aqueous aerosol interface, they appear only partially solvated, with the hydrophilic  $-OH/-O-$  group better immersed in water and the hydrophobic aromatic ring remaining above the interface of aqueous aerosols. Deprotonations of phenolic species accompanying with increasing pH appear to enhance the hydration extent, likely due to the stronger solute-solvent interactions between the negatively charged  $-O^-$  group and water solvent molecules. A significant fraction of neutral phenol is observed along with phenolate at pH of 12.0, indicating that the chemical composition and surface pH at the aqueous aerosol interface deviate from the bulk. The surface pH of phenol aqueous nanoaerosols is estimated  $\sim 2.2 \pm 0.1$  units more acidic than the bulk interior. By tracking the electronic evolutions for phenol and all three DHB isomers from the gaseous phase to the condensed, aqueous nanoaerosol phase, we show that the first ionization energy of phenolic species may be lowered with: 1) increasing degrees of hydration, 2) increasing extents of deprotonation, 3) increasing pH, and 4) increasing numbers of  $-OH$  group, thus allowing them to remove the outermost electrons more readily upon phenolic oxidation. This study provides new insights to understand the valence electronic properties and interfacial solvation of amphiphilic phenol and DHB in the nanoaerosols. Moreover, owing to the surface-sensitivity, the aerosol VUV photoelectron spectroscopy technique also provides a novel way to characterize the surface pH for nanoscaled aqueous aerosols.

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## Imaging Ethylene Sulfide Photodissociation at 217 nm

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The photodissociation dynamics of ethylene sulfide have been studied extensively at 193 nm as well as its electronic absorption spectra in the UV and VUV regions. The molecule is a sulfur containing heterocycle belonging to the  $C_{2v}$  point group which has a ground state  $A_1$  symmetry. The UV absorption studies found several series of Rydberg transitions all of which converge to the first ionization threshold. In the UV spectrum, a peak at 192 nm was assigned to the  $4p_x \leftarrow 3p_x$  transition with  $A_1$  overall symmetry. The source of peaks around 200 – 220 nm was obscure but tentatively assigned to the 4s and 4p states, both are having  $B_1$  symmetry and perhaps of mixed valence-Rydberg character.

In the current work we investigate ethylene sulfide photodissociation at 217 nm. The reason for choosing this specific wavelength is the probing scheme we introduced earlier for  $S(^1D_2)$  detection, which is a 1+1 REMPI at 217 nm. At this wavelength,  $S(^1D_2)$  undergoes one photon excitation to the  $S(^3S)$  intermediate state prior to ionization. Therefore, a one-color pump-probe experiment could readily be performed. The sulfur fragments are then detected using the DC slice imaging technique.

The velocity distribution of the sulfur shows compelling differences compared to that seen earlier at 193 nm. Although the image shows three regions just as at 193 nm, here the angular distributions are perpendicular in our measurements as opposed to parallel at 193nm. We discuss these results in light of high level ab initio calculations of the excited states.

## Demonstration of Multi-hit and Multi-mass capability of 3D Imaging in a conventional Velocity Map Imaging experiment

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Coincidence and 3D ( $x, y, t$ ) imaging has been a highlight in many experiments in past few decades and several methods have been introduced. The basic concept behind all these approaches is to register the position ( $x, y$ ) at which the particle hits the detector and the arrival time ( $t$ ). A novel advance to the time and position sensitive detection was introduced recently by Li, Lee and coworkers. This method utilizes a high-speed digitizer and a computer algorithm designed using Labview language along with the other components used in conventional velocity map imaging apparatus. An inexpensive fast frame camera captures position information while the PMT (photomultiplier tube) through a high speed digitizer records the arrival times of each and every ion. The key factor that enables 3D imaging process is the natural distribution of intensities of ion spots from the microchannelplate (MCP). Due to these intensity variations a correlation can be made and it is possible to assign each ion spot position to their respective arrival times, thereby constructing a 3D distribution.

The technique was primarily introduced for ultrafast ion and electron imaging experiments at high repetition rate. We have recently succeeded in adapting this approach at low repetition rate. The results will be demonstrated in OCS photodissociation at 217 nm. Modifications were done to the initial setup to enhance the acquisition efficiency to attain multi-hits per laser shot rather than single-hit events. The PMT could not be used to obtain timing signal since our phosphor (P47) decay time is long (40 ns) for the PMT to distinguish multiple hits accurately. Therefore, the timing information was taken from the back plate of the MCP. The results show multi-mass multi-hit detection ability with up to 20 events correlated in a single camera frame. Moreover, temporal and spatial slicing capabilities are achieved with good resolution to yield the photofragment velocity and angular distribution in all three planes and for multiple masses simultaneously.

## Dynamics of Molecular Collisions 2017 Poster Abstract

### Resolving the Energy and Temperature Dependence of $C_6H_6^*$ Collisional Relaxation via Time-Dependent Bath Temperature Measurements

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The relaxation of highly vibrationally excited benzene, generated by 193 nm laser excitation, was studied using the transient rotational-translational temperature rise of the  $N_2$  bath, which was measured by proxy using two-line Laser Induced Fluorescence (LIF) of seeded NO. The resulting experimentally measured time-dependent  $N_2$  temperature rises were modeled with MultiWell based simulations of Collisional Energy Transfer (CET) from benzene Vibration to  $N_2$  Rotation-Translation (V-RT). Previously, we found that the average energy transferred in benzene deactivating collisions depends linearly on the internal energy of the excited benzene molecules and depends approximately linearly on the  $N_2$  bath temperature between 300 K and 600 K. The results were consistent with experimental studies and classical trajectory calculations of CET in similar systems. To further examine the dependence of benzene CET on bath temperature, our current experiments are extending the range of initial temperatures of the  $N_2$  bath to between ~58 K – 300 K.

## Geometric Phase Effects in Nonadiabatic Tunneling

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The Born-Oppenheimer (BO) approximation plays an important role in the conventional quantum mechanical description of molecular spectroscopy and reaction dynamics. However, near an electronic degeneracy such as a conical intersection (CI), the BO approximation is inadequate due to the non-zero nonadiabatic couplings (NACs).<sup>1</sup> Even when the dynamics occurs at energies much lower than the CI, such as the tunneling-facilitated photodissociation of phenol ( $S_1$ ),<sup>2</sup> the adiabatic model still fails. This is because a real-valued adiabatic electronic wavefunction changes sign when the system encircles the CI in a closed loop, which makes the wavefunction double valued.<sup>3-5</sup> This sign change ( $-1 = e^{i\pi}$ ) is due to the geometric phase (GP),<sup>3-5</sup> which has to be included in an adiabatic treatment.

Our recent study on the tunneling-facilitated photodissociation of phenol ( $S_1$ ) with a reduced-dimensional model showed that the BO model cannot properly describe the tunneling as it yielded lifetimes two orders of magnitude shorter than the exact ones.<sup>2</sup> In addition, the adiabatic model fails to reproduce a unique nodal structure in the dissociating wavefunction outside the CI. To understand this surprising result, we have established several two-dimensional (2D) adiabatic models, in which the GP is introduced using the vector potential method of Mead and Truhlar.<sup>5</sup> To converge the results, the finite basis representation (FBR) was used to solve the Schrödinger equation in the presence of the singularity at the CI.<sup>6</sup>

Our calculations demonstrated that the failure of the adiabatic model in describing tunneling near a CI can be attributed largely to the neglect of the GP.<sup>6</sup> The GP results in destructive interference between “trajectories” passing around the CI on the opposite sides. This interference leads to the nodal structure and can significantly retard the tunneling. The inclusion of the GP in the BO Hamiltonian leads to much better agreement with the exact results.<sup>6-7</sup> Interestingly, constructive interference can also occur when the coupling mode is excited with odd quanta.<sup>8</sup>

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# Temperature Dependent Study of Microscopic Spectral Diffusion Using Isotopomer-Selective, Background-free IR-IR Double Resonance of Iodide Dihydrate

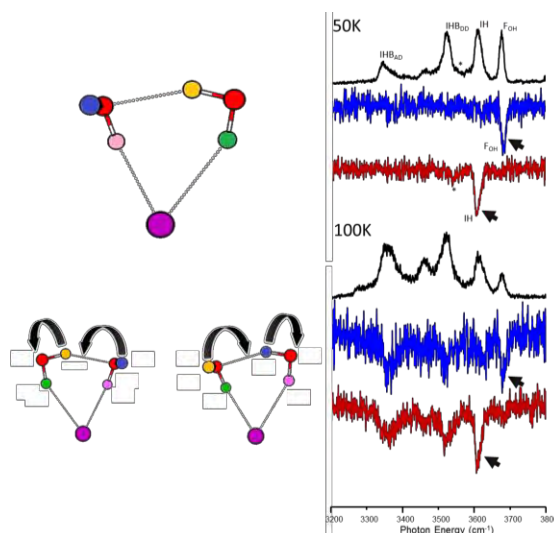
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In aqueous solution, the characteristic time of spectral diffusion associated with water molecules around a halide ion solutions is around 15 ps, much shorter than that reported in pure water. The slower component of spectral diffusion has been attributed to the exchange between ionic hydrogen bonded OH oscillators and inter-water H-bonded OH oscillators. These process has been explained by a molecular jump mechanism involving the exchange of water molecules in the first hydration shell with those in the second shell. This study focuses on the microscopic understanding of spectral diffusion by exploiting the well defined structure and clearly distinguishable OH oscillator frequencies in small anionic water clusters. In particular, the onset of spectral diffusion is observed in mass selected and temperature controlled gas phase clusters of microhydrated halide ions. This is accomplished through trace isotope labeling and double resonance hole burning experiments carried out on a newly developed background free, dual laser, cryogenic ion spectrometer at Yale.

Specifically, the system of interest here is  $\text{I}^-(\text{H}_2\text{O})_2$ , which has four different OH fundamentals. In the  $\text{I}^-(\text{D}_2\text{O})(\text{HDO})$  isopologue, there are four isotopomers that each have a unique location of the single OH oscillator. Large amplitude librational motion of the labeled water molecule then interchange the frequencies of the OH group. Thus, by pumping different isotopomers while monitoring one specific isotopomer, the interconversion between isotopomers can be observed as spectral features from other isotopomers appear in the probed isotopomer.

Moreover, by gradually increasing the temperature, the internal energy required for different types of large amplitude motions that interconvert OH group positions can be determined. The onset of spectral diffusion was observed at around 75 K. Interestingly, the single OH appears to be interchanged with all other OH positions, suggesting that this temperature is sufficient to access multiple pathways for interconversion. These results are analyzed by comparison with calculated trajectories on a realistic potential energy surface, revealing the likely pathways for interconversion.

# Towards Quantum-State-Resolved Ion-Molecule Chemistry

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We are working towards a new platform for quantum-state-resolved ion-molecule chemistry by utilizing a combination of cryogenic buffer gas cooling, laser-cooled ion sympathetic cooling, and integrated mass spectrometry in an RF Paul trap. Cold molecular species produced in a cryogenic buffer gas beam collide with target atomic ions in an linear quadrupole trap. Ion imaging and time of flight mass spectrometry are then used to observe the resulting reaction rates and products. We can utilize the precision control over quantum states allowed by this neutral-plus-ion chemistry environment (N+ICE) to study state-resolved quantum chemical reactions without high-density molecular sample production. We report progress towards cold carbon and water chemistry, including co-trapping and sympathetic cooling of carbon ions with laser-cooled beryllium ions.

# DYNAMIC TIME-RESOLVED CHIRPED-PULSE ROTATIONAL SPECTROSCOPY OF VINYL CYANIDE PHOTOPRODUCTS IN A ROOM TEMPERATURE FLOW REACTOR

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Chirped-pulsed Fourier transform millimeter-wave (CP-FTmmW) spectroscopy is an attractive tool for gas phase chemical dynamics and kinetics studies. A good reactor for such a purpose would have well-defined (and variable) temperature and pressure conditions to be amenable to accurate kinetic modeling. Furthermore, in low-pressure samples with a large enough number of molecular emitters, reaction dynamics can be observable directly, rather than mediated by supersonic expansion. In the present work, we describe *in situ* time-resolved CP-FTmmW spectroscopy in a room temperature flow tube reactor. Vinyl cyanide ( $\text{CH}_2\text{CHCN}$ ), neat or mixed with an inert gas, flows through the reactor at pressures 1–50  $\mu\text{bar}$  (0.76–38 mTorr) where it is photodissociated by a 193 nm laser. The millimeter-wave beam of the CP-FTmmW spectrometer co-propagates with the laser beam along the reactor tube and interacts with nascent photoproducts. Rotational transitions of HCN, HNC, and HCCCN are detected with  $\geq 10 \mu\text{s}$  time-steps for 500 ms following photolysis of  $\text{CH}_2\text{CHCN}$ . The post-photolysis evolution of the photoproducts' rotational line intensities is investigated for the effects of rotational and vibrational thermalization of energized photoproducts. Furthermore, the branching ratios of the observed photoproducts are found to compare favorably with new modelling of vinyl cyanide unimolecular decomposition. Calculated reaction pathways will be discussed, and possible contributions from bimolecular and wall-mediated chemistry will be briefly touched on.

# Vibrational Non-adiabaticity in the $\text{H} + \text{DOH} \rightarrow \text{HD} + \text{OH}$ reaction: A Full Dimensional Quantum Study at the State-to-state Level

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Mode-selectivity and bond-specificity in polyatomic reactions have always been an important goal of physical chemists aiming to control reaction dynamics. Four-atom reactions represent the minimalist prototype involving reactants with multiple vibrational modes. In this aspect, such systems are becoming the proving ground of quantum reaction dynamics.<sup>1, 2</sup> As pointed out by Zare and co-workers in their experimental study of the  $\text{H} + \text{DOH}$  reaction,<sup>3</sup> three factors influence the mode selectivity: (1) preparation of vibrational excitation in reactants, (2) reactant remains in its vibrational state, (3) efficacy of the mode in promoting the reaction.

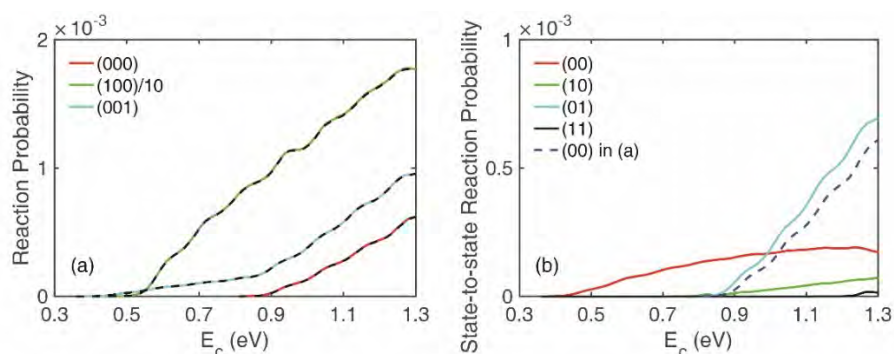


Figure. Reaction probabilities of the  $\text{H} + \text{DOH}(\nu_{\text{OD}}, \nu_{\text{b}}, \nu_{\text{OH}}) \rightarrow \text{HD} + \text{OH}$  reaction with  $J_{\text{tot}}=0$  as a function of collision energy. (a) Total reaction probabilities with DOH reactant in three different vibrational states from flux operator (solid color) and sum of state-to-state reaction probabilities (dashed black). (b) Product vibrational state ( $\nu_1, \nu_2$ ) resolved reaction probabilities from the OH excited DOH (001).

Here, we focus on the second factor by presenting a full-dimensional quantum study of the title reaction at the state-to-state level. The OH bond in the DOH reactant is commonly considered as a spectator in the title reaction, which has been confirmed in experiment at a collision energy of 1.5 eV.<sup>4</sup> However, we report here an interesting behavior of the OH vibration when it is excited. Instead of preserving its initial vibrational excitation, as expected for a spectator, the energy deposited in OH bond may be utilized in promoting the reaction. As shown in above Figure, at a collision energy below 0.9 eV, the OH product is formed solely in the ground vibrational state, which suggests that the OH vibrational energy in DOH(001) is channeled into the reaction coordinate, violating vibrational adiabaticity via intramolecular vibrational energy transfer (IVR). To stimulate future experiment, 3D polar plot of differential cross sections (DCS) will be presented.

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# A Transition-State Based Rotational Sudden (TSRS) Approximation for Polyatomic Reactive Scattering

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Transition-state plays the decisive role in determining how reactants reach the barrier and form products during a chemical reaction. Here we propose a transition-state based rotational sudden (TSRS) approximation in calculating integral cross section (ICS) and differential cross section (DCS) with the scattering S-matrix of vanishing total angular momentum and the geometry of the transition-state. In the TSRS approximation, which can be viewed as an extension of the established J-shifting scheme,<sup>1</sup> we assume separability of rotational and vibrational motions of the molecular system. Different partial waves are approximated by the rotational states of the molecular system fixed at the transition state geometry. Two formulas of the TSRS approximation in both scattering frame and molecular frame are derived for the calculation of ICS and DCS. The choice of the frames is determined by the moment of inertia tensor of the system in the transition-state geometry.

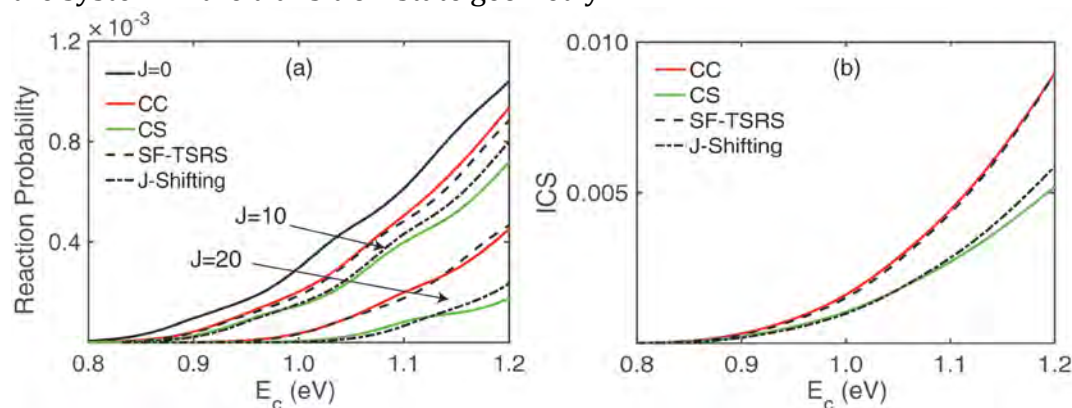


Figure Demonstration of the TSRS approximation on reaction probabilities (with total angular momentum  $J=0,10,20$ ) and ICS of the  $H+H_2O(000) \rightarrow H_2+OH$  reaction. The results obtained from the scattering frame based TSRS (SF-TSRS) and traditional J-shifting are compared to the close-coupling (CC) and centrifugal sudden (CS) ones.

As an example, total reaction probabilities and ICS of the  $H+H_2O(000) \rightarrow H_2+OH$  reaction are shown in above figure, in which the SF-TSRS results agree well with the accurate CC result while the ones from traditional J-shifting scheme are close to the approximate CS results. More examples will be presented in order to test the validity of the TSRS approximation and the applicability will be explained with the help of the moment of inertia tensor.

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## Dynamics of HCl scattering from Au(111)

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The scattering of energetic HCl from Au(111) has been extensively investigated using molecular beams in high vacuum, and significant vibrational inelasticity and translational energy loss have been found in the scattered HCl.<sup>[1-3]</sup> Theoretically, dynamical simulations based on the rigid surface approximation cannot describe the energy transfer between the gaseous molecule and the surface. Ab initio molecular dynamics (AIMD) approaches can give good characterization of the scattering, dissociation, and energy transfer process, but they require a very large number of DFT calculations, thus unable to give good statistics.

Recently, our group developed a high-dimensional HCl-Au(111) interaction potential energy surface (PES) with movable Au surface atoms,<sup>[4]</sup> using the Behler–Parrinello atomistic neural network (AtNN) approach.<sup>[5]</sup> A total of 115,000 DFT energy points covering a large coordinate space far away from equilibrium was fit to the AtNN PES, with a root-mean-square fitting error of 15 meV. Classical trajectory calculations for the scattering of DCl from Au(111) on this PES were found to reproduce the AIMD data, with about 10<sup>5</sup>-fold acceleration.<sup>[6]</sup>

The availability of the PES allows us to explore the dynamics of HCl scattering from Au(111), aiming to gain a more in-depth understanding of the latest state-to-state scattering experiments.<sup>[3]</sup> The calculations were performed with a quasi-classical trajectory (QCT) method, initiated with the HCl molecule located far above the surface ( $Z=7.0$  Å) with different ro-vibrational states. More than ten thousand trajectories were calculated to guarantee good statistics for vibrational inelastic trajectories. The calculations show small excitation probabilities about several percent for HCl( $v=0 \rightarrow v=1$ ) and HCl( $v=1 \rightarrow v=2$ ), comparable with those in the experiment. The calculated scattering angular distributions peak at super-specular angles with narrower widths than those in experiment.

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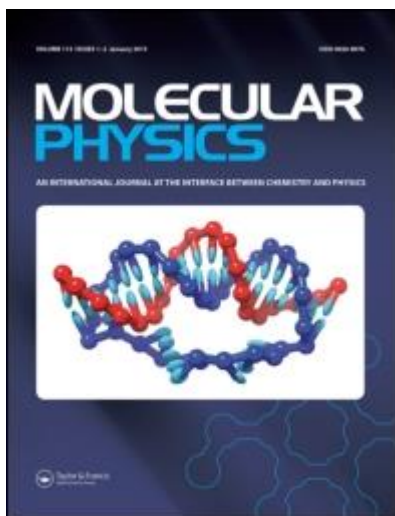
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