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RPPR Final Report
as of 24-Apr-2019

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STEM Degrees:

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Major Goals: The goal of this proposal was to support the 25th Conference n the Dynamics of Molecular Collisions, which was held at Asiolomar Conference Center in Pacific Grove CA, July 12-17, 2015.

Accomplishments: This proposal provided support for students and post-docs to attend the Conference on the Dynamics on Molecular Collisions (DMC). DMC has formed a unique platform for researchers in reaction dynamics and has witnessed its phenomenal growth over the years. The first DMC was held in 1965 in New Hampton, New Hampshire and was chaired by Professor John Fenn, the 2002 Nobel Prize recipient for his work in developing electrospray ionization methods that efficiently introduce biological molecules into molecular beams. The chairman of the second meeting was Professor John Polanyi, the 1986 winner of the Nobel Prize in Chemistry for his work on reaction dynamics. Professor Polanyi shared this Nobel Prize with Professor Dudley Herschbach of Harvard and Professor Y. T. Lee of University of California Berkeley. Professor Lee chaired the seventh DMC meeting in 1978 held at Pacific Grove in California and was the keynote speaker in the 25th DMC held this yearend supported by this proposal. The DMC has also played a key role in educating graduate students and postdoctoral researchers entering this field. It has also served as a gathering place for international cooperation and exchange, and strongly advanced interaction between theorists and experimentalists.

The conference was extremely successful, with over 120 attendees from many countries around the world, many of whom were students and junior researchers supported by this proposal.

Training Opportunities: Nothing to Report

Results Dissemination: The conference was celebrated with a special issue of the Journal of Physical Chemistry published December, 2015. This issue featured 64 papers reporting state-of-the-art results growing out of the meeting.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

RPPR Final Report

as of 24-Apr-2019

Accomplishments – Support for the 25th Conference on the Dynamics of Molecular Collisions

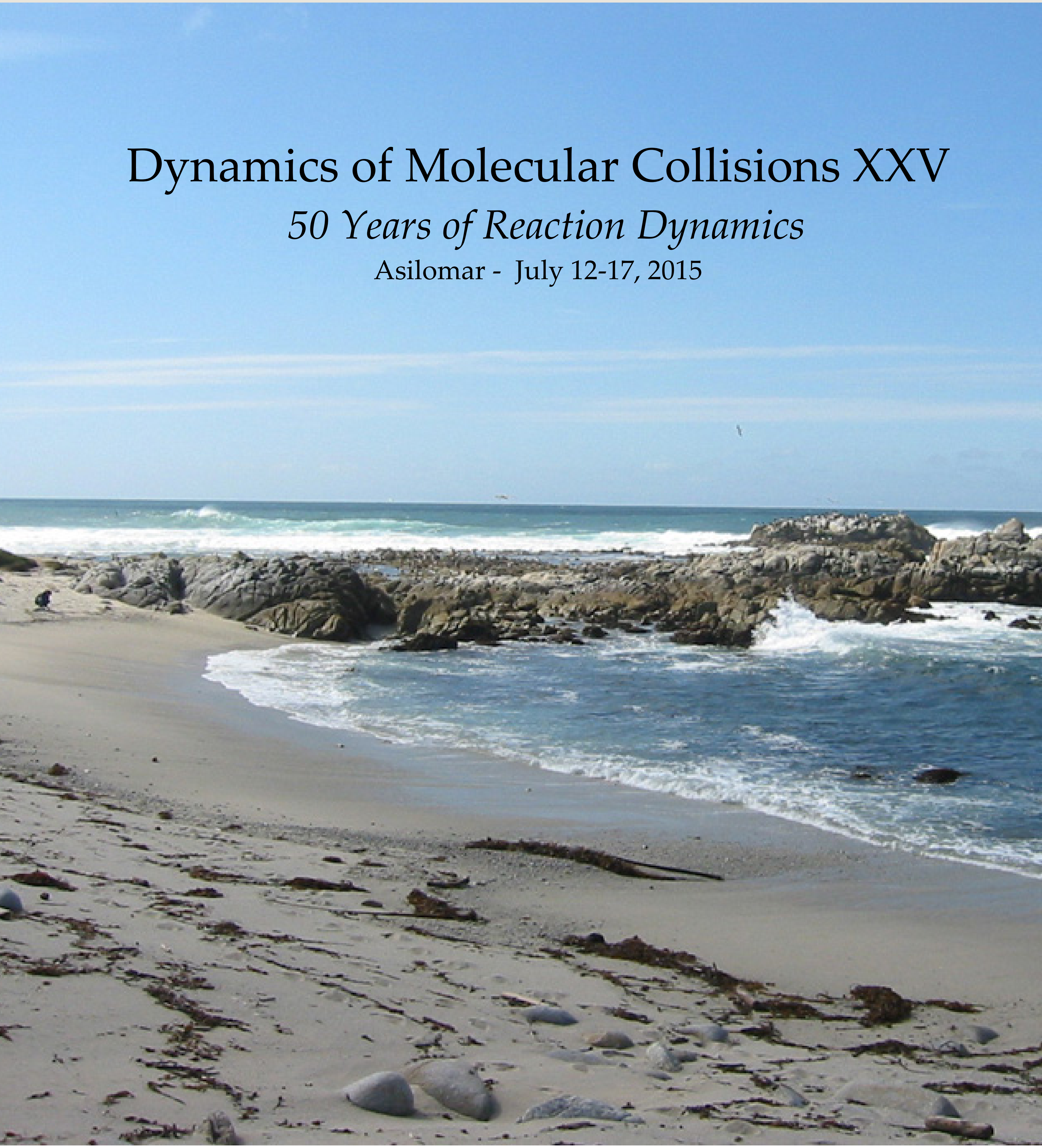
PI Arthur G. Suits

We attach here the book of abstracts that accompanied the meeting.

Dynamics of Molecular Collisions XXV

50 Years of Reaction Dynamics

Asilomar - July 12-17, 2015



Arthur Suits, Chair **David Yarkony, Co-chair**

2015 Dynamics of Molecular Collisions Conference

Asilomar Conference Center – Pacific Grove, California
July 12 – 17, 2015

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

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

Dynamics of Molecular Collisions XXV

July 12-17, 2015
Asilomar Conference Center
Pacific Grove, California

All meals served in Crocker Dining Hall

Lectures will be held in the Chapel

Poster sessions in Evergreen and Oak Shelter

Sunday

4:00	Registration - Chapel
6:00	Dinner
7:00	Reception/Bonfire – Fire Pit

Monday

AM1 *Quantum Collisions*

8:00	Welcome – Arthur Suits, Wayne State University
8:15	H. Floyd Davis, Cornell University
8:30	David Chandler, Sandia CRF *“Imaging the Dynamics of Collision Induced Dissociation”*
9:10	Todd Martinez, Stanford University *“Discovering Chemistry with an Ab Initio Nanoreactor”*
9:50	Coffee
10:20	Donghui Zhang, Dalian Institute of Chemical Physics *"Quantum Dynamics Studies of Differential Cross Sections for Polyatomic Reactions"*
11:00	Amy S. Mullin, University of Maryland *“Dynamics of Optically Centrifuged Molecules in High Angular Momentum States”*
11:20	Robert W. Field, Massachusetts Institute of Technology “*Rydberg Spectroscopy on Steroids: What Can Rydberg States Tell Us about Electron-Ion Collisions?*”
12:00 pm	Lunch
1:00	Free Time
3:30	Refreshments - Chapel

Monday – continued

4:00 Hot topics: Poster Previews
Vanessa Murray, Montana State University
“*Dynamics of Hyperthermal Atomic-oxygen Interactions with Hot Carbon Surfaces – from 675 K to 2200 K*
Huilin Pan, Academia Sinica
“*Imaging the steric effects in Cl + aligned-*$CH_4(v_3 = 1)$*”*
Linsen Pei, University of Rochester
“Velocity Map Imaging Study of Reactions of Carbon Hydrogen Radicals with Cations”
Marissa Weichman, University of California, Berkeley
“High-resolution photoelectron imaging and infrared photodissociation spectroscopy of cryo-cooled anions”
Ralph Welsch, California Institute of Technology
“*Non-equilibrium Ring-Polymer Molecular Dynamics”*
Xiaolei Zhu, Johns Hopkins University
“*A Unified, Efficient Approach to Constructing Quasi-Diabatic Representations of Accurate Wave Functions”*

5:00 Keynote: Y.T. Lee, IAMS, Academia Sinica
“Fifty years of Reaction Dynamics”

PM1 Atmospheric and Astrochemistry

7:00 Anne McCoy, Ohio State

7:15 Ian Sims, University of Rennes
“Molecular collisions in cold supersonic flows: kinetics meets dynamics in the service of astrochemistry”

7:55 R. Benny Gerber, Hebrew Universoty,
“*Mechanisms and Dynamics of Atmospheric Molecular Reactions at Surfaces of Liquid Water and Ice*”

8:35 Marsha Lester, University of Pennsylvania
“Hydrogen transfer pathways for Criegee intermediates in tropospheric chemistry”

8:55 Nadia Balucani, University of Perugia,
"Product branching ratios and extent of intersystem crossing in atomic oxygen reactions with unsaturated hydrocarbons"

9:35 Posters

Tuesday

AM2 *Dynamics at Interfaces & in the Condensed Phase*

8:15	Gil Nathanson , University of Wisconsin
8:30	Ken McKendrick, Heriot-Watt *“'What can reactive-atom scattering reveal about the surface structure of ionic liquids?"*
9:10	Hua Guo, University of New Mexico “*Mode Specificity and Bond Selectivity in Polyatomic Dissociative Chemisorption on Transition Metal Surfaces*”
9:50	Ruth Signorell, ETH-Zurich *“Angle-resolved photoemission from neutral clusters and aerosol particles.”*
10:30	Coffee
11:00	Francesco Paesani, UC-San Diego *“Many-Body Molecular Dynamics: A “First Principles” Approach to Vibrational Spectroscopy in the Condensed Phase”*
11:40	Stephen Bradforth, USC *“Photoelectron processes in liquid water: scattering, ionization and new methods for probing elementary reactivity”*
12:20 pm	Lunch
1:00	Free Time

PM2 Navigating Complex Potential Energy Surfaces

7:00	Stephen Klippenstein, Argonne National Lab
7:15	Stephen Wiggins, University of Bristol *“Roaming: Dynamical Reaction Pathways in Phase Space”*
7:55	Keiji Morokuma, Emory University *"Automatic exploration of crossings of potential energy surfaces for photochemical and excited state reactions"*
8:35	Martin Stei, University of Innsbruck *“Imaging the Influence of the Leaving Group and of Vibrational Excitation on SN2 Reactions”*
8:55	Stuart Althorpe, Cambridge University “*Is there a quantum transition-state theory?”*
9:35	Posters

Wednesday

AM3 Nonadiabatic Dynamics

8:15 am	Simon North, Texas A&M
8:30	Spiridoula Matsika, Temple University *“Nonadiabatic events in photoinitiated processes in molecules”*
9:10	Sang-Kyu Kim, KAIST *“Spectroscopic characterization of the conical intersection in photodissociation reactions of thiophenol and thioanisole”*
9:50	Joseph Subotnik, University of Pennsylvannia *“Surface hopping: A Simple View of Electronic Transitions for Electrochemistry “*
10:30	Coffee
11:00	Graham Worth, Birmingham University *“Direct quantum dynamics simulations of reactions including non-adiabatic effects: DD-vMCG”*
11:40	Greg Hall, Brookhaven National Lab *“Collision-induced intersystem crossing: A talk on* CH_2*-*O_2 *that won't mention the Criegee Intermediate”*
12:20 pm	Lunch
1:30	Free Time

PM3 From Spectroscopy to Dynamics

7:00 pm	John Stanton, UT-Austin
7:15	Gary Douberly, University of Georgia *“Bimolecular Reactions in Helium Droplets”*
7:55	Craig Taatjes, Sandia-CRF *“Testing the intermediate steps in hydrocarbon oxidation”*
8:35	Michael Grubb, University of Bristol *“Into The Abyss: Perfluorinated liquids as an intermediate solvation environment between the gas and solution phases”*

8:55 Mark Johnson, Yale University
“Capturing and characterizing catalytic reaction intermediates with cryogenic ion spectroscopy”

9:35 Posters

Thursday

AM4 Ultracold Collisions

8:15 am Robin Cote, University of Connecticut

8:30 Eric Hudson, UCLA
“Towards quantum-state-resolved charged-neutral chemistry”

9:10 John Bohn, JILA
“Molecular Velcro: Sticking in Ultracold Atom Gases”

9:50 Coffee

10:20 Sebastian van der Meeraker, Radboud University
“Taming molecular collisions”

11:00 Ed Narevicius, Weizmann Insitute
“Molecular Rotor in Cold Reactions”

11:20 Tim Softley, Oxford University
“Cold reactive collisions using laser cooled ions”

12:00pm Lunch

1:00 Free Time

PM4 Herschbach Prize Session

7:30 Dan Neumark, UC-Berkeley

7:45 Carl Lineberger, JILA

“Anion Photoelectron Spectroscopy: From Radicals to the Reaction Co-ordinate”

8:30 Paul Dagdigian, Johns Hopkins

8:45 Millard Alexander, University of Maryland
"*The long (and continuing) saga of the inelastic scattering of* $^2\Pi$ *molecules (NO and OH)*

9:30 Posters

Friday

AM5 Complex Dynamics

8:15 Jingsong Zhang, UC-Riverside

8:30 Scott Anderson, University of Utah
"Chemistry on the surface of nanoparticles using beams and traps"

9:10 A. Jasper, Sandia-CRF
“Microcanonical Rate Coefficients for Unimolecular Reactions in the Low Pressure Limit”

9:50 Coffee

10:20 Claire Vallance, Oxford University
“Multimass imaging of complex molecular fragmentation processes"

11:00 Wen Li, Wayne State University
“3D Coincidence Ion/Electron Imaging with a Fast Frame Camera”

11:20 Larry Harding, Argonne National Lab
“Vinyl + O_2”

12:00 pm Depart

ABSTRACTS

INVITED / CONTRIBUTED TALKS

Determination and Modeling of the Collisional Energy Transfer Distribution Responsible for the Collision-Induced Dissociation of NO_2 with Ar.

Jeffrey D. Steill, Ahren W. Jasper and David W. Chandler
Sandia national laboratory, Livermore CA, 94550, chand@sandia.gov

Abstract.

Collisional energy transfer is an essential aspect of chemical reactivity and maintenance of thermal equilibrium. Knowledge of the distribution of internal and translational energies that are transferred in a bimolecular collision is required for accurate modeling of chemically reacting systems such as combustion. Due to the importance of this quantity many experiments have tried to measure the magnitude and shape of the collisional energy transfer function for various collision partners. In general, average energy transfer values have been obtained and in some specialized cases the shape of the energy transfer function has been partially determined. Here we report the shape of the entire energy transfer function for the final collision that causes dissociation of a molecule. We describe a set of experiments that yield the shape and relative magnitude of the collisional energy transfer function to highly vibrationally excited NO_2. In these experiments we photoexcite NO2 entrained in a molecular beam to within ~40 cm-1 of the dissociation threshold of the ground electronic state. This internally excited molecule then undergoes a single collision with a rare gas atom from a second atomic beam. Any collision that transfers more than ~40 cm^{-1} of translational energy into the NO2 molecule produces a molecule with sufficient energy to undergo rapid dissociation into NO(J) and O atom fragments. We use velocity-mapped ion imaging and REMPI techniques to quantify the kinetic and internal energies of the NO dissociation fragments of NO_2. This momentum- and quantum state-resolved measurement allows us to examine the detailed dynamics of the collision-induced dissociation (CID) process. We directly determine the collisional energy distribution from the experimental data using conservation of energy and a projection analysis method that relates the observed rotational energies and velocities of NO fragments to the initial collisional NO_2 excitation. In this manner we have experimentally determined the shape of the energy transfer function for collisionally induced dissociation of a highly internally excited molecule, the final step in a pyrolysis reaction.

Discovering Chemistry with an Ab Initio Nanoreactor

Todd J. Martínez
Department of Chemistry and The PULSE Institute, Stanford University
SLAC National Accelerator Laboratory, Menlo Park, CA

Traditional approaches for modeling chemical reaction networks such as those involved in combustion have focused on identifying individual reactions and using theoretical approaches to explore the underlying mechanisms. Recent advances involving graphical processing units (GPUs), commodity products developed for the videogaming industry, have made it possible to consider a distinct approach wherein one attempts to discover chemical reactions and mechanisms. We provide a brief summary of these developments and then discuss the concept behind the "ab initio nanoreactor" which explores the space of possible chemical reactions and molecular species for a given stoichiometry. The nanoreactor concept is exemplified with an example to the Urey-Miller reaction network which has been previously advanced as a potential model for prebiotic chemistry. We briefly discuss some of the future directions envisioned for the development of this nanoreactor concept.

Quantum Dynamics Studies of Polyatomic Chemical Reactions: From Gas-Phase to Gas-Surface

Dong Hui Zhang
State Key Laboratory of Molecular Reaction Dynamics
Dalian Institute of Chemical Physics, CAS, Dalian, China 116023
e-mail: zhangdh@dicp.ac.cn

Abstract

The past decade has witnessed significant progress on quantum dynamics studies on polyatomic chemical reactions. The success on the calculation of differential cross sections (DCS) for the HD+OH → H_2O+D reaction in full six dimensions[Science **333**, 440 (2011)], in unprecedented agreement with experiment, declares the four-atom reactive scattering problem is largely solved. In this talk, I will first present some recent developments on computing DCS for polyatomic reactions. A reduced dimensionality quantum reactive scattering theory was developed to calculate DCSs for the $H+CD_4$ and $H+SiH_4$ reactions, with six degrees of freedom included. It is found that the DCS for the $H+CD_4 \rightarrow HD+CD_3$ reaction is largely independent on the rotational state of CD_3, while the DCS for the $H+SiH_4 \rightarrow H_2+SiH_3$ reaction is strongly dependent on the rotational state of SiH_3. Consequently, excellent agreement between theory and experiment on DCS is only obtained for the $H+CD_4$ reaction, but is much difficult for the $H+SiH_4$ reaction, due to lack of rotational information for the CD_3 and SiH_3 in the experiment. I will then show some preliminary results on quantum dynamics studies of chemisorptions of H_2O on Ni(100) surface in full nine dimensions, which can sever as a benchmark for reduced dimensionality quantum studies as well as for quasiclassical trajectory calculations.

Dynamics of Optically Centrifuged Molecules in High Angular Momentum States

Amy S. Mullin, Matthew J. Murray, Hannah M. Ogden and David Burns

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 data indicate that centrifuged molecules act as molecular gyroscopes with a propensity to retain the direction of their angular momentum vectors over the period of many collisions. Doppler-broadened transient line profiles for individual rotational states show that collisions of centrifuged molecules occur with small ΔJ values and lead to large translational energy increases. Recent improvements in experimental design have resulted in increased signal levels, thereby enabling access to the earlier time dynamics for a broader range of rotational states. Recent results on CO and CO_2 offer a comparison of dynamics for molecules with $J_{max}=50$ and $J_{max}=200$, respectively.

Rydberg Spectroscopy on Steroids: What Can Rydberg States Tell Us about Electron-Ion Collisions?

Yan Zhou, David Grimes, Tim Barnum, Barratt Park, Ethan Klein, Stephen Coy, Anthony Colombo, Kirill Prozument, and Robert W. Field

Department of Chemistry, Massachusetts Institute of Technology

Electrons are light; nuclei are heavy. How can energy and angular momentum be transferred between the Rydberg electron and the molecular ion-core? There are two flavors of Rydberg states. In *core-penetrating* states, the electron makes a very hard collision with the ion-core once every Kepler orbit period. In *core-nonpenetrating* states, the electron never collides with the ion-core, but it undergoes resonant, long-range, inelastic interactions with the ion-core via multipole moments and polarizabilities. Multichannel Quantum Defect Theory provides an "all states, all dynamics" physical representation of the multiple infinities of discrete and continuum Rydberg states.

The combination of Chirped Pulse millimeter-Wave spectroscopy with a buffer gas cooled ablation source yields a factor of $\sim 10^6$ increase in "spectral velocity" over "indirect" fluorescence- and ionization-detected schemes. Detection is "direct" via Free Induction Decay. Direct detection is multiplexed. Each 20 GHz chirp at 50 kHz resolution reports 400,000 resolution elements of spectrum. To deal with a deluge of spectroscopic data, powerful real-time assignment schemes are required; foremost among them is "Stark demolition." The strength of each physical mechanism for energy exchange between the Rydberg electron and the ion-core is encoded in a distinct, *a priori* predictable region of state space, the access to which is guided by quantum number scaling rules. Spectroscopy is just another name for scattering at negative energy.

Every molecule has Rydberg states. Clever schemes are required to access them.

This work is supported by grants from the National Science Foundation.

50 Years of Reaction Dynamics

Yuan T. Lee
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It was exactly half a century ago that I received my Ph.D. degree and started my adventure into the field of molecular collisions and chemical dynamics. In this lecture, I will try to describe my personal experiences and perspectives, especially when I was in my young, tender, trying age, and my engagement in the global scientific activities in recent years.

Molecular collisions in cold supersonic flows: kinetics meets dynamics in the service of astrochemistry

Ian R. Sims

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Traditionally, dynamics studies of molecular collisions have been seen as providing a superior test of theoretical models compared to kinetics studies, typically yielding information for which some aspect of thermal averaging has been removed. I hope to show that low temperature kinetics studies performed under carefully controlled conditions can also provide an interesting and insightful challenge to theory, and are highly complementary to dynamics studies.

The use of the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique[1] has enabled us to show that many neutral-neutral reactions may be rapid down to the temperatures of dense interstellar clouds (10—20 K), as well as proving an exacting test for theory.[2] Rate coefficients have been measured as low as 6 K for the reaction $S(^1D) + H_2$.[3] The technique has also been applied to the formation of transient complexes of interest both in atmospheric chemistry[4] and combustion.[5]

Recent results will be presented in two areas of interest for astrochemistry. A series of fast barrierless reactions related to the formation of long chain cyanopolyyne molecules $H(C_2)_nCN$,[6] of interest in both interstellar clouds and Titan's atmosphere, have been studied. The $F + H_2 \rightarrow HF + H$ reaction, on the other hand, does possess a substantial energetic barrier ($\circeq$ 800 K), but is the only source of interstellar HF. I will report direct experimental measurements of the rate of this reaction down to a temperature of 11 K, where essentially all reactivity is due to quantum mechanical tunneling. The results are in remarkable agreement with state-of-the-art quantum reactive scattering calculations by François Lique and Millard Alexander.[7]

[1] I. R. Sims, J. L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B. R. Rowe and I. W. M. Smith, *J. Chem. Phys.*, 1994, **100**, 4229.
[2] H. Sabbah, L. Biennier, I. R. Sims, Y. Georgievskii, S. J. Klippenstein and I. W. M. Smith, *Science*, 2007, **317**, 102.
[3] C. Berteloite, M. Lara, A. Bergeat, S. D. Le Picard, F. Dayou, K. M. Hickson, A. Canosa, C. Naulin, J. M. Launay, I. R. Sims and M. Costes, *Phys. Rev. Lett.*, 2010, **105**, 203201.
[4] S. D. Le Picard, M. Tizniti, A. Canosa, I. R. Sims and I. W. M. Smith, *Science*, 2010, **328**, 1258.
[5] H. Sabbah, L. Biennier, S. J. Klippenstein, I. R. Sims and B. R. Rowe, *J. Phys. Chem. Lett.*, 2010, **1**, 2962.
[6] S. Cheikh Sid Ely, S. B. Morales, J. C. Guillemin, S. J. Klippenstein and I. R. Sims, *J. Phys. Chem. A*, 2013, **117**, 12155.
[7] M. Tizniti, S. D. Le Picard, F. Lique, C. Berteloite, A. Canosa, M. H. Alexander and I. R. Sims, *Nature Chemistry*, 2014, **6**, 141.

Dynamics of Molecular Collisions, Asilomar – July 12-17, 2015

Mechanisms and Dynamics of Atmospheric Molecular reactions at Surfaces of Liquid Water and Ice

R. Benny Gerber [(a), (b), (c)]

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Abstract of Lecture

Reactions at surfaces of liquid water and of ice play an enormous role in the chemistry of the atmosphere. The quest for molecular understanding of such processes is very challenging due to the complexity of systems. Development of sufficiently realistic yet computationally feasible models is essential for adequate microscope description of the processes involved.

In the research, Molecular Dynamics simulations using direct potentials from quantum chemical methods are used to explore the mechanisms of several atmospherically relevant reactions at water and at ice surfaces. In several of the processes, water is involved as a reagent, while in others the water medium catalyzes or inhibits the process.

Specific reactions studied include: (1) Reaction of the ion pair (NO^+) (NO^-_3) with water to produce the atmospherically important HONO and HNO_3. (2) The ionization of the acids HNO_3 and HI on the Quasi-Liquid Layer of ice. (3) The reaction of impacting HCl from the gas phase with N_2O_4 and N_2O_5 adsorbed on liquid water surfaces. These reactions produce ClNO and $ClNO_2$, precursors of atomic chlorine. (4) Proton transfer in $(HCl)_n$ $(H_2O)_n$ clusters, a system of multiple proton donors and acceptors. (5) the reaction of CO_2 impacting on water clusters to produce H_2CO_3.

The role of the hydrogen-bonding network in these reactions is highlighted. The adequacy of small water clusters as models for extended surfaces for some of the processes is analyzed.

Hydrogen transfer pathways for Criegee intermediates in tropospheric chemistry

Fang Liu, Nathanael M. Kidwell, Hongwei Li, Yi Fang, and Marsha I. Lester
Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104-6323

Ozonolysis of alkenes is an important non-photolytic source of OH radicals in the troposphere. The production of OH radicals proceeds though formation and unimolecular decay of carbonyl oxides species, known as Criegee intermediates. Alkyl-substituted Criegee intermediates with an α-H are predicted to undergo an intramolecular 1,4-H atom transfer via a ring-like transition state to form vinyl hydroperoxides, which quickly breaks apart to release OH radical products. This laboratory has focused on IR activation of *syn*-CH_3CHOO and $(CH_3)_2COO$ in the CH overtone region to surmount the barrier, and follow the subsequent unimolecular decay dynamics to OH products.[1,2] Most recently, the OH product internal and translational energy distributions have been characterized, the latter utilizing state-selective ionization and velocity map imaging.[3] The images reveal an isotropic angular distribution, indicating that unimolecular decay is slower than the rotational period ($\tau \geq 2$ ps) of *syn*-CH_3CHOO. In addition, the kinetic energy distribution reveals that most of the available energy is released as internal excitation of the vinoxy co-fragments. Finally, an organic acid catalyzed tautomerization reaction is shown to efficiently convert alkyl-substituted Criegee intermediates with an α-H to vinyl hydroperoxides.[4] A doubly hydrogen-bonded interaction between the Criegee intermediate and carboxylic acid facilitates hydrogen transfer through a double hydrogen shift in a nearly barrierless process.[5] Deuteration of the organic acid results in migration of a D atom to form deuterated vinyl hydroperoxides, which are distinguished from the Criegee intermediates by mass using 10.5 eV photoionization. The generation and identification of stabilized vinylhydroperoxides will enable further investigation of the OH production mechanism from alkene ozonolysis in tropospheric chemistry.

1. F. Liu, J. M. Beames, A. S. Petit, A. B. McCoy, and M. I. Lester, Science 345, 1596 (2014).
2. F. Liu, J. M. Beames, and M. I. Lester, J. Chem. Phys. 141, 234312 (2014).
3. N. M. Kidwell, H. Li, X. Wang, J. M. Bowman, and M. I. Lester, manuscript in preparation (2015).
4. F. Liu, Y. Fang, M. Kumar, W. H. Thompson, and M. I. Lester, submitted for publication (2015).
5. M. Kumar, D. H. Busch, B. Subramaniam, and W. H. Thompson, Phys. Chem. Chem. Phys. 16, 22968 (2014).

Product branching ratios and extent of intersystem crossing in atomic oxygen reactions with unsaturated hydrocarbons

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Because of their relevance in combustion, the rate coefficients for the reactions between ground state ^3P oxygen atoms and unsaturated hydrocarbons have been determined in kinetics experiments as a function of temperature. Much less is known, instead, on the chemical identity of the primary products and their branching ratios (BRs). This piece of information is fundamental, however, because the products of one elementary reaction are the reactants of a subsequent one in the complex scheme of elementary reactions that account for the global combustion process [1]. For multichannel reactions like these, the primary products and their BR are not easy to predict because intersystem crossing (ISC) from the triplet to the underlying singlet potential energy surface (PES) can occur, opening up other reaction channels not accessible on the triplet PES. The quantification of ISC as a function of temperature is a demanding task which requires an experimental or theoretical investigation.

For this reason, following the pioneering work of Y.T. Lee and coworkers [2], we have undertaken a systematic experimental investigation of this class of reactions by means of the crossed molecular beam technique [3] with mass spectrometric detection empowered by soft electron impact ionization.

Results on the reactions of atomic oxygen with alkynes (ethyne and propyne) and alkenes (ethene, propene, 1-butene) will be presented.

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Reactive-Atom Scattering at Liquid Surfaces: Probing Surface Structure through Collision Dynamics

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We are developing reactive-atom scattering (RAS) as a new method to probe the extreme outer layers of liquids. The approach builds on our earlier work on the fundamental mechanisms of collisions of gas-phase radicals with model hydrocarbon liquid and related surfaces. We are now applying these methods to characterize the surfaces of room-temperature ionic liquids (RTILs), a class of materials of both great fundamental and practical interest. In many of their potential applications in, for example, multiphase catalysis and gas separation where gases must transit the gas-liquid interface, the composition of the ionic-liquid outer surface is crucial.

Our current applications are based on RAS using $O(^3P)$ atoms to locate specific groups at the liquid surface. We use complementary experimental approaches based on either laser photolysis or laser detonation to produce $O(^3P)$ atoms with medium or high kinetic energies, respectively. In the medium-energy experiments, the relative yields, internal state distributions and translational energies of the nascent OH products that escape the surface are characterized by laser-induced fluorescence. In the high-energy experiments, mass spectrometric detection provides highly resolved kinetic energy and angular scattering distributions of the reactive OH and other potential products and of inelastically scattered O atoms.

These experiments yield both fundamental insight into the dynamics of the collisions and detailed information on the composition and organization of the liquid surface. We are able to quantify, in particular, the extent to which alkyl chains on the organic cation are exposed to attack by the incoming atoms. We have investigated systematically the family of liquids based on 1-alkyl-3-methylimidazolium cations [1]. We will describe the effects of alkyl chain length and anion volume on the surface properties of single-component RTILs, and in mixtures containing cations with different alkyl chain lengths. The interpretation is enhanced by new molecular dynamics simulations of the liquid structures and by measurements of their physical properties, neutron scattering, and X-ray scattering carried out by our collaborators.

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Mode Specificity and Bond Selectivity in Polyatomic Dissociative Chemisorption on Transition Metal Surfaces

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Dissociative chemisorption is the initial and often rate-limiting step of many important heterogeneous catalytic processes such as ammonia synthesis, steam reforming, and water gas shift reaction. A complete understanding of these processes at the microscopic level is important for a predictive model of catalysis. Recent molecular beam experiments have indicated strong mode specificity and bond selectivity in the dissociative chemisorption of polyatomic molecules such water and methane.[1-3] These observations suggest that all forms of energy are not equal in activating the reactions, which as a result cannot be treated with statistical models.

We will discuss quantum dynamical models for dissociative chemisorption of water and methane on high-dimensional potential energy surfaces constructed by accurate fits of many density functional theory points over the relevant configuration space.[4] These first-principles quantum dynamical investigations successfully reproduced,[5] and in some cases predicted,[6-8] experimental observations, highlighting the importance of dynamics in the experimentally observed mode specificity and bond selectivity. In this talk, we will focus on our recent full-dimensional simulations of water dissociative chemisorption on Ni(111),[9] and discuss the site-specific dynamics and dependence on incident angles.

We further discuss a simple model for predicting mode specificity and bond selectivity in reactions both in the gas phase and between gas molecules and surfaces.[10-12] This Sudden Vector Projection (SVP) model is based on the premise that the collision is much faster than the intramolecular vibrational energy redistribution (IVR) in the reactants. It further assumes that the ability of a reactant mode in promoting the reaction is proportional to its coupling strength with the reaction coordinate at the transition state. This is approximated by the projection of the reactant normal mode vector onto the reaction coordinate vector. The SVP model is used to interpret and predict mode specificity and bond selectivity in dissociative chemisorption reactions.[13-14]

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Angle-resolved photoemission from neutral clusters and aerosol particles

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Light interacts differently with small particles compared with bulk materials or gas phase molecules, producing spectral signatures that strongly depend on particle properties, such as size, shape, or architecture. Our studies focus on a specific class of particles, namely on neutral molecular aggregates that are held together by weak intermolecular forces. We use various spectroscopic methods for the characterization of these aggregates. In this talk, I concentrate on the interaction of ultraviolet light with clusters and nanosized aerosol particles. Three examples are discussed. In the first one, we use angle-resolved photoelectron spectroscopy to probe the structure of sodium nanosolutions. In the second example, we suggest angle-resolved photoemission of aerosol particles as a new way to determine the mean free path of electrons in solids and liquids. In the last example, we combine a uniform Laval expansion with VUV ionization and mass spectrometric detection to study gas phase nucleation at the molecular level.

Many-Body Molecular Dynamics: A “First Principles” Approach to Vibrational Spectroscopy in the Condensed Phase

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Vibrational spectroscopy is a powerful technique to probe the structure and dynamics of water. However, deriving an unambiguous molecular-level interpretation of the experimental spectral features remains a challenge due to the complexity of the underlying hydrogen-bonding network. In this contribution, we present an integrated theoretical and computational framework (named many-body molecular dynamics or MB-MD) which, by systematically removing uncertainties associated with existing approaches, enables a rigorous modeling of vibrational spectra of water from quantum dynamical simulations. Specifically, we extend approaches used to model the many-body expansions of interaction energies to develop many-body representations of the dipole moment and polarizability of water. The combination of these “first principles” representations with centroid molecular dynamics simulations enables the simulation of infrared and Raman spectra of liquid water at ambient conditions that, without relying on any ad hoc parameters, are in good agreement with the corresponding experimental results. Importantly, since the many-body energy, dipole, and polarizability surfaces employed in the simulations are derived independently from accurate fits to correlated electronic structure data, MB-MD allows for a systematic analysis of the calculated spectra in terms of both electronic and dynamical contributions. If time allows, extensions of MB-MD to ionic solutions will also be described.

Photoelectron processes in liquid water: scattering, ionization and new methods for probing elementary reactivity

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Understanding how the electronic structure of an aqueous solute is intricately bound up with the arrangement of the host liquid provides insight into how chemical reactions are influenced by the environment in which they take place. In this talk, I will provide illustrations of these interconnections and describe how new experimental probes can uncover how the solute electronic structure changes during bond breaking, proton transfer and redox reactions.

In the last few years our groups have exploited liquid jet photoelectron (PE) spectroscopy to learn about the orbital energies (and shapes) in pure water, for textbook aqueous inorganic ions and the components of DNA and peptides. [1,2] Such techniques also hold promise for probing chemistry of solutes to varying depths below the water/gas interface, of significance for atmospheric processes. This probing depth is itself intrinsically wrapped up with fundamental electron-water interactions. [3,4] Such scattering interactions are of importance in modeling the passage of ionizing radiation through water-rich media such as those occurring in cellular radiation damage. Recently, we have implemented liquid jet PE spectroscopy with femtosecond time resolution. The non-equilibrium evolution of the valence orbitals involved in a several fundamental solution-phase reactions has been tracked; results show that PE spectroscopy provides new insights into liquid phase reactivity.

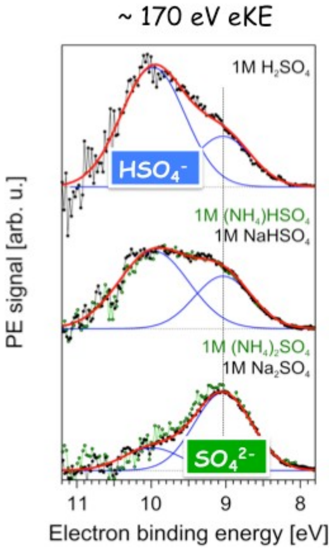

Figure: Depth-dependent speciation in sulfuric acid can be obtained from photoelectron spectra as a function of outgoing PE kinetic energy.

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Roaming: Dynamical Reaction Pathways in Phase Space

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Quoting from a well-known article of Bowman and Suits (J. M. Bowman and A. G. Suits, Roaming Reactions :The Third Way, *Physics Today*, **64**(11), 33 (2011)):

> *Only until very recently it was believed that chemical reactions can occur only by two fundamental ways: i) dissociation over a potential energy barrier and ii) stretching of a bond until it breaks. However, in 2004 a "third way" was discovered, which has been given the name "roaming".*.

In my talk I will discuss the idea of "roaming" from a phase space perspective. In particular, roaming is described as an alternate reaction pathway in phase space that is guided by specific types of phase space structures. I will illustrate this by considering roaming in formaldehyde and demonstrating the existence of the phase space structures that "select" between roaming and dissociating trajectories. If time permits, I will discuss the generality of this approach and roaming in other systems (e.g. ketene isomerization, ion-molecule reactions).

All of the ideas in this talk were developed in collaboration with Peter Collins and Frederic Mauguiere (University of Bristol), Gregory S. Ezra and Zeb Kramer (Cornell University), Stavros Farantos (University of Crete), Barry Carpenter (Cardiff University). This work was supported by the UK Engineering and Physical Sciences Research Council, the US National Science Foundation, the Leverhulme Trust, and the US Office of Naval Research.

AUTOMATIC EXPLORATION OF CROSSINGS OF POTENTIAL ENERGY SURFACES FOR PHOTOCHEMICAL AND EXCITED STATE REACTIONS

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Photochemical reactions start on an excited state potential energy surface (PES) and make transitions to another PES, most likely through a conical intersection (CI, between the same spin states, in f-2 D) or a seam of crossing (SX, between different spin states, in f-1 D), cascading through different PESs before reaching the product. The minimum energy points, MECIs or MESXs, on these crossing hypersurfaces are critical points that define the most likely geometries of non-adiabatic transitions, although real dynamics does not necessarily go through such points. Finding MECIs or MESXs is the most important first task for understanding of photochemical reactions. However, this is not an easy task if guided only by chemical intuition.

The Global Reaction Route Mapping (GRRM) strategy, developed originally for automatic exploration of a single PES for transition states (TSs) and local minima (MINs), consists of two independent methods: the ADDF (anharmonic downward distortion following) and the AFIR (artificial force induced reaction) methods. These methods can also be used for efficient automatic exploration of minima (MECIs or MESXs) and TSs on the crossing hypersurfaces.

In the present talk, I will briefly discuss the GRRM method and show severa examples of applications to photodissociation reactions of small gas phase molecules including photodissociation of complex photodissociation mechanism of formaldehyde H_2CO molecule, the exclusive excited state roaming dynamics of the nitrate NO_3 radical, and all product channels and conformational memory in the photodissociation of formic acid HCOOH, in conjunction with high level ab initio electronic structure methods, as well as photodissociation of acetone and methyl ethyl ketone and the reaction of $N(^2D) + H_2O$, and photoaddition reaction between H_2CO and $CH_2=CH_2$. The application has recently been extended to larger molecules, in conjunction with low cost TD-DFT methods, including the mechanism of quenching of f-f emission of lanthanide complexes and that of multiluminescent acene systems.

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Imaging the Influence of the Leaving Group and of Vibrational Excitation on S_N2 Reactions

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In the last decade our group has developed a crossed-beam apparatus to study differential scattering cross-sections of ion-molecule reactions [1]. With this setup we have gained new insights into the atomistic mechanisms of nucleophilic substitution (S_N2) reactions of halogen anions with halomethanes [2], such as the discovery of the "roundabout" mechanism [3] or the influence of single solvent molecules on these reactions [4]. Here we report on our latest results:

Next to nucleophile and solvent, the leaving group has a significant influence on S_N2 reactions. Its role is frequently discussed with respect to reactivity, but its impact on the reaction dynamics usually remains obscured. The combined approach of crossed-beam imaging and dynamics simulations on an potential energy surface [5] has been used to uncover the influence of the leaving group on the gas phase dynamics of S_N2 reactions. We have studied the reaction $F^- + CH_3Cl$ and compared it to previous work of our group on $F^- + CH_3I$ [6,7]. For the two leaving groups Cl and I we find very similar structures and energetics, but the dynamics show qualitatively different features. Simple scaling of the leaving group mass does not explain these differences. Instead, the relevant impact parameters for the reaction mechanisms are found to be crucial, which is attributed to the relative orientation of the approaching reactants.

The influence of vibration on chemical reactions is a long-standing and continuously active field of research [8,9,10]. For S_N2 reactions, vibrational mode specific influence has been predicted by various theoretical studies [5,11,12,13]. Yet, the exact nature of this influence is still in question. Up to now, only two experimental studies have obtained indirect answers [14,15]. We report on direct measurements of the influence of CH stretch vibration on the reaction of F^- with CH_3I. This reaction features two competing reaction channels - S_N2 and proton transfer - that are supposed to share the same transition state. But while the proton transfer channel sees a 34 fold increase upon vibrational excitation the S_N2 channel is barely influenced, a finding that strengthens the spectator mode picture for this vibrational mode. For the proton transfer channel we conclude that vibrational excitation is approximately as efficient as translational energy in promoting the reaction at threshold. Measuring angle and energy differential cross-sections enables us to discuss the fate of vibrational excitation energy in the course of the reaction.

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Is there a quantum transition-state theory?*

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Transition-state theory (TST) plays a central role in chemistry. It is a classical theory that states that the rate of a direct reaction can be approximated by the instantaneous flux through a dividing surface. This leads to the familiar picture of a reaction rate being dominated by a free-energy bottleneck which gives rise to an Arrhenius temperature-dependence. Various attempts have been made to incorporate quantum effects into TST, most famously the Wigner-Eyring expression (taught to generations of undergraduates). However, quantum rate-theory has seemed to show that a complete quantum generalization of transition-state theory is impossible.

In this talk we will show that a true quantum generalization of transition-state theory does exist, [1] that it appears to be unique, and that it is identical to a very practical rate-expression which was previously obtained heuristically, namely ring-polymer molecular dynamics (RPMD) TST. [2,3] This tells us that RPMD will give a good approximation to the exact quantum rate for reactions which are direct and not strongly influenced by real-time quantum coherence.

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*yes

Nonadiabatic events in photoinitiated processes in molecules

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The fate of molecular systems when they interact with photons is almost always affected by nonadiabatic processes. Conical intersections between two or more electronic states are often present playing a crucial role in the dynamics. We have investigated the importance of nonadiabatic effects in a variety of systems, ranging from radical cations formed during photoionization to complex biological systems such as oligonucleotides. Using surface hopping molecular dynamics we have studied the relaxation of several radical cations initially prepared in excited ionic states. Motivation for this work has been the importance of the dynamics of radical cations in interpreting pump-probe experiments. We have found that radiationless decay to the lowest ionic state occurs very fast, and several factors play a role in the efficiency of the decay. Nonadiabatic events are also important in photoinitiated processes in biological systems where absorption of a photon may lead to photochemistry, electron transfer and other important phenomena. Examples of such processes will also be discussed in this talk.

Spectroscopic characterization of conical intersection in photodissociation reactions of thiophenol and thioanisole

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Nonadiabatic processes are ubiquitous in nature. Those are actually even essential in many important processes such as light-harvesting, vision, or genetic protection from irradiative damages. Despite a number of experimental and theoretical studies on such reactions for decades, chemists are still keenly interested in the detailed mechanism of nonadiabatic transitions at the molecular level. For polyatomic molecules, conical intersection where two different adiabatic surfaces touch has been widely accepted as the dynamic funnel for efficient nonadiabatic transitions. And yet, direct experimental probing of the conical intersection in terms of its topology and energetics has been quite rare. Here, we have investigated the photodissociation dynamics of thioanisole, thiophenol, and their several chemical derivatives using the velocity-map ion imaging method. We have observed strong variation of the nonadiabatic transition probability depending on the nuclear configurations accessed by various initial vibronic transitions. This in turn provides the spectroscopic characterization of the conical intersection as the nonadiabatic transition probability increases when the reactive flux (or wavepacket) passes the phase space in the proximity of the conical intersection.

Surface hopping: A Simple View of Electronic Transitions for Electrochemistry

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Abstract: Electrochemistry represents a big computational challenge for theoretical chemistry: one requires an understanding of solvent motion and statistical mechanics, the electronic structure of a metal surface, and nonadiabatic dynamics at the edge of the electrode. In this talk, I will present the simplest surface hopping view of electrochemistry and a new picture of friction at a molecule-surface interface.

Direct quantum dynamics simulations of reactions including non-adiabatic effects: DD-vMCG

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Simulating the time-evolution of a non-adiabatic process is computationally intensive due to its inherent quantum mechanical nature. Accurate results require quantum dynamics. Propagating a multi-dimensional wavepacket using the time-dependent Schrödinger Equation is a computationally hard problem that scales exponentially with the number of degrees of freedom in the system. In contrast to the traditional grid-based approach, one way to ease the scaling is to describe the evolving wavepacket by a superposition of Gaussian functions, often referred to as Gaussian Wavepackets (GWPs). There are a variety of algorithms for the propagation of the GWPs that provide the time-dependent basis set. All have advantages and disadvantages, but most use classical trajectories which leads to good scaling, but poor convergence and a dependence on the initial selection of basis functions.

One method that promises to overcome the convergence and initial selection problem is based on the MCTDH wavepacket propagation method [1]. This vMCG method will be presented to show its potential. It variationally couples the evolving basis functions as well as the expansion coefficients, and as the result the functions follow "quantum trajectories" [2,3]. In addition, it is possible to use it to run *direct dynamics* in which the potential function is calculated on-the-fly only when required. This introduces a greater flexibility iin the systems that can be treated.

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Collision-induced intersystem crossing:
A talk on CH_2-O_2 that won't mention the Creigee Intermediate

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Collisions of O_2 $(\tilde{X}\ {}^3\Sigma_g^-)$ with singlet CH_2 $(\tilde{a}\ {}^1A_1)$ access a triplet surface of CH_2O_2 at energies far above the global HCOOH singlet minimum. Numerous molecular and radical rearrangement channels are energetically open, although the details of singlet-triplet couplings and surface intersections will play a key role in the process. Previous experimental work[1,2] has identified non-reactive intersystem crossing as the exclusive product in room temperature studies, analyzing the appearance kinetics of reaction products, which all are produced at the slower rates consistent with triplet CH_2 $(\tilde{X}\ {}^3B_1)$ + O_2 reaction rates, rather than matching the initial disappearance rate of singlet CH_2. We have reinvestigated this system, monitoring transient absorption kinetics of selected rotational states of singlet CH_2, including several of the mixed states that mediate intersystem crossing in the non-reactive collisional system. Following 308 nm photolysis of ketene in rare gases, which produces singlet CH_2 in a well characterized initial state distribution, we find multiple relaxation times. With the assistance of master equation modeling[3,4] we interpret the measurements as evidence of reversible intersystem crossing in the absence of molecular oxygen. The addition of perturbative amounts of O_2 causes the relaxation kinetics to change in ways that are inconsistent with a simple acceleration of irreversible loss of singlet CH_2 by O_2. Possible interpretations will be discussed.

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Bimolecular Reactions in Helium Droplets

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The helium nanodroplet isolation method has been applied by several research groups to the study of chemical reactions, such as ion-molecule reactions, aggregation-induced transformations, and bond-forming barrierless reactions. Helium droplets have also provided a versatile platform to study weakly bound ‘entrance-channel’ complexes, stabilized behind small barriers above the asymptotic energy of a bimolecular reaction. Multi-resonance laser schemes coupled to beams of helium droplets will in the future allow one to study the photo-induced chemistry of these highly metastable species, potentially leading to significant insight into issues such as bright state-reaction coordinate coupling and the mode-specificity of product branching ratios. This talk will review some of the past successes and future prospects for studying bimolecular chemistry in helium droplets. Infrared laser Stark and Zeeman spectroscopy has been applied in our group to several hydroxyl radical containing entrance-channel complexes. Recent results on these fascinating systems will be presented. These spectra highlight an amazing hallmark of helium droplet spectroscopy: the rovibrational spectra of weakly bound open-shell systems can be satisfactorily simulated by assuming a gas-phase effective Hamiltonian.

Craig Taatjes

Combustion Research Facility at Sandia National Laboratory.

Abstract

The oxidation of hydrocarbons is an important process in the troposphere and in combustion systems, and investigators in both these arenas seek predictive models of hydrocarbon oxidation chemistry. Especially in complex environments, a predictive model often requires understanding the role of reactive intermediate species in the overall oxidation process. For example, radical chain branching in autoignition relies on the reaction of hydroperoxyalkyl ("QOOH") radicals, and oxidation of unsaturated hydrocarbons by ozone creates carbonyl oxide "Criegee intermediates." I will describe recent investigations that aim to isolate and interrogate the reactivity of these often unstable species.

Into The Abyss: Perfluorinated liquids as an intermediate solvation environment between the gas and solution phases

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Perfluorinated solvents are known to hold large volumes of small gaseous molecules, a property exploited for liquid breathing applications popularized in science fiction films such as James Cameron's *The Abyss*. This property is due to the open structure of the non-interacting perfluorinated molecules, which result in open cavities in the solvent where gas molecules can sit, and even rotate, without significant disruption to the bulk liquid structure. These cavities provide an inert environment in which to study chemical reaction dynamics, almost entirely free from perturbative dipolar and Van der Waals interactions. The solvents consequently offer an intermediate solvation environment between the gas phase and conventional liquids, similar to condensed noble gases but with molecular degrees of freedom, allowing for studies of mode-specific energy transfer in the absence of strong intermolecular coupling. In this talk, we will present the results of transient absorption spectroscopy experiments observing the progress of N_2O_4 -> NO_2 (X) + NO_2 (B) photodissociation at 340 nm in a variety of perfluorinated and conventional solvents. From highly detailed spectra such as those shown in fig. 1, we explore the importance of the solvent's level of interactivity, structure, and density of states on the rate of electronic and vibrational energy transfer from internally excited solute molecules.

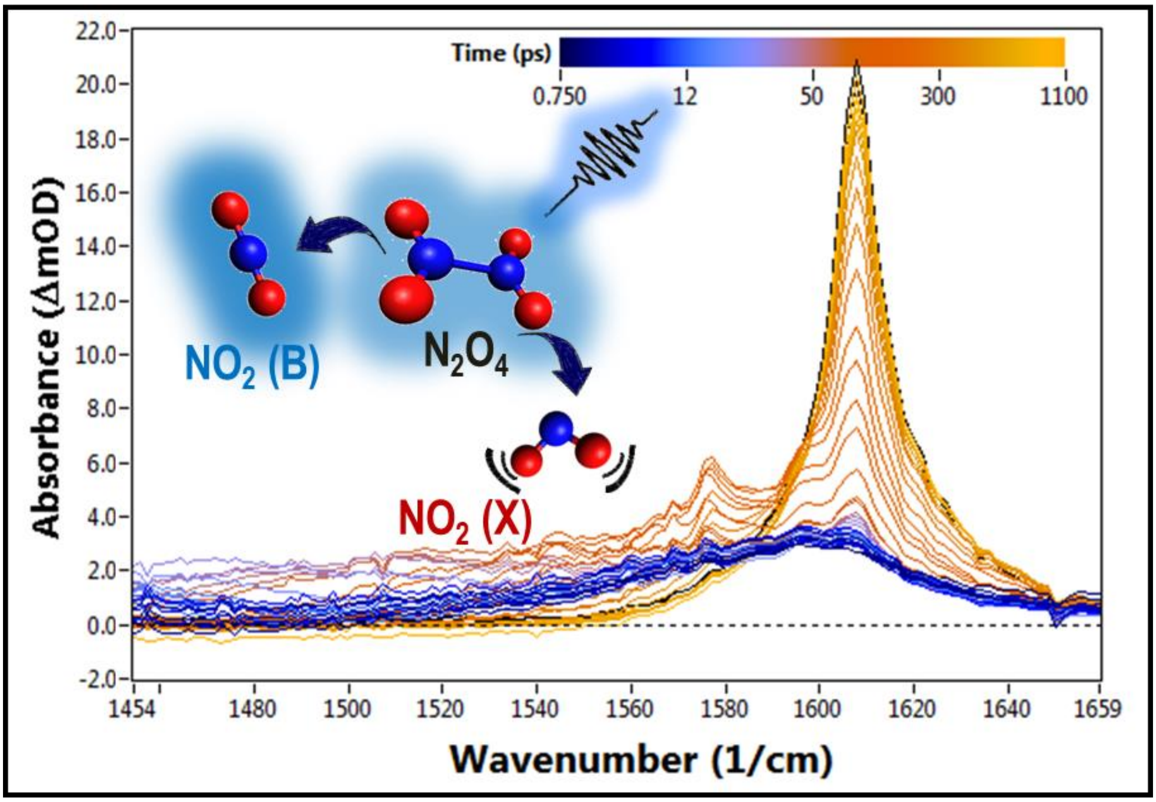

Figure 1: Transient vibrational spectrum of the asymmetric stretch mode of the NO_2 photoproducts resulting from 340nm nm photolysis of N_2O_4 in a liquid solution of perfluorodecalin.

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Probing the onset of large amplitude motion in temperature-controlled, size-selected clusters using isotopomer-selective vibrational spectroscopy

We will discuss how gas phase ion chemistry techniques can be used to explore the embedded correlations in the vibrational spectra of H-bonded networks, information that is inaccessible in the condensed phase due to rapid H/D exchange. In clusters, however, one can introduce a single, intact H_2O molecule into an otherwise homogeneous $(D_2O)_n$ cluster, where the unique water molecule can occupy one of the many distinct local H-bonding environments. The vibrational spectrum associated with each site is then extracted using isotopomer-selective, IR-IR double resonance. We next exploit these site-specific spectral signatures to follow the onset to spectral diffusion as the temperature of the clusters is increased. This broadening is due first to site-to-site exchange, but evolves into long range motion long before the onset of evaporation. Our overall goal in this endeavor is to trace solvent behavior from that best described within the context of small amplitude normal modes, to the regime where the observables are averages of thermodynamic ensembles. Progress toward understanding phase transitions in this regime will be discussed.

Sympathetic cooling of molecules with laser-cooled atoms

Eric R. Hudson, UCLA

Cooling molecules through collisions with laser-cooled atoms is an attractive route to ultracold, ground state molecules [1]. The technique is simple, applicable to a wide class of molecules, and does not require molecule specific laser systems. Particularly suited to this technique are charged molecules, which can be trapped indefinitely, even at room temperature, and undergo strong, short-ranged collisions with ultracold atoms.

I will focus on recent efforts to use the combination of a magneto-optical trap (MOT) and an ion trap, dubbed the MOTion trap, to produce cold, ground state diatomic charged molecules. The low-energy internal structure of these diatomic molecules, *e.g.* the electric dipole moment and vibrational, rotational, and Ω-doublet levels, presents a host of opportunities for advances in quantum simulation, precision measurement, cold chemistry, and quantum information. Recent proof-of-principle experiments have demonstrated that the MOTion trap is efficient at cooling the vibrational motion of molecular ions [2].

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Molecular Velcro: Sticking in Ultracold Molecular Gases

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The reduction of dilute atomic and molecular gases to translational temperatures in the μK range ushers in a new regime of "ultracold" physics. In this limit, collisions are dominated by a handful of the lowest available partial waves, and energy resolution is often adequate to emphasize the role of narrow scattering resonances.

For a particular class of ultracold molecules, namely, heavy alkali dimers, we have estimated the density of these resonant states, finding them to be enormous. Treating the density of states of these resonances within an RRKM-like approach allows us to estimate the dwell time of the molecules within the collision complex. If one is to take these numbers seriously, we find that ultracold alkali dimer molecules will stick upon colliding, for times of tens or even hundreds of milliseconds, before finally dissociating back into the molecules from which they started. This circumstance should have unusual (and not altogether welcome) consequences for maintaining a sample of such a gas.

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Taming Molecular Collisions

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The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Over the last years we have developed methods to get improved control over molecules in a molecular beam [1]. With the Stark decelerator, a part of a molecular beam can be selected to produce bunches of molecules with a computer-controlled velocity and with longitudinal temperatures as low as a few mK. The molecular packets that emerge from the decelerator have small spatial and angular spreads, and have almost perfect quantum state purity. These tamed molecular beams allow for crossed beam scattering experiments with unprecedented levels of precision and sensitivity [2,3].

I will discuss our most recent results on the combination of Stark deceleration and velocity map imaging. The narrow velocity spread of Stark-decelerated beams results in scattering images with an unprecedented sharpness and angular resolution. This has facilitated the observation of diffraction oscillations in the state-to-state differential cross sections for collisions of NO with rare gas atoms [4,5].

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Molecular Rotor in Cold Reactions

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The role of the internal molecular degrees of freedom, such as rotation, in low energy reactions has been unexplored experimentally despite their significance to cold and ultracold chemistry. Particularly important to astrochemistry is the case of the most abundant molecule in interstellar space, hydrogen, where two spin isomers with rotationally ground and excited levels have been detected. Here we demonstrate that quantization of molecular rotation plays a key role in cold reaction dynamics, where rotationally excited *ortho*-hydrogen reacts faster due to a stronger long-range attraction. We observe rotational state dependent non-Arrhenius universal scaling laws in chemi-ionization reactions of *para*-H_2 and *ortho*-H_2 by $He(2^3P_2)$, spanning three orders-of-magnitude in temperature. Different scaling laws serve as a sensitive gauge enabling us to directly determine the exact nature of the long-range intermolecular interactions. Our results show that the quantum state of the molecular rotor determines whether or not anisotropic long-range interactions dominate cold collisions. We will also discuss the effect of molecular rotation on orbiting resonances that we have observed in our earlier work [1,2] in the case of normal H_2. We will demonstrate that orbiting resonance structure is highly dependent on the rotational state of a molecule.

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Cold reactive collisions using laser-cooled ions

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A key objective of our research is to measure the rates and/or cross sections for reactive ion-molecule collisions for polyatomic species at $T < 10K$ and with state selected reactants. In this presentation progress towards achieving these objectives will be discussed [1]. In our experiments we combine sympathetically-cooled molecular ions in a Ca^+ Coulomb crystal with two sources of cold neutrals – either from a Stark decelerator or from a quadrupole guide velocity selector [3, 4]. Decelerated molecules tend to be naturally state selected, whereas the velocity-selected molecules tend to maintain the rotational distribution of the source, for which the temperature can be varied cryogenically [3].

Given that reactions such as $NH_3^+ + ND_3$ have multiple product channels available – e.g., charge transfer, H atom transfer or proton/deuteron transfer, it is necessary to be able to mass selectively detect ionic products to measure branching ratios. The use of trap-ejection and mass spectrometry to measure ionic product branching ratios will be presented [2] along with the latest results from measuring reactions using the Stark decelerator ion-trap combination. The development of a Zeeman decelerator ion-trap combination for studying radical-ion processes will also be discussed [5, 6].

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Photoelectron Spectroscopy and Photochemistry of Ozonide Cluster Anions, $O_3^-(H_2O)_n$ and $O_3^-(Ar)_n$,

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Abstract:

Photofragmentation of ozonide solvated in water clusters, $O_3^-(H_2O)_n$, and argon clusters, $O_3^-(Ar)_n$, $n \leq 16$, have been studied as a function of photon energy as well as the degree of solvation. The O_3^- acts as a visible light chromophore within the cluster, where the photodissociation cross section of the solvated anion exhibits generally the same photon energy dependence as isolated O_3^- throughout the visible spectrum. With the addition of a single water solvent, new photodissociation pathways are opened, including the production of recombined O_3^-. As the degree of solvation of the parent anion increases, recombination to O_3^--based products accounts for 40% of photoproducts for $O_3^-(H_2O)_{16}$, and nearly 90% of photoproducts for $O_3^-(Ar)_{15}$. Time-resolved photodissociation-photoelectron spectroscopy of the ionic species present following photodissociation yields information of the dynamics taking place within the evolving complexes. Finally, we report photoelectron spectra of *cis*-HONO$^-$, providing rich information on high vibrational levels of the ground state of *cis*-HONO, as well as the previously unobserved T_1 (a $^3A''$) HONO near the transition state proceeding along the *cis* Ô *trans* isomerization co-ordinate.

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The long (and continuing) saga of the inelastic scattering of $^2\Pi$ molecules (NO and OH)

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Rotationally inelastic scattering is the most efficient way a molecule can lose (or gain) internal energy. This process plays a key role in non-equilibrium gaseous environments, from high-temperature combustion to low-temperature astrophysics. Experimental accessibility has made collisions of NO with rare gasses a paradigm for rotational energy transfer. In its ground electronic state NO has three π electrons, a $^2\Pi$ electronic state. Consequently, the description of the scattering of a closed-shell system with NO requires two electronic potential energy surfaces, which are degenerate only in linear geometry. Thus, rotationally inelastic collisions of NO involve quantum interference between scattering on these two PES's. This is further complicated by the two-fold spin-degeneracy. The four possible rotational levels of NO (or any $^2\Pi$ molecule) are split apart by spin-orbit coupling and a much-smaller Λ-doubling.

Increasingly sophisticated molecular beam scattering experiments have probed with higher and higher resolution integral and differential scattering of NO by a number of noble gas partners, reaching the elusive goal of four-vector correlation experiments. Quantum scattering studies, based on high-quality *ab initio* potential energy surfaces, allow the interpretation of each new experimentally-detected feature.

Recently, the technique of Stark deceleration has been used to prepare translationally cold beams of OH. This molecule, also with a $^2\Pi$ electronic ground state, is ubiquitous in combustion environments and is the most abundant radical in extragalactic environments. Most recently, it has been possible to study collisions of OH with H_2 (which is the most abundant molecule in similar environments). An intriguing aspect of these experiments and accompanying calculations is the detection of possible quantum mechanical resonances.

The spectroscopy of NO(OH)–Rg weakly-bound complexes provides a alternative experimental probe of the interaction potential, especially in the region of the well. Here, too, theory has been an invaluable complement.

The author is grateful to the National Science Foundation, for continued support of this work, and to a superb set of collaborators over more than 30 years, too many to name here individually. He remains inspired by Dudley Herschbach's excitement for collision dynamics and his love of semiclassical, and evens simpler, dynamical models.

Chemistry on the surface of nanoparticles using beams and traps

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The surface chemistry of small metal nanoparticles can be substantially different than that observed for bulk metal or larger nanoparticles, due to differences in the availability of particular binding sites, and quantum confinement effects on electronic structure. Two approaches to probing size effects will be discussed. For very small particles, in the cluster size regime, it is practical to prepare atomically monodisperse beams of cluster ions, which we deposit on well characterized surfaces and study by surface science or electrochemical techniques. Examples of both electronic and geometric site effects will be presented to illustrate the sorts of effects seen.

For larger particles, with thousands-to-millions of atoms, the size selection approach becomes impractical, but single particle trapping techniques can be used instead. A single particle is trapped, and then its mass is measured non-destructively to high precision while the particle is heated and/or exposed to gaseous reactants. The kinetics of surface reactions can be measured with high sensitivity by tracking the mass; by carrying out measurements on a series of particles, the effects of particle size are determined. Examples will be presented, including the effects of surface reactions on the optical properties of single semiconductor quantum dots, and use of bright probe particles to track dark particles of interests.

Microcanonical Rate Coefficients for Unimolecular Reactions in the Low Pressure Limit

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Abstract: Microcanonical rate coefficients appropriate for characterizing the low pressure limit of unimolecular dissociation reactions (A (+M) → A* → B + C) may be written $\kappa_0(E,J) \equiv Z F(E,J)$, where Z is the A + M collision rate coefficient and F is the fraction of collisions that activate a bound state (E,J) of A above its rotationally adiabatic threshold for dissociation. The two-dimensional (in total energy E and angular momentum J) microcanonical rate coefficients are useful theoretically, as they are intermediate in complexity between $P(E,J;E',J')$, the four-dimensional collisional energy and angular momentum transfer function required for predictive master equation calculations, and k_0, the highly-averaged thermal rate coefficient. Here we calculate κ_0 for several systems using full-dimensional classical trajectories coupled with quantized reaction thresholds. The trajectory-based predictions for κ_0 are used to test the accuracy of calculating κ_0 using a variety of relatively simple parameterized models for P. Based on these comparisons, we quantify the kinetic importance of various physical effects that have been previously identified in P, such as: the long tail in the ΔE-dependence sometimes associated with supercollisions, the sensitivity to the initial rotational state J', and the nonseparability of ΔE and ΔJ. Several systems are considered including two key combustion reactions (CH_4 + M and HO_2 + M) and molecular growth processes relevant to PAH chemistry (e.g., C_6H_4CCH + C_2H_2 + M).

Multimass imaging of complex molecular fragmentation processes

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The domain of velocity-map imaging is rapidly expanding from highly detailed quantum-state resolved studies of diatomic and triatomic molecules to investigations into the photofragmentation dynamics of much larger molecules, many involving model systems of direct relevance to photobiology or organic photochemistry. Such studies present a number of challenges. A diatomic or triatomic molecule generally fragments into only two products, and conservation of energy and linear momentum during the fragmentation process means that by imaging only one of these products in a state-selected manner it is generally possible to gain a fairly complete picture of the photofragmentation dynamics. The key requirement in such an experiment is the existence of a robust REMPI (resonance-enhanced multiphoton ionization) scheme to enable state-resolved ionization and detection of the chosen product. In contrast, a much larger molecule is likely to possess numerous fragmentation channels, forming a variety of different products, and even if suitable REMPI schemes could be identified, it would quickly become unfeasible to obtain state-resolved images for each and every fragment.

Instead, studies of larger molecules tend to rely on employing a universal (or near-universal) ionization scheme to ionize all photofragmentation products, allowing the scattering distribution for each fragment to be imaged, though generally at the expense of quantum-state resolution. Images for each fragment may either be recorded in separate experiments, or with the advent of imaging sensors capable of detecting individual particles with nanosecond time resolution, images of all fragments may be acquired simultaneously in a single image. In the latter case, because multiple fragments may be detected from an individual parent molecule, a covariance analysis of the data set can reveal the correlated scattering distributions of pairs of photofragments, providing similar information to that obtained in more traditional coincidence measurements.

We have recently carried out a number of studies into photoinduced processes in organic molecules, including retrocycloaddition reactions, McLafferty rearrangements, and photo-induced processes in DNA chromophores and model peptide bonds, as well as investigating ionization and fragmentation processes induced by collisions with electrons. This talk will review recent technical advances in the arena of multimass imaging, including an overview of available multimass imaging detectors, and will present data from a number of these studies.

3D Coincidence Ion/Electron Imaging with a Fast Frame Camera

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A new time- and position- sensitive particle detection system based on a fast frame CMOS camera is developed for coincidence electron/ion imaging. The system is composed of three major components: a conventional microchannel plate (MCP)/phosphor screen electron/ion imager, a fast frame CMOS camera and a high-speed digitizer. The system collects the positional information of ions/electrons from a fast frame camera through real-time centroiding while the arrival times are obtained from the timing signal of MCPs processed by a high-speed digitizer. Multi-hit capability is achieved by correlating the intensity of electron/ion spots on each camera frame with the peak heights on the corresponding time-of-flight spectrum. Efficient computer algorithms are developed to process camera frames and digitizer traces in real-time at 1 kHz laser repetition rate. We further show that a time resolution of 30 ps can be achieved when measuring electron TOF spectrum and this enables slicing of electron Newton spheres. A few applications employing this new technique will be demonstrated.

Vinyl + O_2

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The reaction of C_2H_3 with O_2 is a key step in most hydrocarbon flames. The reaction proceeds primarily via an initial addition to form vinylperoxy radical which can then decompose to form either CH_2O + HCO at lower temperatures or CH_2CHO + O at higher temperatures. Because the CH_2O + HCO channel is chain propagating while the CH_2CHO + O channel is chain branching, the product branching ratios between these two channels will have a significant impact on subsequent flame chemistry. We will describe state-of-the-art calculations to accurately determine both the rate of the initial addition reaction and the product branching ratios as a function of both temperature and pressure.

We use a novel hybrid multi-reference/CCSD(T) approach to calculate the interaction potential for the addition of C_2H_3 and O_2. This is an extension of an approach that we have used in the past to treat transition states having a large degree of multi-reference character. This approach relies on the idea that when one is in a region of the potential surface in which the ground state wavefunction is highly multi-reference in character, there will generally be a low-lying, higher spin, excited state, of similar orbital character, which is not highly multi-reference. Our approach uses CCSD(T) to calculate the energy of the high spin state relative to the appropriate asymptote and MRCI (or CASPT2) to calculate the splitting between the high spin and low spin states. Variable reaction coordinate transition state theory (VRC-TST) was then used to compute the microcanonical rate constant for the addition step.

The stationary points controlling the subsequent decomposition of the vinylperoxy radical were first located with UCCSD(T)/cc-pVTZ and then corrections were added for basis set limitations, higher order correlations, core-valence correlations, relativistic effects and anharmonic effects. Variational and conventional TST calculations were then used to compute the rates for the decomposition pathways. The temperature and pressure dependent phenomenological rates were then obtained using RRKM/Master Equation methods. The main conclusions are:

(1) Above 10 atm, collisional stabilization of CH_2CHOO competes directly with the two decomposition channels.
(2) The reaction becomes predominantly chain branching above 1700 K.

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ABSTRACTS

POSTER PRESENTATIONS

Quantitative product branching for multichannel reactions using chirped pulse spectroscopy in pulsed uniform flow

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A new Chirped-Pulse/Uniform Flow (CPUF) spectrometer has been developed and used to determine product branching in a multichannel reaction. With this technique, bimolecular reactions can be initiated in a cold, thermalized, high-density (10^{16} cm^{-3}) molecular flow and a broadband microwave spectrum acquired for all products with rotational transitions within a chosen frequency window. Our recent work on the CN + CH_3CCH reaction yielded HCN via a direct H-abstraction reaction, while HC_3N, CH_3C_3N, and H_2C_3HCN were produced from indirect addition/elimination pathways. From these observations, quantitative branching ratios were established for all products as 12(5)%, 66(4)%, 22(6)% and 0(8)% into HCN, HC_3N, CH_3C_3N, and H_2C_3HCN, respectively. The values are consistent with statistical calculations based on new ab initio results at the CBS-QB3 level of theory. Details of CPUF and its potential as a powerful technique for quantitatively determining the branching of polyatomic products from bimolecular reactions will be discussed.

Computational study of the r_0 structure and the microwave spectra of CH_2OOH

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Understanding of the reactions that occur in the earth's troposphere can give us important information about many processes. Hydroperoxyalkyl (QOOH) radicals are intermediates of low temperature hydrocarbon oxidation that occurs in the earth's troposphere. In this study, the bond lengths, angles, rotational constants, fine and hyperfine couplings of CH_2OOH radical (the simplest QOOH radical) were calculated using Gaussian 09 software to help in the experimental detection of the radical. Before doing direct calculations on hydroperoxyalkyl radicals, a reference point was needed to gauge the accuracy of the calculations and obtain the corrections that are needed in order to get accurate values for CH_2OOH. Hydrogen peroxide and methyl hydroperoxide were used as the reference points. Optimizations of hydrogen peroxide and methyl hydroperoxide were carried out at different levels of theory and the values were compared with available experimental data. The starting point for the calculations was Density Functional Theory (B3LYP) and the highest level of the theory used was CCSD(T). Basis sets ranged from 6-311G(d) to aug-cc-pVTZ. Using the same levels of theory, optimizations were carried out for the CH_2OOH radical and corrections were made. From the structure analysis, it was observed that C-O bond had a partial double bond and that the C-O bond length was smaller compared to the methyl hydroperoxide. The dihedral angle was also smaller compared to both hydrogen peroxide and methyl hydroperoxide. Fine and hyperfine couplings could only be calculated with the HF and DFT level of theory. Therefore, they were calculated with B3LYP/cc-pVTZ using the CCSD/aug-cc-pVTZ geometry.

Spectroscopic and Reaction Studies of Ionic Liquids in a New Ion Trap Electrospray Instrument

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Ionic liquids have several properties which make them very desirable toward Air Force goals to replace current satellite fuels with more efficient and less toxic alternatives. The structures of ionic liquids are not well understood, and gas phase spectroscopy serves as the best benchmark for calculations. This allows theory to guide further development of the ionic liquids with the required properties. For example, ionic liquids can undergo hypergolic reactions with oxidizers, a necessary feature for some types of space propulsion. However, the reaction mechanism is unclear from studying products after combustion from liquid sources, and studying the isolated reactions will identify the initial steps of reaction. To better understand these phenomena, a new ion apparatus is being commissioned. The machine is designed around an electrospray ion source, quadrupole mass selection, and a variable temperature 22-pole ion cryotrap. Conducting spectroscopy in a setup such as this has a rich history, and this will be continued in this apparatus. The novel aspect of this experimental setup will be to conduct reactions within the trap and to interrogate the products of hypergolic reactions at varied temperatures and times. Preliminary results on the hypergolic system between the ionic liquid, EMIM DCA cluster anions, and nitric acid show the sequential addition to the anions. This serves as data to help determine the reaction pathway and energetics which can be determined for the first time experimentally due to isolating the reaction.

193 nm photodissociation of pyridine studied using Chirped Pulse Uniform Flow Spectroscopy (CPUF)

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Chirped - Pulse Fourier-transform microwave spectroscopy has been applied in a uniform supersonic flow (Chirped-pulse/Uniform flow, ‘CPUF”) to study the 193 nm photodissociation of pyridine; a basic nitrogen-containing heterocyclic compound. Rotational spectroscopy was used to detect the possible products. Previous studies have reported six dissociation channels. One direct channel yielding $C_5NH_5 \rightarrow C_5NH_4 + H$ and five ring opening reactions such as $C_5NH_5 \rightarrow C_4H_4 + HCN$, $C_5NH_5 \rightarrow C_3H_3 + C_2NH_2$, $C_5NH_5 \rightarrow C_2H_4 + C_3NH$, $C_5NH_5 \rightarrow C_4NH_2 + CH_3$, $C_5NH_5 \rightarrow C_2H_2 + C_3NH_3$ have been reported. HC_3N and HCN were detected out of the above mentioned products and we report the first detection of HNC. Branching ratios were calculated and will be presented.

Probability of new products formation at simultaneous collision of four ions in system $\mathrm{Cs^{+} + Cl^{-} + Rb^{+} + J^{-}}$

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Dynamics of a recombination at collision of four heavy atomic ions at the energies in several electron-volt is investigated by method of classical trajectories on the example of system $\mathrm{Cs^{+} + Cl^{-} + Rb^{+} + J^{-}}$. The set of all possible channels of such interaction is presented by the following scheme including formation of both ionic and neutral products:

$\mathrm{Cs^{+} + Cl^{-} + Rb^{+} + J^{-}}$ $\mathrm{Cs^{+} + Cl^{-} + Rb^{+} + J^{-}}$ (1)
$\mathrm{CsCl + Rb^{+} + J^{-}}$ (2)
$\mathrm{RbJ + Cs^{+} + Cl^{-}}$ (3)
$\mathrm{CsJ + Cl^{-} + Rb^{+}}$ (4)
$\mathrm{RbCl + Cs^{+} + J^{-}}$ (5)
$\mathrm{CsCl + RbJ}$ (6)
$\mathrm{CsJ + RbCl}$ (7)
$\mathrm{CsClRb^{+} + J^{-}}$ (8)
$\mathrm{CsClJ^{-} + Rb^{+}}$ (9)
$\mathrm{CsJRb^{+} + Cl^{-}}$ (10)
$\mathrm{RbJCl^{-} + Cs^{+}}$ (11)
$\mathrm{CsClRbJ}$ (12)

The probability of realization of this or that channel substantially is defined, in particular, by kinetic collision energy of ions, and dependence of total probability of realization of chemical transformation channels (2) – (12) from collision energy is given in figure 1.

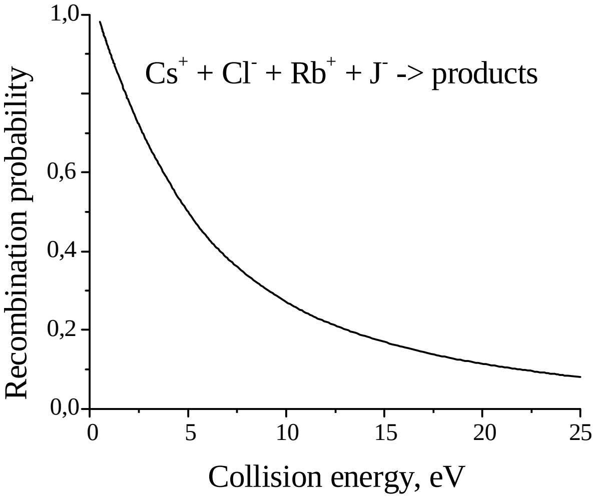

Fig.1. Dependence of total probability of realization of chemical transformation channels (2) – (12) from collision energy of ions.

Spectroscopic Studies of Imidizolium and Pyridinium Based Ionic Liquids

Ryan Booth and Jaime Stearns

Ionic liquids (ILs) have been shown to be extremely useful in areas ranging from chemical synthesis to energetic materials. Furthermore, ILs are thought to be a potential replacement for hydrazine as satellite propellants because a subset are hypergolic with nitric acid. While ILs are useful, however, there is a lack of understanding of the microscopic origins for their macroscopic properties (e.g. viscosity). An example of this is that [emim$^+$][tf2N$^-$] is three times less viscous than its methylated counterpart [emmim$^+$][tf2N$^-$] and there is some discord regarding the reason. We have investigated the molecular properties of such IL pairs using UV and IR spectroscopy in the gas phase on both imidozolium and pyridinium-based ([pyr$^+$]) ILs. UV data show that the photophysics of [emmim$^+$][tf2N$^-$] is different than [emim$^+$][tf2N$^-$] in that there is a lack of evidence for the existence of a charge transfer (CT) state (as was seen in [emim$^+$][tf2N$^-$]). Preliminary UV spectra for the [pyr$^+$] ILs show at least two distinct peaks in the region from 208-270 nm, which are tentatively established as (CT) states between the anion and cation. IR spectra deliver structural information for both sets of ILs and should provide insight into the correlation between microscopic and macroscopic properties.

Pressure Effects Studies of OH, HO_2 and CH_3NO_2 Relaxation in an Ar Bath

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In this work, we use molecular dynamics (MD) simulations to study the effect of pressure on the relaxation of an excited OH and compare this with additional results obtained for HO_2 and previous results for CH_3NO_2.[1] The effect of pressure on relaxation of a chemical species is often described using the isolated-binary collision (IBC) approximation. A key assumption of IBC is that both relaxation and reaction rates are directly proportional to pressure of the system. We designed MD simulations to probe the validity of this assumption under conditions of extreme pressure where the IBC approximation may not be valid. A detailed description of this type of MD simulation can be found in Ref. 1.

We found that the rotational and translational degrees of freedom of these three species quickly equilibrated to match the thermal state of the bath gas, but vibrational energy relaxed on a much longer timescale. For the OH molecule, the vibrational relaxation is much slower when compared to either HO_2 or CH_3NO_2. Figure 1 shows the normalized, excess vibrational energy $E_{\text{nrm-vib}}(t)$ for these three chemical systems for all the simulations done so far. $E_{\text{nrm-vib}}(t)$ is the excess vibrational energy above the expected thermal value as a function of time, this includes the time-dependent temperature increase of the bath gas atoms as energy is transferred to the bath from the initially excited species.

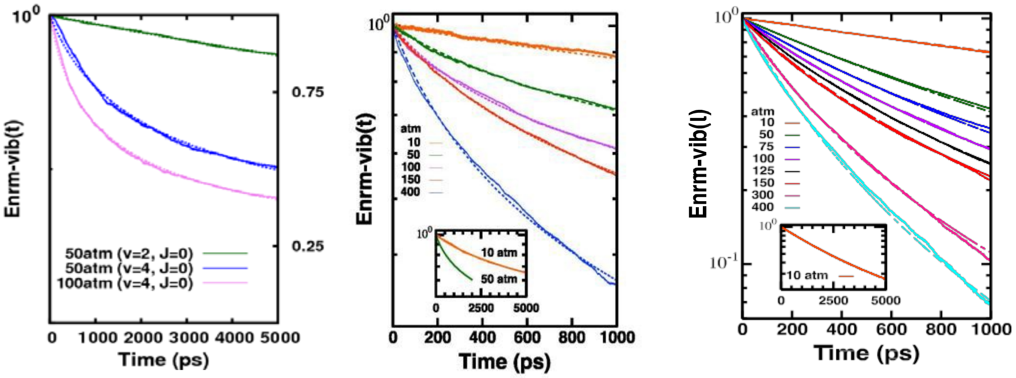

Figure 1. OH (T=300K) (left), HO_2 (T=800K) (middle), CH_3NO_2 (T=300K) (right). The solid curves are the simulation results and the dashed curves are the LS fits.

Analysis of the decay curves of normalized energies (rotational and vibrational) was done by fitting to the Lendvay and Schatz (LS)[2] formula with only two parameters (m, k_i). The parameter k_i is the initial rate of decay at t=0 while m is the curvature of the relaxation curve on a semi-log plot with respect to time. In all cases, the LS functional form fits the results quite well (as seen in the Fig. 1) and shows positive curvature (upward deviation from a straight line [see Fig. 1]) at all pressures for these three species. For OH (see Fig. 1) this effect is more pronounced at higher excitation energies (v = 4). The curvature of the relaxation curves shows that the rate of energy transfer slows as the excited species loses energy. Mechanisms for curvature and non-linear pressure dependence for OH and HO_2 will be discussed in the poster.

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A Density Functional Theory and *Ab Initio* Study of Al + CO_2 Reaction Chemistry

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The reaction between Al and CO_2 is important in the combustion of aluminum under atmospheric conditions, thus there have been several experimental studies of the kinetics of it. We have systematically studied the ground-state potential energy surface of $AlCO_2$ with higher levels of theory, specifically CCSD(T) and M11, than previously employed. Our goal is to determine the reaction pathways and perform transition-state theory calculations to obtain accurate values for rate coefficients. The Al + CO_2 reaction is a multi-channel reaction involving the activated complex $AlCO_2$*, which can be collisionally stabilized or dissociate to either Al + CO_2 or AlO + CO. We have identified and characterized three conformations of $AlCO_2$*: η-$AlCO_2$, *trans*-$AlCO_2$, and C_{2v}-$AlCO_2$. η-$AlCO_2$ is connected to *trans*-$AlCO_2$ by a barrierless pathway with a 0.9 kcal mol^{-1} back-barrier, and *trans*-$AlCO_2$ is connected to C_{2v}-$AlCO_2$ by forward and reverse barriers of 0.7 kcal·mol^{-1} and 2.5 kcal·mol^{-1}, respectively. Our calculated results predict that there are two pathways from Al + CO_2 to $AlCO_2$* with barriers of 0.9 kcal·mol^{-1} and 9.7 kcal·mol^{-1} and three pathways from $AlCO_2$* to AlO + CO (products) with barriers of 22.3 kcal·mol^{-1}, 29.1 kcal·mol^{-1}, and 34.3 kcal·mol^{-1}. We find that the CCSD(T)/CBS//M11/jun-cc-pV(Q+d)Z results are in better agreement with experiment than our present M06-2X and B3LYP results.

Ionization Energy Studies of Free Radical Production and Photodissociation

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Our group has long been interested in the primary photochemistry of neutral free radical species, *e.g.* benzyl (C_7H_7). The recent installation of a new electron ionizer has opened a new avenue for probing these radicals by allowing us to measure the ionization energy of a given species. This technique has been used to demonstrate clean production of the benzyl radical; a species recently studied by our lab. Tunable electron energies also allow for simplification of photodissociation signals, as low energy electrons are less likely to cause fragmentation of a molecule.

Dynamics of hydrogen-abstraction and S_N2 reactions on ab initio analytical potential energy surfaces

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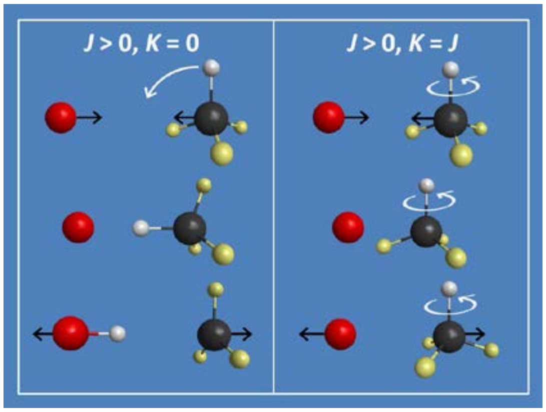
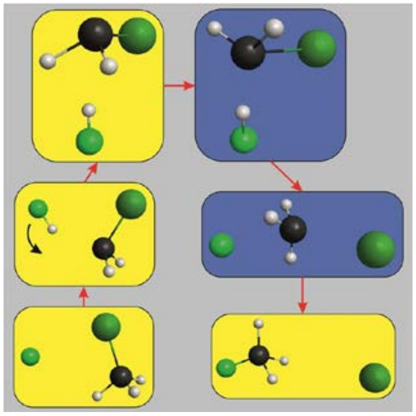
The X + CH_4 abstraction and X^- + CH_3Y substitution reactions have become benchmark systems to study polyatomic chemical reactivity. In order to study the dynamics of these reactions theoretically, we develop chemically accurate ab initio potential energy surfaces (PESs) and perform quasiclassical trajectory (QCT) and/or (reduced-dimensional) quantum dynamics computations using these PESs. Accurate full-dimensional analytical ab initio PESs for the F, O(^{3}P), Cl, Br + CH_4 reactions have already been available [1−4]; however, such PESs did not exist for the X^- + CH_3Y reactions; thus, these S_N2 reactions were usually studied by direct dynamics simulations, in which the potential energies and gradients are computed on-the-fly. We recently reported the first full-dimensional chemically accurate global analytical PESs for the F^- + CH_3Cl [5,6] and F^- + CH_3F [7] reactions, thereby opening the door for efficient QCT and quantum simulations. We focus on our recent results on rotational mode specificity in the Cl and O(^{3}P) + CHD_3 reactions [8,9] and PES developments and dynamics for the F^- + CH_3Cl [5,6] and F^- + CH_3F [7] reactions. We show that the reactivity can depend on the initial JK rotational states [8,9] and we introduce a novel double-inversion mechanism for S_N2 reactions [6,7,10].





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Analysis of hydrogen bonding in the OH stretch region of protonated water clusters

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There are two types of bands in the OH stretch region of the vibrational spectra of hydrogen-bonded complexes; narrow peaks due to isolated OH stretches and a broadened feature reflecting the OH stretches involved in strong hydrogen bonding. This second region can be as wide as several hundred wavenumbers and is shifted to the red of the narrow peaks. In this work we focus on $H^+(H_2O)_n$, where n = 3 or 4.[1] Both of these systems exhibit a very intense, broad H-bonded band. This breadth arises from coupling between the OH stretches and the low frequency modes. To understand the broadening observed in the spectra, we have developed a computational scheme in which we sample displacement geometries from the equilibrium structure based on the ground state harmonic wavefunction.[2] As there are large anharmonicities at play in the HOH bends and OH stretches, we use second-order perturbation theory to solve a reduced-dimensional Hamiltonian for each geometry. Then we combine the anharmonic spectra for each geometry in the OH stretch region to generate the spectrum for each protonated water cluster. We will describe the approach used in these anharmonic calculations and report results for the protonated water clusters.

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Robust methods for the development of high-dimensional diabatic potential energy surfaces

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The quantum dynamics treatment of radicals and excited states in general depends on the availability of coupled multi-dimensional potential energy surfaces (PESs). Therefore, the diabatization of electronic structure data and the development of diabatic PES models is of fundamental importance. Despite the great interest in such diabatic models there is still no well-established methodology available and only few accurate diabatic PESs exist for systems with more than two or three atoms. We found that the core problems are the instability of typical electronic structure *ab initio* calculations, not always immediately obvious, and the lack of robust diabatization techniques for extended regions in nuclear configuration space.

In our quest for a robust PES diabatization we first developed a simple analysis tool to identify non-obvious problems with the electronic structure, which is based on block-diagonalization of the CI eigenvector matrix. The CI vectors are computed in the basis of molecular orbitals diabatized with respect to fixed reference orbitals. By analysing *ab initio* cuts through the PESs, this method immediately reveals where problems occur. We found that such problems are generally due to changes in the adiabatic state space becoming inconsistent with the chosen diabatic state space. The reason for these inconsistencies are either orbital rotations or intruder states.

Our new diabatization strategy is based on this analysis, first solving the electronic structure problems and then generating the diabatic PES model. The data from the block-diagonalization yields the diabatic coupling pattern, identifying the most relevant coupling terms. The diabatic PES model is set up utilizing the block-diagonalization data to find appropriate mathematical representations of the matrix elements and to fit them. Finally we combine the use of the adiabatic energies as in the well-known *diabatization by ansatz* with the CI vectors as utilized for the block-diagonalization in our new hybrid diabatization method. The parameters of the diabatic model matrix are optimized with respect to the eigenvalues reproducing the adiabatic *ab initio* energies as well as to the eigenvectors reproducing the adiabatic CI subspace vectors. This results in a robust diabatization of the *ab initio* data and yields an accurate diabatic PES model suitable for quantum dynamics studies. The power of the new method will be demonstrated on prototypical examples like ozone, propargyl, and the fine structure states of methyl iodide. Systems with up to 9 states in 12 dimensions have been fitted so far.

The effect of energy difference between initially prepared states and conical intersections on photodissociation dynamics

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Non-adiabatic dynamics at conical intersections (CI) extensively affects the photostability of biomolecules by efficiently photoinducing decay routes that dissipate harmful excess ultraviolet energy. Here the predissociation of the model test molecules, methylamine (CH_3NH_2) and its partially deuterated isotopologues CD_3NH_2 and CH_3ND_2, excited to different specific vibrational and rovibrational levels in the electronically excited state has been experimentally investigated. The ensuing H(D) photofragments were detected by two-color reduced-Doppler ion imaging, which allows measurement of the entire velocity distributions of the photofragments in each laser pulse. The fast and slow H(D) products, resulting from N-H and N-D bond cleavage, obtained via different dissociation pathways, showed anomalous distributions for some vibronic or rovibronic states, respectively, as indicated by dynamic resonances in the product branching ratio. The resonances were also exhibited by the anisotropy parameters of the fast H photofragments, resulting from the predissociation of the isotopologues containing the NH_2 moiety. This vibronic and rovibronic specific control is attributed to the sensitivity of the non-adiabatic dynamics to the energy difference between the initially prepared states and the energy of the CIs and to the topography of the potential energy surfaces and not only to the distinctive pre-excited nuclear motions. These findings reveal uniquely detailed insight into the dynamics of state-specific control.

Infrared Multiphoton Dissociation of Vinyl Chloride Yields Cold Vinylidene.

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ABSTRACT

Velocity map imaging of the infrared multiphoton dissociation of vinyl chloride shows the formation of HCl in rotational levels below J=10 that are associated with the 3-center elimination pathway. The total translational energy release is observed to peak at 3-5 kcal/mol, which is consistent with the low reverse barrier predicted for the formation of HCl with vinylidene co-products. Direct dynamics trajectory studies from the 3-center transition state reproduce the observed distributions and show the associated vinylidene is formed with only modest rotational excitation, precluding Coriolis-induced mixing among the excited vibrational levels of acetylene that would lead to distribution of vinylidene character into many vibrationally mixed acetylene vibrational levels. The results suggest that infrared multiphoton dissociation of vinyl chloride is an efficient route to synthesis of stable, cold vinylidene.

Probing Structural Landscapes with Single and Double Resonance Spectroscopy Techniques: Conformation Specific Spectroscopy of the helix-former Z-(Aib)$_n$-X

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2-Aminoisobutyric acid (Aib) is an achiral, α-amino acid having two equivalent methyl groups serving as side chains. Aib is well known for its preference for forming 3_{10} helices in the condensed phase.[1,2] In the work presented here, Z-(Aib)$_n$-X oligomers (n = 1, 2, 4, and 6: X = OH and OMe) have been brought into the gas phase by laser desorption and cooled into their zero-point levels using a supersonic expansion, thereby allowing their intrinsic folding propensities to be probed free from solvent effects. By varying the length of the oligomer backbone and modifying the C-terminal capping agent, a unique perspective is provided on the development of these folding preferences. Similar work done by the Mons group in 2007 investigated the folding propensities of Ac-Aib-Phe-Aib-NH$_2$. Their work showed evidence for initial stages of formation of 3_{10} helices as well as competing motifs.[3]

Conformation specific UV spectra were recorded for the series of molecules in question using resonant two-photon ionization (R2PI) and IR-UV hole-burning spectroscopy techniques. Conformation specific IR spectra were recorded using resonant ion-dip infrared spectroscopy (RIDIRS) in the Amide A (~3200-3500 cm^{-1}) region for each oligomer. Samples with at least four Aib residues are sufficiently long to form the first full turn of a 3_{10} helix, and characteristic 10-member (C10) hydrogen bonded rings are indeed observed. These features are also present in the n = 6 peptide, with a series of overlapping transitions in the frequency region for C10 hydrogen bonds, and two free NH transitions characteristic of the 3_{10} helix. A second structure with a very different amide NH stretch spectrum is present and still under exploration. There is a marked difference between oligomers having COOH or COOMe groups at the C-terminus. In particular, the COOH group contains a strong H-bond donor OH which significantly changes the hydrogen bonding landscape relative to its esterified analog. The gas phase results will be compared to condensed phase data to gain insight regarding the inherent conformational preferences of these prototypical Aib-containing peptides.

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Theoretical tools to aid experimental studies: Dyson orbitals and photoionization cross-sections

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Dyson orbital is a one-electron quantity, which describes the difference between initial N-electron and final (N-1)-electron states of a system undergoing ionizing transition. Having it computed and providing some description for the outgoing electron, one can get various one-electron properties of the ionization process, including photoelectron matrix element. The latter provides a connection to experimental probing of electronic structure, as a key quantity for obtaining [1] photoionization cross-sections and photoelectron angular distributions, which are important parameters for interpretation of photoelectron spectroscopy and photoelectron imaging experiments.

Dyson orbitals can be computed for any initial and final many-electron wavefunctions, however, equation-of-motion coupled cluster (EOM-CC) formalism allows one to include correlation and orbital relaxation effects and provides a straightforward way for evaluation and analysis of the obtained orbitals. Implementation of Dyson orbitals for a variety of EOM-CC flavors provides an access to describing the whole range of experimentally important cases: i.e., ionization from and to ground or excited electronic states, for neutral or charged as well as closed and open-shell species. With the description for outgoing electron as a linear combination of spherical waves, performance of the total model will be shown via comparison with available experimental energy dependences of photoionization/photodetachment cross-sections. Illustrative applications will demonstrate deviations from Koopmans' predictions and will include comparison of valence and dipole-bound anionic states as well as formation of solvated electrons in Na-doped clusters [2].

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CMB-VMI studies of the inelastic scattering dynamics of NH_3 with a series of increasingly bulky hydrocarbons.

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We present Crossed Molecular Beam Velocity Map Imaging (CMB-VMI) studies[1] of the inelastic scattering of ammonia (NH_3) with argon and a selection of hydrocarbons. The hydrocarbons studied are selected for their increasing steric bulk, whilst containing only primary C-H groups. To this end the collisions of NH_3 with Methane (CH_4), Ethane (C_2H_6) and Neopentane ($C(CH_3)_4$) are studied at collision energies of 766, 720 and 547 cm^{-1}, respectively. This work aims to study the effects that scattering with large, non-rigid molecules has on the ammonia, ultimately mimicking the interaction of such gaseous molecules with liquid surfaces.[2]

For comparison inelastic scattering of NH_3 with argon, at a collision energy of 310 cm^{-1}, was also examined as an example of a small collisional partner.[3] These results show a high propensity for forward scattering, with more side scatter at higher total angular momentum quantum number (J) and lower projection quantum number (K), which is in keeping with an attraction dominated scattering model.

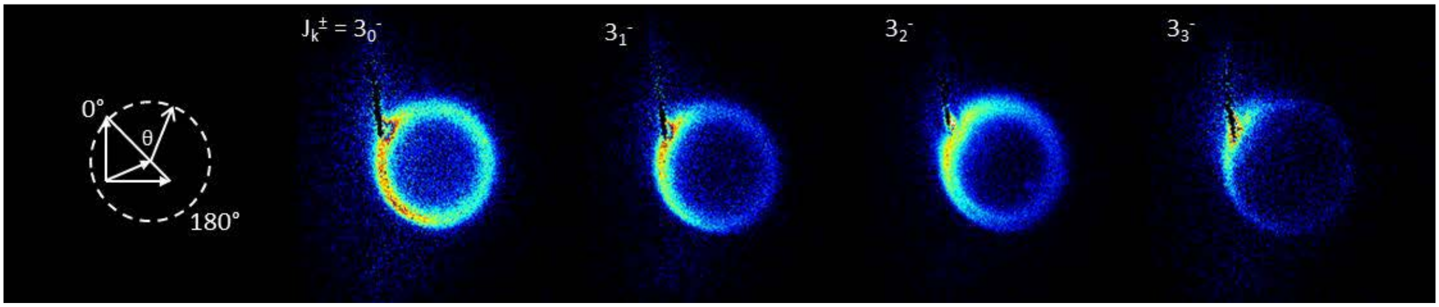

Figure 1: Raw images of inelastic scattering into the J = 3 antisymmetric levels of NH_3 through collision with argon.

Increasing the size of collider, by studying NH_3 collisions with hydrocarbons, shows a small dependency of the differential cross section (DCS) on J and greater scattering into higher J states is observed. However, as with argon, these images are dominated by a large forward scattering signal, suggesting that the scattering process is mostly governed by long range attractive forces between the scattering partners, leading to a majority of “glancing” collisions.

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Exploring the Interfacial Chemistry of Salty Aqueous Solutions: He Evaporation and HCl Scattering

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The aim of our research is to develop a detailed molecular picture of the interactions between gases and liquid surfaces. To explore liquids with high vapor pressures such as water, we couple narrow diameter liquid jets with molecular beam techniques. The liquid microjet provides access to volatile liquids in vacuum because its small surface area and high curvature minimize collisions within the vapor cloud just outside the jet. Scattering and evaporation experiments can then be used to explore collisions and reactions of gases with aqueous solutions.

We have recently measured the velocity distributions of dissolved helium atoms evaporating from water and salty aqueous solutions. The experiments show that He atoms evaporate with super-Maxwellian speeds, while most other gases closely follow a Maxwell-Boltzmann distribution. Molecular dynamics simulations reveal that the He atoms are accelerated by He-water collisions in the interfacial region as the water structure “heals” by expelling the perturbing He atom, and that the weak He-water attraction allows the He atoms to escape before undergoing further collisions in a surface well.

We have also begun DCl scattering experiments that will eventually provide insights into interfacial acid dissociation. Using the deuterated acid as the probe gas allows us to distinguish between DCl molecules that scatter without undergoing reaction and molecules that dissociate at the surface, recombine, and then evaporate as HCl. These studies will reveal how fast proton shuttling in the interfacial region alters DCl → HCl exchange and how this proton transfer is controlled by interfacial ions.

Characterising cold ion-molecule reactions in Coulomb crystals

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Reactive collisions between Coulomb-crystallised ions held within a linear Paul ion trap and neutral molecules are observed, with the examination of a proof-of-principle charge exchange reaction between Xe^+ and ammonia. A new mass-sensitive detection method is introduced, with the ejection of all ions onto an external detector at a selected time. This time-of-flight mass spectrometry (TOF-MS) approach removes ambiguity about the identities of dark ions: both the masses and relative numbers of all trapped species at the point of ejection can be ascertained directly from the TOF spectra (see figure 1). A comparison is made with digital ejection TOF-MS and other mass-sensitive detection methodologies for ensembles of Coulomb-crystallised ions [1-2]. Experimental results and detailed simulations indicate excellent detection efficiency, and the approach is broadly applicable to all ion-molecule reactions examined within an ion trap.

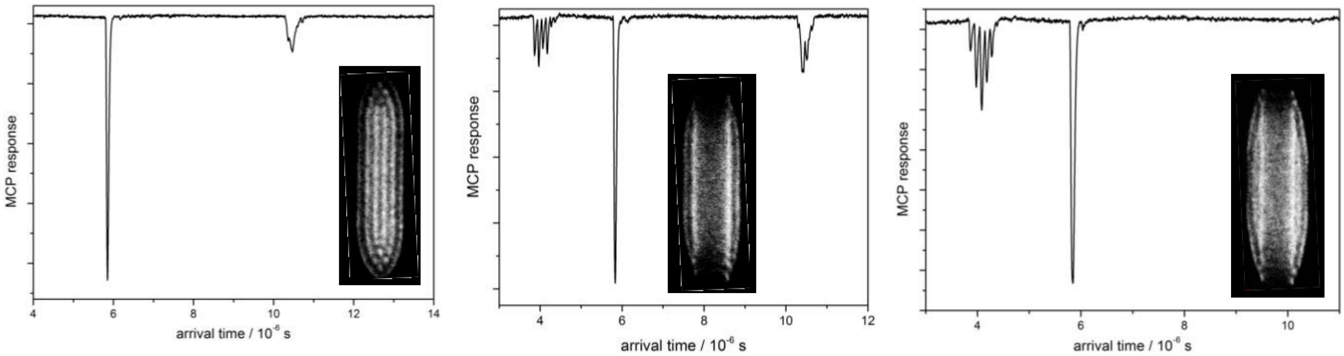

Figure 1. Experimental TOF traces recorded following the ejection of a multi-component Coulomb crystal (inset) at various stages of reaction: (left) composed of Ca^+ and Xe^+ ions, prior to any charge-exchange reactions; (centre) with the addition of ammonia ions, following charge exchange between ammonia and Xe^+; and (right) after all Xe^+ has reacted.

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Permutationally Invariant Polynomial Neural Network Approach: A Simple and Systematic Way to Fit Potential Energy Surfaces with High Fidelity

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The potential energy surface (PES) forms the foundation for understanding molecular spectroscopy and reaction dynamics. With the increasing molecular size, the construction of an efficient and accurate PES from a large number of ab initio data becomes a very difficult task. Among many recent efforts, the permutationally invariant polynomial (PIP)[1] and neural network (NN)[2] fitting approaches have shown great promise for high dimensional problems. The former fits the PES using symmetrized monomials of internuclear distances, which can be systematically obtained.[3] The latter consists of a set of non-linear functions that provides high flexibility to fit the PES with high accuracy. Although the PIP method enforces the intrinsic permutation symmetry in the system, it usually yields a relatively large fitting error due presumably to its simple function form. While the NN fitting approach generally represents the PES more accurately, on the other hand, it does not naturally recognize the intrinsic symmetry existing in a specific system.

Here, we combine the two methods and propose a simple, rigorous, efficient, and systematic way to impose the permutation symmetry in NN fitting procedure. This so-called PIP-NN method uses PIPs, rather than the often used internal coordinates, as the NN input, thus preserving full symmetry without modifying the NN structure.[4] This strategy has been first tested in fitting PESs for gas phase systems,[5] and then applied to PESs for gas-surface interactions with an additional treatment of periodicity using the Fourier expansion.[6, 7] It has been successfully used to fit PESs up to twelve degrees of freedom for gaseous and gas-surface reactions, demonstrating its prowess. In addition, it should be stressed that the PIP-NN method recognizes the importance of the correct rather than “intuitive” but non-existing permutation symmetry. As a result, our PIP-NN scheme is superior to other alternatives in both efficiency and accuracy.

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Imaging the reaction dynamics of chlorine atoms with cycloalkenes

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We report preliminary results for a series of reaction of chlorine atoms with cycloalkenes: cyclohexene, 1,3-cyclohexadiene and 1,4-cyclohexadiene. These reactions were studied using our crossed- beam dc ion imaging apparatus at a collision energy of 12 kcal/mol. Images of the cycloalkenyl radicals were obtained via single photon ionization at 157 nm. The center-of-mass angular and translational energy distribution will be reported and compared to reactions of linear alkenes and cycloalkanes.

Oxygen dissociation and internal energy transfer modeling for non-equilibrium reacting flow simulations

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Many advanced engineering technologies involve nonequilibrium reacting flows. Such flows are generated by re-entry vehicles, plasma environments and detonations. During Earth re-entry gas temperature in the shock region exceeds 10,000 K, which leads to air dissociation. The flow in the shock is highly nonequilibrium and chemical kinetics there cannot be characterized by single-temperature Arrhenius rates[1]. There is currently a lack of high-fidelity nonequilibrium chemistry models for computational fluid dynamics (CFD) and direct simulation Monte Carlo (DSMC) simulations that can account for internal energy specific chemical processes. Therefore, modern CFD and DSMC codes depend on phenomenological collision models that are calibrated to reproduce equilibrium measurements but their accuracy in reproducing nonequilibirium conditions is uncertain[2]. Due to its importance in reentry and combustion, our work focuses on modeling oxygen reactions.

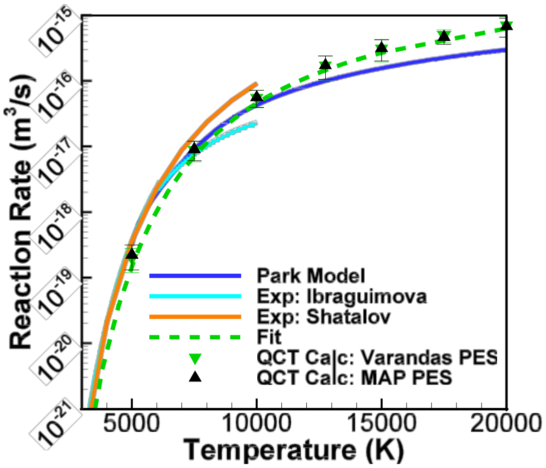

Figure:1 Comparing of O_2+O-->3O equilibrium dissociation rates calculated via QCT with Varandas (green triangles) and MAP (black triangles) potentials and a compact model fit (dashed green). Experimental data can be found in [4]

State-specific models can be constructed based on quasi-classical trajectory (QCT) calculations. There are three main challenges for implementation of QCT-based models within CFD and DSMC. The first is related to the need for potential energy surfaces for a few dozen of possible collision pair species combinations. Second, oxygen has approximately 3,000 ro-vibrational levels. A database of O_2+O reaction cross sections would exceed 3,000*N elements while a database of state-to-state cross section would exceed $3{,}000^2$*N elements, where N is the number of considered relative translational energies. A database of all needed state-to-state cross sections for all collision partners would be too large to be used efficiently within DSMC or CFD. Third, due to relatively low lying electronic states the high energy collisions of oxygen cause non-adiabatic transitions that need to be considered.

To adapt QCT-derived models into flow calculations we first study the sensitivity of rates and cross sections to PES. Fig 1 shows that $O_2(^3\Sigma)+O(^3P)$è□$3O(^3P)$ reaction rates calculated by simplified Morse-additive pairwise (MAP) and a detailed DMBE potential by Varandas and Pais[3] match within 12% in the 5,000 – 20,000 K range. Rates calculated by both potentials are bound by experimental measurements of Shatalov and Ibgraguimova. Next, we reduce the number of state-to-state cross sections using a compact model based on modified total collision energy (TCE) cross sections. Fig. 2 shows that the compact model is able to reproduce dissociation cross sections within 2% while using just 72 parameters. Dissociation rates calculated via this fit match rates calculated directly from QCT within 23 %, as shown in Fig. 2. The final poster will also discuss approaches to account for non-adiabatic transitions and consistent implementation of QCT model within a DSMC calculation.

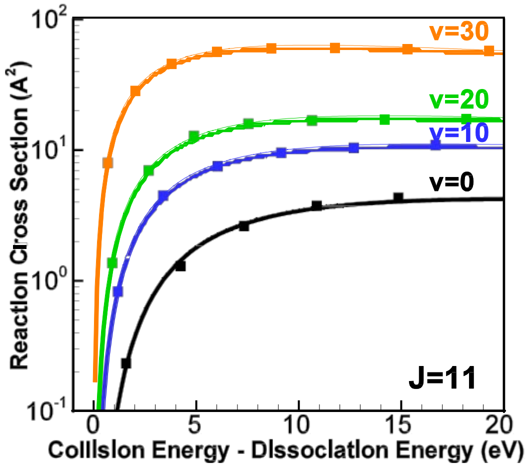

Figure 3: Comparison of reaction cross sections predicted by a compact model fit (lines) and QCT calculations (dots).

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Dynamics of electron attachment to uracil, thymine, and imidazole

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Electron attachment to the DNA bases uracil and thymine and to imidazole, a subunit of the DNA bases adenine and guanine, was investigated using femtosecond time-resolved photoelectron imaging to examine iodide-base binary clusters. An ultraviolet pump pulse initiates charge transfer of an electron from iodide to the base to form a transient negative ion. Pump excitation energies were selected to sample electron attachment dynamics both near and significantly above the vertical detachment energy (VDE) of the iodide binary complex. Iodide-uracil complexes were found to form both the dipole-bound (DB) and the valence-bound (VB) anion when excited with energies near (110 meV below – 100 meV above) the VDE (4.11 eV), but form only the VB anion at energies significantly (550 meV) above the VDE. Below the VDE, the DB anion forms with approximately a 250 fs rise time but at higher excitation energies the DB anion forms more quickly and eventually the rise becomes cross-correlation limited. At excitation energies for which both DB and VB anions form, VB anions have a 200-300 fs rise time. This indicates that the DB anion may act as a "doorway" state to form the VB anion at energies near the VDE. Iodide-thymine clusters exhibited similar rise times (220-250 fs) for energies both near (120 meV below – 90 meV above) and significantly (550-740 meV) above the VDE of the complex (4.05 eV), and also showed only VB state formation at high excitation energies. Additionally, a DB to VB transition was also observed for thymine anions. Thymine exhibits fairly similar electron attachment dynamics as uracil, and calculations indicate that energetic and geometric differences between the two bases affect the exact rise times and DB:VB formation ratios. Iodide-imidazole binary clusters, however, cannot support a VB state and only form DB anions. The rise times of these DB states (180-340 fs) appear to be much more dependent on the specific excitation energy used (90 meV below – 0 meV, directly at the VDE of 3.90 eV) than is observed for uracil or thymine. The dynamics of the DB state appear to be affected more greatly by the distribution in vibrational states of the initially formed anion. These studies indicate that for species that form both DB and VB anions, the DB state appears to act as a doorway to the VB anion at energies near the VDE. Species that cannot support a VB state may experience more excitation energy dependent electron attachment dynamics.

A Step Closer to Understanding Acid Solvation: Imaging the Dissociation Dynamics of Mixed HCl and H_2O Clusters

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Abstract

The prototype system of HCl in water is a topic of fundamental importance for acid solvation and ionization, yet details regarding the energetics and dissociation dynamics of small $(HCl)_m(H_2O)_n$ clusters are still missing. We present a study of the vibrational predissociation dynamics of these mixed clusters, focusing on those with m:n=1:3 and 1:2. These clusters dissociate via excitation of the bound-OH stretch fundamental vibration, which was recently assigned and characterized by Zischang *et al*.[1] Vibrational predissociation is induced by IR laser excitation. HCl and H_2O fragments are monitored state-selectively by using 2+1 resonance enhanced multiphoton ionization (REMPI) combined with time-of-flight mass spectroscopy. Velocity map imaging (VMI) of state-selected fragment levels is used to determine translational energy distributions in the pair-correlated fragments. Accurate dissociation energies for different dissociation pathways are determined as well, and the results compared with the previously studied HCl-H_2O dimer.[2,3]

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Ab initio kinetics for the decomposition of unsymmetrical di-methylhydrazine $(CH_3)_2NNH_2$

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Hydrazines, are an important class of chemical propellants. They have been found to be energetically powerful, yet stable enough to find utility in the propulsion of satellites and rockets. A quantitative understanding of their decomposition kinetics is central to the development of quantitative models for their use as a propellant. We have made a priori predictions for the decomposition kinetics of unsymmetrical di-methyl hydrazine (UDMH), which is both a technologically and kinetically interesting representative of this class of propellants. Our analysis employs a combination of high level ab initio electronic structure theory, potential energy surface fitting, rigid body reduced dimensional dynamics, transition state theory, and master equation calculations.

A key feature of hydrazines is that they contain weak N-N bonds and any C-N bonds are only slightly stronger. The simple N-N and C-N bond fissions produce two radicals that interact generally through both strong dipole-dipole interactions and through hydrogen bonding interactions. As a result, the potential energy surface (PES) for the interactions between the two incipient radicals is remarkably complex showing multiple minima and multiple pathways to a variety of products. In this work, we present a detailed exploration of the PES for UDMH on the basis of high level ab-initio calculations. For illustrative purposes we have generated a set of planetary plots, which highlight the topography of the long-range interactions, for a range of N-N and C-N fragment separations. Analytic representations of the interactions for the N-N and C-N fissions are obtained via fits to $\sim 10^5$ CASPT2(2,2)/avdz ab initio data points. These analytic surfaces are utilized in rigid body dynamics (RBD) simulations of the branching between simple bond fission and other roaming related channels involving various H abstractions. Finally, utilizing the results of these RBD calculations, and the high level ab initio calculations for the tight transition state, the master equation (ME) is solved to obtained high level predictions for the full set of thermal rate coefficients over a range of temperatures and pressures. Our total rate constants are then compared to previous experimental work.

One interesting finding is that, due to the presence of long range complexes, a false high pressure limit is accessed, which gradually transforms to the true high pressure limit as the pressure is increased to very high values. This highlights the need to show care when performing kinetic analyses for azine-like compounds, as they may require much larger pressures to access the true high pressure limit.

A theoretical study of vibronic perturbations in magnesium carbide (MgC)

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Studying molecules related to group IIA metal carbide clusters like the magnesium carbide family (MgC, MgC_2, Mg_2C_3 etc.) has been of great interest to experimental and theoretical chemists for many years. It is important to understand and relate the bulk properties of clusters to those of its simplest molecule in the quest for advanced materials. Given the relative cosmic abundances of magnesium and carbon, there has been an increasing interest in the MgC species from the astrophysics and astrochemistry community as they seek to detect it in interstellar space. Dynamically weighted multi-reference configuration interaction (MRCI/DW-SA-CASSCF) *ab initio* calculations have been used to generate adiabatic potential energy curves for MgC near the complete basis limit (CBS). Highly accurate triplet (4 $^3\Sigma^-$, 4 $^3\Pi$ and 2 $^3\Delta$) and quintet (1 $^5\Sigma^-$ and 1 $^5\Pi$) curves were constructed up to 50,000 cm^{-1} above the ground state minimum. Energies and dipole transition moments were transformed into a quasi-diabatic representation to simplify coupled vibronic calculations. Vibronic levels have been computed for four interacting $^3\Pi$ states using individually optimized complex absorbing potentials (CAPs). Predicted transitions, vibronic wavefunctions, band origins and spectroscopic constants were computed and reported to facilitate experimental detection.

Ultraviolet photodissociation dynamics of 1-methylallyl and 2-methylallyl radicals

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The ultraviolet (UV) photodissociation dynamics of the 1-methylallyl (1-MA) and 2-methylallyl (2-MA) radicals were studied using the high-*n* Rydberg atom time-of-flight (HRTOF) technique in the photolysis region of 226-244 nm. The two C_4H_7 radicals were produced by 193 nm photodissociation of suitable precursors: 1-MA from 3-chloro-1-butene and 2-MA from 3-chloro-2-methyl-1-propene. The H-atom photofragment yield (PFY) spectrum of 1-MA contains a broad peak centering around 230 nm. The translational energy distributions of the H-atom loss product channel, $P(E_T)$'s, show a bimodal distribution indicating two dissociation pathways for 1-MA. The slow pathway is isotropic with $\beta \sim 0$ and has a fraction of average translational energy in the total excess energy, $\langle f_T \rangle$, in the range of 0.12-0.15, corresponding to the unimolecular dissociation of 1-MA after internal conversion. The fast pathway has a $\langle f_T \rangle \sim 0.55\text{-}0.60$ and is also isotropic. This fast pathway is consistent with direct H-atom dissociation on a repulsive excited state surface or on the repulsive part of the ground state surface, possibly through a conical intersection. The fast/slow branching ratio is ~0.06. The intensity in the PFY spectrum of 2-MA increases towards the shorter wavelengths. The $P(E_T)$'s of the H-atom loss product channel in 2-MA peak at ~7 kcal/mol and have a single component; the $\langle f_T \rangle$ value is nearly constant at ~0.13 in the region of 226-244 nm. The H-atom product angular distribution of 2-MA is isotropic. The dissociation mechanism of 2-MA is consistent with unimolecular dissociation of a highly vibrationally excited hot radical on the ground electronic state after internal conversion from the electronically excited state.

Christopher L Malbon

Application of fitted, coupled potential energy surfaces via a *quasi*-diabatic Hamiltonian to the multichannel, multistate photodissociation of hydroxymethyl.

[*J. Chem. Phys.* **2014**, 140, 024112] introduced a method for fitting coupled, adiabatic potential energy surfaces using a *quasi*-diabatic Hamiltonian. This procedure is applied to the multichannel photodissociation of hydroxymethyl. We present our most current surfaces, comparison to previous surfaces, and recently reported results simulating excitation to the 2^2A state [*J. Phys. Chem. A* **2015**] and results simulating excitation to the 3^2A state not yet reported.

Binning Methods for Trajectory Results: A Closer Look at Gaussian Binning

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Quasiclassical trajectory methods continue to be an attractive method of studying molecular collisions due to their tractability despite the number of degrees of freedom or total energy involved. Although the selection of an initial state may be be constrained by quantum mechanical considerations, a trajectory evolves entirely classically. One of the ongoing issues is the assignment of the trajectory results to quantum states and the calculation of the associated cross sections and rate coefficients.

An effective method of doing this should be computationally efficient, free of systematic errors, and consistent with the physics of the system with respect to reproducing the properties of the final energy distributions and obeying detailed balance and microscopic reversibility. In addition, it should offer the potential of good agreement with quantum mechanical and experimental results.

A number of methods have been proposed with varying success, from the bin histogram method to the more recent Gaussian methods. It has been established that the bin histogram method gives rise to cross sections that are ”hot” relative to experimental and full quantum results for atom-diatom systems (Mandy et al. 1994). This is aggravated when there are more quantum numbers involved. Recently there has been increased interest in Gaussian binning methods. Earlier attempts at Gaussian binning used separate distributions for each quantum number which gave rise to poor convergence, even with large batches of trajectories. More recent attempts utilize a single Gaussian distribution of a chosen width based on the energy of the quantum state, regardless of the number of quantum numbers involved (Conteet al. 2013).

An examination of this Gaussian binning method indicates that it converges with number of trajectories at the same rate as the bin histogram method. While it does give cross sections that are less “hot” than those determined by bin histogram methods, it does not and cannot completely eliminate “hot” cross sections. The implications of this are discussed.

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Oscar Martinez Jr.

DMC Abstract

Observation of a Rotational Effect in the Temperature Dependence of Ion-Neutral Reactions

Experimental thermal rate coefficients measured between 100 and 600 K using a variable temperature selected ion flow tube instrument are compared to those calculated using a quasi-classical trajectory method on an accurate global potential energy surface fitted to many high-level ab initio points for the following two reaction systems:

$$H_2O^+ + H_2/D_2 \rightarrow H_3O^+/H_2DO^+ + H/D$$

and

$$OH^+ + H_2/D_2 \rightarrow H_2O^+/HDO^+ + H/D$$

Approximately 81,000 high-level ab initio points were calculated for the H2O$^+$ system and approximately 30,000 points for the OH$^+$ system. Excellent agreement between theory and experiment is found across the entire temperature range for each system. In particular, the H_2O^+ system shows a subtle, but unusual temperature dependence of its rate coefficients; a maximum appears around 350 K, which is a result of H_2O^+ rotations increasing the reactivity, while kinetic energy is decreasing the reactivity. A strong isotope effect is found, although the calculations slightly overestimate the kinetic isotope effect. Similar, though less-accentuated results occur for the OH$^+$ system. The overall excellent agreement between theory and experiment not only validates the accuracy of the potential energy surface but also provides more accurate kinetic data in a large temperature range. The abovementioned reactions are of high importance to astrophysical models and the temperature dependence of the rate constants determined here should now allow for an extrapolation to temperatures more relevant to the interstellar medium.

Dissociative Photoionization of Ethylenediamine

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Abstract

Preliminary results of the photodissociation of ethylenediamine by threshold photoelectron photoion coincidence spectroscopy (TPEPICO) are presented. Time-of-flight spectra of energy-selected EN ions have been collected in the 8.6-10.6 eV photon energy range using the custom-built instrument at the University of the Pacific in Stockton, California. In the examined photon energy range, five parallel dissociation channels were determined: (1) $NH_2CH_2CH_2NH_2^{\cdot+} \rightarrow NH_2CH_2CHNH_2^{+} + H$; (2) $NH_2CH_2CH_2NH_2^{\cdot+} \rightarrow NH_2CHCH_3^{+} + NH_2$; (3) $NH_2CH_2CH_2NH_2^{\cdot+} \rightarrow NH_2CHCH_2^{+} + NH_3$; (4) $NH_2CH_2CH_2NH_2^{\cdot+} \rightarrow NH_2CH_3^{+} + NHCH_2$; (5) $NH_2CH_2CH_2NH_2^{\cdot+} \rightarrow NH_2CH_2^{+} + NH_2CH_2$. The first dissociation channel is the slow NH_3-loss around 9.13 eV and is overtaken by the H-loss and NH_2-loss fragment ions. The bisection of ethylenediamine (NH_2CH_2 loss) is the dominant channel within this energy range. Optimized structures and potential energy surfaces are computed at the CBS-QB3 level of theory and underline the influence of internal hydrogen bonding in the cationic state, including the gauche and anti-gauche structures of ethylenediamine. The fragments, their geometries, and mechanisms to formation are compared to a previous study on the dissociative photoionization of ethylenediamine using vacuum ultraviolet (VUV) photoionization mass spectrometry. In addition, a statistical modeling program is utilized to fit the breakdown diagram and the time-of-flight mass spectra to determine the dissociation rates via RRKM theory. Appearance energies and enthalpies of formation of the fragments are currently being evaluated.

DYNAMICS OF HYPERTHERMAL ATOMIC-OXYGEN INTERACTIONS WITH HOT CARBON SUFACES – FROM 675 K TO 2200 K

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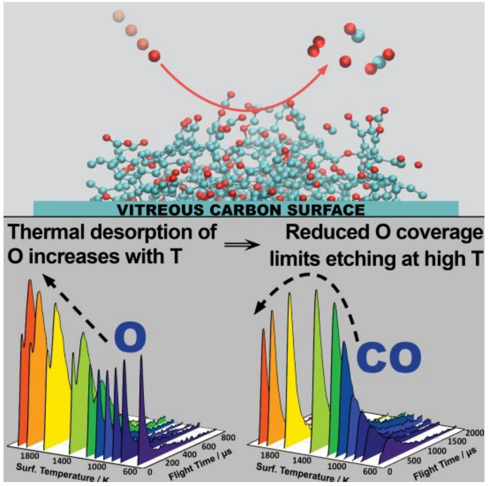
Gas-surface interactions at high temperatures are of great importance to atmospheric re-entry of spacecraft. Hypersonic flows generate the most extreme thermal conditions experienced by any flight vehicle. For a flight vehicle to survive in this environment, it requires a thermal protection system (TPS) 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 surface 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 oxygen, O(^3P), with both highly oriented pyrolytic graphite (HOPG) and vitreous (or glassy) carbon surfaces were investigated with a broad range of surface temperatures from 675 K to approximately 2200 K. Beams of 5 eV O atoms were directed at surfaces, and angular and translational energy distributions were obtained for inelastically and reactively scattered products using a rotatable mass spectrometer detector. Inelastically scattered O atoms exhibited both thermal and non-thermal components. The inelastic scattering from HOPG showed mostly nonthermal (impulsive) scattering with very sharp and superspecular angular distributions. In contrast, thermal scattering was much more important on the vitreous carbon surface and the angular distributions for impulsive scattering were broader. Surprisingly, an increasing fraction of inelastically scattered O atoms was observed on both HOPG and vitreous carbon as the surface temperature was increased, which corresponded to a significant increase in thermally scattered O atoms and a concomitant shift in the angular distribution of the scattered atoms toward the surface normal. For both surfaces, CO and CO_2 were produced at lower temperatures and the primary reaction product was carbon monoxide (CO), which was formed through direct (nonthermal) and indirect (thermal) mechanisms. The flux of CO produced reached a maximum at surface temperatures between 1500 and 1900 K, depending on heating rate, and decreased with increasing temperature. Similar non-Arrhenius behavior was observed decades ago in the oxidation of carbon with thermal O and O_2, but we have explained it for the first time. The increasing thermal desorption of O atoms with temperature signifies a decrease in surface oxygen coverage, and with fewer reagent O atoms to react with carbon the reactivity of the surface is limited even though the it is being constantly bombarded with highly reactive (hyperthermal) O atoms.

Combined time dependent and time independent study of inelastic scattering of the CO dimer

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ABSTRACT

Carbon monoxide is the second most abundant molecule in the universe after molecular hydrogen. Its importance was demonstrated in various processes occurring in the atmosphere, hydrocarbon combustion and interstellar space. In astrophysics for instance, the CO emission spectrum is frequently used to detect H_2 and other molecules that do not have a spectrum visible from earth. However, as molecular level populations are generally not in equilibrium, the prediction of spectral lines depends on the magnitude of collisional excitation rate coefficients with dominant species (H_2, He, H but also CO). Rate coefficient data for inelastic scattering of CO with various colliders have been reported in the literature in the past decades, but none with CO itself. The reason behind this is the high computational cost of close-coupling calculations of the cross-sections which arises from the small rotational constant of CO combined with the heteronuclear nature of the diatom. To overcome these limitations, we performed rigid rotor non-reactive scattering quantum mechanical calculations on the CO dimer by combining time independent close-coupling calculations at low energies with time dependent calculations using the MCTDH method[1] at high energies. We obtain rotational excitation cross-sections and thermal rates for collision from the ($\boldsymbol{j}_1 = 0, \boldsymbol{j}_2 = 0$) initial rotational states. The cross-sections and rates[2] exhibit an excitation propensity where symmetric excitations of the monomers (both excited equally) are favored over other transitions. The approach presented here is viable for systems where ”heavy” colliders are involved and is currently being applied to study other Van der Waal systems.

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Structure and Thermochemistry of *o*-, *m*-, and *p*-Didehydromethylphenol

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Using Negative Ion Photoelectron Spectroscopy (NIPES), the photoelectron spectra of the distonic radical anions *o*-, *m*-, and *p*-didehydromethylphenoxide have been measured, and the EAs of the *o*-, and *p*-didehydromethylphenoxyl biradicals were determined to be 1.217(6), 1.097(6) eV, respectively. They were shown to have Franck Condon active ring distortion vibrational modes at 564(50) and 444(36) cm^{-1} in addition to C-O and C-C (with respect to the bond between the ring and methyl group) active vibrational modes at 1565(50) and 1617(36) cm^{-1}. In the photoelectron spectrum of *m*-didehydromethylphenoxide, only one peak could be uniquely identified at 0.868(6) eV; however, its identification is uncertain due to low signal and conflicting quantum chemical calculations. The thermochemistry of these molecules was also investigated using Flowing Afterglow-Selected Ion Flow Tube (FA-SIFT) mass spectrometry and acid bracketing, and the proton affinities of *o*-, *m*-, and *p*-hydroxybenzyl radicals were determined to be 334.8(4.3), 341.7(2.6), and 334.8(4.3) kcal/mol respectively. Building a thermodynamic cycle allows for an experimental determination of the surprisingly small dissociation energy of the O-H bond in all three of these isomers, 49(4), 48(3), and 47(4) kcal/mol. Most of the trends and behaviors observed here can be explained by resonance and the effects of electron withdrawing groups in aromatic chemistry.

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Photoelectron Spectroscopy of the *cis*-Nitrous Acid Anion (*cis*-$HONO^-$)

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Abstract

We report gas-phase photoelectron spectra of *cis*-$HONO^-$. In this experiment, $HONO^-$ is formed in an association reaction of HO^- and NO in a pulsed plasma-entrainment source.[1] In our photoelectron spectra we observe the presence of only the *cis*-$HONO^-$ isomer, which is predicted to be the global minimum on the anion potential energy surface. The photoelectron spectra obtained with 1613, 1064, 532, 355 and 301 nm show electron photodetachment of $HONO^-$ to access both the ground $X\ ^1A'$ state and excited $a\ ^3A''$ state of neutral HONO. The ground state spectrum shows a long vibrational progression which is dominated by the central O–N stretching vibration (ν_4) and combination bands thereof indicating a significant change in central O–N bond length upon photodetachment. Moreover a strong resonance of ν_4 with the ν_2 and ν_5 modes is indicated by large Franck-Condon intensity in the combination bands of these modes. The observation of these vibrations leads to vibrational frequencies of $\nu_2 = 1633(11)$, $\nu_4 = 857(8)$ and $\nu_5 = 624(34)$ cm^{-1}, in very good agreement with the previously determined frequencies from IR absorption experiments.[2] We observe the origin transition at 0.358(5) eV, corresponding to the first measurement of the electron affinity (EA) of *cis*-HONO. With the measurement of the EA, we also report the dissociation energy (D_0) of the HO^-–NO bond as 0.610(6) eV or 14.1(2) kcal/mol, almost a four-fold decrease in bond strength when compared to neutral *cis*-HO–NO (D_0 = 2.079 eV).[3] The $a\ ^3A''$ state is shown to lie ~2.3 eV above $X\ ^1A'$, and exhibits broad features spaced by the terminal N=O stretching frequency. The projection of the anion geometry onto the $a\ ^3A''$ state potential energy surface places the molecule in a saddle-point which results in prompt dissociation to HO + NO with a time constant of around 50 fs, as indicated by width of the peaks, as it vibrates in the bound N=O coordinate. Electronic structure calculations and photoelectron spectra simulations reported here showed very good agreement with the experimental data, providing confidence to our assignments.

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Imaging the steric effects in Cl + aligned-$CH_4(\nu_3 = 1)$

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Recently, our laboratory reported an in-depth study on the stereo requirements of the Cl + $CHD_3(v_1 = 1)$ reaction by pre-aligning the reactants in space.[1,2] In that study, the vibrational energy deposited into CHD_3 is localized in the C-H stretching mode ($v_1 = 1$) with the C-H bond aligned by a linearly polarized infrared (IR) pump laser. A profound dependence of dynamics on the alignment of CHD_3 reactant was brought to light. In contrast to CHD_3, when CH_4 (a spherical top molecule) is optically excited to the antisymmetric stretching state $v_3 = 1$, all four C-H bonds are excited simultaneously and any of the four H atoms could be abstracted by Cl. Intuitively, how the excited CH_4 is aligned and how it will change the reactive outcomes are not obvious *a priori*. Preliminary experiments revealed a striking effect on reactivity by polarizing the $CH_4(v_3 = 1)$ reactants.[3] Here, a full alignment study of the title reaction is reported, using the crossed molecular beam method and the time-sliced ion imaging technique.[4] Through an inversion scheme, the complete sets of polarization-dependent differential cross sections (PDDCSs)[5] are disentangled from a series of images under multiple crossed-beam geometries at the same collision energy. The results help to unveil the steric view of how the reaction proceeds.

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Velocity Map Imaging Study of Reactions of Carbon Hydrogen Radicals with Cations

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We report crossed beam studies of reactions $CH_3 + H_3^+$ and $C_3H_5 + C^+$ using the velocity mapping method. It is found that there are two main product channels, the proton transfer ($CH_4^+ + H_2$) and the charge transfer ($CH_3^+ + H_2 + H$), for reaction of $CH_3 + H_3^+$ over the collision energy range from 1.2 to 3.4 eV. Vibrational excitation in the H_3^+ reactants plays an important role both in promoting endoergic charge transfer and in supplying energy to the products of the proton-transfer reaction. Excited H_3^+ reactants with vibrational energy in excess of the barrier lead to energy-resonant charge transfer via long-range collisions. A small fraction of collisions that take place at low impact parameters appear to form charge-transfer products with higher levels of internal excitation. The proton-transfer reaction exhibits direct, stripping-like dynamics. Consistent with the kinematics of proton transfer, incremental kinetic energy supplied to the reactants is strongly directed into product relative kinetic energy, as predicted by the concept of "induced repulsive energy release". The reaction of $C_3H_5 + C^+$ exhibits C-C bond formation ($C_4H_3^+ + H_2$) in addition to charge transfer ($C_3H_5^+ + C$).

Semiclassical Approaches for Modeling the Effects of Nonadiabatic Excited State Dynamics on Electronic Spectroscopy

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We recently developed an approach for directly calculating dipole-dipole correlation functions and hence electronic spectra from swarms of semiclassical trajectories propagated using Tully's fewest switches surface hopping (FSSH) algorithm.[1-2] Here, we describe benchmarking our approach on model three-state systems in which the two excited states are vibronically coupled together as well as each coupled to a harmonic bath. We compare the linear absorption spectral lineshapes calculated using our approach to the results of exact quantum dynamics as well as to other semiclassical methods, including Kubo theory and Ehrenfest dynamics.[3-4] In doing so, we will demonstrate that semiclassical methods that include dynamical information from both the ground and excited potential energy surfaces are more reliable for modeling spectral lineshapes than approaches that only include dynamical information on one potential energy surface. Finally, we will discuss the use of our approach for modeling time-resolved, pump-probe spectroscopy as well as combining FSSH and Ehrenfest dynamics to model 2D electronic spectra.[5]

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Dynamics of the O-Atom Exchange Reaction $^{16}O(^3P) + ^{18}O^{18}O(^3\Sigma_g^-) \rightarrow$ $^{16}O^{18}O(^3\Sigma_g^-) + ^{18}O(^3P)$ at Hyperthermal Energies

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ABSTRACT

The O-atom exchange reaction, $^{16}O(^3P) + ^{18}O^{18}O(^3\Sigma_g^-) \rightarrow ^{16}O^{18}O(^3\Sigma_g^-) + ^{18}O(^3P)$, was investigated at a hyperthermal center-of-mass collision energy (E_{coll}) of 86 kcal mol^{-1}, using a crossed-molecular-beams apparatus and quasi-classical trajectory (QCT) calculations. The inelastically scattered ^{16}O and reactively scattered $^{16}O^{18}O$ products were detected with a rotatable mass spectrometer employing electron-impact ionization. The inelastically scattered ^{16}O atoms scatter sharply in the forward direction, with the majority of the available energy partitioned into translation ($\langle E_T \rangle$ = 90%). The $^{16}O^{18}O$ products of reactive collisions are mainly formed through impulsive dynamics and are scattered in the forward as well as sideways directions, also with a substantial fraction of the available energy partitioned into translation ($\langle E_T \rangle$ = 57%). QCT calculations were carried out on the ground state singlet electronic potential energy surface, and the center-of-mass angular and translational energy distributions of $^{16}O^{18}O$ products obtained from these calculations agree well with the experiment. The calculations reveal that $^{16}O^{18}O$ is both highly rotationally and vibrationally excited, with $j''(^{16}O^{18}O)$ up to 150 and $v''(^{16}O^{18}O)$ up to 15, respectively.

Unimolecular Reaction Dynamics of Atmospherically Relevant α-keto Carboxylic Acids: Capturing Hydroxycarbene Intermediates

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α-keto carboxylic acids, such as glyoxylic and pyruvic acids, and their CO_2, aldehydes and hydroxycarbenes decomposition products are important in combustion and atmospheric chemistry, as well as in interstellar and planetary processes relevant to astrochemistry. In spite of their facile thermal decomposition and photodissociation under UV radiation, little is known about the details of the unimolecular reaction dynamics of these α – keto carboxylic acids, and even less is known about their hydroxycarbene products. In recent work we were able to identify *cis*- and *trans*-hydroxymethelene (HCOH), the prototype hydroxycarbene, in the UV photodissociation of the CH_2OH radical, by monitoring H atoms cofragments. Using time-sliced velocity map images of H products, we assigned highly vibrationally excited states of HCOH, up to and above its dissociation limit, as well as its triplet state. Evidence for its dissociation to HCO + H following isomerization to formaldehyde was obtained. In ongoing experiments, HCOH is produced as a product of pyrolysis and photolysis of glyoxylic acid with CO_2 as the cofragment. CO_2 is detected by 3+1 resonance enhanced multiphoton ionization (REMPI) using several intermediate Rydberg states. In addition to CO_2, we have identified CO products, which are rotationally and vibrationally excited, and we will discuss their production from photolysis of glyoxylic acid and/or HCOH. Glyoxylic acid has a broad absorption in the near UV, and by detecting CO_2 and CO reaction products, its photodissociation dynamics is revealed.

Vinoxy and HNO Products from Photodissociation at 193 nm of a Substituted Alkyl Nitrite

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The alkyl nitrites are important atmospheric species, where they form as intermediates in numerous processes including the formation of chemical smog. In this work we explore the photochemistry of a halogenated alkyl nitrite, $BrCH_2CH_2ONO$, in a crossed laser-molecular beam experiment using 193 nm photodissociation. This laser wavelength can excite either the O–NO or C–Br moieties, allowing us to probe the dynamics of both the parent nitrite and the nitrosooxy ethyl radical CH_2CH_2ONO. Our results show significant branching to HNO (nitrosyl hydride) and CH_2CHO (vinoxy) products from both species, which we attribute to a roaming mechanism, by analogy with the very recent work of other groups on thermal decomposition of methyl and ethyl nitrites. The secondary dissociation to HNO + CH_2CHO from the radical is especially interesting, as roaming of the NO must produce an energetically unfavorable incipient diradical. Moreover, a consideration of barrier heights suggests that secondary dissociation is disfavored in the radical's *trans*-ONO conformer; we employ a natural bonding orbital analysis to investigate this result.

Mixed Quantum/Classical Theory (MQCT) for Rotationally and Vibrationally Inelastic Scattering

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We developed a mixed quantum/classical theory (MQCT) for molecule + atom inelastic scattering where translational motion of collision partners is treated classically, while the internal degrees of freedom – rotational and vibrational motion – are treated quantum mechanically. Within this framework, we carried out calculations of rotationally inelastic cross sections in a broad range of collisional energies and compared results against the exact full quantum results for several real systems. For Na + N_2 the agreement is excellent through six orders of magnitude range of cross sections values and in a broad range of collision energies, $5 < E < 1800$ cm^{-1}, even near excitation thresholds. Moreover, even the differential cross sections are accurately reproduced, including quantum oscillations. For He + H_2, which is the lightest possible system and the most stringent test of our theory, we also observed very good agreement with exact quantum results in a broad range of collisional energies, $10 < E < 10000$ cm^{-1}, including the case of high rotational excitation, $j = 22$. For H_2O + He, one of the most important systems in astrochemistry, we found that below $E = 1{,}000$ cm^{-1} the typical errors for cross sections are on the order of 10%, which is acceptable. At higher collision energies our MQCT method always produces very accurate results (1-2%) and remains computationally affordable. We found that computational cost of the fully-coupled MQCT scales as n^2, where n is the number of channels, which is more favorable than the full-quantum inelastic scattering calculations that scale as n^{5-6}. This allows caring out calculations on larger molecules and at higher collision energies, than was possible using the standard approach. For example, we carried out MQCT calculations for rotational excitation of methyl formate, $HCOOCH_3$ + He, a process important for interpretation of astrochemical observations. At energies below $E = 30$ cm^{-1}, where quantum calculations are affordable, the agreement is very good (5%). It is important that even for this heavy molecule MQCT remains computationally affordable at higher energies, up to $E = 1000$ cm^{-1}, which makes this theory a practical tool for obtaining the state-to-state transition rates for astrochemical modeling and other applications.

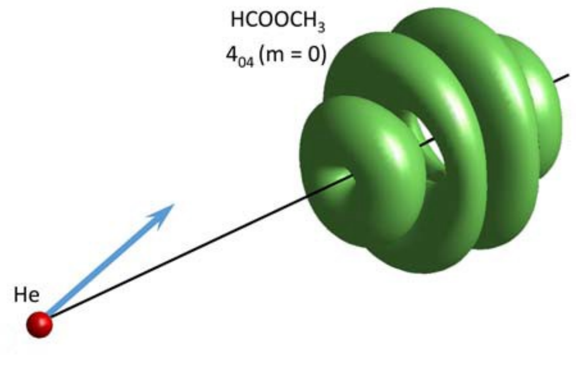

Fig. 1. Schematic of MQCT calculations for $HCOOCH_3$ + He in the BF reference frame.

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DCl Uptake through Sodium Dodecyl Sulfate Films on Salty Glycerol: Modeling Gas Entry into Sea Spray

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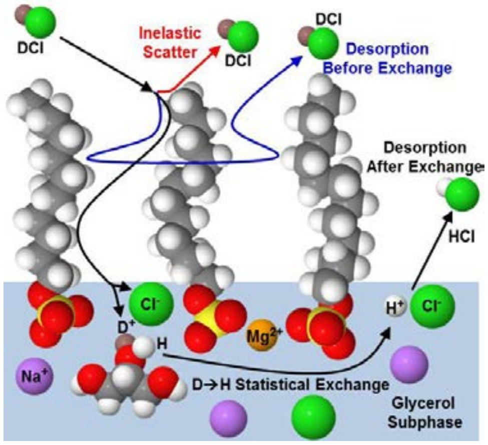
Sea spray aerosol particles convert ambient N_2O_5 into HNO_3 and $ClNO_2$, removing nitrogen oxides from the atmosphere and altering the abundances of key species such as O_3, OH, and CH_4. Gas entry into these aerosol particles can be hindered by organic molecules at the surface. We use molecular beam scattering experiments to measure the transport and dissociation of DCl in salty glycerol coated with a dodecyl sulfate film ($DS^- = CH_3(CH_2)_{11}OSO_3^-$). DS^- is used as a proxy for long-chain anionic surfactants found in the ocean, while salty glycerol is a low vapor pressure, protic liquid containing ocean-relevant ions. We used five salt solutions: 0.25 and 0.5 M NaCl, 0.25 M $MgCl_2$, 0.25 $CaCl_2$, and sea salt. Bulk DS^- concentrations were chosen from 0 to 11 mM, which generate surface concentrations as high as 1.8×10^{14} DS^-/cm^2 (~70% of a monolayer) determined by surface tension and Ar scattering measurements. We find that the addition of salt enhances the surface segregation of DS^- in the order: 0.25 M $MgCl_2$ ~ 0.25 M $CaCl_2$ > sea salt > 0.5 M NaCl > 0.25 M NaCl. Mg^{2+} and Ca^{2+} likely promote higher surface coverages because their +2 charge better shields the negative charges of the sulfate headgroups.

The DCl scattering experiments reveal that the DCl entry fraction for bare salty glycerol is 0.70, independent of the cation. The addition of DS^- lowers the entry fraction as more DCl molecules are caught in the long carbon chains of the surfactant and desorb rather than diffuse into the subphase glycerol solution, where they undergo DCl→HCl exchange and emerge as HCl. Our lowest observed entry fraction is 0.11 at ~70% DS^- coverage. A comparison of all measurements suggests that the entry probability depends solely on the surface concentration of DS^-, independent of Na^+, Ca^{2+}, or Mg^{2+} cation. At this low entry probability, gas permeation through the SDS monolayer limits uptake into aerosol particles that are smaller than one µm in radius.



Stereodynamics of Rotationally Inelastic Scattering of Electronically Excited Molecules: NO($A^2\Sigma^+$) with Rare Gas Colliders

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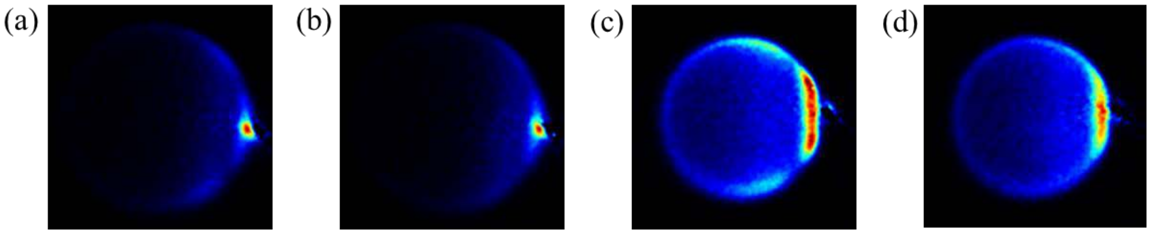
We present experiments conducted using a Crossed Molecular Beam Velocity Map Imaging (CMB-VMI) apparatus newly-constructed at Heriot Watt University, and optimized for the measurement of the stereodynamics of collisions of *electronically excited* species. We present the first systematic study of NO($A^2\Sigma^+$) scattered from Ne and Ar, building on our previous collaborative work on the dynamics of NO(A) + rare gas collisions.[1-3] NO($A^2\Sigma^+$, v = 0, N = 0) is prepared at the crossing point of the two molecular beams by laser excitation, followed by N' state-resolved detection of the products of rotational energy transfer within the $A^2\Sigma^+$, v = 0 manifold. An important feature of this method is that, since collisions only occur in the well-defined (400 ns) window between NO(A) state preparation and detection, the measurement is a true reflection of the scattered flux, and the density-flux transform necessary in the analysis of conventional CMB experiments is not required.

Example images for NO(A, v = 0. N' = 7) + Ar/Ne at collision energies, E_{coll}, centred at 504 cm^{-1} and 500 cm^{-1}, respectively, are shown below. Images have been acquired with the probe laser parallel and perpendicular to the scattering plane, revealing a strong variation of the rotational angular momentum polarization with scattering angle that does not follow the hard-shell, kinematic apse, limit.



Scattering images for production of NO($A^2\Sigma^+$; v = 0; N' = 7). (a) and (b) show scattering from Ar (E_{coll} = 504 cm^{-1}) with horizontal and vertical probe polarization, respectively. (c) and (d) show scattering from Ne (E_{coll} = 500 cm^{-1}) with horizontal and vertical probe polarization, respectively.

These experiments are complemented by quantum scattering calculations performed on recently calculated potential energy surfaces (PESs). In addition to the insight gained from the effect of the different PESs for the NO(A) + Ar and NO(A) + Ne systems, experiments and calculations have been conducted at different collision energies to explore dynamics accessing different regions of the PESs.

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Photochemistry of aldehyde clusters

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Chemical kinetics and dynamics of unimolecular reactions of isolated molecules in the gas phase are well understood for many processes. The influence of the environment on a unimolecular reaction in a solid or a liquid is, however, a major open problem in condensed phase dynamics. A cluster of five pentanal molecules, a medium-sized aldehyde, is chosen as a model for photochemical reactions in condensed phases e.g. in atmospheric aerosols. The photochemistry of aldehyde clusters is investigated theoretically. This study employs “on the fly” dynamics simulations using a semi-empirical MRCI electronic code for the singlet and triplet states involved. Previous studies have shown that the triplet-state photochemistry of an isolated pentanal molecule is dominated by Norrish I and II reactions. In this talk the importance of cross-molecular reactions in condensed phases is discussed and the effect on reaction yields of Norrish I and II reactions is evaluated. The main findings for the cluster are: (1) 55% of the trajectories lead to a unimolecular or cross-molecular reaction within a timescale of 100 ps; (2) cross-molecular reactions occur in over 70% of the reactive trajectories; (3) the main cross-molecular processes involve an H-atom transfer from the CHO group of the excited pentanal to an O atom of a nearby pentanal; and (4) the unimolecular Norrish II reaction is suppressed by the cluster environment. The predictions are qualitatively supported by experimental results on condensed-phase photolysis of an aliphatic aldehyde, undecanal. The very large effect of the environment on such a unimolecular reaction comes as a surprise on the background of present assumptions.

The computational approach should be useful for predicting the mechanisms of other condensed-phase organic photochemical reactions. The cross-molecular reactions discussed in this work are relevant to photolysis-driven processes in atmospheric organic aerosols. It is expected that the condensed-phase environment of an organic aerosol particle should support a multitude of similar cross-molecular photochemical processes.

Reference:

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Crossed-beam DC slice imaging of fluorine atom reactions with linear alkanes

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We report the reaction dynamics of F atom with selected alkanes studied by crossed beamscattering with DC slice ion imaging. The target alkanes are propane, *n*-butane, and *n*-pentane. The product alkyl radicals are probed by 157 nm single photon ionization following reaction at a collision energy of ~10 kcal mol^{-1}. The analyzed data are compared with the corresponding theoretical studies. Reduced translational energy distributions for each system show similar trends with little of the reaction exoergicity appearing in translation. However, the pentanereaction shows a somewhat smaller fraction of available energy in translation than the other two, suggesting greater energy channeled into pentyl internal degrees of freedom. The center-of-massangular distributions all show backscattering as well as sharp forward scattering that decreases in relative intensity with the size of the molecule. Possible reasons for these trends are discussed.

Scattering of O(^{3}P) from 1‐Alkyl‐3‐Methylimidazolium Tetrafluoroborate Ionic Liquids

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Quantitative characterization of the vacuum-liquid interface of room temperature ionic liquids (RTIL) is a challenging problem with applications in CO_2 capture and multiphase catalysis. We use ground-state oxygen-atom scattering to probe the vacuum-liquid surface structure of the RTIL 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]). Previous work found encouraging correlations between experimental scattering spectra and estimates of surface accessible RTIL atoms computed from molecular dynamics trajectories. However, a more realistic description of the oxygen-surface collision is necessary to predict product formation and to simulate experiment. This study combines hybrid QM/MM-MD direct dynamics simulations with two experimental reactive atom scattering (RAS) methods that differ in O atom energy and detection method: RAS-laser induced fluorescence (RAS-LIF) and RAS-mass spectrometry (RAS-MS). It is found that QM/MM-MD simulations add mechanistic insight by reporting on phenomena that are poorly resolved in experiment including projectile penetration depth and the dynamics of multi-step product formation (e.g. formation of water). Correlation of QM/MM-MD collision-site structure with product branching and product angular distributions are found to be a fruitful means of interpreting scattering trends in RAS-LIF and RAS-MS experiments.

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Ab initio study of H + CO rotation-vibration inelastic collision for astrochemical applications

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As the second most abundant molecule in the universe, carbon monoxide (CO) is rapidly becoming one of the best tracers of the astrophysical conditions. It is often not appropriate to assume local thermal equilibrium (LTE) in the dilute gas of astronomical sources. Accurate non-LTE modeling requires reliable collision rate coefficients of CO with its dominant collision partners H, H_2 and He.[1] Progress in ro-vibrational rate coefficients calculations has been slow. The difficulty of reliable H-CO ro-vibrational rate coefficients is related to the fact that HCO is a chemically bound species, in contrast with He-CO and H_2-CO that are bound only by weak Van der Waals forces. Lack of accurate three dimensional H-CO potential also blocks the availability of the accurate ro-vibrational rate coefficients.[2]

In this work, we present our new three dimensional H-CO potential[3], which can produce multiple experimental data precisely. Based on the new potential, ro-vibrational rate coefficients for transitions of v=1-5, j=0-30 to v'<v, j' have accurately been calculated and extrapolated at the temperature range T=10-3000K. Our new rates are very different from what have recently been used in astrophysical modeling[1]. The tests reveal that our work provides more comprehensive and accurate ro-vibrational de-excitation rate coefficient of H-CO system than any previously available data for astrophysical modeling.

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A Comprehensive Study of Ozonolysis of Ethylene

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Abstract

The textbook reaction of ozone with ethylene, which produces the simplest Criegee intermediate and plays an important role in the atmosphere, has been studied using highly accurate coupled-cluster calculations and advanced chemical kinetics (steady-state two-dimensional master equation) techniques. Our calculated results show that about 40% of nascent carbonyl oxide is cool, in excellent agreement with (indirect) experimental measurements; the remaining fraction is hot (see Figure 1). Hot Criegee has a short lifetime, so it rapidly isomerizes to dioxirane/formic acid and then subsequently to different products such as H_2O + CO, H_2 + CO_2, so on (see Scheme 1). The fate of cool Criegee in the atmosphere is believed to be through reaction with water dimer to form hydroxyl-methyl-hydroproxide, $HOCH_2OOH$. In addition, yields of HO and HO_2 radical products are predicted to be 13 ± 6% and 17 ± 6%, respectively. In the kinetic simulation, the HO radical product is produced mostly from the stepwise decomposition mechanism of primary ozonide rather than from dissociation of hot CH_2OO.

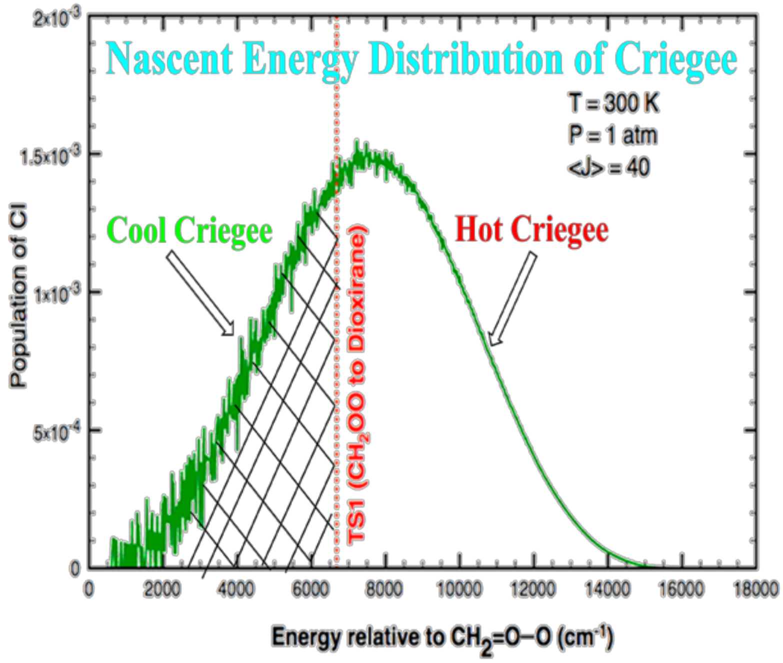
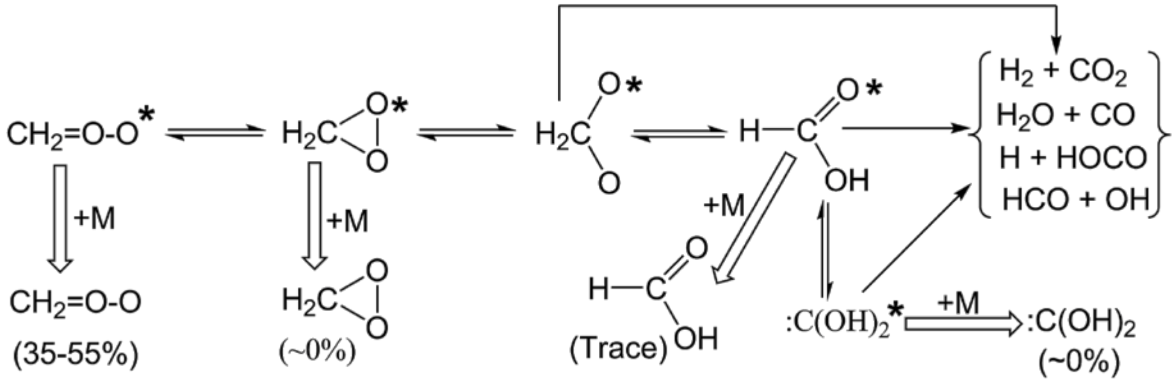


Figure 1: Nascent energy distribution function of vibrationally excited Criegee $CH_2{=}O{-}O$ intermediate, which is just formed from the $O_3 + C_2H_4$ reaction at the conditions of 300 K and 1 atm and an expectation angular momentum of 40.



Scheme 1: Schematic reaction mechanism of vibrationally excited Criegee CH_2OO intermediate. Species designated with an asterisk are present only in highly excited vibrational states.

Radiation induced dynamics in iodide-adenine anionic complexes

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A key issue in DNA damage caused by low energy electrons is the mechanism for electron attachment. The low energy electron is posited to initially interact with the dipole moment of a nucleobase and form a dipole-bound (DB) anion that possibly acts as gateway for valence bound (VB) anion formation. Electronic coupling facilitates subsequent electron transfer from the nucleobase VB anion to the DNA backbone, where cleavage can occur. The ability of DB states to serve as doorway for VB states is however still not well-understood. In order to gain new insight into the interaction of low energy electrons with adenine, we have studied iodide-adenine anionic complexes using photoelectron imaging combined with quantum chemical calculations taking the three most abundant adenine tautomers into account. Using a pump-probe scheme, a UV photon first induces electron transfer from iodide to adenine, while a subsequent IR pulse probes the resulting anion dynamics. The experimental results show evidence for two different adenine tautomers comprising the canonical and biologically relevant A9 and the less abundant A3 tautomer. A3 constitutes an excellent example illustrating that a DB state *can* provide gateway to VB anion formation, when the VB state is energetically accessible. This is manifested in the data as matching decay and rise components of the A3 DB and VB features. Conversely, A9 appears less susceptible to electron capture: Due to a smaller dipole moment, A9 forms DB anions in a narrower excitation energy range, and when formed, the DB anion auto-detaches rather than transitioning into the VB state. The VB state of A9 was found to be higher in energy than both the DB state and the neutral, and consequently the anion conversion is not feasible. Indications of the metastable A9 VB anion were instead observed as a shape resonance in one-color photoelectron spectra, when photon energies overlapping with the $\pi \rightarrow \pi^*$ absorption band of A9 were used. This resonance was interpreted to result from UV absorption by A9 followed by electron transfer from iodide into the empty π-oribtal – essentially corresponding to formation of the metastable A9 VB anion that auto-detaches efficiently.[1]

Overall the investigation – a succession of previous work on uracil[2] and thymine[3] – shows that while DB anions can act as gateway for the VB state and thereby possibly play a role in DNA damage, biological adenine is less prone to electron capture and VB anion formation compared to uracil, thymine and its tautomeric analogue A3.

Acknowledgments

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Efficient calculations of bound and resonance ro-vibrational states of ozone

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Ozone is one of those molecules which exhibit anomalous isotopic effect, also known as mass-independent fractionation (MIF) of oxygen isotopes [1]. It is understood that it comes from the ozone forming recombination reaction, which proceeds in two steps. First, an excited molecule of O_3^* is being form in O + O_2 encounter. This excited molecule is characterized by a spectrum of bound and resonance states. Second, O_3^* is stabilized by collision with bath gas (such as Ar), so that scattering resonances are quenched and a stable molecule of O_3 is formed.

Many theories, both classical and quantum, has been applied to describe this process. They explain some features of the MIF, but many questions remain. One of the recent studies was based on the mixed quantum/classical theory (MQCT) for Ar + O_3^* collision, but it also involved a dimensionally-reduced assumption for O_3^*, in which excitation of the bending motion was neglected [2]. It was concluded that development of the full-dimensional description of vibrations in O_3^* is need in order to describe the MIF quantitatively.

Thus, we develop a numerically efficient and physically accurate approach for computing ro-vibrational spectrum of ozone, including scattering resonances O_3^*, with all degrees of freedom included. We use hyper-spherical coordinates [3] that allow incorporating the symmetry of O_3 molecule exactly, and result in a simple Hamiltonian operator. Example of wave function for one of the resonance states is presented in Fig. 1. Such states are characterized by large spatial extent and exhibit complicated structure, which corresponds to the very-large-amplitude vibrational motion.

Unfortunately, we found that straightforward calculations of accurate (fully converged) energies and wave functions for such metastable states are too demanding computationally. They require large grids and lead to a huge Hamiltonian matrix. In order to increase the efficiency of these calculations substantially, we are implementing the method of sequential diagonalization-truncation [4]. Preliminary results are encouraging.

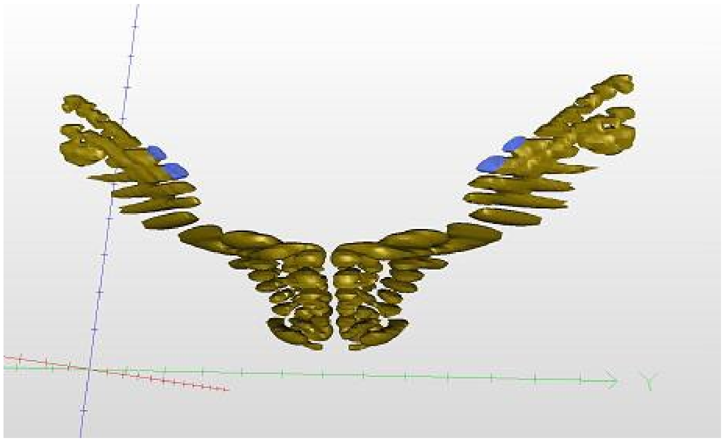

Figure 1: Example of wave function for a metastable state of ozone, when nuclear motion extends into the dissociation channels on the potential energy surface. The middle part of the "owl" structure corresponds to the highly excited vibrational motion in the deep covalent well (short-range), while the "wings" correspond to the large-amplitude vibrational motion in the van der Waals regions (long-range).

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Computing Vibrational Spectra of Polyatomic Molecules using Wavefunctions in Low-Rank Tensor Format

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Quantum dynamics calculations enable one to obtain accurate cross sections, rate constants and vibrational spectra. However, the CPU and memory cost of such calculations is notoriously high and increases sharply with the number of atoms. Using a "standard" direct-product representation of the wavefunction one is limited to molecules with no more than four atoms since one must explicitly store n^D wavefunction components per state, where D is the number of degrees-of-freedom (DOF) and n is the number of basis-functions-per-DOF. For instance, to treat a seven-atom (15 vibrational DOF) molecule with a modest 10 basis-functions-per-DOF, one requires ~15000 TB of memory to store even one state, and typically many states are wanted! This exponential scaling is a manifestation of the "curse of dimensionality".

Recently our group used the canonical-polyadic (CP) (also called CANDECOMP/PARAFAC) tensor format to represent high-dimensional wavefunctions and a block power method to compute vibrational spectra. The memory cost of this method nominally scales linearly with the number of DOF. This strategy exploits the fact that many vibrational wavefunctions are well-approximated by a sum of only a few products of well-chosen basis functions, that is, they are "low rank". Using this idea it was possible to solve a 20-D model problem and to compute the vibrational spectrum of acetonitrile (CH_3CN, 12-DOF) with less than 1 GB of memory; however, CPU times were long (~1-2 weeks) for these systems.

In this work we devise a method for solving the time-independent Schrödinger equation in which a system of many DOF is arranged into hierarchical groups of sub-systems, and each subsystem is solved in CP-format. We are able to compute the vibrational spectra of a 64-D coupled oscillator Hamiltonian as well as acetonitrile (CH_3CN) and ethylene oxide (C_2H_4O), the latter having 12 and 15 DOF, respectively. The CH_3CN calculation presented here required only 7 MB of memory and was 5 orders of magnitude faster and achieved higher accuracy for the first 70 energy levels relative to the previous CP-format calculation. For ethylene oxide we are able to predict the fundamental frequencies with accuracies similar to those obtained without exploiting the advantages of CP-format. Work is currently underway to compute spectra of even larger molecules.

Photochemistry and Reaction Dynamics of Halogen Oxide Radicals

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Abstract

The iodine dioxide free radical (OIO) has strong electronic absorption features at visible wavelengths in the 400 - 650 nm range. The photochemistry of OIO has potential implications in the balance of ozone in coastal areas but remains poorly understood. We are studying the photodissociation dynamics of this radical using photofragment translational energy spectroscopy with VUV photoionization detection of nascent products. A molecular beam containing OIO is produced using a novel photolytic source employing the reaction $OI + OI \rightarrow OIO + I$. At excitation wavelengths greater than 500 nm, the sole products from OIO photodissociation are $I + O_2$. Translational energy distributions of the ground state $I(^2P_{3/2})$ products indicate that the O_2 is produced in both the ground $^3\Sigma^-_g$ and electronically excited $^1\Delta_g$ states.

We are also investigating the bimolecular reaction dynamics of halogen oxide radicals in crossed molecular beams. Reactions of interest include those with stable molecules, such as $IO + NO \rightarrow I + NO_2$. We are also pursuing studies of radical-radical reactions such as IO + ClO. Energetically accessible product channels include OClO + I, OIO + Cl, ICl + O_2, and $I + Cl + O_2$.

Improved Semiclassical Tunneling

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The analytic multidimensional semiclassical tunneling formula[1] based on a second order vibrational perturbation theory (VPT2) description of the barrier is incorrect for deep tunneling at energies well below the top of the barrier. The origin of this deficiency is that the formula uses an effective barrier weakly related to the true energetics but correctly adjusted to reproduce the VPT2 anharmonic description of the reaction path at the saddle point. We have developed[2] an analytic improved semiclassical formula that correctly includes energetic information and allows a qualitatively correct representation of deep tunneling. Our approach consists of construction of a multi-segment composite Eckart potential that is continuous everywhere in both value and derivative, incorporates all relevant VPT2 information plus correct forward/reverse barriers, and has an analytic barrier penetration integral from which the semiclassical action and semiclassical tunneling probability can be derived. Our new theory is identical to the original theory at energies near or above the barrier but significantly improves the description of the deep tunneling regime. Unlike many methods that require the calculation of a reaction path, semiclassical tunneling requires only VPT2 calculations at the saddle point that can be readily parallelized and are options in popular electronic structure code packages.

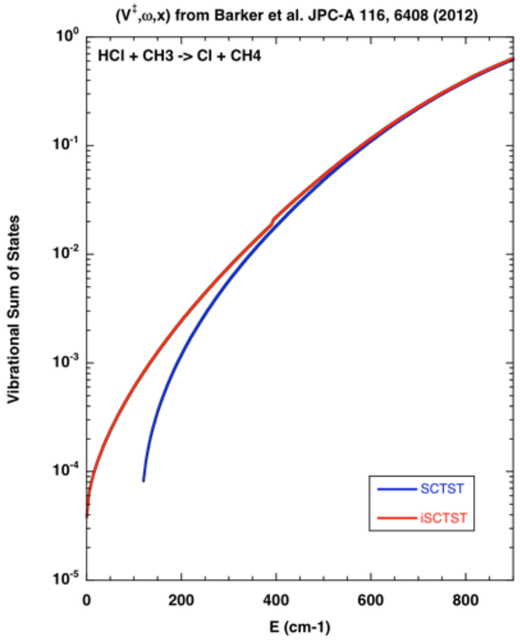

Figure 1. Sum of states with conventional (blue) and improved (red) semiclassical tunneling plotted versus the energy above the base of the barrier.

We will discuss applications and extensions of this approach to a variety of reactions for which VPT2 calculations have recently been carried out, including $H_2CCO+H_2O \rightarrow CH_3COOH$, $F+H_2O \rightarrow FH+OH$, and $HCl+CH_3 \rightarrow Cl+CH_4$. The resulting sum of states for the last reaction are in the figure and show significant differences between conventional and improved semiclassical tunneling in the deep tunneling regime where the correct threshold behavior is recovered by only the improved method. This approach will be included in the next release of the program suite Multiwell.[3]

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Imaging Spin Polarized Hydrogen from Photodissociation

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ABSTRACT: As a novel approach to spin polarized hydrogen studies, Rydberg tagging with slice imaging was incorporated into the study of photodissociation dynamics. Spin polarization of H photofragment is a rank-one photofragment orientation which can be characterized by three laboratory frame anisotropy parameters. Measurement of all three parameters with high sensitivity was possible using this method. Since the H atom TOF separation in the prevailing experimental conditions was ~30 ns, to achieve an effective slicing 30ps time gate should be provided at the MCP, which was not achievable by controlling hardware settings. Three dimensional imaging is a contemporary technique, which was introduced as a modification to velocity map imaging, which was used in obtaining thin slices. This technique requires a high speed digitizer and a computer algorithm designed using Labview language in addition to other components used in velocity map imaging. The key factor that enables 3D imaging process is the natural distribution of intensities of ion spots. Camera captures positional information while photomultipliertube through a high speed digitizer records the arrival times of each and every ion. Due to intensity variations of ion spots, a correlation could be made and, it was possible to assign each ion spot position with their respective arrival times, constructing a 3D distribution of the expanding ion sphere.

High-resolution photoelectron imaging and infrared photodissociation spectroscopy of cryo-cooled anions

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Two high-resolution techniques, slow photoelectron velocity map imaging (SEVI) spectroscopy and infrared photodissociation (IRPD) spectroscopy are used to probe cryogenically cold anions. Systems of interest studied recently are polycyclic aromatic hydrocarbons, transition states of bimolecular reactions, and transition metal oxide clusters.

Anion photoelectron spectroscopy (PES) is a versatile technique for studying transient neutral species via photodetachment of a stable closed-shell anion. Cryo-SEVI is a variant of anion PES which combines tunable laser energy, a velocity-map imaging detection scheme, and cryogenically cold ions.[1] Slow photoelectrons are preferentially detected, yielding high-resolution (sub-meV) spectra over a limited range of electron kinetic energy. SEVI yields detailed information on the geometry, vibrational frequencies, and electronic structure of the neutral molecule.

Using cryo-SEVI, we have recently studied the anthracyl radicals, which are intermediates in the combustion of organic matter and the formation of interstellar dust grains. We report photoelectron spectra of the ground and first excited states of distinct radical isomers, with detailed vibrational structure resolved and assigned for the first time. We also report a new cryo-SEVI study of the benchmark $F+H_2$ and $F+D_2$ reactions, wherein we probe the transition state region through detachment of FH_2^- and FD_2^- and directly observe new reactive resonances. Comparison to accurate theoretical calculations allows for assignment of these newly resolved features to resonances associated with quasi-bound states of the $F+H_2$ transition state and HF+H and HD+D products.

IRPD spectroscopy is complementary to photoelectron imaging for the structural characterization of exotic anionic species. Anions of interest (A^-) are mass selected, collected in a ring-electrode ion trap held as cold as 15 K, and tagged with D_2 to form A^-D_2.[2] The trapped ions are irradiated with intense, tunable IR light from the Fritz Haber Institute free electron laser, then extracted into a time-of-flight mass spectrometer. The vibrational absorption spectrum of A^- is constructed by measuring the depletion of the A^-D_2 species and formation of A^- as the IR wavelength is scanned.

We report IRPD spectra of the anionic titanium oxide clusters $(TiO_2)_n^-$ with n=(3-8) at a resolution of ~3 cm^{-1}. Point defects in bulk materials can be important catalytic sites, and gas-phase clusters are structural and reactive analogues that are more tractable for both experimental and theoretical study. Metal oxide clusters have been predicted by theory to exhibit many different structural motifs, but there is little experimental work in the literature confirming these structures. With comparison to *ab initio* results, our spectra identify the most stable $(TiO_2)_n^-$ cluster geometries and provide detailed information on their vibrational structure.

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Full-dimensional state-to-state reaction probabilities for $H + CH_4 \rightarrow H_2 + CH_3$

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Understanding chemical reactivity is one of the fundamental goals in chemical physics. Full-dimensional state-to-state differential cross sections can be calculated for triatomic and selected tetratomic systems. In the last decade impressive experiments studied polyatomic reactions in full detail. Reactions of methane with atoms like H, F, Cl and O provide prototypical examples studied. Most theoretical studies rely on quasi-classical trajectory calculations while advanced wave packet calculations employ reduced dimensional models explicitly including six of the twelve coordinates. For six atom reactions, only thermal rate constants and initial state-selected reaction probabilities could be studied by rigorous theory.

Full-dimensional state-resolved reaction probabilities for the $H + CH_4(v_{CH_4}, j, m) \rightarrow H_2(v_{H_2}) + CH_3(v_{CH_3})(J = 0)$ reaction are presented. These calculations are facilitated by flux correlation functions, the quantum transition state concept, the multi-layer extension of the multiconfigurational time-dependent Hartree (MCTDH) approach and an efficient scheme to evaluate the accurate Shepard interpolated potential energy surface on modern graphics processing units (GPUs). The mode-selectivity of the title reaction and the influence of rotational energy will be discussed. Furthermore, product distributions will be examined.

Non-equilibrium Ring-Polymer Molecular Dynamics

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During the last decade the Ring-Polymer Molecular Dynamics (RPMD) approach has proven to be an efficient method to approximately simulate quantum mechanical effects in chemical systems. Based on the path integral formulation, RPMD incorporates quantum effects using classical trajectories in an extended ring-polymer phase space. It exhibits appealing features including preservation of detailed balance, being exact in several limiting cases and it can be run efficiently exploiting techniques known from molecular dynamics. However, the current formalism has been limited to the calculation of correlation functions associated with the equilibrium Boltzmann distribution. In this talk the extension of the RPMD approach to simulate processes with non-equilibrium initial conditions is discussed.

Products of Mutual Neutralization Measured in a Flowing Afterglow

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Mutual neutralization (MN), $A^+ + B^- \rightarrow$ neutrals, is a very exothermic process in plasmas that typically occurs at large internuclear separations. As such, MN has been difficult to characterize theoretically except for very simple (e.g. monatomic-monatomic) systems. Experimentally, we have greatly expanded the kinetic database using the Variable Electron and Neutral Density Attachment Mass Spectrometry (VENDAMS) technique on a Flowing Afterglow-Langmuir Probe (FALP) apparatus. A recent upgrade to orthogonal time-of-flight detection of the ions has allowed characterization of MN products, which have historically been difficult to identify except with large error bars on the branching fractions, if at all. We present results for the reactant pairs CF_3^+/Cl^-, CF_3^+/Br^-, CF_3^+/I^-, and NF_2^+/Br^-. MN for these pairs creates the interhalogens FX among a few other species. Measurements of the attachment rate coefficients for the interhalogens will further constrain the product branching analysis.

Bimolecular reactions of silicon (Si) and silylidyne (SiH) with small unsaturated hydrocarbon molecules

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By combing the crossed molecular beam techniques with *ab initio* calculations as well as quasi classical trajectory (QCT) calculations, we explore the energetics, dynamics, and potential energy surfaces of the silicon atom and the silylidyne radical (SiH) with prototype hydrocarbons (allene and 1,3-butadiene), to untangle the underlying molecular processes leading to the formation of organosilicon molecules. We discover that, organosilicon molecules (SiC_mH_n, m, n ≤ 6) can be formed in bimolecular gas phase reactions via atomic and/or molecular hydrogen loss channels, and exhibit unusual chemical bonding and uncommon cyclic structures. As a hitherto poorly explored radical in chemical dynamics, $SiH(X^2\Pi)$ is also compared to its isovalent counterpart $CH(X^2\Pi)$ to shed more lights on the similarities and discrepancies in reaction mechanisms including isomerization processes of stabilized collisional complexes, decomposing channels, structures of formed products, energetics and branching ratios. Our studies therefore bring forward the novel concepts about the formation of organosilicon molecules, which eventually enrich our understanding of silicon-bearing molecules in astrochemistry and physical-organic chemistry.

A Single-longitudinal Mode Laser System for Probing Resonances in Cl + HD(v=1)→DCl + H Reaction

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Abstract

Recently, we set up a single-longitudinal mode(SLM) nanosecond laser system for Raman pumping of HD molecules to vibrationally excited states, which consists of two injection seeded Nd: YAG lasers and a home-built SLM optical parameter oscillator/amplifier system (OPO/OPA). More than 90% population transfer from v=0 to 1 of HD was demonstrated in a small volume with the scheme of Stark-induced adiabatic Raman puming [1]. About 13% of HD molecules was pumped to (v=1,j=0) level in crossed molecular beam experiment, which gives us a great opportunity to study the dynamical effect of HD vibrational excitation [2,3].

Combined this laser system with the high resolution time-of-flight Rydberg tagging apparatus, we found extremely short-lived resonance states in the reaction of Cl+HD(v=1)→DCl+H, which is originated from the mechenism of "chemical bond softening". We anticipate that similar resonance phenomena may occur in a broad range of chemical reactions involving vibrationally excited molecules [3].

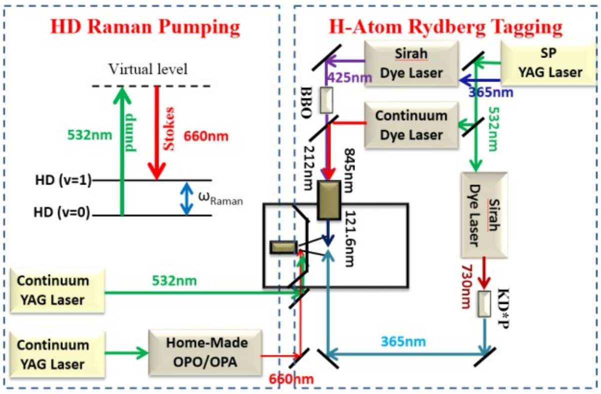

Figure: The schematic diagram for the laser system and the experimental setup.

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Photodissociation dynamics of thiophenol: A new dynamic facet near the conical intersection

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Ultrafast S-D bond dissociation reaction of thiophenol-d_1 has been experimentally investigated by the photofragment excitation (PHOFEX) spectroscopy and velocity-map ion imaging technique. As reported from our group's works relevant to photodissociation dynamics of thiophenol and its chemical derivatives, in the planar geometry, two conical intersections ($\pi\pi^*/\pi\sigma^*$ and $S_0/\pi\sigma^*$) are encountered along the reaction pathway leading to the S-H(D) bond fragmentation. The phenylthiyl radical at the asymptotic level is produced with its singly occupied molecular orbital (SOMO) either perpendicular ($\tilde{X}$) or parallel ($\tilde{A}$) to the molecular plane.

The ultrafast S-D bond rupture accounted for broad S_1-S_0 origin in PHOFEX spectrum is reflected in the angular distribution of fragments as the linearly polarized pump laser pulse interacts with the transition dipole moment of which the direction is well defined with respect to the dissociating S-D bond axis. Interestingly, however, it is found that anisotropy parameter (β) of +0.25 at the S_1 origin decreases to -0.60 at ~ 600 cm^{-1} above the S_1 zero-point level, giving a broad peak in β with a bandwidth of ~ 200 cm^{-1}. Our theoretical calculations reveal that the peak in β is ascribed to in-plane S-D bending mode excitation by which the nuclear configuration in the proximity of the S_1/S_2 conical intersection seam is accessed, showing a mixed character of parallel (S_1-S_0) and perpendicular (S_2-S_0) transition dipole moments at the same time. As a results, our report here on detailed dynamics of thiophenol-d_1 on the close-lying S_1 and S_2 states reveals a new dynamic aspect for chemical reactions taking place near the conical intersection.

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Applications of Chirped Pulse Microwave Spectroscopy in Uniform Supersonic Flows: The Photodissociation of Methyl Isothiocyanate

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Methyl isothiocyanate (CH_3NCS, MITC) is a volatile decomposition product of metam sodium, one of the most commonly used agricultural fumigants. Once in the atmosphere, MITC can photodissociate to CH_3NC, among other products, which could potentially oxidize to form toxins such as CH_3NCO. Thus, the photodissciation of MITC has been the focus of several previous investigations. These studies have shown the main reaction channels from 193 and 248 nm photolysis of MITC to be:

$$CH_3NCS \rightarrow CH_3 + NCS \quad (1)$$

$$CH_3NCS \rightarrow CH_3S + CN \quad (2)$$

$$CH_3NCS \rightarrow CH_3NC + S \quad (3)$$

The observation of CH_3S, as well as electronically excited CN and vibrationally excited NCS and CH_3NC has led to the proposal of a dissociation mechanism involving excited state isomerization of CH_3NCS to CH_3SCN.

Recently, the Suits lab has revisited the 193 nm photolysis of MITC using chirped-pulse microwave spectroscopy. The rotational spectrum showed signatures of NCS and CH_3NC, consistent with previous works. Additional products HCN, HNC, H_2CS, and CH_3CN were observed for the first time. Notably, CH_3S was not present, nor was there any evidence of vibrationally excited NCS or CH_3NC. This contradiction, and the observation of new products, could indicate that mechanisms other than excited state isomerization are relevant to this system.

How is C-H vibrational energy redistributed in the reaction $F + CHD_3 (v_1=1) \rightarrow HF + CD_3$?

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Abstract

Polyatomic reaction $F+CHD_3$ is a typical early barrier reaction and its reactivity is extremely impacted by the C-H stretching excitation. From the impressive results shown by Kopin Liu's group, we know that the vibrational excitation of C-H bond greatly suppresses the breaking of this bond, causing a much smaller cross section for the $HF + CD_3$ channel [1].

Recently, the title reaction was performed in our lab using the self-built crossed beam apparatus combined with time-sliced velocity map imaging [2] at a collision energy of 9kcal/mol. By determining the fraction of the vibrational excited CHD_3 reagent in the crossed-beam region accurately, we investigate the effects of C-H stretching excitation on the title reaction quantitatively. Experimental data show that the vibrational energy in the excited C-H bond of CHD_3 is almost exclusively deposited into the HF product vibration, and hence, the HF products from the excited-state reaction are about one vibrational quantum hotter than those of the ground-state reaction, while the vibrational state distribution of the CD_3 products is only slightly affected. The reaction is suppressed by the C-H stretching excitation, and the overall reactivity of the vibrational excited reaction is 74 ± 4% of that of the ground-state reaction for CD_3 ($v_2 = 0, 1, 2, 3$) product channels [3].

Key Words

Reaction dynamics, Crossed beam, Vibrational excitation

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State-to-state Quantum Dynamics of the X + $H_2O \leftrightarrow$ HX + OH (X=H, F, Cl) Reactions with a Transition-State Wave Packet Theory

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State-to-state quantum dynamics of the X + $H_2O \leftrightarrow$ HX + OH (X = H, F, Cl) reactions are investigated using a recently proposed transition-state wave packet (TSWP) theory.[1] The state-to-state TSWP theory is based on the quantum transition-state theory of Miller,[2, 3] which was first proposed for the direct and efficient calculation of cumulative reaction probability (CRP) and thermal rate coefficient by using flux correlation functions. In this approach, an ensemble of initial TSWPs is prepared as the eigenstates of a thermal flux operator, defined in the transition-state region on a dividing surface. These TSWPs are then propagated into the asymptotic region each arrangement channel, and as a result, the bases/grids required are significantly smaller than those needed in state-to-state approaches based on a single set of scattering coordinates. Finally, *S*-matrix elements are obtained from the thermal flux cross-correlation functions obtained in both the reactant and product arrangement channels. Within TSWP theory, the entire *S*-matrix can be obtained at all energies, which is unlike the initial state specific wave packet (ISSWP) approach. Furthermore, the propagation of multiple TSWPs can be carried out in parallel. We have implemented the TSWP method for triatomic and tetratomic reactions.[4, 5]

The state-to-state TSWP method is used to address several central issues in chemical dynamics, which are concerned with how chemical reactions are activated by various forms of energy and how the energy is disposed into product translational and ro-vibrational energies. The mode specificity and product energy disposal in the title reactions have been investigated with an focus on the transition-state control[6] and its modifications by other features on the potential energy surface.[7] These phenomena are rationalized by the Sudden Vector Projection (SVP) model.[8, 9]

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A Unified, Efficient Approach to Constructing Quasi-Diabatic Representations of Accurate Wave Functions

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Using newly developed tools, we are able to compute residual couplings of diabatic representations constructed using methods that do not utilize derivative coupling data. Using NH_3 as an example we are able, for the first time, to analyze and compare the diabaticity of popular diabatization approaches that avoid computation of derivative couplings, and show how to improve their quality using derivative coupling data.

This scheme can also be used to provide an initial guess for our algorithm that simultaneously constructs and fits a quasi-diabatic Hamiltonian, $\mathbf{H}^d$, resolving the multiple local minima problem and dramatically reducing the time to solution of the initial $\mathbf{H}^d$.

Using phenol – four states, all 33 internal coordinates, > 100 million CSFs- as an example, these new tools are used to conveniently adjust and select single coordinate functions and the monomial expansion used as the basis to expand H^d. This method provides a convenient, reliable and objective procedure to select an expansion basis to fit H^d, significantly improving the quality of the resulting representation

Angle-Resolved Molecular Scattering of Supersonically Cooled Nitric Oxide from Low Vapor Pressure Liquids

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Collision dynamics at the gas-liquid interface are explored with state-to-state resolved molecular scattering of NO. Liquid surfaces are probed with an incident beam of supersonically cooled NO ($^2\Pi_{1/2}$, J = 0.5) that strikes the surface at $\theta_{inc} = 45^o$ and scattered molecules are detected using laser induced fluorescence, which yields full rovibrational and electronic population distributions. Scattering pathways and dynamics are investigated as a function of (i) scattered angle, ranging from $\theta_{scatt} = -60^o$ to 60^o with respect to surface normal, (ii) incident collision energy, and (iii) liquid identity, specifically squalane, PFPE and [bmim][Tf_2N]. Results from these experiments show strong correlations between scattering angle and quantum state population distributions, which provide insight into the nature of the NO-liquid surface collision dynamics.

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Breakers East	Rooms 821-832	C5
Breakers West	Rooms 833-840	C5
Cypress	Rooms 717-724	H5
Deer Lodge	Rooms 1121-1130	H3
Director's Cottage		C3
Embers	Rooms 1313-1324	F2
Engineer's Cottage		G3
Forest Lodge	Rooms 1202-1211	F1
Guest Inn	Rooms 901-903	F2
Hearth	Rooms 1325-1336	F1
Live Oak	Rooms 1101-1110	G3
Lodge	Rooms 201-218	D4
Long View North	Rooms 101-110	A3
Long View Middle	Rooms 111-120	A3
Long View South	Rooms 121-130	A3
Manzanita	Rooms 1001-1012	B4
Oak Knoll	Rooms 1013-1024	C4
Pirates' Den	Rooms 501-510	G5
Sand	Rooms 605-610	G6
Scripps	Rooms 301-323	D4
Shores	Rooms 709-716	H5
Spindrift North	Rooms 849-856	C5
Spindrift South	Rooms 841-848	C6
Stuck-up Inn	Rooms 401-414	F4
Surf	Rooms 601-604	H6
Tree Tops	Rooms 1111-1120	H3
Whitecaps North	Rooms 809-820	C5
Whitecaps South	Rooms 801-808	D5
Willow Inn	Rooms 1025-1036	B4
Windward	Rooms 701-708	H5
Woodside	Rooms 1212-1223	G1

MEETING ROOMS

Acacia	B4
Chapel Auditorium	D5
Curlew	C4
Dolphin	C5
Evergreen	F1
Fred Farr Forum	E2
Heather	C4
Kiln	E2
Madrone	G3
Manzanita I & II	B4
Marlin	D4
Merrill Hall	G4
Nautilus	H4
Oak Knoll I & II	C4
Oak Shelter	F1
Sanderling	C6
Scripps	D4
Surf & Sand	G5
Toyon	B4
Triton	H4
Willow I & II	B4
Whitehead	G3

OTHER

BBQ Area	E6
Crocker Dining Hall	F6
Fire Pits	E6/H5
Guest Check-In	E5
Hearst Social Hall	E5
Human Resources	F1
Meditation Space	A3
Mott Training Center	G2
Park Ranger Office	G1
Park Store	E5
Phoebe's Café	E5
Seascape	F6
Swimming Pool	A5
Group Sales	E4
Viewpoint	E4
Volleyball Court	H5
Woodlands	F5
Yoga Room	A3

PARKING LOTS

Parking Lot A	E5
Parking Lot B	G5
Parking Lot C	H4
Parking Lot D	F2
Parking Lot E	E3
Parking Lot F	D4
Parking Lot G	D3
Parking Lot H	B3
Parking Lot J	A4
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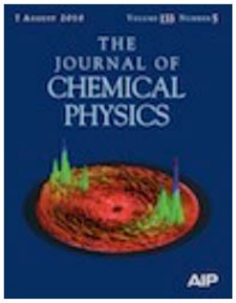

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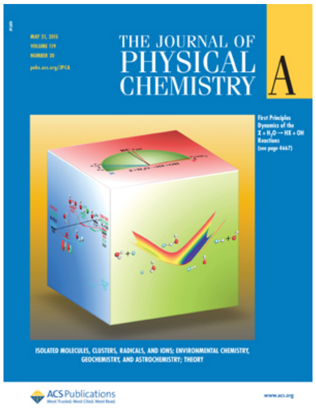

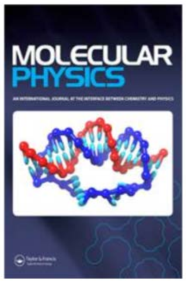

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