Dynamics of Molecular Collisions
28th Conference

Richard Dawes, Chair
Amy Mullin, co-Chair

July 9–14, 2023 | Snowbird, Utah
The Dynamics of Molecular Collisions (DMC) meeting is back!

We are excited to welcome you to Snowbird, Utah, for the 28th meeting in this series. The DMC, since 1965, has a great history of providing a unique platform and focal point for the gathering of experimentalists and theoreticians in the field of chemical dynamics.

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**Keynote Speaker**

Anne McCoy  
University of Washington

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**Herschbach Medals**

Marsha Lester  
University of Pennsylvania  
Hua Guo  
University of New Mexico

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**Organizers**

Richard Dawes  
Chair, Missouri S&T  
Amy Mullin  
co-Chair, University of Maryland

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**Featured Sessions**

- **Bimolecular Collision Dynamics**  
  Monday (morning) and Thursday (evening)

- **Quantum Control & Cold Reaction Dynamics**  
  Thursday (morning)

- **Nonadiabatic Dynamics**  
  Tuesday (evening)

- **Collision Dynamics in the Condensed Phase**  
  Monday (evening)

- **Photodissociation Dynamics**  
  Tuesday (morning)

- **Dynamics of Interfacial Collisions**  
  Wednesday (morning)
The Dynamics of Molecular Collisions (DMC) Conference provides a tremendous opportunity for the gathering of experimentalists and theoreticians in the field of chemical dynamics. At this biannual conference which spans five days, the latest developments in bimolecular collisional dynamics, dynamics in the condensed phase, photodissociation dynamics, reactions at interfaces, nonadiabatic dynamics, quantum control and cold reactions, and applications to combustion, atmospheric, and interstellar chemistry are discussed by experts in these fields. In addition to delivering a robust schedule of invited talks, young scientists are encouraged to present contributed talks as well as posters. The meeting has a Gordon Conference format, leaving afternoons free for the students and scientists to mingle and discuss their work in informal settings. Mornings and evenings are scheduled for talks and every night will feature a poster session for those not speaking to showcase their research.

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

**History**

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

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

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

D. R. Herschbach

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

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

Since 2007, the DMC has honored pioneers in the field via the Herschbach Medal Symposium as part of the meeting format. The awardees will deliver a special lecture on their work following the meeting banquet. The 2023 Herschbach Medals are dedicated to the contributions of two long-standing leaders in Chemical Physics, Professor Marsha Lester and Professor Hua Guo.

2023 Herschbach medalists

Professor Lester is known for her work on the spectroscopy and dynamics of important atmospheric radicals, and the development of action spectroscopy techniques. She is a great collaborator for theorists, with her work provoking many new ideas.

Professor Guo is known for his work on time-dependent quantum wavepacket simulations. He is a great friend to experimentalists, providing predictions and insight into a wide variety of systems ranging from cold molecules to hot radicals, to reactions on surfaces.
## Program

### SUNDAY, July 9

<table>
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<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>3:00 pm – 6:00 pm</td>
<td>Check in and Badge pickup</td>
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<tr>
<td>6:00 pm – 7:30 pm</td>
<td>Dinner</td>
</tr>
<tr>
<td>7:30 pm – 9:00 pm</td>
<td>Welcome and Keynote Address</td>
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<tr>
<td>7:30 pm – 7:45 pm</td>
<td>Welcome by Richard Dawes (Missouri S&amp;T)</td>
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<tr>
<td>7:45 pm – 8:00 pm</td>
<td>Keynote Introduction by Ned Sibert (University of Wisconsin)</td>
</tr>
<tr>
<td>8:00 pm – 8:45 pm</td>
<td>Keynote Address by Anne McCoy (University of Washington) “Decoding signatures of large amplitude vibrational motions: Exploring the stories encoded in vibrational spectra”</td>
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<tr>
<td>8:45 pm – 9:00 pm</td>
<td>Discussion</td>
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<tr>
<td>9:00 pm – 10:45 pm</td>
<td>Reception</td>
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### MONDAY, July 10

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>7:00 am – 8:10 am</td>
<td>Breakfast</td>
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<tr>
<td>8:10 am – 12:00 pm</td>
<td>Bimolecular Collision Dynamics I</td>
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<tr>
<td>8:10 am – 8:25 am</td>
<td>Session Introduction: Piergiorgio Casavecchia (University of Perugia)</td>
</tr>
<tr>
<td>8:25 am – 8:55 am</td>
<td>Ian Sims (Rennes) “Experimental studies of gas phase molecular collisions for astrochemical and astrophysical applications”</td>
</tr>
<tr>
<td>8:55 am – 9:05 am</td>
<td>Discussion</td>
</tr>
<tr>
<td>9:05 am – 9:35 am</td>
<td>Xingan Wang (USTC) “High resolution bimolecular reactive scattering experiments on the H/F/N+HD reactions”</td>
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<tr>
<td>9:35 am – 9:45 am</td>
<td>Discussion</td>
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<td>9:45 am – 10:00 am</td>
<td>Bin Zhao (Shenzhen) “Product angular distribution in the H + CD₄ → HD + CD₃ reaction”</td>
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<tr>
<td>10:00 am – 10:10 am</td>
<td>Discussion</td>
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<tr>
<td>10:10 am – 10:40 am</td>
<td>Coffee Break</td>
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<tr>
<td>10:40 am – 11:10 am</td>
<td>Francois Lique (Rennes) “The excitation of CO in cometary comae”</td>
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<tr>
<td>11:10 am – 11:20 am</td>
<td>Discussion</td>
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<tr>
<td>11:20 am – 11:50 am</td>
<td>Ed Narevicius (TU Dortmund) “Collisions with cold molecules: Tomography of Feshbach resonances”</td>
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<tr>
<td>11:50 am – 12:00 am</td>
<td>Discussion</td>
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<td>Time</td>
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<tr>
<td>12:00 pm – 1:00 pm</td>
<td><strong>Lunch</strong></td>
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<td>1:00 pm – 5:00 pm</td>
<td><strong>Afternoon Break</strong></td>
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<tr>
<td>5:00 pm – 6:00 pm</td>
<td><strong>Hot Topics</strong></td>
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<td>5:00 pm – 5:30 pm</td>
<td><strong>Zlatko Bačić</strong> (NYU)</td>
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<td></td>
<td>“Hydrogen-bonded molecular trimers: Full-dimensional quantum calculations of vibrational states”</td>
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<td>5:30 pm – 5:40 pm</td>
<td><strong>Discussion</strong></td>
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<tr>
<td>5:40 pm – 6:00 pm</td>
<td><strong>Hot Topic Poster Previews</strong></td>
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<tr>
<td></td>
<td>A9 (Nathanael Kidwell)</td>
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<td>A19 (Tianlin Liu)</td>
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<td>B2 (Dandan Lu)</td>
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<td>B12 (N. Balakrishnan)</td>
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<td></td>
<td>B21 (Patricia Vindel-Zandbergen)</td>
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<tr>
<td>6:00 pm – 7:15 pm</td>
<td><strong>Dinner</strong></td>
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<tr>
<td>7:15 pm – 9:30 pm</td>
<td><strong>Collision Dynamics in the Condensed Phase</strong></td>
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<tr>
<td>7:15 pm – 7:30 pm</td>
<td>Session Introduction: <strong>Hanna Reisler</strong> (University of Southern California)</td>
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<td>7:30 pm – 8:00 pm</td>
<td><strong>Andrew Orr-Ewing</strong> (Bristol)</td>
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<tr>
<td></td>
<td>“Photochemical dynamics of nitroaromatic compounds in aqueous solution”</td>
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<tr>
<td>8:00 pm – 8:10 pm</td>
<td><strong>Discussion</strong></td>
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<tr>
<td>8:10 pm – 8:40 pm</td>
<td><strong>Ruth Signorell</strong> (ETH Zurich)</td>
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<td></td>
<td>“Chaperon complexes and dielectrons: Transient species in reaction dynamics”</td>
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<td>8:40 pm – 8:50 pm</td>
<td><strong>Discussion</strong></td>
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<tr>
<td>8:50 pm – 9:20 pm</td>
<td><strong>Francesco Paesani</strong> (University of California San Diego)</td>
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<td>“Unveiling the quantum behavior of ions in water: From tunneling dynamics to bulk hydration with data-driven many-body potentials”</td>
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<td>9:20 pm – 9:30 pm</td>
<td><strong>Discussion</strong></td>
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<tr>
<td>9:30 pm – 11:30 pm</td>
<td>**Poster Session 1</td>
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**TUESDAY, July 11**

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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<tbody>
<tr>
<td>7:00 am – 8:10 am</td>
<td><strong>Breakfast</strong></td>
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<tr>
<td>8:10 am – 12:00 pm</td>
<td><strong>Photodissociation Dynamics</strong></td>
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<tr>
<td>8:10 am – 8:25 am</td>
<td>Session Introduction: <strong>Curt Wittig</strong> (USC)</td>
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<tr>
<td>8:25 am – 8:55 am</td>
<td><strong>Jingsong Zhang</strong> (UC Riverside)</td>
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<td>“Quantum interferences in photodissociation of small free radicals”</td>
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<tr>
<td>8:55 am – 9:05 am</td>
<td><strong>Discussion</strong></td>
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<tr>
<td>9:05 am – 9:35 am</td>
<td><strong>Floyd Davis</strong> (Cornell)</td>
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<tr>
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<td>“Casting light on alkylcarbene formation and unimolecular reactions”</td>
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<tr>
<td>9:35 am – 9:45 am</td>
<td><strong>Discussion</strong></td>
</tr>
</tbody>
</table>
9:45 am – 10:00 am  Yeonjun Jeong (Argonne)
“Electron spin coherences in photosystem I”

10:00 am – 10:10 am  Discussion

10:10 am – 10:40 am  Coffee Break

10:40 am – 11:10 am  Kristie Boering (Berkeley)
“Kinetics and reaction dynamics of oxygen isotope exchange reactions and their applications in earth and planetary science”

11:10 am – 11:20 am  Discussion

11:20 am – 11:50 am  Stephen Bradford (University of Southern California)
“New tools for unraveling solution phase photochemistry”

11:50 am – 12:00 am  Discussion

12:00 pm – 1:00 pm  Lunch

1:00 pm – 5:00 pm  Afternoon Break

5:00 pm – 7:15 pm  Nonadiabatic Dynamics

5:00 pm – 5:15 pm  Session Introduction: Ben Levine (Stonybrook)

5:15 pm – 5:45 pm  Ad van der Avoird (Nijmegen)
“Collision-induced spectrum of O₂ in collisions with O₂ and N₂”

5:45 pm – 5:55 pm  Discussion

5:55 pm – 6:25 pm  Sebastian van der Meeraker (Nijmegen)
“Cold and controlled collisions using tamed molecular beams”

6:25 pm – 6:35 pm  Discussion

6:35 pm – 7:05 pm  Jesus Perez Rios (Stony Brook University)
“Ion-atom-atom three-body recombination: from cold chemistry to plasma physics”

7:05 pm – 7:15 pm  Discussion

7:15 pm – 8:15 pm  Dinner

8:15 pm – 10:15 pm  Poster Session 2 | Group A (posters A1—A24)

Wednesday, July 12

7:00 am – 8:10 am  Breakfast

8:10 am – 12:00 pm  Dynamics of Interfacial Collisions

8:10 am – 8:25 am  Session Introduction: David Nesbitt (University of Colorado)

8:25 am – 8:55 am  Steven Sibener (University of Chicago)
“On-surface chemical dynamics probed with supersonic beam scattering, STM imaging, and infrared spectroscopy”

8:55 am – 9:05 am  Discussion

9:05 am – 9:35 am  Gil Nathanson (University of Wisconsin)
“Creation and reaction of solvated electrons at and near the surface of water”
9:35 am – 9:45 am  Discussion

9:45 am – 10:00 am  Matthew Costen (Heriot-Watt University)
“Real-space laser-induced fluorescence imaging of OH inelastic scattering at the gas-liquid interface”

10:00 am – 10:10 am  Discussion

10:10 am – 10:40 am  Coffee Break

10:40 am – 11:10 am  Chris Reilly (Lausanne)
“Probing rovibrational dynamics of CH₄-surface scattering with optothermal spectroscopy”

11:10 am – 11:20 am  Discussion

11:20 am – 11:50 am  Bin Jiang (USTC)
“First-principles dynamics simulations of adiabatic and nonadiabatic energy transfer of molecular scattering from metal surfaces”

11:50 am – 12:00 am  Discussion

12:00 pm – 1:00 pm  Lunch

1:00 pm – 5:00 pm  Afternoon Break

5:00 pm – 6:00 pm  Business Meeting

6:00 pm – 7:15 pm  Banquet

7:15 pm – 9:30 pm  Herschbach Medal Session

7:15 pm – 7:30 pm  Session Introduction: Bob Continetti & Richard Dawes

7:30 pm – 7:45 pm  Introduction of Marsha Lester: Bob Continetti

7:45 pm – 8:30 pm  Marsha Lester (University of Pennsylvania)
“Unimolecular decay dynamics of reactive intermediates in atmospheric and combustion Chemistry”

8:30 pm – 8:45 pm  Introduction of Hua Guo: Bob Continetti

8:45 pm – 9:30 pm  Hua Guo (University of New Mexico)
“Sudden vector projection model, mode specificity and bond selectivity made simple”

9:30 pm – 11:30 pm  Poster Session 3 | Group B (posters B1—B24)

THURSDAY, July 13

7:00 am – 8:10 am  Breakfast

8:10 am – 12:00 pm  Quantum Control and Cold Reaction Dynamics

8:10 am – 8:25 am  Session Introduction: David Chandler (Sandia)

8:25 am – 8:55 am  Brian Kendrick (Los Alamos)
“Quantum dynamics of ultracold chemical reactions: Quantum interference, excited electronic states, and long-lived complexes”
<table>
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<th>Time</th>
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<tbody>
<tr>
<td>8:55 am – 9:05 am</td>
<td>Discussion</td>
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</tbody>
</table>
| 9:05 am – 9:35 am | **Leah Dodson** (University of Maryland)  
“Fundamental studies of ion/molecule and neutral/neutral interactions for astrochemistry applications” |
| 9:35 am – 9:45 am | Discussion                                                          |
| 9:45 am – 10:00 am | **Mark Babin** (Harvard)  
“Controlling the unimolecular dissociation rate of an ultracold reaction” |
| 10:00 am – 10:10 am | Discussion                                                          |
| 10:10 am – 10:40 am | Coffee Break                                                       |
| 10:40 am – 11:10 am | **John Bohn** (University of Colorado Boulder)  
“Electro-association of field-linked tetramer states in ultracold gases” |
| 11:10 am – 11:20 am | Discussion                                                          |
| 11:20 am – 11:50 am | **Jeremy Hutson** (Durham University)  
“Making ultracold molecules by merging tweezers” |
| 11:50 am – 12:00 am | Discussion                                                          |
| 12:00 pm – 1:00 pm | Lunch                                                               |
| 1:00 pm – 5:00 pm | Afternoon Break                                                     |
| 5:00 pm – 7:15 pm | **Bimolecular Collisions II**                                       |
| 5:00 pm – 5:15 pm | Session Introduction: **Roland Wester** (Universität Innsbruck)      |
| 5:15 pm – 5:45 pm | **Stephen Klippenstein** (Argonne)  
“Formation and decay of criegee intermediates through bimolecular collisions” |
| 5:45 pm – 5:55 pm | Discussion                                                          |
| 5:55 pm – 6:25 pm | **Nick Shuman** (Air Force Research Laboratory)  
“Oxygen three ways: \( O \), \( O_2 \), and \( O_3 \) in upper atmospheric discharges, metal oxidation, and ionospheric processes” |
| 6:25 pm – 6:35 pm | Discussion                                                          |
| 6:35 pm – 7:05 pm | **Ahren Jasper** (Argonne)  
“Inefficient IVR and negative internal energy dependence for the \( H + HO_2 \) reaction” |
| 7:05 pm – 7:15 pm | Discussion                                                          |
| 7:15 pm – 8:15 pm | Dinner                                                              |
| 8:15 pm – 10:15 pm | **Poster Session 4 | Group B (posters B1—B24)**                                        |

**FRIDAY, July 14**

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<tr>
<th>Time</th>
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<tr>
<td>7:00 am – 8:10 am</td>
<td>Breakfast</td>
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<tr>
<td>8:10 am – 12:00 pm</td>
<td><strong>Applications of Molecular Collision Dynamics</strong></td>
</tr>
<tr>
<td>8:10 am – 8:25 am</td>
<td>Session Introduction: <strong>David Osborn</strong> (Sandia-Livermore)</td>
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</tbody>
</table>
8:25 am – 8:55 am  
**Mark Johnson** (Yale)  
“Temperature- and size-dependent, water-cluster-mediated long range proton transfer in microhydrated 4-aminobenzoic acid”

8:55 am – 9:05 am  
Discussion

9:05 am – 9:35 am  
**Ryan Steele** (Utah)  
“Taming the beast: New developments & demonstrations of anharmonic vibrational simulations for large(r) chemical systems”

9:35 am – 9:45 am  
Discussion

9:45 am – 10:00 am  
**Simone DeSouza** (University of Maryland)  
“Dynamics of optically centrifuged N₂O in extreme rotational states studied with transient IR absorption spectroscopy”

10:00 am – 10:10 am  
Discussion

10:10 am – 10:40 am  
Coffee Break

10:40 am – 11:10 am  
**Krzysztof Szalewicz** (University of Delaware)  
“Interactions of H₂ with CO: High-accuracy computational spectroscopy and scattering versus experiment and astronomic observations”

11:10 am – 11:20 am  
Discussion

11:20 am – 11:50 am  
**Dmitri Babikov** (Marquette)  
“MQCT2023 – A program for calculations of inelastic scattering of two molecules”

11:50 am – 12:00 am  
Discussion

12:00 pm – 12:05 pm  
THANKS! and DMCXXVIII / **Amy Mullin** (Maryland)
TALKS
Decoding Signatures of Large Amplitude Vibrational Motions: Exploring the Stories Encoded in Vibrational Spectra

Anne B. McCoy

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

ABSTRACT

In this talk, I will discuss recent work in our group in exploring spectral signatures of large amplitude vibrational motions, focusing on water-containing complexes and radicals. The vibrational spectra of these systems contain features that cannot be understood by the usual harmonic description of molecular vibrations, and often contain more peaks than one would expect. The breakdown of the harmonic treatment of molecular vibrations reflects both the anharmonicity along this coordinate and coupling between this mode and other low frequency modes in these systems. It also reflects changes in the electronic structure as molecules vibrate. The presentation will draw from reported vibrational. The focus will be on how we can use an array of methods, including harmonic treatments, vibrational perturbation theory in internal coordinates and analysis of electronic wave functions to unravel the insights that can be obtained from the spectra of these molecular systems. Implications of these studies into the condensed phase dynamics and spectroscopy will also be discussed.
Thanks to advances in astronomical techniques, the past few years have seen a significant increase in the rate of detection of interstellar molecules. State-of-the-art astrochemical models fail to predict accurately the observed abundances of these gas-phase (mainly) organic molecules, sometimes by many orders of magnitude. This is principally due to a lack of knowledge of important input parameters – the rate constants and in particular product branching ratios for formation and destruction reactions of these species, especially at the low temperatures (down to 10 K and even below) prevailing in the richest molecular sources, dense molecular clouds. Furthermore, transformation of radioastronomical detections into absolute abundances requires knowledge not only of radiative transitions but also collisional (de-)excitation by the most abundant species in these environments (hydrogen, helium, ...). I will describe experimental measurements made in the gas phase down to 10 K of these important collisional parameters using innovative combinations of the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique coupled with pulsed laser photolysis and a range of spectroscopic detection methods including laser-induced fluorescence\(^1\)\(^2\) and chirped-pulse mm-wave rotational spectroscopy.\(^3\)

Homogeneous nucleation in the gas phase is a key process in the formation of clouds and dust particles in a range of systems including combustion, planetary atmospheres and circumstellar shells. Experimental measurements on the formation of the small, weakly bound clusters implicated in the early stages of nucleation are few and far between.\(^4\) In Rennes we have made a number of measurements of homodimer formation rate constants at low temperatures, exploiting the temperature jump afforded by the CRESU technique in ‘flow tube’ mode coupled to molecular beam sampling and mass spectrometric detection.\(^5\)\(^6\) Here, we extend these measurements for the first time to heterodimer formation using a completely new detection scheme employing chirped-pulse Fourier transform mm-wave rotational spectroscopy combined with molecular beam sampling, which has enabled us to follow both monomer and dimer concentrations at a variable distance (and therefore, reaction time) along the cold, uniform flow. The high sensitivity of the technique has allowed us to employ pseudo-first-order conditions to obtain absolute rate constants. Time permitting I will report preliminary measurements of rate constants for formation of formic acid – CO\(_2\) heterodimers at temperatures down to 50 K.

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**High resolution bimolecular reactive scattering experiments on the H/F/N+HD reactions**

Xingan Wang

*Department of Chemical Physics, University of Science and Technology of China. Jinzhai road 96, Hefei, 230026, China. Email: xawang@ustc.edu.cn*

**ABSTRACT**

Crossed molecular beam method is a mature technique and has played an important role in the development of molecular physics and chemical reaction dynamics. Over the past decade, various interesting quantum effects have been investigated in detail in crossed molecular beam scattering experiments,\(^1\)\(^2\)\(^3\) which are of great value in understanding molecular quantum dynamics.

Here we report the studies of reactive collisions by using time sliced velocity map ion imaging technique together with the near threshold ionization method. We acquired quantum state resolved ion images for the F+HD,\(^4\) H+HD/D\(_2\) and N+HD reactions. The high resolution results are beneficial in the study of detailed reaction mechanism of elementary chemical reactions.

**Acknowledgements:** This work was supported by the National Natural Science Foundation of China (Grant No. 22125302), Strategic Priority Research Program of the Chinese Academy of Sciences, and the Ministry of Science and Technology of China.

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Product angular distribution in the H + CD₄ → HD + CD₃ reaction

Bin Zhao,¹,² Uwe Manthe,² Donghui Zhang¹

¹Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, People’s Republic of China. Email: zhaobin@sustech.edu.cn
²Theoretische Chemie, Fakultät für Chemie, Universität Bielefeld, Bielefeld 33615, Germany

ABSTRACT

First-principles based study of quantum state-to-state reaction dynamics aims to provide insights into the most detailed dynamical processes of chemical reactions and has achieved great success in predicting and explaining fascinating quantum effects in various tri-atomic systems. This field has now advanced to polyatomic reaction systems, and reactions of CH₄ with various atoms are the most studied systems.

Recently, counterintuitive effects are found in the H+CHD₃→H₂+CD₃ reaction:¹ Increasing the energy in the reactant’s CD₃ umbrella vibration reduces the energy in the corresponding product vibration. An in-depth analysis reveals the crucial role of the effective dynamical transition state: Its geometry is controlled by the vibrational states of the reactants and subsequently controls the quantum state distribution of the products.

![Figure](image_url)

Figure. (a) Counterintuitive CD₃ umbrella vibrational excitation in the H+CHD₃→H₂+CD₃ reaction; (b) The velocity and angle-resolved state-specific differential cross sections of the H+CD₄→HD+CD₃ reaction at a collision energy of 0.72 eV.

Very recently, we performed a theoretical study of the H+CD₃→HD+CD₃ reaction² with the time-dependent wave packet method using a seven-dimensional model Hamiltonian developed by Palma and Clary. The velocity and angle-resolved state-specific differential cross sections (DCSs) at a collision energy of 0.72 eV are investigated in detail. Two detection schemes based on measuring the state-selective HD(v₁,j₁) and CD₃(v₂,j₂) products are compared. The very interesting angular distribution of the CD₃ product is explained with the concept of the effective dynamical transition state.

¹ R. Ellerbrock, B. Zhao, U. Manthe, Sci. Adv. 8, eabm9820 (2022)
² In preparation
The excitation of CO in cometary comae

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ABSTRACT

An accurate determination of the physical conditions in astrophysical environments relies most of the time on the modeling of molecular spectra. In such environments, densities can be so low ($n << 10^{10}$ cm$^{-3}$) that local thermodynamical equilibrium (LTE) conditions cannot be maintained$^1$. Hence, radiative and collisional properties of molecules are needed to correctly model molecular spectra. CO is one of the most abundant molecules in the interstellar medium in planetary and cometary atmospheres and is even found to be dominant in comae of comets at large heliocentric distances. It is then of high interest to study the excitation of CO induced by collisions with H$_2$O and CO, the dominant collisional partners in cometary comae.

In this talk, I will present new scattering calculations for the collisional energy transfer in CO-H$_2$O$^2$ and CO-CO$^3$ collisions. Using quantum close coupling and statistical approaches, excitation cross sections and rate coefficients are provided for collisional energy transfer between the first 11 levels of CO. In comparison with data available in the literature, significant differences were found, especially for the dominant transitions. Using these new collisional data, non-LTE excitation models were performed and compared to recent CO observations in CO-rich cometary comae. These new data allow an accurate modelling of the physical conditions cometary comae that are keys for understanding stars and planets formation.

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Figure 1: SACM rate coefficients for the rotational excitation of CO by water

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$^3$ Zoltowski, M. et al., The excitation of CO in CO-dominated cometary comae, MNRAS 520, 3887 (2023)
Collisions with Cold Molecules: Tomography of Feshbach resonances

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ABSTRACT

During collisions coupling between relative and internal atomic and molecular degrees of freedom leads to the formation of Feshbach resonances. The large phase space volume that particles explore in this metastable scattering state supports interference between many different quantum pathways that include inelastic and reactive processes. We present a new method that allows us to measure simultaneously all the quantum channels for Feshbach resonances that appear in collisions between vibrationally excited $\text{H}_2^+$ ion and noble gas atoms. Our quantum state mapping is based on ion-electron coincidence velocity map imaging spectroscopy.
Hydrogen-bonded molecular trimers: Full-dimensional quantum calculations of vibrational states

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ABSTRACT

Noncovalently bound molecular trimers hold a special place in the hierarchy of molecular clusters. These are the smallest clusters in which the nonadditive many-body (three-body in this case) interactions arise, that are essential for accurate description of the structural and dynamical properties of condensed phases. Consequently, molecular trimers are the obvious, most natural candidates for testing the accuracy of the computed three-body interactions through a comparison of high-level bound-state calculations on the potential surfaces (PESs) that incorporate them with the spectroscopic data. This presupposes the existence of such rigorous quantum methods. However, while powerful methods for full-dimensional quantum calculations of rovibrational states of noncovalently bound molecular dimers are available,\textsuperscript{1} until our work within the past year\textsuperscript{2,3} no comparable methodology existed for hydrogen-bonded molecular trimers. Very recently, building on our rigid-monomer nine-dimensional (9D) quantum treatment of molecular trimers,\textsuperscript{2} we presented the computational methodology which for the first time allows rigorous full-dimensional (12D) quantum calculations of fully coupled intramolecular and intermolecular vibrational states of hydrogen-bonded trimers of flexible diatomic molecules.\textsuperscript{3} At the foundation of our methodology is the partitioning of the full vibrational Hamiltonian of the trimer in two reduced-dimension Hamiltonians, one in 9D for the intermolecular degrees of freedom and another in 3D for the intramolecular vibrations of the trimer, and a remainder term. These two Hamiltonians are diagonalized separately, and a fraction of their respective 9D and 3D eigenstates is included in the final 12D product contracted basis in which the full vibrational Hamiltonian of the trimer is diagonalized. This methodology has been implemented in the 12D quantum calculations of the coupled HF-stretch excited intra- and intermolecular vibrational states of the hydrogen-bonded HF trimer\textsuperscript{3} on \textit{ab initio} calculated PES of Quack and Suhm. These 12D calculations show that the frequencies of the HF-stretch excited states of the trimer are strongly redshifted in comparison to those of the isolated HF. Moreover, the magnitudes of these trimer redshifts are much larger than the redshift of the bound HF stretch in HF dimer, a manifestation of the cooperative hydrogen bonding in HF trimer. The 12D calculations also reveal strong coupling between the intramolecular HF-stretch vibrations and the intermolecular vibrational states of HF trimer.

Photochemical Dynamics of Nitroaromatic Compounds in Aqueous Solution

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ABSTRACT

Brown carbon aerosol in Earth’s atmosphere absorbs solar radiation at visible wavelengths and contributes to the overall warming of the troposphere. It is released directly to the troposphere by biomass burning, whether from wild fires, domestic fuels, or agricultural practices. Analysis of atmospherically sampled brown carbon particles reveals a complex matrix of constituents, including various partially oxidized organic compounds. Of these molecular constituents, the most significant contributors to absorption of near-UV and visible light at tropospheric wavelengths (λ > 290 nm) are nitroaromatic compounds such as nitrophenols and nitrocatechols. Photochemical processing of these nitroaromatic compounds by sunlight and oxidants in the atmosphere will change the composition of the brown carbon aerosol over time. Here, we consider the primary steps in this photochemical processing by studying the response of nitroaromatic compounds over femtosecond to microsecond timescales using transient absorption spectroscopy. Experiments are conducted in aqueous solution to mimic the conditions in water droplets in the atmosphere. The absorption spectra and the photochemical pathways are sensitive to the pH of the solution, hence the effects of acidification of the solutions are explored. Measurements over extended timescales reveal multiple sequential steps in the photochemical dynamics from ultrafast autoionization and radical formation to recombination, the consequences of which will be discussed.

Chaperon complexes and dielectrons: 
Transient species in reaction dynamics

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ABSTRACT

Transient species play a crucial role in reaction dynamics. With the help of supersonic expansions, such species can be isolated and their role in the dynamics be studied. Here, we report on chaperon complexes and their role in gas phase nucleation, and on dielectrons as a source of low-energy electrons for reduction reactions.

New particle formation through vapor condensation is an important source of atmospheric aerosols. However, the question how the volatility of different vapor components affects the nucleation kinetics has hardly received any attention yet - mainly due to the lack of suitable experiments to answer this question. To solve this problem, we have developed a special nucleation instrument that combines a Laval expansion with soft mass spectrometric cluster detection. The setup allows us to probe transient heteromolecular clusters (chaperon complexes) directly during the very first step of vapor nucleation. We find that higher volatility vapor components catalyze the nucleation of lower volatility vapor components, thus providing an alternative, previously unknown route for more efficient nucleation.

Electrons solvated in liquid ammonia or water are powerful reducing agents. Here we report a new way to generate low-energy electrons in situ that might even enhance such reduction reactions. Using double-imaging photoelectron-photoion coincidence spectroscopy, we demonstrate for sodium-doped ammonia cluster how ultraviolet photoexcitation generates spin-paired solvated dielectrons, which subsequently relax through electron-transfer-mediated decay. When the dielectrons decay, an electron is formed that recombines with the solvent molecules together with a second low-energy electron that is ejected. The latter is available for reduction reactions.

Unveiling the Quantum Behavior of Ions in Water: From Tunneling Dynamics to Bulk Hydration with Data-Driven Many-Body Potentials

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ABSTRACT

This talk will provide a comprehensive exploration into the quantum behavior of ions in water, from tunneling dynamics to bulk hydration, using data-driven many-body potential energy functions (PEFs) developed within the many-body energy (MB-nrg) formalism.\textsuperscript{1,2} I will begin describing the MB-nrg theoretical and computational framework for molecular simulations of ion-water systems across different phases. The accuracy and predictive power of the MB-nrg PEFs will be assessed through extensive comparisons with results obtained using both ab initio models and polarizable force fields. Our group’s investigations into the nature of ion-water interactions using many-body models and density functional theory will also be highlighted, particularly focusing on the importance of capturing close-range interactions such as charge transfer and charge penetration.\textsuperscript{3,4} I will then cover our group’s findings on the vibrational spectra of halide-water dimers\textsuperscript{6} and specific ion effects on tunneling and hydrogen-bond rearrangements in halide-dihydrate complexes.\textsuperscript{7,8,9} Finally, I will present our group’s work on the hydration structure of halide and alkali-metal ions in solution. I will show that our MB-nrg PEFs predict X-ray spectra in close agreement with experimental results,\textsuperscript{10-13} thus enabling realistic simulations of ions in water across various phases and providing a unified picture of ion hydration from gas-phase clusters to bulk solutions.

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\textsuperscript{12} Zhuang, D. \textit{et al.} Hydration structure of Na\textsuperscript{+} and K\textsuperscript{+} ions in solution predicted by data-driven many-body potentials, J. Phys. Chem. B 126, 9349, 2022.
Quantum Interferences in Photodissociation of Small Free Radicals

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ABSTRACT

The near-UV state-to-state predissociation dynamics of SH(A\(^2\Sigma^+, v', N\)) are probed as a function of rovibrational levels of A\(^2\Sigma^+, v\)', from v'=0 to 7 up to the S(1D) threshold. The S(3P_J) product spin-orbit branching fractions change drastically as the A\(^2\Sigma^+ v\)' level tunes across the crossing points of the repulsive states \(^4\Sigma^-, \(^2\Sigma^-,\) and \(^4\Pi,\) manifesting quantum interferences among the three repulsive states. Furthermore, near the H + S(1D) threshold, the bound A\(^2\Sigma^+ v\)'=5 or 6 level and the continuum \(^2\Sigma^−\) state can both be optically excited with good Franck-Condon factors from X\(^2\Pi v\)\(^>=3\). Since these two excited states are coupled via spin-orbit interactions and lead to the same S(3P_J) products, quantum interferences (predissociation of discreet level of A\(^2\Sigma^+ vs.\) direct dissociation of \(^2\Sigma^−\) continuum) would result, and the S(3P_J) product spin-orbit branching ratios and angular distributions vary drastically across the discreet-continuum resonance. The S(3P_J) product distributions could provide deeper insights into the quantum interference phenomenon.

The \(^2\Sigma^-\)\(^−\)\(^2\Pi\) predissociation dynamics of the HCO radical is examined at a state-to-state level in a combined experimental and theoretical study.\(^1,2\) The complete CO (v, J) product state distributions from various vibrational levels of the \(^2\Sigma^-\) state are obtained from the H-atom product translational energy distributions. The CO product rotational distributions are highly inverted, and furthermore, intensity oscillations at high J states are observed. The quantum reaction dynamics show that the oscillations in the CO product state distributions are attributed to an interference effect stemming from unique features on the ground-state potential energy surface (PES) of HCO, following the decay of the excited \(^2\Sigma^-\) state to the ground \(^2\Pi\) state via Renner-Teller coupling at linearity. This interference effect is exquisitely sensitive to the PES and thus can be used to probe dynamically important regions of the reactive PES.

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Casting Light on Alkylcarbene Formation and Unimolecular Reactions

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ABSTRACT

Simple alkylcarbenes such as methylcarbene (CH\textsubscript{3}CH), dimethylcarbene (CH\textsubscript{3}CCH\textsubscript{3}), and ethylcarbene (CH\textsubscript{3}CH\textsubscript{2}CH) have been remarkably elusive to experimental characterization. Our interest in alkylcarbenes began with the finding that they are produced by C-C bond fission in the UV photodissociation of alkyl radicals.\textsuperscript{1} Lying ~ 300 kJ/mol (~ 3 eV) above their stable ground state alkene isomers, singlet alkylcarbenes undergo rapid isomerization via a 1,2-hydrogen atom shift. Most previous attempts at formation of alkylcarbenes involved UV photodissociation of diazoalkanes or diazirines (e.g., CH\textsubscript{3}CHN\textsubscript{2}). Unfortunately, this forms singlet alkylcarbenes with high internal energies and very short lifetimes, precluding their observation.

Methylcarbene (CH\textsubscript{3}CH, also called ethylidene) can be produced in its triplet ground state at energies below threshold for intersystem crossing by photolysis of methylketene.\textsuperscript{2} We use photofragment translational energy spectroscopy, with 8.8 or 9.9 eV pulsed vacuum ultraviolet (VUV) photoionization, to probe the dynamics. Our observations are consistent with a high potential energy barrier for isomerization of methylcarbene on the triplet surface. Electronically excited singlet methylcarbene is also produced, isomerizing by a 1,2-hydrogen atom shift after departure of CO, producing highly vibrationally excited ethylene. Product translational energy distributions, measured at m/e = 28 and 26, verify the theoretically calculated enthalpy of formation of triplet methylcarbene, and are consistent with a singlet-triplet energy gap of about 12.5 kJ/mol.

Dimethylcarbene (CH\textsubscript{3}CCH\textsubscript{3}) and ethylcarbene (CH\textsubscript{3}CH\textsubscript{2}CH) are produced by UV photolysis of the appropriate alkylketene.\textsuperscript{3,4} Product translational energy distributions are consistent with theoretical predictions that ground state ethylcarbene lies ~34 kJ/mol higher in energy than its dimethylcarbene (CH\textsubscript{3}CCH\textsubscript{3}) isomer. A second dissociation channel involves direct formation of propene prior to, or concurrent with, CO elimination.

Upon photolysis of propenal (also called acrolein), a 1,3 H atom shift produces methylketene, which exclusively undergoes C=C bond fission yielding methylcarbene + CO, as described above.\textsuperscript{2} Recently, we initiated time-resolved studies using a time of flight mass spectrometer. By varying the delay between the UV pump and VUV photoionization laser pulses, nanosecond timescales are measured for isomerization of propenal to methylketene, and its dissociation forming methylcarbene. Some initial time-resolved measurements will be presented.

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Electron Spin Coherences in Photosystem I

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ABSTRACT

Microsecond coherence times are observed in the $P^+A_1^-$ entangled electron spin pair created upon excitation of photosystem I in cyanobacteria. Important environmental features in the spin pair’s decoherence, such as protein residues and the distance of the bath spins from the central spins, are identified using spin dynamics calculations under the cluster-correlation expansion (CCE) approximation. Notably, the protons within the distance range of 5-8Å are found to be the dominant contributors. In a more microscopic picture, important two-spin decoherence drivers, as well as individual nuclear spins, are characterized by controlling the spin-spin couplings in the system’s interaction Hamiltonian.

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Reactions of the ground and first excited states of atomic oxygen, O(^3P) and O(^1D), with small molecules such as O_2, CO, CO_2, and NO_2 continue to be of interest in aeronomy, atmospheric chemistry, and paleoclimate studies, thus providing additional motivation to understand the kinetics and dynamics of these reactions and how well they are predicted by theory. I will present an overview of current understanding of several of these reactions through kinetics and dynamics experiments and their comparison with theory as well as updates on their applications in Earth and planetary science.
New tools for unraveling solution phase photochemistry

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ABSTRACT

In the liquid phase, intermolecular interactions often control electronic structure, and therefore chemical reactivity and excited state dynamics, but these interactions are complex to quantify and are frontier problems for theory. Our group has developed several experiments to quantify how electronic interactions with the local environment affect overall reactivity, in ionization, electron transfer, bond breaking and photochemistry. In each case, we seek to challenge the latest theoretical approaches to understand reactivity within complex molecular environments.

Cycloadditions and ring closings leading to highly strained cyclobutane motifs are targets in synthesis planning. They are also a constant reality in solar photodamage inflicted on cellular DNA leading to skin cancer. Our recent efforts are to characterize photochemical pathways from the perspective of high-throughput excited state reaction discovery. We are designing a closed loop between theory and photochemical experiment at the level of individual observables - screening tens of substrate substituents and reaction conditions in a single excited state dynamics experiment.

Hexafluorobenzene will serve as an example for unraveling the excited state forces that guide an intramolecular 4π-electrocyclic ring closing that largely parallels the gas phase behavior. On the other hand, pyrimidine nucleosides have different photochemistry when moved into water and we have explored these differences using our new high-throughput ultrafast photochemistry apparatus.


2 Bain, M., Godinez, Bradforth, S.E, J. High Throughput Screening of Ultrafast Photochemistry, submitted (2023)
Collision-induced spectrum of O\textsubscript{2} in collisions with O\textsubscript{2} and N\textsubscript{2}

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ABSTRACT

Collision-induced absorption (CIA) is the phenomenon that interactions between colliding molecules lead to absorption of light, even for transitions that are forbidden for the isolated molecules. Collision-induced absorption contributes to the atmospheric heat balance and is important for the electronic excitations of O\textsubscript{2} that are used for remote sensing. Absorption by O\textsubscript{2}-O\textsubscript{2} pairs has been put forward as biomarker to be observed in exoplanetary transit spectra.

The X\textsuperscript{3}Σ\textsubscript{g}→a\textsuperscript{1}Δ\textsubscript{g} and X\textsuperscript{3}Σ\textsubscript{g}→b\textsuperscript{1}Σ\textsubscript{g} electronic transitions in O\textsubscript{2} are electric-dipole forbidden by both spin and spatial selection rules. We calculated CIA spectra of these transitions in O\textsubscript{2} in collisions with N\textsubscript{2} and O\textsubscript{2}. In line shape calculations for colliding molecules, which have previously been made only for roto-translational and vibrational transitions, we obtained the absorption spectrum from dipole coupling between the scattering wave functions that describe the colliding molecules. The scattering calculations, performed with the coupled-channels or close-coupling method, require the interaction potentials and transition dipole moments for the electronic ground and six electronically excited states of the complex as functions of its geometry. These four-dimensional potential energy and exchange-induced transition dipole moment surfaces were obtained from \textit{ab initio} electronic structure calculations. The essential innovation that enabled these calculations was diabatization of these surfaces, which includes non-adiabatic couplings beyond the Born–Oppenheimer approximation. To this end, we used a novel multiple-property-based diabatization algorithm\textsuperscript{1} which has been developed as a part of this project. In the scattering calculations the transition dipole coupling was propagated simultaneously with the scattering wave functions of the states involved and integrated over the radial coordinate to obtain the absorption intensity as a function of the frequency.

We unambiguously identified the underlying absorption mechanism, which —contrary to textbook knowledge— is shown to depend explicitly on the collision partner: N\textsubscript{2} or O\textsubscript{2}. This explains experimentally observed qualitative differences between O\textsubscript{2}-O\textsubscript{2} and O\textsubscript{2}-N\textsubscript{2} collision-induced spectra in the overall intensity, line shape, and vibrational dependence of the absorption spectrum\textsuperscript{2}. Moreover, we provided explicit analytical expressions\textsuperscript{2,3} for the spectral line shape depending on the underlying mechanism, which can be applied in the calibration of satellite and ground based spectrometers such as OCO-2, OCO-3, GOSAT, COCCON, SCIAMACHY, Microcarb, and TCCON that measure the concentrations of various gases in the atmosphere\textsuperscript{3}.

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\textsuperscript{1} T. Karman, A. van der Avoird, and G. C. Groenboom, Multiple-property-based diabatization for open-shell van der Waals molecules, \textit{J. Chem. Phys.}, \textbf{144}, 121101 (2016).


\textsuperscript{3} E. M. Adkins, T. Karman, A. Campargue, D. Mondelain, and J. T. Hodges, Parameterized model to approximate theoretical collision-induced absorption band shapes for O\textsubscript{2}-O\textsubscript{2} and O\textsubscript{2}-N\textsubscript{2}, \textit{J. Quant. Spectrosc. Radiat. Transfer}, submitted (2023) and references therein.
Cold and controlled collisions using tamed molecular beams

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ABSTRACT

The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Experimentally, the level of detail obtained in these studies depends on the quality of preparation of the collision partners before the collision, and on how accurately the products are analyzed afterward.

Over the last years, methods have been developed to get improved control over molecules in a molecular beam. 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 are excellent starting points for high-resolution crossed beam scattering experiments.

I will illustrate the possibilities this technology offers to study molecular collisions with unprecedented precision and at low collision energies. 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 several quantum effects in state-to-state cross sections, such as diffraction, scattering resonances and product pair correlations in bimolecular collisions. Finally, I will present recent results on bimolecular collisions at collision energies down to 0.1 cm⁻¹ obtained by merged beam configurations.

8 G. Tang et al., Quantum state-resolved molecular dipolar collisions over four decades of energy, Science 379, 1031, 2023.
Ion-Atom-Atom Three-Body Recombination: From Cold Chemistry to Plasma Physics

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ABSTRACT

Three-body recombination, or ternary association, is a termolecular reaction in which three free particles collide, yielding a bound state between two of them; at the same time, the third one carries away the excess of kinetic energy. Three-body recombination plays a significant role in many areas of physics and chemistry, such as cold chemistry, atmospheric physics, action spectroscopy, atmospheric physics, and plasma physics, to cite a few.\textsuperscript{1}

Three-body recombination is a complicated chemical process, and a full quantal approach is not feasible in many relevant scenarios. However, a classical approach could be applied in various physical scenarios, particularly ion-atom-atom three-body recombination.

In our group, we have developed classical trajectory calculations in hyperspherical coordinates to treat three-body recombination processes in a \textit{direct} approach, i.e., without invoking the existence of an intermediate complex.\textsuperscript{2} This technique brings new insights into the role of different proposed reaction mechanisms for termolecular reactions and the possibility of dealing with complex termolecular reactions, otherwise hardly studied. Ion-atom-atom three-body recombination presents two reaction products: (i) $A^+ + A + A \rightarrow A_2^+ + A$ and (ii) $A^+ + A + A \rightarrow A_2 + A^*$. Using our classical trajectory approach, we have derived a threshold law based on the long-range nature of the ion-atom potential leading to a predominance of the channel (i), as shown in the Figure. However, for systems in which the atom-atom long-range coefficient is substantial compared to the ion-atom one, (i) and (ii) will be equally important, as seen in the Figure. Nevertheless, this scenario will change once the collision energy overcomes the dissociation energy of the molecular ion, entering the high-energy regime dominated by short-range details of atom-atom and atom-ion potentials. To fully understand this behavior, we have conducted calculations in different ion-atom-atom systems, from the cold up to the hyperthermal regime, showing the universality of our findings.\textsuperscript{3}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure1}
\caption{Heat map of visualizing the effective long-range three-body parameter, $\beta$, as a function of long-range two-body interaction coefficients $C_4$ and $C_6$ in the log-log scale. The schematic illustrations display the dominant reactions at low collision energies.}
\end{figure}

\begin{thebibliography}{9}
\end{thebibliography}
On-Surface Chemical Dynamics Probed with Supersonic Beam Scattering, STM Imaging, and Infrared Spectroscopy

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ABSTRACT

We have developed the capability to elucidate interfacial reaction dynamics using an arguably unique combination of supersonic molecular beams combined with in situ STM visualization. These capabilities have been implemented in order to reveal the complex spatio-temporal correlations that govern heterogeneous reactions spanning atomic, nano, and meso length-scales. For example, time-lapse visualization of reacting interfaces is allowing us to probe the reactivity of specific sites at interfaces and how the presence of a reacted site or local region influences the subsequent reaction probability at proximal sites. Such correlations are important in chemisorption, catalysis, materials oxidation and erosion, and film processing. This approach also opens up a new view for interfacial reaction dynamics where incident beam kinetic energy and angle of incidence can be used for reaction control parameters with outcomes such as site-specific reactivity, changes for overall time-evolving mechanisms, and where the on-surface fate of chemisorbed species can be ascertained. In this work the time-evolving interface can be probed either in real-time or, for reactions occurring under extreme thermal conditions, using time-lapse sequential imagery. This presentation will examine illustrative examples from our recent work on H reactivity with SAMs, the atomic and multiscale oxidative reactivity of HOPG graphite, O interactions with single and multilayer graphene including moiré superlattices, and briefly N₂ chemisorption on Ru. In situ studies of molecular embedding, reactivity, and sticking under non-equilibrium gas-surface collision conditions will also be discussed, including the demonstration of notable isotope and isotopologue dependencies in condensation. Taken together, these results provide a direct and information-rich complement to traditional gas-surface scattering experiments which monitor only volatile products, especially with respect to uncovering the important on-surface chemical and physical events that inform energy transfer dynamics and interfacial reactivity.

Creation and Reaction of Solvated Electrons at and near the Surface of Water

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ABSTRACT

Solvated electrons ($e_s^-$) are among nature’s most powerful reactants, with over 2600 reactions investigated in bulk water. These electrons can also be created at and near the surface of water by exposing an aqueous microjet in vacuum to gas-phase sodium atoms, which ionize into $e_s^-$ and Na$^+$ within the top few layers. When a reactive surfactant is added to the jet, the surfactant and $e_s^-$ become co-reactants localized in the interfacial region. I will describe the reaction of $e_s^-$ with the surfactant benzyltrimethylammonium in a 6.7 M LiBr/water microjet at 235 K and pH = 2. The reaction intermediates trimethylamine (TMA) and benzyl radical are identified by mass spectrometry after they evaporate from solution into the gas phase. Their detection demonstrates that TMA can escape before it is protonated and benzyl before it combines with itself or a H atom. Diffusion-reaction calculations indicate that $e_s^-$ reacts on average within 20 Å of the surface and perhaps within the surfactant monolayer itself, while unprotonated TMA evaporates from the top 40 Å. The escape depth exceeds 1300 Å for the more slowly reacting benzyl radical. These proof-of-principle experiments establish an approach for exploring the near-interfacial analogs of aqueous bulk-phase radical chemistry through the evaporation of reaction intermediates into the gas phase.
Real-Space Laser-Induced Fluorescence Imaging of OH Inelastic Scattering at the Gas-Liquid Interface

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ABSTRACT

Gas-Liquid interfaces, and the heterogeneous processes that occur at them, have been the subject of much less experimental and theoretical study than the gas-phase or gas-solid interface. Relatively little is known about the structure of liquid surfaces, and the interplay between the surface structure and the elementary chemical processes resulting from gas-liquid interaction. In recent years, new experimental techniques and theoretical methodologies have begun to provide detailed understanding in this area. We have developed a gas-liquid scattering apparatus with planar laser-induced-fluorescence imaging of the real-space scattering distribution. Combined with a pulsed supersonic DC discharge source of OH, we have used this apparatus to study the dynamics of the inelastic collisions of OH radicals with the surfaces of the inert liquid perfluoropolyether (PFPE), and also the surfaces of the potentially reactive hydrocarbons squalane (saturated) and squalene (unsaturated).

Analysis of images taken in a time-series that spans before and after collision reveals that the OH radicals are scattered from all 3 liquids, and for both normal and 45° incident angles, with a predominately superthermal speed distribution, with no strong evidence for a substantial thermalized component. Angular scattering distributions are determined from both time-series and single-time images for each incident angle, each liquid and as a function of OH rotational state. Significant anisotropy is observed in the scattering for 45° incident angle, with the scattering angle distribution varying as a function of liquid and final N'. We discuss the observed differences in the scattering dynamics in the context of both the inelastic and reactive processes occurring at the surfaces of the three liquids.
Probing Rovibrational Dynamics of CH₄-Surface Scattering with Optothermal Spectroscopy

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ABSTRACT
Quantum state-prepared and quantum state-resolved molecular-surface scattering experiments offer a highly detailed glimpse into the fundamental interactions underlying a number of important surface chemistry applications, including heterogeneous catalysis. Recently we have completed the fabrication and testing of a new apparatus designed to perform such experiments with independent control of the incident and final scattering angles of the detected molecules. Rovibrational state-preparation and state-detection are accomplished using a pair of lasers for infrared excitation of molecular vibrations in combination with a rotatable silicon bolometer detector operating at liquid helium temperatures. The technique is applicable to any molecular species possessing a rotationally-resolved infrared spectrum (CH₄, H₂O, CO₂, NH₃, etc.).

We present in this talk some first results obtained with the new apparatus. We begin with a study of the rotational dynamics investigating the influence of surface oxidation on the strength of molecule-surface energy exchange in methane-nickel collisions. From an analysis of the scattering intensity as a function of rotational state, scattering, and surface temperature, we find a pronounced enhancement in energy exchange between the molecule and the surface upon surface oxidation. We then move to the subject of surface collision-mediated coupling between the different vibrational modes of the CH₄ molecule. Previous experimental and theoretical work on vibrationally inelastic CH₄-surface scattering hinted at a possible correlation between the probability of collision-mediated conversion between antisymmetric (v3) and symmetric (v1) CH₄ stretching vibrations and the surface’s ability to catalyze methane dissociative chemisorption. To test this hypothesis, we measure the v3 → v1 conversion efficiency for the chemically reactive Ni(111) surface and the chemically inert Au(111) surface. Our results are in favor of the hypothesis, with the measured conversion efficiency more than 5 × stronger on the Ni(111) surface. We conclude with a brief presentation of new unpublished results on alignment effects in methane-surface scattering. For example, we find in CH₄/Au(111) collisions remarkable population imbalances in the scattered flux among quasi-degenerate states of equal rotational quantum number J (see figure). Further analysis reveals these imbalances to imply a strong tendency for the production of a “tumbling” rotational motion in scattering.

4 Floß, P. et al. Surface-induced vibrational energy redistribution in methane/surface scattering depends on catalytic activity, currently under review.
First-Principles Dynamics Simulations of Adiabatic and Nonadiabatic Energy Transfer of Molecular Scattering from Metal Surfaces

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ABSTRACT

Energy transfer among different degrees of freedom (DOFs) is of fundamental importance to chemical processes at the gas-solid interface. At metal surfaces, the energy of incident species can be transferred to either surface phonons via an adiabatic mechanism or surface electrons via a non-adiabatic mechanism. Given the high-dimensionality of a gas-surface system, a first-principles description of this process has been challenging. Constructing potential energy surfaces (PESs) including all relevant nuclear DOFs represents the first challenge. The second challenge is the effective inclusion of electronic DOFs in dynamical simulations. To overcome these difficulties, we have developed embedded atom neural network (EANN) approaches for constructing PESs\textsuperscript{1} and electron friction tensors (EFT)\textsuperscript{2} with surface DOFs, which enable the description of the energy transfer to surface phonons and low-energy electron-hole pairs at metal surfaces in the weak-coupling case. More recently, by combining the constrained density functional theory (CDFT) to determine charge transfer states at metal surfaces\textsuperscript{3} and the independent electron surface hopping approach\textsuperscript{4}, we were able to simulate nonadiabatic energy transfer during molecule-surface scattering in the strong-coupling case involving charge transfer. These theoretical advances allow us to discuss the realistic energy transfer dynamics for representative systems like NO and CO scattering from Au(111) with an unprecedented level of accuracy\textsuperscript{4,7}. Our results suggest that both adiabatic and nonadiabatic energy transfer are important in such systems and emphasize the importance of the dissociation barrier on the adiabatic PES in describing the vibrational energy transfer in molecular scattering on metal surfaces.

\textsuperscript{2} Y. Zhang, R.J. Maurer, B. Jiang, J. Phys. Chem. C 124(1), 186, (2020)
\textsuperscript{7} C. L Box, et al., JACS Au, 1(2), 164-173, (2021)
Unimolecular Decay Dynamics of Reactive Intermediates in Atmospheric and Combustion Chemistry

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ABSTRACT

Our research aims to characterize important, yet often elusive, reaction intermediates in atmospheric and combustion chemistry. A recent thrust is focused on hydroperoxyalkyl radical (•QOOH) intermediates containing a carbon radical (•Q) center, which are transient intermediates in the atmospheric oxidation of volatile organic compounds and low temperature combustion (< 1000 K) of hydrocarbon fuels. •QOOH intermediates are the “central switchyard” in the oxidation mechanism, controlling the branching between unimolecular decay to hydroxyl (OH) radicals and epoxides or, alternatively, O₂ addition leading to extremely low-volatility organic compounds or fuel autoignition. In addition, our research continues to explore carbonyl oxides (Criegee intermediates, R₁R₂C=O’O”) with novel zwitterionic character, which are short-lived intermediates in tropospheric alkene ozonolysis reactions. Criegee intermediates undergo unimolecular decay to OH radicals, increasing the oxidative capacity of the atmosphere, and their bimolecular reactions can generate secondary organic aerosols. In both systems, our experiments yield spectroscopic signatures of the reaction intermediates and time-resolved measurements of their unimolecular decay dynamics. Moreover, our experiments demonstrate the importance of quantum mechanical tunneling¹,² and/or roaming²,⁴ in their unimolecular decay dynamics, generally releasing OH radicals that are detected. Our experimental studies and complementary theoretical analyses show the importance of these dynamical pathways under controlled laboratory conditions as well as their impact in realistic atmospheric and combustion chemistry.

Sudden Vector Projection Model, Mode Specificity and Bond Selectivity Made Simple

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ABSTRACT

Dynamics of chemical reactions shed important light on chemical transformation, which might or might not be statistical. Non-statistical dynamics are often observed in gas phase reactions, but also in some gas-surface reactions. An important manifestation is mode specificity, and the associated bond selectivity, which exhibit differing reactivity for excitations in different reactant modes or bonds. More than half a century ago, Polanyi suggested propensities based on the location of the prevailing transition state, but these rules of thumb provide no guidance on the efficacies of different vibrational modes in a polyatomic molecule and on rotational excitation. We have proposed the Sudden Vector Projection (SVP) model,\textsuperscript{1-2} which attributes the ability of a reactant mode (or a bond) for promoting the reaction to the projection of the corresponding normal mode onto the reaction coordinate at the transition state. The premise of the SVP model is based on the observation that collisions typically occur so much faster than intramolecular vibrational energy redistribution (IVR), so that a large projection signifies strong coupling with and facile energy flow into the reaction coordinate, and vice versa. The SVP model has been successfully applied to a large number of gas phase and gas-surface reactions,\textsuperscript{3-5} as serves as a guide for understanding mode specificity and bond selectivity in reactions.

\textsuperscript{2} Jiang, B.; Guo, H., Control of mode/bond selectivity and product energy disposal by the transition state: The X + H\textsubscript{2}O (X=H, F, O\textsuperscript{3}P), and Cl) reactions. \textit{J. Am. Chem. Soc}. 2013, \textbf{135}, 15251-15256.
Quantum Dynamics of Ultracold Chemical Reactions: Quantum Interference, Excited Electronic States, and Long-lived Complexes

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ABSTRACT

Experimental techniques for cooling, trapping and colliding cold (T < 1 K) and ultracold (T < 1 mK) molecules continue to develop at an astounding pace. Recent techniques using external fields and/or initial quantum state selection have demonstrated exquisite control of the collision outcome including chemical reactions. Recent experiments have also identified collision complexes (also known as metastable states or resonances) and have measured their lifetimes. For Rb colliding with KRb these lifetimes exceed statistical based theoretical estimates by five orders of magnitude! Thus, an accurate theoretical treatment of ultracold chemical reactions is needed for the understanding of the reaction mechanisms and interpreting the experimental measurements. However, accurate calculations are challenging and require a fully quantum mechanical first-principles description of both the electronic and nuclear motion. A numerically exact quantum reactive scattering methodology for atom-diatom (A + BC) collisions/reactions will be reviewed. This methodology is ideally suited for treating ultracold chemical reactions and has recently identified a novel quantum interference mechanism that could be exploited to effectively turn the chemical reaction on or off (i.e., a quantum molecular switch). This mechanism is general and has been shown to occur in a variety of ultracold chemical reactions: O + OH → H + O₂, H + HD → H + HD (and isotopic variants), and Li + LiNa → Li₂ + Na. Of particular interest is the crucial role of an excited electronic state that becomes degenerate with the ground electronic state. The geometric phase associated with this degeneracy is shown to control the constructive or destructive nature of the quantum interference and hence the reaction outcome. For many ultracold reactions, the excited electronic state is energetically accessible even at ultracold collision temperatures. Thus, a fully coupled two-electronic state (non-adiabatic) calculation is required. The excited electronic state can also lead to very long-lived complexes that might be the origin of the experimentally observed lifetimes for Rb + KRb.
Fundamental Studies of Ion/Molecule and Neutral/Neutral Interactions for Astrochemistry Applications

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ABSTRACT

Many of the new molecules discovered in astrophysical objects are totally outlandish by traditional perspectives: long linear unsaturated carbon chains, metals in surprising charge states, and strained ring structures have all challenged chemists to think beyond terrestrial conventions in explaining how these molecules form and react, and where they fit into the overall cycle of planetary and stellar evolution. The challenge to the molecular dynamics community is to study this exotic chemistry under the relevant physical conditions—most importantly the low temperatures of space. In this talk, I will describe two orthogonal research projects occurring in our group that are unified by their study of the fundamental physical processes that impact low-temperature (down to 10 K) experiments.

In the first part of my talk, I will describe our efforts to measure reaction rate constants for radiative association reactions, a special class of chemical reactions that is most relevant under the low-temperature, low-pressure conditions of space. In these experiments, gaseous ions are generated in a glow-discharge ion source, mass selected, and trapped in a multipole ion trap. Reaction kinetics are monitored in real time by mass spectrometry.\(^1\) Our plans for incorporating buffer-gas cooling in the ion trap, as well as injection of the buffer-gas-cooled neutral co-reactant will also be discussed.

In the second part of my talk, I will share a second research avenue we are pursuing in investigating weakly bound complexes that form under low-temperature conditions. This effort couples matrix-isolation spectroscopy with quantum chemistry calculations to investigate the formation of unique complexes,\(^2\) and probe the role that solvation plays in determining structural properties at low temperature.\(^3\)

\(^1\) Palotás, J., Kisuryna, D., Palko, J. Dodson, L.G., in preparation.


\(^3\) Hockey, E.K., McLane, N., Vlahos, K., McCaslin, L., Dodson, L.G., in preparation.
Controlling the Unimolecular Dissociation Rate of an Ultracold Reaction

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ABSTRACT

Transient intermediate reaction complexes connect reactants and products along the reaction path, controlling not only the overall reaction rate but also the dynamics of chemical transformation. While transient in nature, the lifetime of these species can be extended from a few vibrational periods, on the order of picoseconds, to the nanosecond or even millisecond timescale when prepared under ultracold conditions (T < 1 μK).

Here, we show that this extension in lifetime can be actively controlled in the endothermic KRb + Rb ↔ KRb₂ reaction at 500 nK not only by judicious choice of reactant state, but also by external magnetic fields. In our experiment, a bulk gas of ultracold KRb molecules in a single hyperfine level of their ground rovibronic state and Rb atoms in their ground hyperfine (F = 1) level are prepared and trapped in an optical dipole trap. The hyperfine levels of both KRb and Rb can be controlled coherently, allowing for molecular and atomic state preparation with near-unit fidelity. Stochastic reactive collisions are initiated upon formation of the atom-molecule cloud and measurements of the KRb₂ collisional complex lifetime, the inverse of its unimolecular dissociation rate, are performed by single-photon UV ionization and subsequent ion-imaging. Despite the stochastic nature of these collisions, we have previously observed that our optical trapping light rapidly photoexcites these complexes, allowing us to set a clear starting time of these dynamics by shutting off the trapping light and probing at various delay times. We interrogate myriad reactant state combinations, as well as various external electric and magnetic fields, revealing that the dissociation rate of KRb₂ can be controlled continuously by over an order of magnitude and is relatively insensitive to the initial molecular hyperfine state. As the first demonstration of control over a unimolecular reaction, this work is a crucial step towards an era of fully-controlled chemistry.

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Electro-Association of Field-Linked Tetramer States in Ultracold Gases

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ABSTRACT

Dipolar molecules in an ultracold gaseous environment, say at sub-microKelvin temperatures, are subject to sensitive control by exploiting their native dipole-dipole interaction. This talk will focus on a particular manifestation of this control, namely, the existence 1 and formation 2 of tetramer states, consisting of pairs of ground-state diatomic molecules, clinging together in extremely weak, long-range potential energy surfaces. I will describe the fundamental physics of these surfaces, which are tunable in either electric 3 or microwave 4,5 fields that are applied to the gas. Further, I show that these tetramers can be created by dynamically altering the potential energy surface. 2 This capability, recently observed experimentally 6,7 opens new opportunities for controlled chemistry and many-body physics of ultracold molecular gases.

Making Ultracold Molecules by Merging Tweezers

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ABSTRACT

Optical tweezers are shallow potential wells formed at the waist of a tightly focussed laser beam, which confine particles through their polarizability. It is now possible to load a pair of ultracold atoms into a separate tweezers and then merge them to study interactions and collisions. We have collaborated with Kang-Kuen Ni’s group at Harvard to form an NaCs molecule by magnetoassociation from Na and Cs atoms in a tweezer,\(^1\) and with Simon Cornish’s group at Durham to form an RbCs molecule.\(^2\)

For RbCs, we were surprised to discover that a molecule can be formed when tweezers are merged \textit{without} needing magnetoassociation. This occurs because there is an avoided crossing (as a function of tweezer separation \(z_0\)) between states of the confined atom pair and a weakly bound state of the molecule. An RbCs molecule is formed by adiabatic passage over this avoided crossing as the tweezers are merged. We refer to this as \textit{mergoassociation}. We have modelled this with coupled-channel calculations for both isotropic and anisotropic tweezers and find good agreement between experimental and theoretical probabilities of molecule formation.

Mergoassociation offers a route to forming ultracold molecules in systems that do not possess Feshbach resonances suitable for magnetoassociation.

More generally, optical tweezers offer a rich platform for highly selective studies of atomic and molecular collisions and reactions. Configurable tweezer arrays offer further possibilities for quantum science, ranging from fundamental studies of few-body dipolar physics to quantum simulation and quantum computing.\(^4\) They present many fascinating challenges for theory at both the single-particle and few-particle levels.

\(3\) R. C. Bird, C. R. Le Sueur and JMH, "Theory of mergoassociation: two atoms in adjacent nonspherical optical traps", in preparation.
Formation and Decay of Criegee Intermediates through Bimolecular Collisions

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ABSTRACT

Criegee intermediates (CIs) play an important role in atmospheric chemistry through their production of OH and as key intermediates in the formation of aerosols. In recent work we have examined theoretically a variety of bimolecular reactions of relevance to both the formation and decay of CIs. These theoretical studies involve a combination of high-level electronic structure theory, transition state theory and trajectory studies, as well as master equation kinetic analyses. Their coupling with complementary experimental work led by Caravan, Lester, Taatjes, and Percival allows us to unravel the detailed dynamics and kinetics of these ephemeral species. In this talk we will summarize various dynamical features of these studies as well as the relevance of their kinetics to the chemistry of the atmosphere.

The production of CIs generally occurs through the ozonolysis of alkenes, which leads to highly vibrationally excited CIs. The unimolecular dissociation of these CIs commonly yields OH, with recent studies indicating an important role for roaming reactions in altering the product distributions away from OH production. There are interesting dynamical questions for the ozonolysis process related to the degree of vibrational excitation of the incipient CIs as well as the coupling of their collisional cooling and thermal dissociation processes. A recent experimental study of Zhang and coworkers indicates a significant discrepancy with the predictions of our detailed theoretical analysis. We will suggest a possible resolution of this discrepancy and how that would relate to both chamber experiments and the atmosphere.

The thermal dissociation of the CIs occurs in competition with a variety of bimolecular reactions. Reactions of CIs with formic acid provide an important loss route. Both the unimolecular and bimolecular processes are strongly conformer dependent, as directly explored in our study of the reaction of CH₃CHOO with dimethylamine. Interestingly, successive additions of CIs to formic acid yield an oligomerization sequence that appears to have been observed in a field study in the Amazon. Meanwhile, their reactions with SO₂ produce SO₃ at a rate that is sufficient to have a major effect on the extent of aerosol formation from further reactions of SO₃. Our theoretical analyses allow us to examine various chemical effects on the kinetics such as the effect of resonance stabilization on the kinetics.

Oxygen Three Ways: O⁻, O₂, and O₃ in upper atmospheric discharges, metal oxidation, and ionospheric processes

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ABSTRACT

Three stories of ion-molecule reactions involving oxygen allotropes are discussed. First, the kinetics of associative detachment of O⁻ + N₂ are investigated at temperatures up to 1300 K. The reaction is important for modeling of transient luminous events, electrical phenomena that occur in the upper atmosphere. Current models rely on a single prior rate constant determination, the accuracy of which has been questioned. The present results are well below the literature and indicate a pronounced enhancement of the reaction through N₂ vibrational excitation. The results are supported by calculation of the N₂O and N₂O⁻ potential surfaces at the CCSD(T) level and reveal an interesting case of the Polanyi rules. Second, a number of similarities between O₂ incident on an Al(111) surface and O₂ reacting with Alₙ⁻ cluster anions are noted and interpreted as due to similarities in the long-range potentials. In both cases, the kinetics are controlled by a small barrier coinciding with charge transfer at large internuclear distance, not through spin-conservation as previously proposed. The kinetics of several transition metal cluster anions show evidence of an analogous barrier, suggesting the mechanism is quite common. Most interestingly, the kinetics of lanthanide atoms and atomic cations with O₂ show a similar early barrier, although in these cases it may be due not to charge transfer, but to an excited state promoting covalent bonding. We suggest that the general scheme may offer additional control of oxygen activation processes. Finally, the kinetics of O₃ with meteoric metal ions and their higher oxides are reported. Ablated meteoric material consolidates in the upper mesosphere and lower thermosphere causing Sporadic E events; the conversion of atomic cations to polyatomic cations by reaction with O₃ leads to termination of the Sporadic E. The literature is plagued by underestimation of these reaction rates due to analyses not properly accounting for sequential chemistry with O₃. Here, corrected rate constants are reported and the general mechanism of O₃ leading to both oxidized and reduced cation products is deduced. The data for Ca⁺ is used to update an atmospheric model resulting in improved agreement with field measurements.

Inefficient IVR and Negative Internal Energy Dependence for the H + HO₂ Reaction

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ABSTRACT

Quasiclassical trajectories (QCT) are used to quantify the effects of inefficient intermolecular vibrational energy redistribution (IVR) in thermal and nonthermal rate constants for the H + HO₂ reaction. The thermal QCT rate constants are found to be up to 50% smaller than transition state theory (TST) rate constants based on the same level of electronic structure theory. This reduction is demonstrated to result from inefficient IVR in the transient H₂O₂ well, with a significant fraction of trajectories promptly dissociating back to reactants instead of via the heavily statistically favored OH + OH channel. The nonstatistical reduction factor, κ_IVR, that quantifies this effect increases in importance with temperature. Notably, this same effect causes nonthermal rate constants mediated by H₂O₂ to depend inversely on the initial vibrational excitation of HO₂, which in turn leads to non-Boltzmann HO₂ populations as vibrationally excited HO₂ cools. Inefficient IVR has been previously reported in the related reaction, O + OH, and new calculations are carried out here for this system and comparisons are made with results for H+ HO₂.

Nonthermal rate constants for HO₂* + H as a function of the initial excitation of HO₂ and at a relative temperature of 1000 K. Quasiclassical trajectories predict a negative energy dependence (black solid line) in contrast to the conventional picture predicted by a statistical model (blue dashed line).

Temperature- and Size-Dependent, Water-Cluster-Mediated Long Range Proton Transfer in Microhydrated 4-Aminobenzoic Acid

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ABSTRACT

I will discuss our recent efforts to directly measure water-mediated proton transfer between two spectroscopically distinct protonation sites adopted by 4-aminobenzoic acid (4ABA). This is achieved by following the spectroscopic behavior of \( \text{H}^+\cdot4\text{ABA}\cdot\text{(H}_2\text{O})_{n=0-4} \) cluster ions held in a temperature-controlled ion trap. The method is derived from the classic “T-jump” approach introduced by Eigen in the 1950s, which involves interrupting the dynamic equilibrium between reactants and products and following the kinetics that restore steady state populations of reactants and products. In the present case, protonation occurs at the acid (O-protomer) and amine (N-protomer) functionalities, which display dramatically different ultraviolet (UV) absorption bands. After most of the O-protomer population is depleted by UV excitation with a 6 ns pulse width laser near 310 nm, the time evolution of the protomer populations is determined over tens of milliseconds by monitoring the characteristic vibrational bands of two protomers. Temperature-dependent interconversion with retention of the water molecules is observed for \( n = 3 \) and \( 4 \) but not \( n = 2 \). These results thus support an earlier theoretical prediction that the transfer mechanism changes from \( n = 2 \) to \( 3 \).
Taming the Beast: New Developments & Demonstrations of Anharmonic Vibrational Simulations for Large(r) Chemical Systems

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ABSTRACT

Recent advances in cold ion sources and tandem mass spectrometry-based spectroscopies have provided unprecedented information regarding the vibrational dynamics of hydrated ions, radicals, and biomolecules. Theory and computer simulation have become critical partners in these advances, and the shared insight gained from this partnership continues to promote new advancements in our understanding of these challenging systems.

A suite of methods is now available for this purpose, ranging from variational solvers—on all or a targeted subset of vibrational modes—to generically applicable methods that often analogues of techniques in electronic structure theory. The latter methods include vibrational self-consistent (VSCF) approaches, perturbation theory (VMP2/VDPT2), configuration interaction (VCI), coupled-cluster theory (VCC), or even correlations from a harmonic reference (VPT2).

The central computational challenge common to all of these approaches is the need to account for non-local (or at least semi-local) representations of vibrational coupling. This presentation will first survey some of our recent methodological progress in addressing both computational-speed and qualitative aspects of these approaches, including (a) local-mode, multilevel methods, (b) convergence algorithms for VSCF calculations, and (c) approaching convergence in the n-mode representation with local modes. It will then demonstrate applications of these new methods for challenging spectra of hydrated ions and biomolecules. The outcome of these new methods—and conceptual understanding of these methods—is considerable new hope in extending these general anharmonic simulation methods toward the type large(r) systems currently being studied with modern experimental spectroscopic techniques.

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Dynamics of Optically Centrifuged N$_2$O in Extreme Rotational States
Studied with Transient IR Absorption Spectroscopy

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ABSTRACT

The behavior of molecules with large amounts of rotational energy is a largely unexplored area in physical science. Molecules in high energy rotational states are observed as products of reactions and collisional energy transfer, but they are not easily prepared by traditional experimental methods. High rotational states can be prepared using an optical centrifuge, which is an ultrafast laser-based method that selectively populates molecules with inverted rotational distributions. Investigating the behavior of molecules in extreme rotational states enhances our understanding of fundamental energy transfer processes, energy partitioning in vibration and rotation, and centrifugal distortion in molecules in extreme J states. In this project, an optical centrifuge is combined with a high-resolution transient IR absorption spectrometer to explore the dynamics of optically centrifuged N$_2$O (00$^1$1-00$^0$0) with J=100-200 and rotational energies up to 16,000 cm$^{-1}$.

A tunable optical centrifuge was used to selectively optimize N$_2$O population by controlling the bandwidth of the optical pulses. Figure 1a shows optical trap intensity profiles as a function of instantaneous angular frequency $\omega_{OC}$ for the full bandwidth pulses and for pulses with reduced bandwidth to preferentially populate the J=140 and 160 rotational states. The nascent distributions of centrifuged molecules were measured with high-resolution transient IR absorption spectroscopy at $\lambda=4.4$ µm and a spectroscopic pressure of 2.5 Torr. The IR transitions used for this study were first identified using transient spectroscopy of optically centrifuged N$_2$O.$^{1,2}$ Figures 1b and 1c show the inverted nascent rotational distributions for the two reduced-bandwidth traps at t=300 ns. Transient IR Doppler line profiles were measured to characterize the translational energy transfer of optically centrifuged molecules and polarization-sensitive spectroscopy was used to investigate orientational anisotropy dynamics and relaxation kinetics of the optically centrifuged molecules. The orientational anisotropy of the centrifuged molecules increases as a function of J and lower J-states have higher translational energies as a result of impulsive collisions between centrifuged molecules and thermal bath molecules. The translational energies of lower J-states increase as a function of time as rotational energy is converted to translational energy through inelastic collisions. The time-dependence of the high-J tail populations shows that the collisional relaxation rate constants are approximately half that of the Leonard-Jones collisional rate constant. The results are compared with previous dynamics studies on optically centrifuged CO molecules.$^3$ This project has been funded through the NSF.

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2 Ogden, H. et al. Transient IR (00$^1$1–00$^0$0) Absorption Spectroscopy of Optically Centrifuged N$_2$O with Extreme Rotation up to J=205. JSOR 246, 106867, 2020.
Interactions of H$_2$ with CO: High-Accuracy Computational Spectroscopy and Scattering Versus Experiment and Astronomic Observations

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ABSTRACT

Interactions of H$_2$ with CO are of great importance to astronomy, astrophysics, and astrochemistry. In particular, the dominant cooling mechanism in molecular clouds is the collisional excitation of CO by H$_2$ followed by a radiative deexcitation. This cooling allows the gas to collapse and leads to the formation of stars. H$_2$ and CO form a dimer, and if it were detected in space, such observations would provide a wealth of information about molecular clouds. Generally, most of our knowledge about molecules in space comes from their spectral signal, and while H$_2$ cannot be detected, CO is the easiest molecule to detect in space and it is the main probe of dark regions of the universe. The observed spectral lines can be identified since they are known to extremely high precision of about 0.0001 cm$^{-1}$ from laboratory measurements. For such identification, the measured spectral lines have to be assigned to the quantum states they originate from. This is not always possible and one example is orthoH$_2$-CO. We have developed a synergistic method which combines highest possible accuracy quantum mechanical calculations with analysis of experimental spectra to fully interpret the spectrum of orthoH$_2$-CO. In particular, we were able to increase by a factor of two the number of assigned transitions and, for the first time, deduce the experimental energy levels. The use of high-accuracy theoretical information to interpret spectra can be applied to other van der Waals dimers, extending in this way the range of systems for which spectroscopy can provide physical insights. To realize the goal of complete interpretation of the orthoH$_2$-CO spectra, high-accuracy, full-dimensional calculations were performed, including calculations of the potential energy surface at the highest practically achievable level of electronic structure theory, and 6D nuclear dynamics calculations for bound states that are virtually exact. The resonance states, an essential component of the measured spectrum, were obtained from 4D scattering calculations on a potential energy surface (PES) obtained by averaging the 6D PES over nuclear motion within monomers. Also the intensities of transitions were computed from the 4D PES. Despite pushing the current limits of theory, computed transitions have at least one order of magnitude larger uncertainties than experiment. However, they can very effectively guide extractions energy levels from measured spectra. In an earlier work, absolute state-to-state collisional rotational energy transfer rate coefficients at interstellar temperatures were measured and computed,$^1$ resulting in an excellent agreement. Previous versions of the 4D and 6D PESs were used in the computations. This work increases confidence in predictions for star-forming regions based on computed rates.

MQCT2023 – A Program for Calculations of Inelastic Scattering of Two Molecules

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ABSTRACT

We developed theoretical methodology and wrote a user-ready computer program to carry out the calculations of rotational-vibrational-translational energy transfer in a collision of two molecules, within a framework of the mixed quantum/classical theory (MQCT). In this approach the translational motion of scattering partners is treated classically, while the internal motion of each molecule (rotation, vibration) is described by quantum mechanics.\(^1\) Time-dependent framework is adopted, which includes the propagation of mean-field trajectories for the translational motion (the Ehrenfest approach), and the time-evolution of probability amplitudes for the internal quantum states of the molecules, driven by their collision process. Energy is exchanged between the translational, rotational, and vibrational degrees of freedom but the total energy is conserved (on average).

The most demanding part of the full-coupled MQCT calculations is calculations of the potential gradient averaged over all quantum states of collision partners (the mean-field potential) at each time step. But recently, we proposed a simplified version of MQCT, in which the classical and quantum degrees of freedom are partially decoupled. This method, named adiabatic trajectory, or AT-MQCT, happens to be both efficient and accurate,\(^2,3\) see Fig. 1.

In MQCT program there are ten system types, from the simplest rigid-diatom + atom, to the most general case of collision between two asymmetric-top rotor molecules. For each system, MQCT calculations can be initiated by indicating the rotational and vibrational constants of collision partners. Those are used by the code to set up and diagonalize Hamiltonian matrix for the rotational motion (using the basis set of symmetric-top functions) in order to determine the rotational states of the system (energies and wave-functions).

Potential energy surface for the interaction of collision partners, expressed in Euler angles of the fragments is also required. State-to-state transition matrix is computed in body-fixed reference frame. A detailed user manual and examples of input files for all system types are available.\(^4\) In this version of MQCT the vibrational motion is supported for the diatomic molecules only, but we plan is to introduce vibration for other system types.

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\(^3\) B. Mandal, C. Joy, A. Semenov, D. Babikov, ACS Earth Space Chem. 6, 521-529, 2022.
High temperature reactions of individual nanoparticles

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ABSTRACT

Understanding structure-reactivity relationships for nanoparticles (NPs) is complicated by the fact that each NP has a different distribution of surface sites, and by the evolution of the NP structure as reactions add or remove material. We have developed a single NP mass spectrometry method that allows the absolute kinetics for gas-surface reactions of individual NPs to be measured as a function to time, while varying NP temperature and gas pressure/composition, with or without various pre-treatments such as melting or heating to drive sublimation or composition changes for the surface layer.

A single nanoparticle (NP) of the material of interest is electrodynamically trapped in either inert or reactive atmospheres, and laser heated to a temperature of interest, which is measured by fitting the particle’s thermal emission spectrum. Kinetics for mass-changing processes such as sublimation, oxide formation, and addition or etching reactions, are measured by simply tracking the NP mass vs. time as the reaction proceeds. By monitoring reactivity over time, the effects of evolution of the surface (passivation, roughening, etc.) can be followed, and comparing results for different NPs provides insights into the effects of NP heterogeneity on reactivity. The upper temperature limit for the experiment is determined only by the sublimation kinetics of the NPs, thus for refractory materials, kinetics can be measured to temperatures above 3000 K. For materials with modest vapor pressure at their melting points, chemistry can also be studied for molten nanodroplets.

The method will be illustrated with results for O\textsubscript{2} oxidation and sublimation of silicon (T\textsubscript{melt} = 1687 K) and hafnium carbide, HfC (T\textsubscript{melt} = 4170K). The figure shows one type of experiment, in which a HfC NP was trapped, cleaned by preheating to 1900 K in argon (white background), then subjected to a temperature ramp from 1400 K to 2000 K, measuring both the sublimation rates in argon (white background) and the etching rates in O\textsubscript{2} (aqua background). The slope of the mass vs. time plot gives the absolute mass loss rates (Da/sec), and it can be seen that the sublimation rates increased as the temperature increased, but that the O\textsubscript{2} etching rates decreased, due to partial passivation of the NP surface. The second part of the experiment followed the NP mass for >~10 hours at constant O\textsubscript{2} pressure with T\textsubscript{NP} initially at 1500 K, then at 1600 K. Here, the NP passivated, with kinetics slowing by two orders of magnitude. By comparing experiments at different temperatures and pressures, it is possible to map out how the etching, sublimation, and passivation kinetics vary with reaction conditions.
Simulating the Anion Photoelectron Spectrum of Tetrazolyl with the Time-Independent Multimode Vibronic Coupling Approach

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ABSTRACT

Tetrazolyl has recently shown promise as the basis of high-energy-density materials.\textsuperscript{1,2} It is an azolyl ($N_x(CH)_y$; $x + y = 5$), a class of 35-electron neutral radicals which are substitutional isomers of cyclopentadienyl. The high $D_{5h}$ symmetry of cyclopentadienyl results in its electronic ground state being doubly degenerate, having $^2E_1''$ symmetry.\textsuperscript{3} This has consequences for the closely-related potential energy surface (PES) of tetrazolyl, which has a conical intersection seam between its two lowest-energy electronic states, near the ground state equilibrium geometry.

The present work aims to simulate the anion ultraviolet photoelectron spectrum of tetrazolyl. A quasidiabatic Hamiltonian is used with a time-independent multimode vibronic coupling approach to yield the vibronic eigenstates and, by extension, the spectral intensity distribution.\textsuperscript{4} Most applications of this approach only include up to quadratic terms in the Hamiltonian, but this is expected to be insufficient, so quartic terms will be included.\textsuperscript{3,5}

$Ab initio$ electronic structure calculations are performed using the COLUMBUS suite of electronic structure codes. This consists of the multi-configurational self-consistent field method followed by multireference configuration interaction with single and double excitations and generalized interacting space restrictions. Dunning’s cc-pVDZ basis set is used for the neutral radical. Geometry optimizations were performed, which identified, among others, three key critical points. Minima were found on the ground and first electronic excited states, both having $C_{2v}$ symmetry. In addition, a minimum energy crossing (MEX) was found between these states. The quasidiabatic Hamiltonian will be generated using a variant of Surfgen (produces coupled PESs by fitting to provided $ab initio$ points) for bound systems, and NadVibS (nonadiabatic vibrational spectrum simulation package) will be used to simulate the spectrum.

Controlling the unimolecular dissociation rate of an ultracold reaction

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ABSTRACT

Transient intermediate reaction complexes connect reactants and products along the reaction path, controlling not only the overall reaction rate but also the dynamics of chemical transformation. While transient in nature, the lifetime of these species can be extended from a few vibrational periods, on the order of picoseconds, to the nanosecond or even millisecond timescale when prepared under ultracold conditions ($T < 1 \mu K$). Here, we show that this extension in lifetime can be actively controlled in the endothermic $\text{KRb} + \text{Rb} \leftrightarrow \text{KRb}_2$ reaction at 500 nK not only by judicious choice of reactant state, but also by external magnetic fields. In our experiment, a bulk gas of ultracold KRb molecules in a single hyperfine level of their ground rovibronic state and Rb atoms in their ground hyperfine ($F = 1$) level are prepared and trapped in an optical dipole trap. The hyperfine levels of both KRb and Rb can be controlled coherently, allowing for molecular and atomic state preparation with near-unit fidelity. Stochastic reactive collisions are initiated upon formation of the atom-molecule cloud and measurements of the $\text{KRb}_2$ collisional complex lifetime, the inverse of its unimolecular dissociation rate, are performed by single-photon UV ionization and subsequent ion-imaging. Despite the stochastic nature of these collisions, we have previously observed that our optical trapping light rapidly photoexcites these complexes, allowing us to set a clear starting time of these dynamics by shutting off the trapping light and probing at various delay times. We interrogate myriad reactant state combinations, as well as various external electric and magnetic fields, revealing that the dissociation rate of $\text{KRb}_2$ can be controlled continuously by over an order of magnitude and is relatively insensitive to the initial molecular hyperfine state. As the first demonstration of control over a unimolecular reaction, this work is a crucial step towards an era of fully-controlled chemistry.

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**ABSTRACT**

Bimolecular collisions involving diatomic molecules are topics of active investigation due to the continuing interest in cooling and trapping of molecules and their applications in sensing, precision spectroscopy, quantum information processing, and ultracold chemistry, to name a few. By combining optical state-preparation using the Stark-induced adiabatic Raman passage (SARP) method with co-expansion of the colliding species in the same molecular beam Mukherjee and coworkers have been able to explore the stereodynamics of atom-molecule and molecule-molecule collisions at collision energies in the vicinity of 1 K. In this regime, collision outcomes are dominated by isolated partial waves allowing measurements of differential cross sections (DCSs) with partial wave resolution.

Recently, Mukherjee and coworkers have reported DCS for collisions between two aligned D₂ molecules prepared in the v=2 vibrational level and J=2 rotational level using the SARP method. They attributed key features of the angular distributions to a ℓ=2 partial wave resonance in the incident channel.

Here we provide a first principles simulation of the experiment using explicit quantum close-coupling calculations. Our calculations takes both aligned-aligned collisions of D₂ molecules in the v=2 vibrational level as well as collisions between state-prepared D₂ in v=2 and unprepared D₂ in v=0 that are present in the experiment. As shown in the Figure our calculations using a full-dimensional interaction potential for the H₂+H₂ system nearly quantitatively reproduces the experimental angular distribution for both H-SARP and V-SARP preparations. However, a key difference is that our calculations show that the DCS is dominated by a ℓ=4 shape resonance than a ℓ=2 resonance ascribled in the experiment.

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1 Zhou, H., Perreault, W. D., Mukherjee, N. and Zare, R. N. Anisotropic dynamics of resonant scattering between a pair of cold aligned diatoms. Nat. Chem 14, 658-663, 2022

Long-range molecular interactions play an essential role in atmospheric and environmental chemistry, astrochemistry, and many other relevant fields. For modeling purposes, these interactions can be better understood by constructing a potential energy surface (PES) for the system of interest.\(^1\) The contributing interactions in the long-range region of a PES (namely electrostatic, induction, dispersion, ...) are usually evaluated by perturbation theory techniques after expanding the electronic charge distribution in the well-known multipolar series.\(^2\) However, although its theoretical description is a well-studied subject, the implementation of its mathematical formulation can be extremely challenging, considering that the analytical expressions (which can be written as a sum of terms for each of the different interactions) could be several pages long of explicit algebra just for a single term and changes from system to system. Our program “Long-Range-Fit” (LRF), is an interactive user-friendly interface designed to assist in fitting the long-range region of a PES for systems composed of (any) two rigid molecules. Once the symmetry of each of the fragments is specified, LRF is programmed to automatically generate and fit the corresponding analytical expressions for the most common symmetry groups (up to the desired order of accuracy, defined by the maximum order in the expansion of each interaction, also specified by the user). LRF is designed to complement programs such as AUTOSURF\(^3\) in providing a more robust and accurate representation in the long-range region of a PES.

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**Figure 1:** (a) LRF flowchart: The program starts with the “System Definition” (specifying each molecule by symmetry group, net charge, and some initial coefficient values such as the charge and/or dipole, if known) and reading in the \textit{ab initio} data to be fit. Once the order of accuracy (order in the expansion of each interaction) is selected by the user, LRF generates the corresponding analytical expression and performs a fit. Finally, the fit quality is analyzed to decide whether the fit has converged and is good enough to be used. (b) LRF main control window.

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Poster B15

Gas Phase Infrared Investigation of the Water Catalyzed Isomerization of N1- to N6-Methyl-Adenosine

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ABSTRACT

Protonated 1-methyladenosine (m¹A+H⁺) and 6-methyladenosine (m⁶A+H⁺) are naturally occurring molecules that play important roles in RNA chemistry. Previous studies demonstrated that isomerization between m¹A and m⁶A occurs most efficiently at pH values between 8-9. This dependence was rationalized by invoking an initial isomerization step where hydroxide attacks the m¹A scaffold at either the C₂ or C₆ position. The Dimroth rearrangement was the mechanism proposed for this isomerization, and Engel later demonstrated using NMR spectroscopy and isotopically labeled (¹⁵N) nitrogen that methyladenosine does in fact undergo the ring opening mechanism as indicated in Figure 1. Here we explore a mechanism that involves a nucleophilic attack by hydroxide at the 6-membered pyrimidine ring of m¹A+H⁺ (between ring positions 1 and 2). This would lead to a ring-opening that allows for a rotation around the C₅-C₆ bond. Subsequent ring closure with loss of hydroxide would then yield the m⁶A+H⁺ product. While this mechanism is known, we aim to capture and structurally characterize key reaction intermediates utilizing cryogenic ion chemistry and isomer-selective vibrational spectroscopy to reaffirm the current isomerization mechanism. We will report high-resolution mass spectra and cryogenic vibrational spectra of m¹A+H⁺, m³⁶A+H⁺ (m/z = 282 Da), and the proposed reaction intermediate corresponding to the stoichiometry m¹A+H⁺+H₂O (m/z = 300 Da). Preliminary results indicate that a species at m/z=282 Da (which could be m¹A+H⁺ or m³⁶A+H⁺) can be generated upon collisional activation of the 300 Da intermediate. The implications of these findings on the isomerization mechanism will be discussed in the context of the computed potential energy barriers and structures of the transition states.

Crossed-Beam Studies of the O(3P, 1D) Reactions with Cyanoacetylene and Cyanoethylene: Product branching Fractions and Role of Intersystem-Crossing

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ABSTRACT

Cyanoacetylene (HCCCN) and cyanoethylene (acrylonitrile) (CH\textsubscript{2}CHCN) are of considerable interest in astrochemistry being ubiquitous in space (molecular clouds, solar-type protostars, circumstellar envelopes) and also relatively abundant. They are also abundant in the upper atmosphere of Titan. Since oxygen is the third most abundant element in the universe, the reaction O(3P) with these two nitriles can be of relevance in the chemistry of extraterrestrial environments. In addition, the oxidation of cyanacetylene and acrylonitrile is also relevant in combustion environments, because the thermal decomposition of pyrrolic and pyridinic structures present in fuel-bound nitrogen generates many nitrogen-bearing compounds, including cyanoacetylene and acrylonitrile. Despite their relevance, limited information exists on the reactions of oxygen atoms with these important nitriles. Here, we report on a combined experimental and theoretical investigation of the reactions of cyanoacetylene and acrylonitrile with both ground (3P) and excited (1D) atomic oxygen. From product angular and time-of-flight distributions in crossed molecular beam experiments with mass spectrometric detection at the collision energy of about 31 kJ/mol, we have identified the primary reaction products and determined their branching fractions (BFs). Theoretical calculations of the relevant triplet and singlet potential energy surfaces (PESs) were performed to assist the interpretation of the experimental results and elucidate the reaction mechanisms. Adiabatic statistical calculations of product BFs for the decomposition of the main triplet and singlet intermediates were carried out. Combining the experimental and theoretical results, we have reached the following conclusions. (i) The O(3P)+HCCCN reaction exhibits a minor adiabatic channel leading to OCCCN(cyanoketyl)+H (BF=0.10±0.05), while the dominant channel (BF=0.90±0.05) occurs via intersystem crossing (ISC) to the underlying singlet PES forming HCCN(cyanomethylene)+CO. The O(1D) reaction exhibits the same two channels, with the relative CO/H yield slightly larger. (ii) The O(3P)+CH\textsubscript{2}CHCN reaction leads to two main product channels, among a variety of possible open channels: (a) CH\textsubscript{2}CNH(ketenimine)+CO (dominant, BF=0.87±0.05), formed via efficient ISC, (b) HCOCHCN+H (BF=0.13±0.05), occurring adiabatically on the triplet PES. Both ketenimine and acrylonitrile have been detected toward the same star-forming regions (as in Sagittarius B2(N) hot core). Ketenimine is often neglected by astrophysical modelers, with respect to its more abundant CH\textsubscript{3}CN isomer, and also the reaction O(3P)+acrylonitrile is overlooked in models. The O(1D)+CH\textsubscript{2}CHCN reaction mainly leads to formation of CH\textsubscript{2}CNH+CO adiabatically on the singlet PES; these results can help improving models related to the chemistry of interstellar ice and cometary comas, where O(1D) reactions are believed to play an important role. Overall, our results on the title reactions are expected to be useful for improving models of combustion and extraterrestrial environments.

An Experimental and Theoretical Investigation of the N(\textsuperscript{2}D) + Benzene Reaction with Implications for the Photochemical Models of Titan

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ABSTRACT

We report on a combined experimental and theoretical investigation of the N(\textsuperscript{2}D) + C\textsubscript{6}H\textsubscript{6} (benzene) reaction of relevance in the atmospheric chemistry of Titan. Experimentally, the reaction was studied (i) under single-collision conditions by the crossed molecular beams (CMB) scattering method with mass spectrometric detection and time-of-flight analysis at the collision energy (E\textsubscript{c}) of 31.8 kJ/mol to determine the primary products and their branching fractions (BFs),\textsuperscript{1,2,3} and (ii) in a continuous supersonic flow reactor to determine the rate constant as a function of temperature from 50 K to 296 K.\textsuperscript{4} Theoretically, electronic structure calculations of the doublet C\textsubscript{6}H\textsubscript{6}N potential energy surface (PES) were performed to assist the interpretation of the experimental results and characterize the overall reaction mechanism. The reaction is found to proceed via barrierless addition of N(\textsuperscript{2}D) to the aromatic ring of C\textsubscript{6}H\textsubscript{6}, followed by formation of several cyclic (five-, six-, and seven-membered ring) and linear isomeric C\textsubscript{6}H\textsubscript{6}N intermediates that can undergo unimolecular decomposition to bimolecular products. Statistical (RRKM/Master Equation) calculations of product BFs on the theoretical PES were carried out under the conditions of the CMB experiments and at the temperatures relevant for Titan’s atmosphere. In all conditions the ring-contraction channel leading to C\textsubscript{5}H\textsubscript{6} (cyclopentadiene) + CN is dominant, while minor contributions come from the channels leading to o-C\textsubscript{6}H\textsubscript{5}N (o-N-cycloheptatriene radical) + H, C\textsubscript{5}H\textsubscript{5}N (pyrrolyl) + C\textsubscript{2}H\textsubscript{2} (acetylene), C\textsubscript{5}H\textsubscript{5}CN (cyano-cyclopentadiene) + H, and p-C\textsubscript{6}H\textsubscript{5}N + H.\textsuperscript{5} Rate constants (which are close to the gas kinetic limit at all temperatures, with the recommended value of (21.9±3.0)×10\textsuperscript{-11} cm\textsuperscript{3} s\textsuperscript{-1} over the 50-296 K range) and BFs have been used in a photochemical model of Titan’s atmosphere to simulate the effect of the title reaction on the species abundances (including any new products formed) as a function of the altitude.\textsuperscript{5}

\textsuperscript{4} Hickson, K. M. \textit{et al.} A kinetic study of the N(\textsuperscript{2}D) + C\textsubscript{2}H\textsubscript{2} reaction at low temperature. \textit{PCCP} 22, 14026-14035, 2020.
\textsuperscript{5} Balucani, N. \textit{et al.} An experimental and theoretical investigation of the N(\textsuperscript{2}D) + C\textsubscript{6}H\textsubscript{6} (benzene) reaction with implications for the photochemical models of Titan, \textit{Faraday Discuss.}, in press (DOI: 10.1039/D3FD00057E), 2023.
ABSTRACT

Gas-Liquid interfaces, and the heterogeneous processes that occur at them, have been the subject of much less experimental and theoretical study than the gas-phase or gas-solid interface. Relatively little is known about the structure of liquid surfaces, and the interplay between the surface structure and the elementary chemical processes resulting from gas-liquid interaction. In recent years, new experimental techniques and theoretical methodologies have begun to provide detailed understanding in this area. We have developed a gas-liquid scattering apparatus with planar laser-induced-fluorescence imaging of the real-space scattering distribution. Combined with a pulsed supersonic DC discharge source of OH, we have used this apparatus to study the dynamics of the inelastic collisions of OH radicals with the surfaces of the inert liquid perfluoropolyether (PFPE), and also the surfaces of the potentially reactive hydrocarbons squalane (saturated) and squalene (unsaturated).

Analysis of images taken in a time-series that spans before and after collision reveals that the OH radicals are scattered from all 3 liquids, and for both normal and 45° incident angles, with a predominately superthermal speed distribution, with no strong evidence for a substantial thermalized component. Angular scattering distributions are determined from both time-series and single-time images for each incident angle, each liquid and as a function of OH rotational state. Significant anisotropy is observed in the scattering for 45° incident angle, with the scattering angle distribution varying as a function of liquid and final N'. We discuss the observed differences in the scattering dynamics in the context of both the inelastic and reactive processes occurring at the surfaces of the three liquids.
Dynamics of Optically Centrifuged N\textsubscript{2}O in Extreme Rotational States Studied with Transient IR Absorption Spectroscopy

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ABSTRACT

The behavior of molecules with large amounts of rotational energy is a largely unexplored area in physical science. Molecules in high energy rotational states are observed as products of reactions and collisional energy transfer, but they are not easily prepared by traditional experimental methods. High rotational states can be prepared using an optical centrifuge, which is an ultrafast laser-based method that selectively populates molecules with inverted rotational distributions. Investigating the behavior of molecules in extreme rotational states enhances our understanding of fundamental energy transfer processes, energy partitioning in vibration and rotation, and centrifugal distortion in molecules in extreme J states. In this project, an optical centrifuge is combined with a high-resolution transient IR absorption spectrometer to explore the dynamics of optically centrifuged N\textsubscript{2}O (00\textsubscript{1}1-00\textsubscript{0}0) with J=100-200 and rotational energies up to 16,000 cm\textsuperscript{-1}.

A tunable optical centrifuge was used to selectively optimize N\textsubscript{2}O population by controlling the bandwidth of the optical pulses. Figure 1a shows optical trap intensity profiles as a function of instantaneous angular frequency \(\Omega_{DC}\) for the full bandwidth pulses and for pulses with reduced bandwidth to preferentially populate the J=140 and 160 rotational states. The nascent distributions of centrifuged molecules were measured with high-resolution transient IR absorption spectroscopy at \(\lambda=4.4\) \(\mu\text{m}\) and a spectroscopic pressure of 2.5 Torr. The IR transitions used for this study were first identified using transient spectroscopy of optically centrifuged N\textsubscript{2}O\textsuperscript{1,2}. Figures 1b and 1c show the inverted nascent rotational distributions for the two reduced-bandwidth traps at \(t=300\) ns. Transient IR Doppler line profiles were measured to characterize the translational energy transfer of optically centrifuged molecules and polarization-sensitive spectroscopy was used to investigate orientational anisotropy dynamics and relaxation kinetics of the optically centrifuged molecules. The orientational anisotropy of the centrifuged molecules increases as a function of J and lower J-states have higher translational energies as a result of impulsive collisions between centrifuged molecules and thermal bath molecules. The translational energies of lower J-states increase as a function of time as rotational energy is converted to translational energy through inelastic collisions. The time-dependence of the high-J tail populations shows that the collisional relaxation rate constants are approximately half that of the Leonard-Jones collisional rate constant. The results are compared with previous dynamics studies on optically centrifuged CO molecules\textsuperscript{3}.

This project has been funded through the NSF.


\textsuperscript{2} Ogden, H. \textit{et al.} Transient IR (00\textsubscript{1}1–00\textsubscript{0}0) Absorption Spectroscopy of Optically Centrifuged N\textsubscript{2}O with Extreme Rotation up to J=205. \textit{JSQRT} 246, 106867, 2020.

CPUF in an Extended Laval Nozzle: Low Temperature Kinetics of the HCO + NO Reaction with Conditions Measured Using REMPI

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ABSTRACT

In the CRESU technique, pioneered in Rennes, a uniform supersonic flow serves as a wall-less reactor for low temperature kinetics measurements. The traditional method of detection employed with CRESU is laser induced fluorescence (LIF). One of the major drawbacks of LIF is the limited number of species that can be probed, and this range can be greatly expanded by using chirped-pulse rotational spectroscopy, an approach we term CPUF for chirped-pulse/uniform flow. Detection by CPUF requires monitoring the free induction decay of the species. However, the high collision frequency in high-density uniform supersonic flows can interfere with the free induction decay and attenuate the signal. One way to overcome this is to use sampling methods, such as airfoil or skimmer sampling. However, this requires complicated experimental designs with differential pumping systems and can have interference from shocks in the sampling region and thus may not be ideal for studying reaction kinetics. This has led us to develop an extended Laval nozzle which creates a uniform flow within the nozzle itself, after which the gas undergoes a shock-free secondary expansion to a cold, low pressure condition ideal for CP-FTMW detection. However, impact pressure measurements, commonly used to characterize Laval flows, cannot be used to monitor the flow within the nozzle. Hence, we have implemented a REMPI (resonance-enhanced multiphoton ionization) detection scheme which allows interrogation of the conditions of the flow directly inside the extended nozzle, confirming fluid dynamics simulations of the flow environment. We have built an extended nozzle designed for a 20 K He flow and characterized the flow within the nozzle using (1+1) REMPI of a very dilute sample of NO. We will describe the development of the new extended flow along with its characterization using REMPI and application to studies of the low temperature reaction kinetics of HCO with NO as co-reactant. The data gathered in this study demonstrates the potential of both the REMPI and CPUF methods for low temperature kinetics.


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The Collisional 2:1 Rotation-Vibration Quasiresonance

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ABSTRACT

At low rotational angular momentum \( j \), atom-diatom collisions at thermal energies are typically rotationally sudden but vibrationally adiabatic, resulting in large rotationally inelastic and small vibrationally inelastic rate constants. In contrast, at elevated \( j \), the molecular rotational frequency can be a small-integer submultiple of the vibrational frequency. At such resonances, collisional energy transfer between rotation and vibration becomes extremely facile, leading to dramatically increased level-to-level vibrationally inelastic rate constants. The resonance condition also leads to sharply-peaked rotational distributions governed by the rule \( \Delta j^{\text{peak}} = -n\Delta v \); where \( v \) denotes the vibrational action or quantum number and \( n \) is the order of the resonance.

The 4:1 resonance in Li\(_2\) \((1)^1\Sigma_u^+\) has been studied experimentally at \( j = 64 \) in previous work.\(^1\) The 4:1 rule persists well away from resonance, leading to the term quasiresonance to describe the phenomenon, in which the adiabatic invariants \( j \) and \( v \) are transiently replaced by a linear combination. In experiments and calculations, quasiresonance dominates rovibrationally inelastic energy transfer between \( j = 42 \) and 76 in this system.\(^1\) The dynamical origin of quasiresonance has been explored by Ruiz and Heller.\(^2\)

Using the same laser-induced fluorescence technique as in previous studies, we have extended measurements to initial values of \( j \) as high as 96 and final values up to 112. Making these measurements necessitated increasing the range of spectroscopic measurements of the Li\(_2\) A-X system. We determined the frequencies of 4818 previously unmeasured transitions, up to the X-state predissociation limit for some \( v'' \) values. These results made possible the first observation of a quasiresonant transition, between the 4:1 and 2:1 quasiresonant regions in Li\(_2\)-X, with X=Li and Xe. While the 2:1 resonance itself remains beyond the reach of the experiments, the 2:1 quasiresonant rule \( \Delta j^{\text{peak}} = -2\Delta v \) is very clearly dominant at the highest values of \( j \). The very strong peaking and large rate constants previously observed near \( j = 64 \) are further enhanced. The figure shows rate constants for \( \Delta v = -1 \) in the Li\(_2\)-Li system.

At some initial values of \( j \), both the 2:1 and 4:1 quasiresonances are observable in a single rate constant distribution. We have explored the classical origins of this behavior and found that the two resonant peaks arise from different classes of collisions with rotational and orbital angular momentum either aligned or anti-aligned. While classical mechanics seems to capture the essence of the dynamics, quantitative comparison is made challenging by the shortcomings of available binning methods in the presence of sharp resonance features.


Toward Understanding Dynamics of Associative Ionization in Hypersonic Flows

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ABSTRACT

Rapid variation of flow thermodynamics in shocks during hypersonic flight leads to dissociation of O$_2$ and N$_2$ to atomic constituents and ablate surfaces that are encountered to produce carbon atoms. Associative ionization of C, N, and O atoms, primarily N + O → NO$^+$ + e$^-$, form a plasma that can interfere with radio communication and compromise the performance of onboard sensors. Complex chemistry due to rapidly varying nonequilibrium flow conditions in hypersonic systems has been modeled, but suitable experimental data is lacking. Only a single direct measurement of associative ionization under conditions relevant to hypersonic flows has been made.\(^1\) Dissociative recombination measurements have indirectly obtained associative ionization cross sections for NO$^+$, CO$^+$, and O$_2$$^+$ assuming detailed balance.\(^2\) However, only ground state ions were used in these dissociative recombination studies, despite evidence of branching to vibrationally excited ions by Ringer and Gentry.

Modifications to a crossed molecular beam apparatus are being made to allow for fast atom beam production to study associative ionization processes. A well-defined fast atom beam is crucial for understanding associative ionization dynamics and must be versatile, tunable, and has a narrow kinetic energy spread. Here, atomic ion beams are produced via a pulsed discharge from a Trickl valve. High velocity atom beams are then produced via charge exchange of atomic ions with various gases. Furthermore, implementation of 3D electron-ion coincidence detection by velocity map imaging will allow for identification of contributing electronic states and determination of the vibrational distribution of the product ions.\(^3\) We will measure the associative ionization excitation functions and electronic state dependence for C, N and O atoms. The internal state distribution of the product ions provide a key test of the theoretical description of the process. The results will then be available for use in multiscale computer modeling of plasma formation in hypersonics.

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Steric effects in rotationally inelastic collisions: Imaging $k$-$j$-$k'$ correlations in NO(A) + Ne scattering.

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ABSTRACT

We report what we believe to be the first ever experimental measurement of state-to-state $k$-$j$-$k'$ correlations in rotationally inelastic scattering.

We have used crossed-molecular beam scattering with velocity-map imaging, combined with optical state-selection, to study the stereodynamics of rotational energy transfer of electronically excited NO(A\textsuperscript{2}Σ\textsuperscript{+}, $v = 0$, $N = 4$, $j = 3.5$) in collisions with Ne. A linearly polarized laser prepares this initial state with a rotational alignment, $j$, that is preferentially either perpendicular to the pre-collision velocity vector, $k$, or near parallel to $k$. The products of rotationally inelastic scattering, NO(A\textsuperscript{2}Σ\textsuperscript{+}, $v = 0$, $N' = 0, 1, 3, 5, 9, 10$), are probed by 1+1' REMPI. The saturated probe step is essentially insensitive to product rotational alignment, $j'$, resulting in velocity-map images that contain $k$-$j$-$k'$ correlations. Analysis of the images provides the conventional differential cross sections, and two polarization-resolved differential cross sections, which describe the dependence of the observed scattering on the initial $j$ alignment as a function of scattering angle. Strong $k$-$j$-$k'$ correlations, that vary systematically with final state $N'$ and with $\Delta N'$ negative or positive are observed. The results are consistent with theoretical predictions from quantum scattering calculations performed on a literature ab initio potential energy surface. Representing the results as the respective differential cross sections for limiting ‘propeller’, ‘cartwheel’ and ‘frisbee’ alignments of $j$ provides physical insight into the observed scattering dynamics.

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Velocity mapped images for $N'=0$ NO(A)-Ne scattering. Images left to right are Horizontal, Vertical, V-H (red = high). Top is data, bottom is fit to QS calculations.
Theoretical investigation of the reactions of OH with ethane and glycine

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ABSTRACT

We perform a high-level study of the dynamics of the OH + ethane reaction. In the first place, we optimized the geometries of the stationary points of the reaction with the CCSD(T)-F12b method using aug-cc-pVTZ basis set. Three reaction paths are taken into account: hydrogen-abstraction, hydrogen-substitution and methyl-substitution. In the case of substitution two different mechanisms are considered: Walden inversion and front-side attack. In order to further advance the punctuality, we carry out single-point energy calculations at the level of CCSD(T)-F12b/aug-cc-pVQZ utilizing the above-determined structures. Furthermore, five different energy corrections are taken into consideration to go below the sub-chemical accuracy: the effect of the core electrons, δT, δ(Q), the scalar relativistic and the spin-orbit contributions. After the characterization of the stationary points of the OH + ethane reaction, we aim to develop an analytical \textit{ab initio} full-dimensional potential energy surface (PES) to study the dynamics in detail. The PES development is carried out at the level of a composite method (CCSD(T)-F12b/aug-cc-pVDZ + (MP2-F12/aug-cc-pVTZ − MP2-F12/aug-cc-pVDZ) using the ROBOSURFER program package. All in all, 85 000 quasi-classical trajectories are run and we determine the following quantities: classical and adiabatic energies of the stationary points, reaction probability values, integral cross sections, scattering angle distributions, attack angle distributions of the reactants, translational, rotational, vibrational and internal energy distributions, and rotational quantum number distributions. As a next step, we investigate the dynamics utilizing the current PES by exciting several normal-modes (one for OH and five for ethane). Quasi-classical simulations are carried out and we compute the same quantities as before. Furthermore, we also calculate the mode-specific vibrational state distributions in case of the H$_2$O product molecule.

We also study the OH + glycine reaction being interested in only the hydrogen-abstraction pathways. The abstraction can happen from three different groups of the glycine molecule: NH$_2$, CH$_2$ and COOH. The reactants and products and their conformers were already revealed previously. We determine the most possible conformer-structures of the transition states and post-reaction minima at the level of CCSD(T)-F12b/aug-cc-pVDZ. Higher level energy calculations are carried out with the CCSD(T)-F12b method using two different basis sets, aug-cc-pVTZ and aug-cc-pVQZ. The previously-mentioned energy corrections are also calculated. All in all, we successfully identify 5 transition states and 2 post-reaction minima in the case of the CH$_2$ group, 5 transition states and 19 post-reaction minima considering the NH$_2$ pathway, as well as 5 transition states in the COOH region. Utilizing these structures an analytical \textit{ab initio} full-dimensional PES development is performed using a ManyHF-based coupled-cluster-quality composite method.

\begin{itemize}
\end{itemize}
ABSTRACT

Microsecond coherence times are observed in the $P^+A_1$ entangled electron spin pair created upon excitation of photosystem I in cyanobacteria. Important environmental features in the spin pair’s decoherence, such as protein residues and the distance of the bath spins from the central spins, are identified using spin dynamics calculations under the cluster-correlation expansion (CCE) approximation. Notably, the protons within the distance range of 5-8Å are found to be the dominant contributors. In a more microscopic picture, important two-spin decoherence drivers, as well as individual nuclear spins, are characterized by controlling the spin-spin couplings in the system’s interaction Hamiltonian.

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Intermolecular Interactions Drive Chemical Outcomes: Infrared Activation of Open-Shell Collision Complexes

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The accurate prediction of bimolecular collision outcomes is crucial for understanding chemical transformations on multidimensional potential energy surfaces. A comprehensive understanding of the reactive and nonreactive pathways demands that all factors affecting the collision be characterized to accelerate the predictive modeling of chemical reactivity. To this end, the bimolecular collision outcomes can be systematically explored by preparing reactants in the entrance channel prior to reaction. Experimental studies in this laboratory have utilized infrared action spectroscopy and velocity map imaging of products to probe the structure, vibrational frequencies, and nonreactive energy-exchange mechanisms of open-shell collision complexes between nitric oxide (NO) and alkane partners (CH₄ and C₂H₆). As shown in Figure 1, the isomer-specific infrared spectroscopy of NO-CH₄ and NO-C₂H₆ complexes in the CH stretch region reveals the intermolecular interactions between the collision partners. Furthermore, the spectra indicate that ultrafast vibrational predissociation takes place when the asymmetric CH stretch is activated, signifying that this vibrational mode couples more directly with the intermolecular reaction coordinate. The figure also illustrates that the ion image anisotropy is largely determined by the probed rotational quantum number of NO (J′′) products. For a subset of NO (J′′) fragments, the ion images and total kinetic energy release distributions show an anisotropic component at low relative translation (~225 cm⁻¹) indicating a prompt dissociation mechanism. However, for other detected NO (J′′) products, the ion images and total kinetic energy release distributions are bimodal, in which the anisotropic component is accompanied by an isotropic feature at high relative translation (~1400 cm⁻¹) signifying a slow dissociation pathway. The mechanistic pathways prior to and following infrared activation of NO-CH₄ and NO-C₂H₆ complexes will be presented to assess the bimolecular collision impacts in the atmosphere and non-thermal environments.

Figure 1: (a) Infrared action spectra of (top) NO-CH₄ and (bottom) NO-C₂H₆ collision complexes. (b, c) Velocity map ion images and total kinetic energy release distributions of NO (X²Π, v″=0, J′′, Fₙ, Λ) + CH₄ products from infrared activation of NO-CH₄ complexes.
Sulfur ($^3\text{P}$) reaction with conjugated dienes forms thiophenes under single collision conditions

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ABSTRACT

Sulfur's abundance and presence in organic molecules, notably thiophenes, make it a vital element in understanding the origin and evolution of life and the chemistry of the universe. While detailed dynamics studies on S($^3\text{P}$) are lacking, Gunning and Strausz conducted studies exploring the kinetics and product branching.1 A highly stereospecific addition of S($^3\text{P}$) across a double bond was observed, resembling the behavior of S($^1\text{D}$) and singlet species in general. They attributed this stereospecificity to asymmetric addition, forming a long-lived triplet biradical followed by rapid intersystem crossing (ISC).

Here, we utilized crossed-beam velocity map imaging and high-level ab initio/transition state theory modeling to investigate the reaction of S($^3\text{P}$) with 1,3-butadiene and isoprene under single collision conditions.2 Coupled cluster calculations using KinBot3 indicate intersystem crossing to the singlet surface, leading to the formation of various long-lived intermediates, including 5-membered heterocycles. In the case of the butadiene reaction, our experimental observations revealed the detected 2H-thiophenyl radical through H loss and confirmed the predicted formation of thiophene through H$_2$ loss and thioketene through ethene loss. Complementary chirped pulse microwave measurements in a uniform flow reinforced the formation of thioketene. For the isoprene reaction, we experimentally observed analogous products, but also the methyl loss (C$_4$H$_5$S) radical. Theoretical calculations suggest a range of reaction products analogous to reaction of S($^3\text{P}$) with butadiene. Interestingly, the results obtained for S($^3\text{P}$) + 1,3-butadiene highlight a direct cyclization pathway to the aromatic product, contrasting significantly with the behavior observed in the analogous O($^3\text{P}$) reaction. The different behavior is primarily attributed to the substantial differences in C-O and C-S bond energies among the potential products.

The Role of the Pre-reaction Complex in the Dynamics of the CH$_3$ + HBr $\rightarrow$ CH$_4$ + Br Reaction

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ABSTRACT

The potential surface of the exothermic hydrogen abstraction reaction by CH$_3$ radicals from HBr involves a weakly bound hydrogen-bonded complex separated from the products by a submerged barrier. This kind of reaction is generally handled by statistical rate theories, although the energy redistribution in the weakly bound van der Waals complex is probably not fast. We studied the reaction using the quasiclassical trajectory (QCT) method to explore the correlation between reaction dynamics and the potential energy surface. The adequacy of the QCT method for this system was validated by the good agreement of the excitation functions with those derived from reduced dimensionality quantum scattering calculations.

To understand the microscopic mechanism of the reaction, for each collision, the complex lifetime was calculated as the delay induced by the interaction with respect to free flight (which can be negative when the reactants attract each other). The lifetime distribution for nonreactive collisions is structured and depends on the collision energy. The peaks of the distribution were assigned by analysis of the correlations between the impact parameter, the minimum reactant separation and the lowest energy accessed by the reacting system, recorded for each collision. In addition to reactive collisions, three classes of inelastic collisions were identified: quasi-elastic, trapped in the van der Waals well and frustrated reaction. Quasi-elastic collisions are fast and sample the repulsive wall of the potential energy surface. Among trajectories entering the potential well (forming a complex), the minority at low and the majority at high temperature leave the van der Waals well without reaction. The majority of the remaining “complex-forming” collisions lead to reaction, in the minority, called “frustrated reaction” the system visits regions of configuration space with potential energy below the bottom of the potential well, which is possible only on the product side of the barrier to reaction, temporarily forming a C-H bond and breaking the H-Br bond, but gets reflected from the repulsive C-H potential.

The vibrational energy of the breaking HBr bond speeds up the reaction at any collision energy. Although the barrier is early, an extra attraction arises when the H-Br vibration is close to the outer turning point, because the bond is “half broken”. The H-Br amplitude is so large even in the vibrational ground state that the reaction is much faster than without the extra attraction, which is an interesting quantum effect. The reaction can be frozen by artificially reducing the H-Br amplitude.

The thermal rate coefficients obtained by trajectory calculations perfectly match the recent experiments, according to which the activation energy is negative at low temperatures, but switches to positive above about 600 K. The calculated excitation functions reveal that the negative activation energy, as expected, is induced by the attraction between the reactants: the reaction cross sections diverge when the collision energy is reduced towards zero. The large change of the activation energy can be reconciled with the existing thermochemical data only if one assumes that the activation energy of the reverse reaction also increases with the temperature.

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OH Roaming in the Unimolecular Decay of the Alkyl Substituted Criegee Intermediates


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ABSTRACT

Alkene ozonolysis generates short-lived Criegee intermediates ($R_1R_2C=O'–O^-$), which are a significant source of hydroxyl (OH) radicals in the atmosphere. While unimolecular decay of Criegee intermediates to OH products can occur promptly or following thermalization, recent experimental and theoretical studies suggest that an alternative roaming pathway leading to hydroxycarbonyl products may also occur. Experiments under thermalized conditions utilizing multiplexed photoionization mass spectrometry with tunable vacuum ultraviolet radiation have identified hydroxybutanone as a stable product arising from OH roaming in the unimolecular decay of the methyl-ethyl substituted Criegee intermediate [(CH$_3$)(CH$_3$CH$_2$)COO, MECI]. Hydroxybutanone is distinguished from isomeric MECI (m/z 88) by its distinctive photoionization threshold and a kinetic appearance profile that matches that for unimolecular decay of MECI. A comprehensive theoretical kinetic analysis has been conducted to characterize the OH roaming pathway for unimolecular decay of MECI, and evaluate rate constants and branching yields under laboratory and atmospheric conditions. Additional experiments generating CH$_3$CHOO, (CH$_3$)$_2$COO, and MECI in a capillary reactor tube followed by jet-cooling detect hydroxymethyl (CH$_2$OH) radicals utilizing 2+1 resonance-enhanced multiphoton ionization. The CH$_2$OH radical is a characteristic C-C fission product of hydroxycarbonyls due to insufficient collisional stabilization. The formation of hydroxycarbonyl and C-C fission products is expected to be a general result of roaming, which can reduce the yield of OH radicals produced from alkene ozonolysis.

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ABSTRACT

It is well established that electronically excited atomic species are much more reactive than their ground state counterparts. In the high-temperature boundary layer of a (re-)entry vehicle, atomic excitation could be facilitated by hyperthermal collisions with atmospheric molecules such as $\text{N}_2$. The dynamics and kinetics of the nonadiabatic excitation of $\text{C}(^3\text{P})$ to $\text{C}(^1\text{D})$ and of $\text{N}(^4\text{S})$ to $\text{N}(^2\text{D})$ induced by hyperthermal collisions with $\text{N}_2$ molecules are investigated on coupled *ab initio* potential energy surfaces (PESs). These nonadiabatic spin-forbidden processes are modelled using both a quantum wave packet (WP) method and the semi-classical coherent switches with decay of mixing (CSDM) method. The multi-state quantum scattering calculations at selected partial waves found small transition probabilities, due to the weak spin-orbit coupling. Strong oscillations are also found in the probabilities for these two excitation processes, which are attributable to resonances supported by deep wells on PESs. The semi-classical method semi-quantitatively reproduces the quantum results when the zero-point energy of the product is properly taken into consideration. The calculated hyperthermal rate coefficients are expected to help constrain kinetic models for hypersonic simulations.
ABSTRACT
Pressure broadening measurements in the 3-0 vibrational overtone band of CO are reported with neon and nitrogen as colliders. The Ne measurements, spanning the CO initial state range from j=2 to j=20, are compared with computed values based on the XC(fit) potential energy surface of Dham et al. The computed values match well with the experimental results. The nitrogen measurements are compared with published experimental results from other authors that were later retracted on the basis of concerns that the data analysis may have been in error. We find no evidence of errors in the earlier work.
Studying rotational-state and conformational effects in chemi-ionisation reactions

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ABSTRACT

Conformers are the dominant isomers of complex molecules. The conformation of a molecule can have pronounced effects on its chemical reactivity. However, because they often interconvert into one another under ambient conditions, individual molecular conformations are difficult to isolate. Consequently, only sparse experimental data exists on the chemical properties of distinct conformers. Over the past years, we have developed experimental methods to study conformational effects in ion-molecule reactions under single-collision conditions. We have recently built a new crossed-molecular-beam setup to extend our methodology to neutral-neutral reactions. This setup is equipped with an electrostatic deflector which enables the spatial separation of different conformers or individual rotational states of molecules based on their effective dipole moments.

As the first application of this new method, rotational-state-dependent chemi-ionisation reactions of carbonyl sulfide (OCS) with metastable neon atoms were investigated. A pronounced state-specific effect on the product branching ratio was observed. Our result suggests that OCS molecules in the rotational ground state \(j = 0\) are a factor of 2.5 more reactive for dissociative ionisation than Penning ionisation compared to the \(j = 1\) state. Moreover, for heavier molecules, the disentanglement of conformational and rotational-state effects can be difficult to analyse due to the involvement of several rotational states. Choosing conformers that can be chemically separated and have high interconversion barriers could disentangle the conformational and rotational state dependencies. Therefore, we chose to study the chemi-ionisation reaction of 1,2-dibromoethylene (DBE), the conformers of which can be chemically separated. Additionally, in a collaboration with the Korean Advanced Institute of Science and Technology (KAIST), we are also currently undertaking a comparative study of the photochemistry, photoionization, and chemi-ionisation of individual stereoisomers using 1,2-dibromoethylene (DBE) as a prototypical system. These investigations aim to gain a comprehensive understanding of the role of molecular conformations in unimolecular and bimolecular reactivity.

5 Ploenes 1, L. et al. in prep. 2023.
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ABSTRACT

Organic reactions carried out in microdroplets are accelerated compared to their bulk-phase counterparts. This remarkable phenomenon is attributed to the unique environment of the microdroplet. At the air-water interface, partial solvation of the reagents reduces the solvent reorganization energy and the increased surface area-to-volume ratio leads to high surface concentrations. Additionally, extraordinary pH conditions lead to the formation of products that otherwise require catalysts and heating to synthesize in the bulk phase. While promising for the future of small-scale synthesis, all mechanistic investigations of microdroplet reactions have been restricted by the limitations of mass spectrometry (MS). Although MS/MS provides fragmentation patterns that can be used to identify the presence of structural motifs, it falls short of providing unequivocal evidence of molecular connectivity.

We employ cryogenic ion vibrational spectroscopy (CIVS) to study two previously reported reactions carried out in microdroplets: Baeyer-Villiger (BV) oxidation of 2-hydroxybenzophenone and the nucleophilic addition of protonated formic acid to 1,2-diaminobenzene to produce benzimidazole. In the case of BV oxidation, CIVS reveals that the reported product does not share the same structure as that produced via electrospray ionization. For nucleophilic addition, CIVS reveals that benzimidazole is produced in the microdroplet. Additionally, we employ cluster chemistry to identify the size in which formic acid becomes protonated and a potential intermediate along the reaction pathway. These two cases demonstrate that spectroscopy is necessary in order to assign structures and invoke mechanism in microdroplet synthesis.
Capture, Angular Acceleration, and Release of CO$_2$ and CO in a Tunable Optical Centrifuge

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ABSTRACT

The capture, angular acceleration, and release of CO$_2$ and CO molecules in a tunable optical centrifuge were investigated using high-resolution transient IR absorption spectroscopy to elucidate the mechanisms by which an optical centrifuge ramps molecules into extreme rotational states. A tunable optical centrifuge uses ultrafast, oppositely-chirped laser pulses with tunable bandwidth to trap and angularly accelerate molecules into selected rotational states. Centrifuged molecules are released from the trap when the interaction energy between the optical field and the molecule is insufficient to drive them into the next higher rotational state. Reducing the optical bandwidth of the chirped pulses reduces the effective angular frequency of the optical trap, and enables control of the ultimate angular acceleration of the molecules, leading to molecules with lower rotational frequencies.

Here, the nascent distributions for CO (J=41-49) and CO$_2$ (J=200-240) were measured as a function of the optical centrifuge bandwidth under low pressure conditions. A series of “clipped” optical centrifuge traps, as shown in Figure 1, were used to prepare molecules with classic rotational frequencies of $\Omega_f$=3-3.6 $\times$ 10$^{13}$ radians s$^{-1}$. Transient fingerprint spectroscopy was used to identify new IR frequencies for CO$_2$ (00$^0$1-00$^0$0) $\nu_3$ R-branch transitions with J=200-240. Number densities for the nascent CO and CO$_2$ distributions were used to characterize capture and acceleration efficiencies. The molecular aspects of the capture and acceleration are elucidated. The nascent distributions undergo collisional decay, and the Clip 3 time-dependent data were analyzed to determine rotational energy transfer rate constants for CO (J>40) and CO$_2$ (J>200). The results are compared to previous CO and CO$_2$ studies to elucidate the dynamics of molecules with large amounts of rotational energy.$^{1,4}$ This work is supported by the National Science Foundation.

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Theoretical insights into the Cl$^- + CH_3I$ and the F$^- + CF_3CH_2I$ reactions

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ABSTRACT

For the Cl$^- + CH_3I$ reaction, we have developed a full-dimensional *ab initio* potential energy surface (PES)\(^1\) using a composite method, defined as CCSD-F12b + BCCD(T) – BCCD, with the aug-cc-pVTZ(-PP) basis set. The fitting was done by the permutationally-invariant polynomial approach. For an initial data set, we randomly displaced the previously-determined stationary points of the PES and fit an initial PES, later did further refinement with the ROBOSURFER program system, which improves the accuracy by iteratively adding points to the fitting set. The quasi-classical trajectory (QCT) simulations on the final PES showed two product channels to be active in our collision energy (\(E_{\text{coll}}, 1–80\ \text{kcal/mol}\) range: the S\(_2\)N reactions leading to I$^- + CH_3Cl$ and iodine abstraction resulting in the ICl$^- + CH_3$ products. Detailed analysis of more than 1.5 million trajectories (reaction probabilities, integral cross sections, scattering angle, initial attack angle, product translational energy and product internal energy distributions) gave us deeper insights into the dynamics and mechanisms of the Cl$^- + CH_3I$ reaction. Finally, we could compare our results with crossed-beam experiments and previous direct dynamics simulations, and quantitative and/or qualitative agreement could be observed.

We also investigated the F$^- + CF_3CH_2I$ 9-atomic reaction.\(^2\) The F$^- + CH_3CH_2I$ reaction has already been studied, however substituting the three hydrogen atoms with fluorine atoms can drastically change the reaction dynamics as the bimolecular elimination (E2) reaction pathway will be blocked. The stationary points of the PES were characterized at the CCSD(T)-F12a/cc-pVDZ(-PP)-F12 level of theory and we started a PES development. However, the *ab initio* computations at the randomly displaced points mostly did not converge, so we utilized a recently-developed method, ManyHF, which solves most of the convergence problems occurring during the creation of the initial data set.


ABSTRACT

Our research revealed cases of spontaneous N₂ cleavage without further activation. This was achieved by some naked transition metal (TM) clusters under cryo conditions within an ion trap. Choice of TM, of cluster size, and of cluster charge turned out crucial. We find this cleavage mediated by some cationic clusters, and by some anionic clusters. Most noteworthy, we find cases where the adsorption of multiple N₂ hampers activation – self poisoning – and cases where it enables the activation – self promotion. We embed these investigations into a long standing scheme of concerted studies that combine reaction kinetics, IR spectroscopy, electronic spectroscopy, and reaction path modeling by DFT quantum chemistry.¹⁻¹³

Spin-orbit changing collisions of highly vibrationally excited NO molecules

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ABSTRACT

Collision studies involving the open shell nitric oxide (NO) molecule have been central in many detailed investigations of molecular reaction dynamics as a prototype system for probing inelastic collisions. These processes have proven a powerful means of investigating molecular interactions, and much current effort is focused on the cold and ultracold regime where quantum phenomena are clearly manifested. Here I present our recent work on state-to-state spin-orbit changing collisions of highly vibrationally excited NO molecules prepared in single rotational and parity levels at $v=10$ using stimulated emission pumping (SEP).\(^1\) This state preparation is employed in a near-copropagating beam geometry that permits very wide tuning of the collision energy, from far above room temperature down to 2 K where we test the theoretical treatment of the attractive part of the potential and the difference potential for the first time. We have obtained differential cross sections for state-to-state collisions of NO($v=10$) with Ar/Ne in spin-orbit excited manifold using velocity map imaging.\(^2\) Overall good agreement of the experimental results was seen with quantum mechanical close-coupling calculations done on coupled-cluster potential energy surfaces. Probing cold collisions of NO carrying $\sim$2 eV of vibrational excitation allows us to test state-of-the-art theory in this extreme nonequilibrium regime. The current experimental setup is now modified to permit a near-counterpropagating geometry for the molecular beams which allows us to look into really high collision energies to study chemistry in high temperature hypersonic flows. This takes us to a new direction where vibrationally inelastic processes may appear and the latest results along these experiments will also be presented.


Unimolecular decay dynamics of the simplest Criegee intermediate to OH products

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ABSTRACT

The simplest Criegee intermediate, formaldehyde oxide (CH$_2$OO), is produced by ozonolysis of terminal alkenes in the troposphere, where its unimolecular decay leads to hydroxyl (OH) radicals and other products. Isolated and jet-cooled CH$_2$OO prepared in the laboratory is characterized by IR action spectroscopy with time-resolved UV laser-induced fluorescence detection of the OH radical products. The IR action spectrum of CH$_2$OO is obtained in the overtone CH stretch region (5940-6280 cm$^{-1}$). The observed vibrational features and relative intensities are in good agreement with computed anharmonic frequencies and intensities. The IR excitation energies (17.0-17.4 kcal mol$^{-1}$) are below the transition state (TS) barrier via 1,3 ring closure (19.1 kcal mol$^{-1}$) predicted at a high level of theory.$^1$ As a result, the unimolecular decay of CH$_2$OO to OH products proceeds exclusively by quantum mechanical tunneling, specifically heavy-atom tunneling associated with ring closure. Experimental measurements reveal a relatively slow rate for appearance of OH products, which is compared with calculated Rice-Ramsperger-Kassel-Marcus energy-dependent rates $k(E)$ implemented with 1D Eckart tunneling. The latter is extended to thermal rate calculations $k(T,P)$ and compared with prior kinetic studies on unimolecular decay of CH$_2$OO under thermal conditions.$^2$


Vibrational energy levels and predissociation lifetimes of the $A^2\Sigma^+$ state of SH/SD radicals by photodissociation spectroscopy

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ABSTRACT

Photo-predissociation of SH and SD radicals in the $A^2\Sigma^+$ state are investigated using the high-$n$ Rydberg atom time-of-flight (HRTOF) technique. By measuring the photoproduct translational energy distributions as a function of excitation wavelength, contributions from overlapping $A^2\Sigma^+$ ($v'$) $\rightarrow X^2\Pi$ ($v''$) transitions can be separated, and the H/D + S($^3P_J$) photofragment yield (PFY) spectra are obtained across various rovibrational levels (SH $v' = 0$-7 and SD $v' = 0$-8) of the $A^2\Sigma^+$ $\rightarrow X^2\Pi$ bands. The upper $A^2\Sigma^+$ state vibrational levels $v' = 5$-7 of SH and $v' = 3$-8 of SD are determined for the first time. The PFY spectra are analyzed with the simulation program PGOPHER, which gives vibrational origins and linewidths of the rovibrational levels of the $A^2\Sigma^+$ state. The linewidths ($\geq 1.5$ cm$^{-1}$) of the SH $A^2\Sigma^+$ $v' = 3$-7 and SD $A^2\Sigma^+$ $v' = 2$-8 states are characterized for the first time in this work, demonstrating that these levels undergo rapid predissociation with lifetimes on the order of picosecond. The lifetimes of the SD $A^2\Sigma^+$ $v' = 0$, $N = 1$ and 2 levels are determined to be $247\pm50$ ns and $176\pm60$ ns by pump-probe delay measurements, respectively. The experimentally measured lifetimes are in a reasonable agreement with the theoretical predictions.

Two-photon dissociation dynamics of the mercapto radical

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ABSTRACT

Two-photon dissociation dynamics of the SH/SD radicals are investigated using the high-$n$ Rydberg atom time-of-flight (HRTOF) technique. The H/D($^2S$) + S($^1D$) and H/D($^2S$) + S($^1S$) products are observed in the dissociation of the SH/SD radicals on the $2^2\Pi$ and $B^2\Sigma^+$ repulsive states, from sequential two-photon excitation via the $A^2\Sigma^+$ ($v' = 0, J' = 0.5-2.5$) state. The angular distributions of both H/D($^2S$) + S($^1D$) and H/D($^2S$) + S($^1S$) product channels are anisotropic. The anisotropy parameter ($\beta$) of the H($^2S$) + S($^1D$) products is $-0.8 \pm 0.1$ ($-0.9 \pm 0.05$ for SD), and that of the H($^2S$) + S($^1S$) products is $1.3 \pm 0.3$ ($1.2$ for SD). The anisotropic angular distributions indicate that the SH/SD radicals promptly dissociate on the repulsive $2^2\Pi$ and $B^2\Sigma^+$ potential energy curves (PECs) along with some non-adiabatic crossings, leading to the H/D($^2S$) + S($^1D$) and H/D($^2S$) + S($^1S$) products, respectively. The bond dissociation energy of the ground-state $X^2\Pi_{3/2}$ SH/SD to the ground-state H/D($^2S$) + S($^3P_2$) products is measured to be $D_0(S-H) = 29253 \pm 20$ cm$^{-1}$ and $D_0(S-D) = 29650 \pm 20$ cm$^{-1}$, respectively. The dissociation energy of the $A^2\Sigma^+$ state SH/SD to the H/D($^2S$) + S($^1D$) products is derived to be $D_0[S-H(A)] = 7659 \pm 20$ cm$^{-1}$ and $D_0[S-D(A)] = 7940 \pm 20$ cm$^{-1}$.

Temperature- and Size-Dependent, Water-Cluster-Mediated Long Range Proton Transfer in Microhydrated 4-Aminobenzoic Acid

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ABSTRACT

We explore water-mediated proton transfer between two spectroscopically distinct protonation sites adopted by 4-aminobenzoic acid (4ABA). This is achieved by following the spectroscopic behavior of H⁺-4ABA-(H₂O)ₙ₋₀₄ cluster ions held in a temperature-controlled ion trap. Protonation occurs at the acid (O-protomer) and amine (N-protomer) functionalities, which display dramatically different ultraviolet (UV) absorption bands. After most of the O-protomer population is depleted by UV excitation with a 6 ns pulse width laser near 310 nm, we record time evolution of the protomer populations over tens of milliseconds by monitoring the characteristic vibrational bands of two protomers. Temperature-dependent interconversion with retention of the water molecules is observed for n = 3 and 4 but not n = 2. These results thus support an earlier theoretical prediction that the transfer mechanism changes from n = 2 to 3.

Scheme 1. Schematic of water mediated proton transfer.
A tunable optical centrifuge is used to investigate high rotational energy states of N$_2$O that have not previously been reported. A full-bandwidth optical centrifuge angularly accelerates N$_2$O molecules to rotational states as high as J=380. Tuning the optical centrifuge is accomplished by reducing the spectral bandwidth, thereby lowering the rotational states of molecules that are released from the optical trap, as shown in Figure 1. Population in selected states is optimized by tuning the optical centrifuge bandwidth to correspond to selected rotational frequencies. High-resolution transient IR absorption spectroscopy is used to probe rotationally-resolved transition frequencies of the N$_2$O (00$^0$1-00$^0$0) band at $\lambda$=4.4 $\mu$m. Prior to our studies, IR transitions from the (00$^0$0) state had been reported up to J=92 in long path absorption measurements$^1$. The selectivity of the tunable optical centrifuge enables us to observe nearly all N$_2$O R-branch rotational transitions with J=100-205 and P-branch transitions up to J=135, based on the tuning range of the IR probe lasers. Figure 1 shows a four-fold enhancement in transient absorption signals at t=300 ns for the R134 transition when the optical centrifuge bandwidth is reduced. This work expands on previous IR measurements from our group of a number of N$_2$O R-branch transitions using a tunable optical centrifuge between J=93 and 205$^{2,3}$. The experimental results are compared to two models. In the first model, rotational energies for N$_2$O (00$^0$0) and (00$^0$1) up to J=205 are extrapolated using a third-order expansion of the rigid rotor model and low-J spectral constants reported by Toth$^1$. The second model by Perevalov and coworkers is semi-empirical and uses an effective Hamiltonian that includes rotationally resolved polyads of more than 40 vibrational modes$^4$. The observed R200 transition frequency is within 0.05 cm$^{-1}$ of the first model and within 0.021 cm$^{-1}$ of the second model. Finally, rotational energies for the (00$^0$0) vibrational state up to J=134 and the (00$^0$1) vibrational state up to J=135 are determined using combination differences and results are compared to the models. This study lays the groundwork for identifying new probe transitions for J=250-380 that will be used in future dynamics studies.
Nonadiabatic Dynamics with Only Potential Energies and Gradients

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ABSTRACT

We often employ mixed-quantum classical (MQC) algorithms to simulate nonadiabatic processes involve multiple electronic states. There are in general two categories of MQC algorithms, namely, trajectory surface hopping (TSH), and self-consistent potential (SCP) methods. The electronic equation of motion (EOM) of TSH and SCP methods involve nonadiabatic coupling vector (NACs) terms that can be expressed as time derivative couplings (TDCs). While the nuclear EOM of SCP methods involves terms that are explicitly in NACs. Evaluating NACs from the electronic structure theory is cumbersome, for reasons that the number of NACs scales quadratically with the number of electronic states and therefore it is expansive to evaluate, and it limits the possible electronic structure theories that MQC algorithms can be interfaced with. One can address this issue partly in TSH by evaluating TDCs from overlap integrals of electronic wave functions at successive time steps. However, such approach still requires wave functions to be available for electronic structure theory. In addition, this advantage cannot be fully utilized for SCP methods because it requires an explicit evaluation of NACs. In this talk, I will introduce the recent development on how we circumvent such difficulty by accurately approximate TDCs from the information of only potential energies and gradients, and therefore, one can propagate accurate nonadiabatic dynamics without evaluating NACs or overlap integrals (which are often used to approximate TDCs). This new category of MQC algorithm is called curvature-driven algorithm. ¹² Not only the curvature-driven algorithms are more efficient without losing accuracy, ¹ but also can be interfaced with electronic structure theories for which the wave functions are not available (and therefore one cannot evaluate TDCs from overlap integrals). The latter involves many popular machine learning electronic structure methods and multi-state pair density functional theories. Specifically, I will show you how to apply this curvature approximation to TSH and coherent switching with decay of mixing (CSDM), and the result methods are called κTSH and κCSDM. And how to extend these methods to simulate both internal conversion and intersystem crossing processes.

ABSTRACT

Penning ionization is a process of the general form:

\[ A^* + M \rightarrow A + M^+ + e^- \]

in which target atom or molecule \( M \) is ionized by collision with electronically excited reagent \( A^* \). Typically, \( A^* \) is a noble-gas atom in its excited metastable state, such as \( \text{He}(^3\text{S}) \) or \( \text{Ne}(^3\text{P}) \). The target \( M \) can be any atom or molecule as long as its lowest ionization potential is below the internal energy of \( A^* \). Due to its unique characteristics, for many years Penning ionization has been the subject of significant experimental research by means of molecular beam techniques\(^1\). In the past 10 years, several breakthrough experiments with Penning ionization have demonstrated how pure quantum phenomena can be observed in cold chemistry\(^2\). Yet, despite the importance of Penning ionization reaction in many experimental settings and fundamental research, its first-principle modeling remains challenging, even for the smallest atomic/molecular systems. The major difficulty in the theoretical description of this process arises from the autoionizing nature of the electronic state which governs the entrance channel of the reaction. If coupling with the electronic continuum is to be included within the framework of Born-Oppenheimer approximation, then complex-valued potential energy surfaces are needed.

Here we present a novel approach to calculate complex-valued optical potentials for molecular systems which undergo Penning ionization. Our method combines Fano-Feshbach resonance theory with equation-of-motion coupled-cluster (EOM-CCSD) wave function, and explicit description of the unbound electron. We show how to construct effectively Feshbach projectors within the EOM-CCSD framework, designed specifically to target systems undergoing Penning ionization. In the method we approximate state of the outgoing electron with a Coulomb wave, expanded in terms of auxiliary basis set composed of products of plane wave and Gaussian type orbitals. The proposed computational scheme is an extension of our recent work on calculating Auger decay rates in core-ionized/core-excited molecules\(^3\).

As a numerical illustration, we present complex-valued potential energy surfaces for a few benchmark systems such as \( \text{He}(^3\text{S}) + \text{Ar}, \text{He}(^3\text{S}) + \text{H}_2, \) or \( \text{Ne}(^3\text{P}) + \text{Ar} \). The reported complex potentials are compared with available empirical surfaces derived from the experimental data. Presented method opens up a possibility for fully ab initio quantum-dynamical studies of Penning ionization reaction, even for systems containing sizable molecular targets.

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\(^{1}\) Siska P.E., Molecular-beam studies of Penning ionization. Rev. Mod. Phys. 65, 337, 1993.


ABSTRACT

Vibrational spectroscopy is a powerful experimental tool that can be used to decipher the properties and potential energy surface for molecules and ensembles. Anharmonicity—deviation from the typical harmonic-oscillator reference picture—often indicates important details, such as strong hydrogen bonding, bond rearrangements, or even resonant vibrational interactions. These effects frequently differ from the results of often-used harmonic scaling factors, yet direct inclusion of such effects is often prohibitively costly compared to harmonic simulations, due to the need for inclusion of mode-coupling effects. Recent research in the Steele group has demonstrated the opportunity to examine molecular vibrations in a local-mode context, which allows for distance-based truncation of mode couplings and orders-of-magnitude acceleration of vibrational simulations. However, this approach has nonetheless been limited to heavily truncated versions of the so-called “n-mode representation”, wherein pairs, triples, etc., of modes are included in the vibrational potential. In this presentation, we demonstrate that heretofore-inaccessible convergence of this n-mode representation can be achieved within the local-mode picture, as shown in Figure 1 for a water-displacement motion in \( \text{(H}_2\text{O)}_{17} \), thereby providing the possibility of fully converged, exact anharmonic simulations for molecules beyond small reference systems. In addition to these computational accelerations, such simulations provide new insight into the nature and distance dependence of the electronic coupling between vibrational motions.

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Simulating Bimolecular Collisions with Machine Learning Potential

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ABSTRACT

Machine learning has grown in use for constructing potential energy surfaces for their ability to theoretically recreate any function given enough training as well as their fast predictive powers after being trained. When trained on ab initio data, this enables simulation of an unprecedented number of ab-initio-quality trajectories. Herein, rigorous benchmarking of these machine-learned potential energy surfaces - both in terms of their static errors and dynamics errors - is carried out for two multi-product-channel ion-molecule bimolecular collisions (HBr⁺ + HCl and HBr⁺ + CH₄). Comparison with ab initio molecular dynamics (AIMD) simulations provides one of the first direct evidence of ML potential’s ability of recreating the dynamic, ensemble-average properties such as the cross section of the reaction, time of flight of the products, etc. It is also of interest to note that ML potential with smaller static error, identified with a limited size of the validations set, does not necessarily lead to better dynamic, ensemble-average properties in MLMD. Finally, once carefully calibrated, the large number of MLMD trajectories does not only provide better statistics, but they are also essential in applying other post-process techniques (e.g., zero-point energy restraint) that are critical to reach remarkable agreement with guided-beam experimental results.
ABSTRACT

Cold and ultracold systems attract researchers’ attention because the universe’s quantum nature clearly manifests under such conditions, and research into such systems provides new insight into the quantum theory of matter and matter-light interaction. Ultracold atoms, ions, and molecules offer numerous exciting research prospects ranging from quantum-controlled chemical reactions and quantum simulations to precision spectroscopic measurements probing the fundamental laws of nature.

I will present our recent results of ab initio electronic structure and multichannel scattering calculations proposing, guiding, and explaining ultracold quantum physics experiments. I will start with our efforts related to hybrid systems of laser-cooled trapped ions and ultracold atoms combined in a single experimental setup. In collaboration with experimental groups in Amsterdam and in Freiburg, we reached and explained the quantum regime of ion-atom collisions manifested via shape resonances\(^1\) and their quantum control with an external magnetic field observed with magnetic Feshbach resonances.\(^2\) Giant second-order spin-orbit coupling is responsible for measured Feshbach resonances. I will conclude with explaining the mechanism\(^3\) of recently observed magnetic Feshbach resonances in ultracold atom-molecule mixtures.\(^4\) In collaboration with groups at MIT and in Nijmegen, we showed that these Feshbach resonances result from spin-rotation and spin-spin couplings in combination with the anisotropic atom-molecule interaction.\(^5\)

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Trapping and sympathetic cooling of conformationally selected ions

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ABSTRACT

The different effective dipole moment of conformational isomers allows for their spatial separation by means of electrostatic deflection, enabling their individual reactivity to be investigated. Recently, the conformer-specific polar cycloaddition of dibromobutadiene (DBB) with trapped propene ions has shown that both gauche and s-trans DBB conformers display capture-limited reaction rates. The reaction was found to occur through both a concerted and a stepwise reaction mechanism, despite the spatial rearrangement of atoms necessary in s-trans DBB for the latter to take place. These results were obtained by selectively aiming the molecular beam containing either one of the two conformers at a static target of propene ions embedded within a laser-cooled Coulomb crystal of calcium ions. In order to gain further control over the reaction partners, we also wish to select the conformational isomer of the ionic reactant.

Here, we demonstrate for the first time the sympathetic cooling of different conformational isomers within a Coulomb crystal, setting the scene for fully conformationally selected ion–molecule reaction studies. Following the successful isomer-selective ionisation and loading of the two m-aminostyrene conformers into Coulomb crystals of trapped and laser-cooled calcium ions, we now aim to investigate their isomer-specific reactivity.

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1 Y.-P. Chang et al., Specific Chemical Reactivities of Spatially Separated 3-Aminophenol Conformers with Cold Ca+ Ions, Science 342, 98, 2013.
2 A. Kilaj et al., Conformer-specific polar cycloaddition of dibromobutadiene with trapped propene ions, Nat. Commun. 12, 6047, 2021.
Hydrofluoroolefins (HFOs), referred to as ‘fourth generation’ refrigerants, are being considered as replacements for chlorofluorocarbons (CFCs) and hydrofluorocarbons (HFCs). Compared to CFCs and HFCs, HFOs, in general, have lower global warming potentials (GWP) and zero ozone depletion potential (ODP). However, atmospheric degradation of HFOs containing the CF$_3$CH$_2= $ moiety can lead to the formation of trifluoroacetaldehyde (CF$_3$CHO). Upon UV photolysis, CF$_3$CHO has the potential to form trifluoromethane (CHF$_3$), a potent greenhouse gas (GWP=14,700 on the 100-year time horizon). Therefore, accurate measurement of quantum yields, $\phi(\lambda)$, in the UV photolysis of CF$_3$CHO is critical for understanding its climate impacts.

This study directly quantifies $\phi_{\text{CHF}_3}(\lambda)$ and $\phi_{\text{CF}_3\text{CHO}}(\lambda)$ in the pulsed laser photolysis of CF$_3$CHO at 248, 266, 281, and 308 nm and pressures between 100 and 650 Torr (N$_2$/NO) using Fourier transform infrared spectroscopy (FTIR) and gas-chromatograph mass-spectrometry (GC/MS) detection methods. Our results indicate that photolysis of CF$_3$CHO at 308 nm, a tropospherically relevant photolysis wavelength, leads to a small, but measurable, $\phi_{\text{CHF}_3}(308 \text{ nm})$ of $\sim$10$^{-4}$ at atmospheric pressure. Figure 1 illustrates the CF$_3$CHO quantum yield results measured in this work. The experimental methods, range of conditions, and interpretation of the $\phi_{\text{CHF}_3}(\lambda)$ and $\phi_{\text{CF}_3\text{CHO}}(\lambda)$ measurements will be discussed. The present results will be critically compared with previous indirect broadband photolysis, low-pressure, and theoretical studies of $\phi_{\text{CHF}_3}(\lambda)$ and $\phi_{\text{CF}_3\text{CHO}}(\lambda)$ to resolve existing discrepancies and limitations in previous studies.

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**ABSTRACT**

Trifluoromethane (CHF$_3$) Quantum Yields in the Pulsed Laser Photolysis of Trifluoroacetaldehyde (CF$_3$CHO) at 248, 266, 281, and 308 nm at Pressures between 100 and 650 Torr

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Figure 1. Stern-Volmer plot of CF$_3$CHO photolysis measured in this work at various wavelengths.
ABSTRACT

This project investigates the state-resolved dynamics of vibrationally excited CO\textsubscript{2} prepared by direct overtone pumping. vibrationally excited states populated by overtone excitation are important in Earth's atmosphere as they can contain enough energy to break chemical bonds and have relatively slow emission lifetimes.\textsuperscript{1} Collisional relaxation competes with radiative decay, and the product energy partitioning into rotational and translational energies is determined by the energy transfer mechanisms. Previous studies have investigated the dynamics of overtone-excited C-H and O-H stretches, but less is known about CO\textsubscript{2}.\textsuperscript{2,3,4} Here, two methods of overtone pumping are used to prepare the vibrationally excited molecules, as shown in Figure 1. In Scheme 1, the (1001) state is excited with a CW single-mode mid-IR OPO near \( \lambda = 2.7 \) \( \mu \)m. The pump beam is chopped for transient detection. In Scheme 2, the (1003) state is pumped by a pulsed near-IR OPO near \( \lambda = 1.2 \) \( \mu \)m. High-resolution transient IR absorption spectroscopy of one quantum of the \( \nu\text{\textsubscript{3}} \) stretching mode near \( \lambda = 4.4 \) \( \mu \)m is used to characterize the excitation and monitor the subsequent relaxation dynamics.

The experiment uses a 3-meter cell that contains 20-65 mTorr of CO\textsubscript{2} and nearly-collinear pump and probe beams, as shown in Figure 2. Absorption of overtone excitation light for the CO\textsubscript{2} (10\textsuperscript{0}3) state centered at the P12 transition shows a linear pressure dependence, as shown in Figure 3. Three types of transient IR absorption measurements are collected in this study: 1) direct detection of the optically pumped state to characterize the nascent distribution and subsequent rotational energy transfer within that state and vibrational relaxation to other states; 2) detection of neighboring vibrational states that are collision products of the overtone-pumped states; and 3) Doppler-broadened line profiles to characterize the translational energy of the collision products. These studies will identify the major collisional relaxation pathways and provide insight into the role of vibrationally excited CO\textsubscript{2} molecules in hot environments.

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\textsuperscript{2} Christopher G. Elles, \textit{et al.} “Vibrational relaxation of CH\textsubscript{3}I in the gas phase and in solution” \textit{J. Chem. Phys.}, 120, 6973–6979 (2004)


\textsuperscript{4} Joann M. Pfeiffer, \textit{et al.} “Probing the new bond in the vibrationally controlled bimolecular reaction of O with HOD(4\nu\textsubscript{OH}).” \textit{J. Chem. Phys.} November 2000; 113 (18): 7982–7987.
Rigorous quantum calculations of rovibrational states of fluxional molecular complexes

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ABSTRACT

The interaction between HCN and its closely related molecule HNC, with H2O is of considerable theoretical and experimental interest due to its important role in astrophysics. Hydrogen cyanide is one of the most observed molecules in the interstellar medium (ISM). The interpretation of HCN, and its isotope HNC, emission in comets requires the knowledge of accurate spectroscopical data and the calculation of rate coefficients for the rotational excitation of HCN and HNC by water.

In this study, we investigate the HCN-H2O and HNC-H2O complexes, where H2O and HCN (or HNC) can act as proton donors or proton acceptors. We present quantum calculations for the bound-state properties of the fully coupled intermolecular rovibrational states of these van der Waals (vdW) complexes using a five-dimensional (5D) approach, considering the rigid-monomer approximation for total angular momentum J values of 0 and 1. Our analysis employs a newly developed ab initio five-dimensional potential energy surface (PES). This treatment offers a comprehensive and rigorous description of the intermolecular rovibrational level structure of both isomers, enabling us to characterize their vibrationally averaged nonplanar ground-state geometries as well as the rotational constants of the vdW complexes. We employ two different approaches in our calculations, which vary in terms of the definition of the dimer-fixed (DF) frame and the associated coordinates. We demonstrate that using the approach introduced in this work, H2O-HCN and HNC-H2O exhibit unusually strong coupling, with reduced probability density plots that display signatures of simultaneous excitation in multiple internal coordinates. The calculated rotational constants show excellent agreement with experimental data. These results, along with the rotational transition frequencies, confirm that the employed PES accurately describes the rotational properties of both vdW complexes.

Elucidating the reaction dynamics of dissociative chemisorption of nitrogen on Ru(0001)

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ABSTRACT

The reactive surface dynamics of energy- and angle-selected N\textsubscript{2} dissociation on a clean Ru(0001) surface are analyzed through STM images showing the results of highly energetic N\textsubscript{2} impinging on Ru(0001) terrace sites.\textsuperscript{1} An in situ STM in line with a supersonic molecular beam provides atomically resolved visualization of individual N\textsubscript{2} dissociation events to elucidate the fundamental reactive dynamics of the N\textsubscript{2}/Ru(0001) system. The distance and angle between nitrogen atoms from the same dissociated N\textsubscript{2} molecule, site specificity and coordination of binding on terrace sites are precisely measured over a range of impinging N\textsubscript{2} kinetic energies and angles, revealing previously unattainable information about the energy dissipation channels that govern the reactivity of the system. The experimental results provide insight into the fundamental N\textsubscript{2} dissociation mechanism that, in conjunction with ongoing theoretical modeling,\textsuperscript{2} will help determine the role of dynamical processes such as energy transfer to surface phonons and nonadiabatic excitation of electron–hole pairs (ehps).

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\textsuperscript{2} Wang, Y. and Guo, H. Post-dissociation Dynamics of N\textsubscript{2} on Ru(0001): How Far Can the “Hot” N Atoms Travel? \textit{J. Phys. Chem. C} 127, 8, 4079–4086, 2023
Optical cycling in polyatomic molecules

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ABSTRACT

An electronically excited state decays after a characteristic lifetime to any of the available molecular states of lower energy. The decay populates various electronic, vibrational, rotational, and spin states. Some molecules however, feature an excited state that decays almost exclusively back to the ground state. In that case a repeated laser excitation followed by spontaneous decay forms a closed optical cycle. Optical cycling on a bright transition enables rapid transfer of momentum from photons to molecules forming a basis for laser cooling. Laser-cooled molecules find applications as probes in tests of fundamental physics, hosts of a high fidelity qubits, or platforms for studying quantum state controlled chemistry.\(^1\)\(^-\)\(^5\) The first demonstration of molecular laser cooling was achieved in 2010.\(^6\) The breakthrough fueled more efforts in the field resulting in laser cooling of three- and six-atomic molecules in respectively 2017 and 2020.\(^7\)\(^,\)\(^8\) This progress promises optical cycling for even larger polyatomic molecules. I will present recent work from our group that focuses on exploring the domain of molecules with optical cycling centers, in particular, I will highlight applications enabled by increased chemical complexity of polyatomics.\(^9\)\(^-\)\(^11\)

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Gas-Phase Formation of the Resonantly Stabilized 1-Indenyl (C₉H₇⁺) Radical in the Interstellar Medium

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ABSTRACT

The 1-indenyl (C₉H₇⁺) radical - a prototype aromatic and resonantly stabilized free radical (RSFR) carrying a six- and a five-membered ring - has emerged as a fundamental molecular building block of non-planar polycyclic aromatic hydrocarbons (PAHs) and of carbonaceous nanostructures in deep space and in combustion systems. However, the underlying elementary mechanisms of formation of 1-indenyl in these extreme environments have remained largely elusive. Here, we reveal an unconventional low-temperature gas-phase formation of 1-indenyl (C₉H₇⁺) via barrierless ring annulation involving reactions of atomic carbon (C(3P)) with styrene (C₆H₅C₂H₃) and of the propargyl radical (C₃H₅⁺) with the phenyl radical (C₆H₅⁺). Macroscopic environments like molecular clouds act as natural low-temperature laboratories, in which rapid molecular mass growth processes to interstellar 1-indenyl and subsequently to more complex PAHs involving vinyl side-chained aromatics and aromatic aryl radicals can occur. This sequence of reactions and versatile mechanism to prepare aromatic RSFRs under the extreme low temperature conditions in molecular clouds might augment PAH production in deep space thus explaining the presence of PAHs along with their derivatives in the interstellar medium and carbonaceous chondrites and closing the gap of timescales of their production and destruction in our Universe.
**Poster B9**

**Theoretical Study of Formate Decomposition on Cu Catalysts**

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**ABSTRACT**

In this work, *ab initio* molecular dynamics (AIMD) calculations based on density functional theory (DFT) have been carried out to understand the post-transition state dynamics for formate (HCOO) decomposition on three model surfaces of Cu — Cu(111), Cu(110) and Cu(100). Formate, which is an important reaction intermediate in many catalytical processes, is known to adsorb with a bidentate configuration. Its decomposition proceeds to the conversion to a mono-dentate configuration, followed by the cleaving of the H-C bond. Our AIMD simulations showed that the CO\(_2\) product is translationally hot with angular distributions sharply collimated along surface normal, in agreement with experimental measurements.\(^1\) Furthermore, the CO\(_2\) product was found to have rotational and vibrational excitations, mostly in the bending mode.\(^2\) These product state distributions are rationalized by the Sudden Vector Projection model,\(^3\) revealing the key role of the transition state in product energy disposal. Specifically, the CO\(_2\) bending excitation originates from the bent geometry at the decomposition transition state.


**Product angular distribution in the H + CD₄ → HD + CD₃ reaction**

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**ABSTRACT**

First-principles based study of quantum state-to-state reaction dynamics aims to provide insights into the most detailed dynamical processes of chemical reactions and has achieved great success in predicting and explaining fascinating quantum effects in various tri-atomic systems. This field has now advanced to polyatomic reaction systems, and reactions of CH₄ with various atoms are the most studied systems.

Recently, counterintuitive effects are found in the H+CHD₃→H₂+CD₃ reaction:¹ Increasing the energy in the reactant’s CD₃ umbrella vibration reduces the energy in the corresponding product vibration. An in-depth analysis reveals the crucial role of the effective dynamical transition state: Its geometry is controlled by the vibrational states of the reactants and subsequently controls the quantum state distribution of the products.

Very recently, we performed a theoretical study of the H+CD₄→HD+CD₃ reaction² with the time-dependent wave packet method using a seven-dimensional model Hamiltonian developed by Palma and Clary. The velocity and angle-resolved state-specific differential cross sections (DCSs) at a collision energy of 0.72 eV are investigated in detail. Two detection schemes based on measuring the state-selective HD(v₁,j₁) and CD₃(v₂,j₂) products are compared. The very interesting angular distribution of the CD₃ product is explained with the concept of the effective dynamical transition state.

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¹ R. Ellerbrock, B. Zhao, U. Manthe, Sci. Adv. 8, eabm9820 (2022)

² in preparation
The persistent $l = \text{even}$ feature of the $\text{D}_2$-Rg(He,Ne) $\Delta j = 2$ scattering?

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ABSTRACT

Low-energy collisions are important to understand molecular interactions. In particular, dynamics of a scattering resonance is sensitive to the shape of the potential energy surface, hence providing the most detailed probe. In the past few years, we have conducted a series of $\Delta j = 2$ rotationally inelastic scattering between rovibrationally excited $\text{D}_2$ ($v = 2, j = 2$) molecules with rare gas atoms He, Ne at cold temperatures ~1 K. Despite the different vibrational levels and different collision partners involved, we have repeated discovered similar $l = \text{even}$ features by fitting the product angular distributions using partial wave analysis. These features are consistent between various collision geometries, which we attribute to the $l = 2$ resonance of the collision complex.$^{1,2}$ However, our experimental findings do not agree well with theory. For $\text{D}_2$-He, previous theoretical calculations$^3$ have identified a more predominant $l = 1$ resonance in our collision temperature range. There are less works on $\text{D}_2$-Ne, but an earlier spectroscopic measurement$^4$ found an $l = 5$ resonance complex. But since both resonances are $l = \text{odd}$, they would result in completely different scattering angular distributions than the experiment.

We are currently looking for the cause of this discrepancy. In a intrabeam setup, cold collisions are realized between the faster and slower velocities in a single molecular beam. This poses a challenge in defining the collision energy. Detailed characterization should be further performed for the coexpansion process. But in general, the dominance of a single partial wave and the similarity across different scattering partners seem to indicate a common feature in our current experimental setup which has not been identified.

Figure 1. Comparison between the scattering angular distributions for $\text{D}_2(v = 2)$ and ($v = 4)$ with He (top), and $\text{D}_2(v = 4)$ with He and Ne (bottom). Two different alignments ($m = 0$) and ($m = \pm 1$) are presented. All distributions are normalized to the same height.

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