Abstracts for Posters

Poster A13

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

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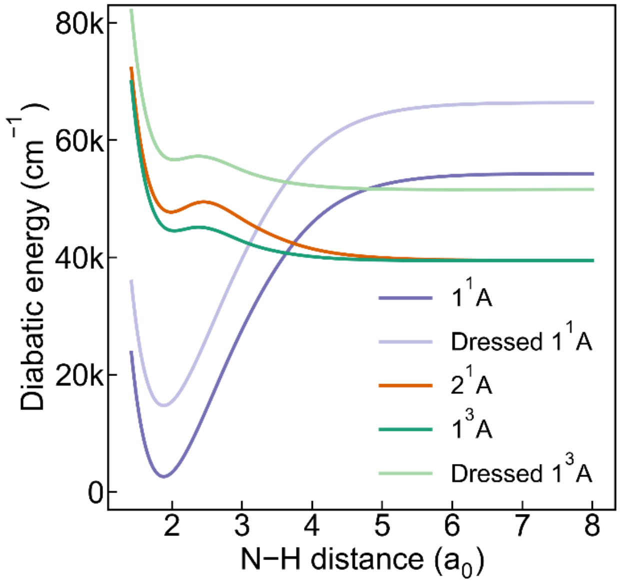
ABSTRACT

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

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



The product branching ratios were drastically altered by the laser–dipole interaction, which is a signature of nonadiabatic effects induced by light. Without the electric field, 27% of trajectories throughout the entire energy range yielded excited-state NH_2. With the electric field present, this value decreased to below 1%, and the excited-state population lifetime decreased.[4] Significant changes were also observed in the molecular channel. With the field off, 0.04% of trajectories with a total energy of 8.4 eV yielded triplet NH. With an electric field strength of 0.02 Ha/ea$_0$, over 0.3% of trajectories yielded triplet NH (an 8-fold increase), and this value was even larger for higher field strengths.

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Poster A12

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

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ABSTRACT

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

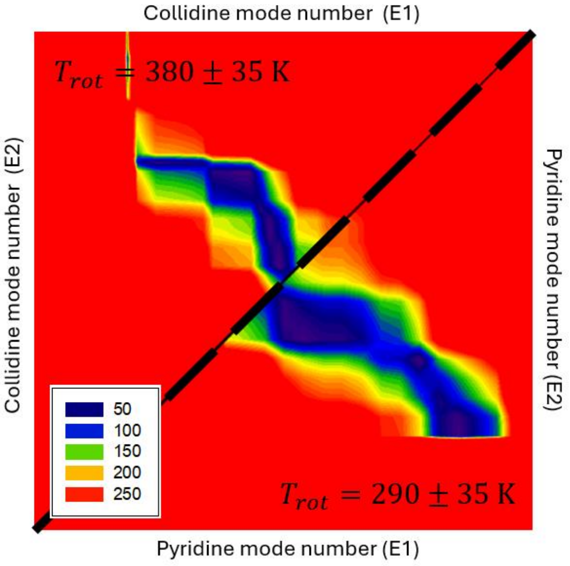

Figure 1. Heat map of energy mismatch (up to 250 cm^{-1}) between CO_2 (00^01) vibrational energy and donor combination modes. T_{rot} values are the observed nascent rotational temperature of scattered CO_2 (00^01). Inset values have units of cm^{-1}.

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

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Poster A21

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

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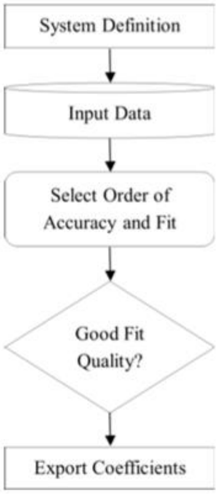
ABSTRACT

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



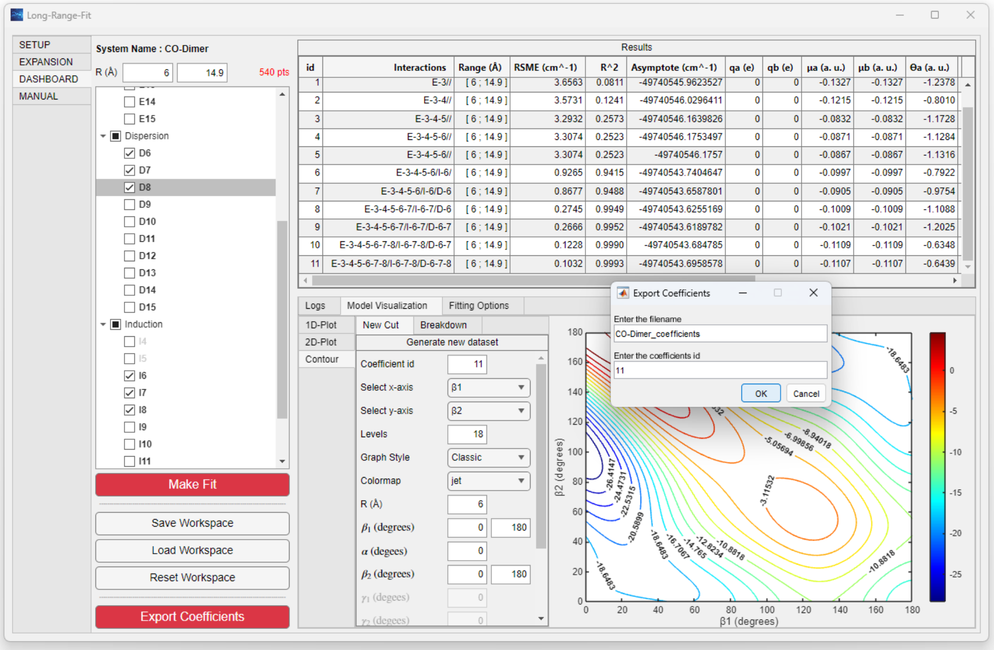
System Definition

Input Data

Select Order of Accuracy and Fit

Good Fit Quality?

Export Coefficients



System Name : CO-Dimer

R (Å) 6 14.9 540 pts

☐ E14
☐ E15
■ Dispersion
  ☑ D6
  ☑ D7
  ☑ D8
  ☐ D9
  ☐ D10
  ☐ D11
  ☐ D12
  ☐ D13
  ☐ D14
  ☐ D15
■ Induction
  ☐ I4
  ☐ I5
  ☑ I6
  ☑ I7
  ☑ I8
  ☐ I9
  ☐ I10
  ☐ I11

Results

id	Interactions	Range (Å)	RSME (cm^-1)	R^2	Asymptote (cm^-1)	qa (e)	qb (e)	µa (a. u.)	µb (a. u.)	Θa (a. u.)
1	E-3//	[6 ; 14.9]	3.6563	0.0811	-49740545.9623527	0	0	-0.1327	-0.1327	-1.2378
2	E-3-4//	[6 ; 14.9]	3.5731	0.1241	-49740546.0296411	0	0	-0.1215	-0.1215	-0.8010
3	E-3-4-5//	[6 ; 14.9]	3.2932	0.2573	-49740546.1639826	0	0	-0.0832	-0.0832	-1.1728
4	E-3-4-5-6//	[6 ; 14.9]	3.3074	0.2523	-49740546.1753497	0	0	-0.0871	-0.0871	-1.1284
5	E-3-4-5-6//	[6 ; 14.9]	3.3074	0.2523	-49740546.1757	0	0	-0.0867	-0.0867	-1.1316
6	E-3-4-5-6/I-6/	[6 ; 14.9]	0.9265	0.9415	-49740543.7404647	0	0	-0.0997	-0.0997	-0.7922
7	E-3-4-5-6/I-6/D-6	[6 ; 14.9]	0.8677	0.9488	-49740543.6587801	0	0	-0.0905	-0.0905	-0.9754
8	E-3-4-5-6-7/I-6-7/D-6	[6 ; 14.9]	0.2745	0.9949	-49740543.6255169	0	0	-0.1009	-0.1009	-1.1088
9	E-3-4-5-6-7/I-6-7/D-6-7	[6 ; 14.9]	0.2666	0.9952	-49740543.6189782	0	0	-0.1021	-0.1021	-1.2025
10	E-3-4-5-6-7-8/I-6-7-8/D-6-7	[6 ; 14.9]	0.1228	0.9990	-49740543.684785	0	0	-0.1109	-0.1109	-0.6348
11	E-3-4-5-6-7-8/I-6-7-8/D-6-7-8	[6 ; 14.9]	0.1032	0.9993	-49740543.6958578	0	0	-0.1107	-0.1107	-0.6439

Coefficient id 11
Select x-axis β1
Select y-axis β2
Levels 18
Graph Style Classic
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R (Å) 6
β_1 (degrees) 0 180
α (degees) 0
β_2 (degrees) 0 180
γ_1 (degees) 0
γ_2 (degees) 0

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Poster B12

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

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ABSTRACT

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

Poster A1

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

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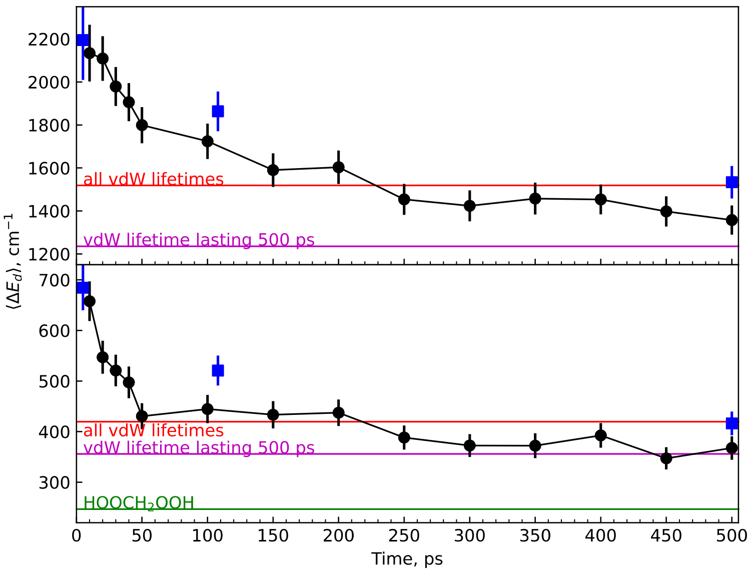
ABSTRACT

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



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

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Poster B15 Hot Topic

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

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ABSTRACT

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

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

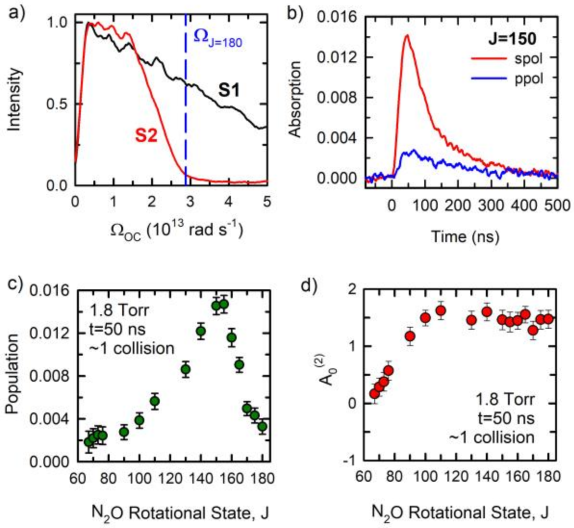

Figure 1. a) Optical centrifuge trap profiles. b) Transient absorption signals for N_2O J=150. C) N_2O populations at 50 ns. d) N_2O alignment moments $A_0^{(2)}$ at 50 ns.

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Poster B9

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

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ABSTRACT

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

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

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

Poster A6 Hot Topic

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

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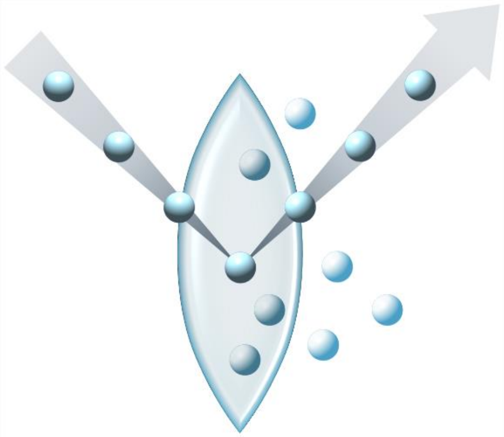
ABSTRACT

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

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



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Poster A7

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

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ABSTRACT

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

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

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

Poster A9

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

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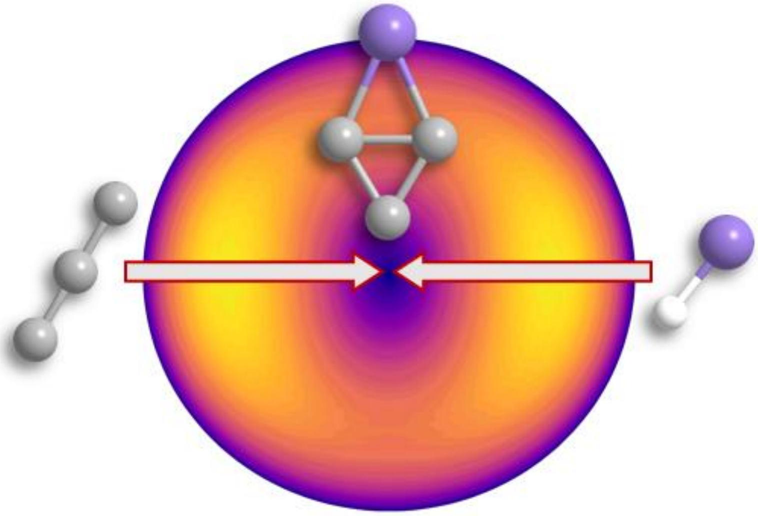
ABSTRACT

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



Poster B13 Hot Topic

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

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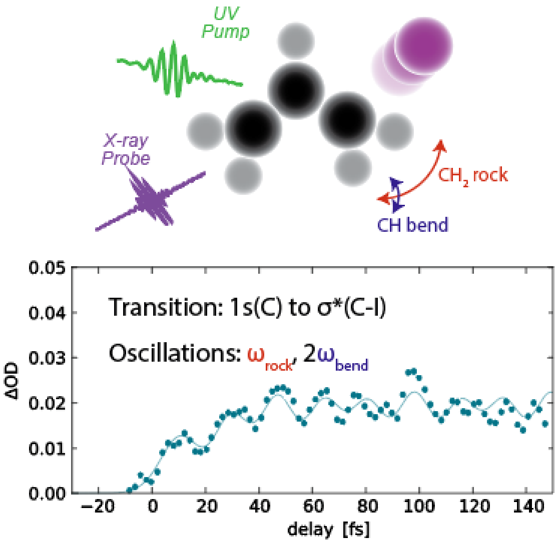
ABSTRACT

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



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

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Poster B8

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

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ABSTRACT

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

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Poster A2 Hot Topic

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

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ABSTRACT

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

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

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Poster B10

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

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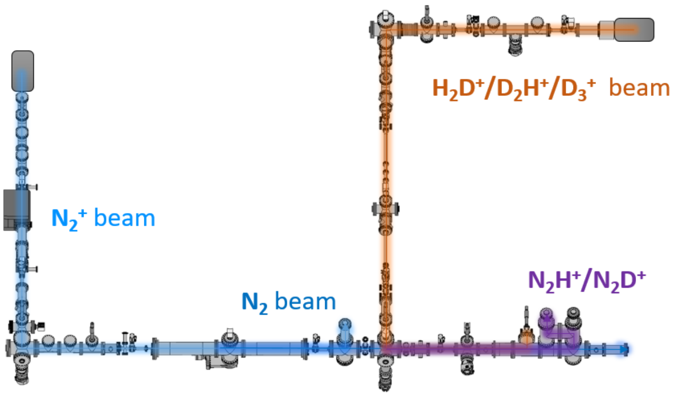
ABSTRACT

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



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

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

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

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Poster A3 Hot Topic

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

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ABSTRACT

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

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Poster B2

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

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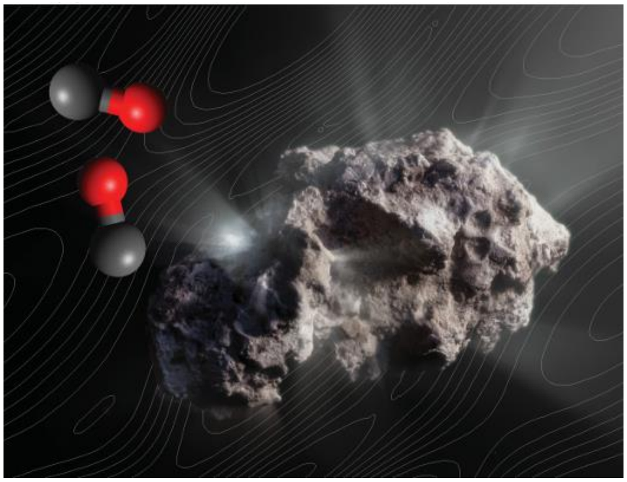
ABSTRACT

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



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Poster B11

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

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ABSTRACT

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

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Poster A14

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

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

Ultrahigh velocity resolution for inelastic scattering dynamics

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

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Poster B3 Hot Topic

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

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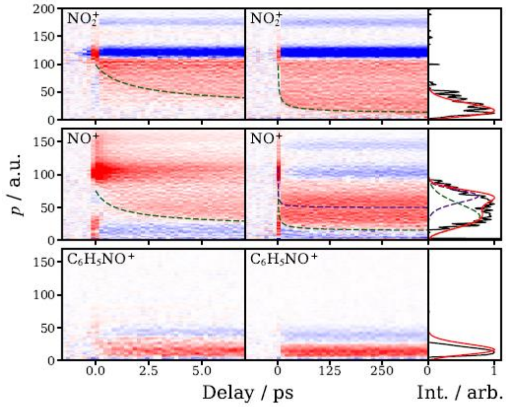
ABSTRACT

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



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

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

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Poster B5

Comparing How CO and CO_2 Are Optically Centrifuged

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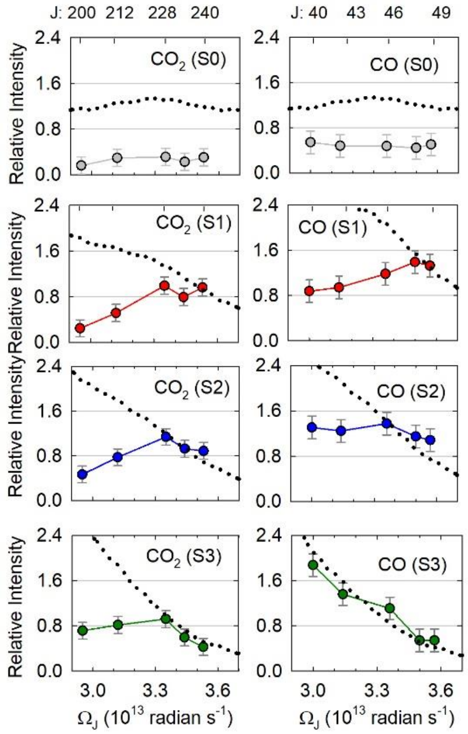
ABSTRACT

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



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

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Poster B14

Unimolecular Dynamics of Hydroperoxyalkyl (•QOOH) Intermediates

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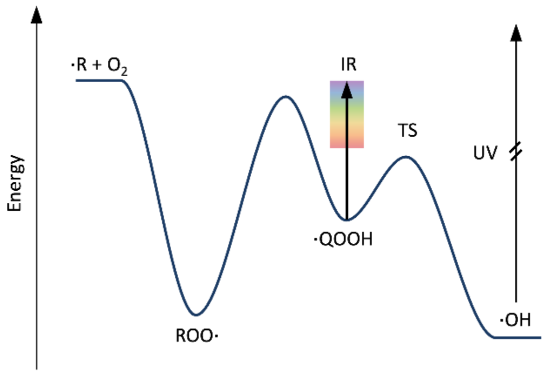
ABSTRACT

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



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Poster A10

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

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ABSTRACT

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

Poster A18

Photoacoustic Spectroscopy in a Supersonic Flow

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

Poster A19

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

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Abstract

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

Poster B20

Advancing reaction dynamics with ultracold molecules

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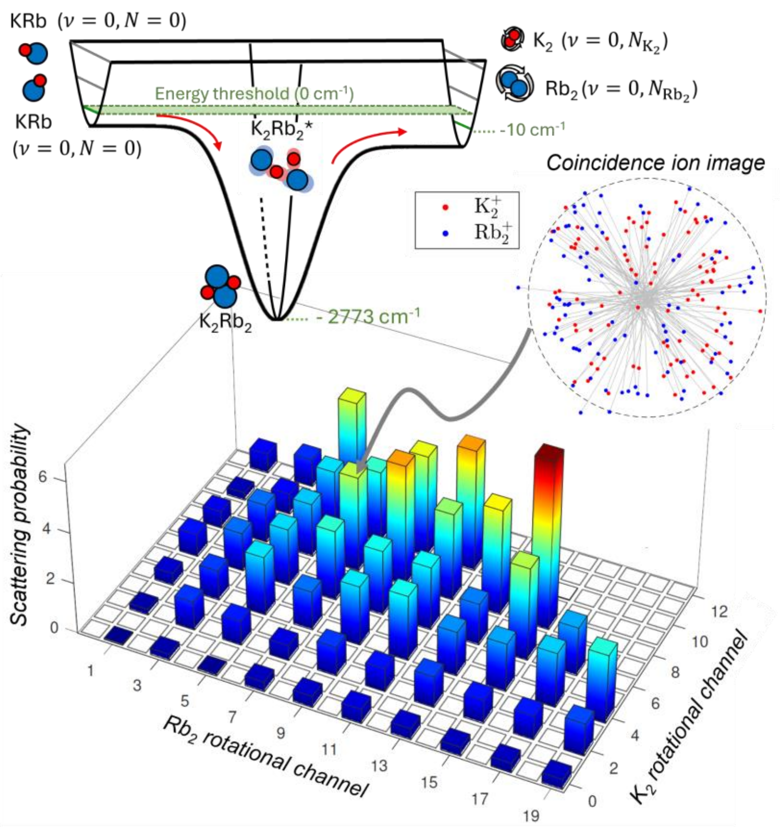
ABSTRACT

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



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Poster B18

Stereodynamics of cold molecules in collision with rare gas atoms

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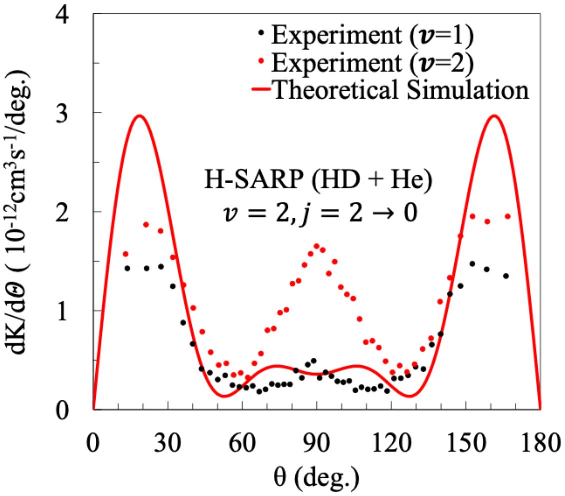
ABSTRACT

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

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



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

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

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Poster A4

The Stereodynamics of Two Orientated Molecules

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ABSTRACT

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

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

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Poster B21

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

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ABSTRACT

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

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

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Poster B7

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

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ABSTRACT

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

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

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Poster A16

Modelling of CO Superrotor Collisions with Fitting Laws

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ABSTRACT

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

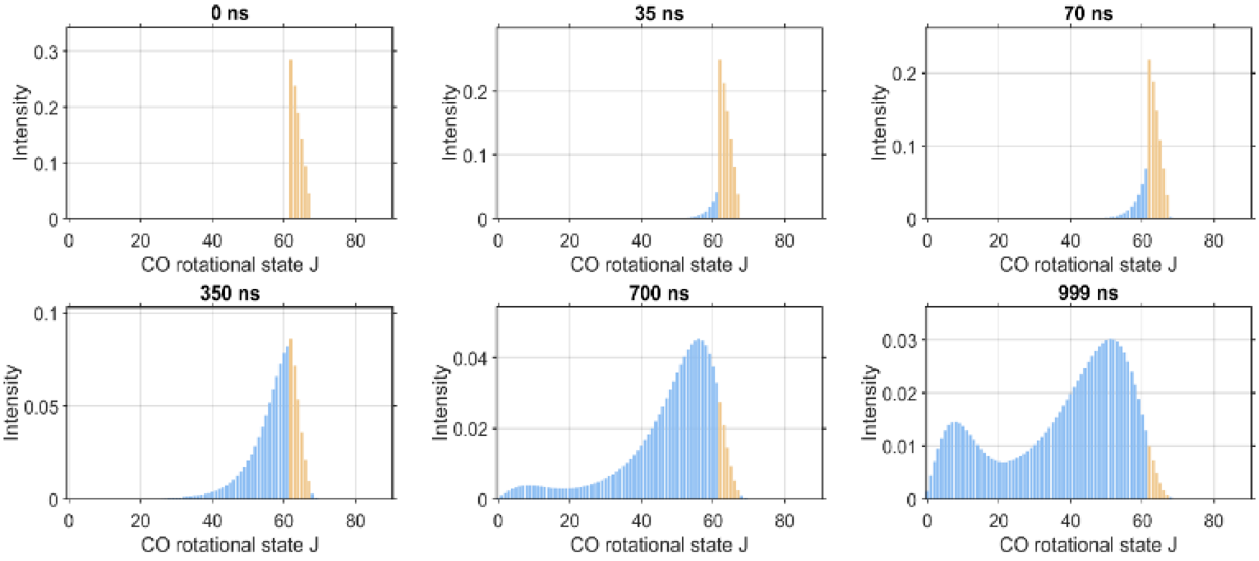

Figure 1. Simulated population decay of CO superrotors with J>60 based on experimental state-to-state rate

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Poster A20

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

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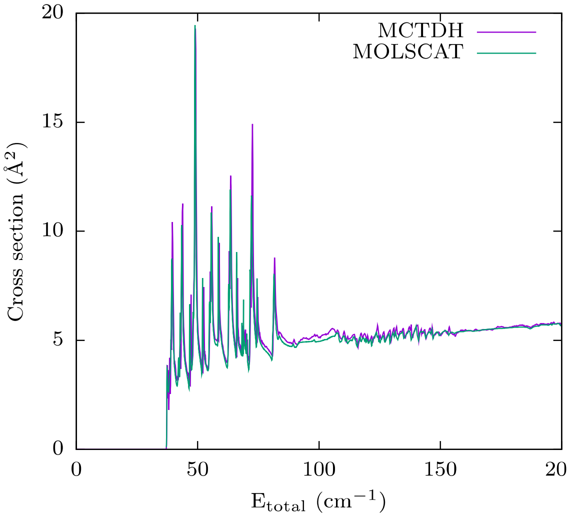
ABSTRACT

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



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Poster A15

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

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ABSTRACT

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

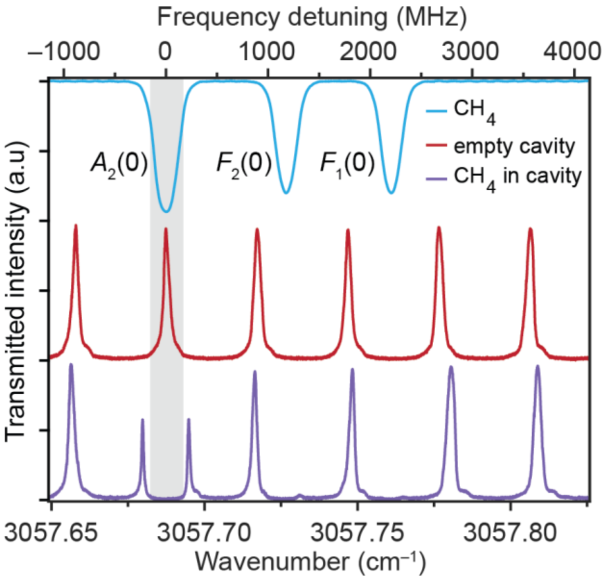

Figure 1: Transmission spectra of polariton system in CH_4

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

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Poster B4

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

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ABSTRACT

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

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Poster B19

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

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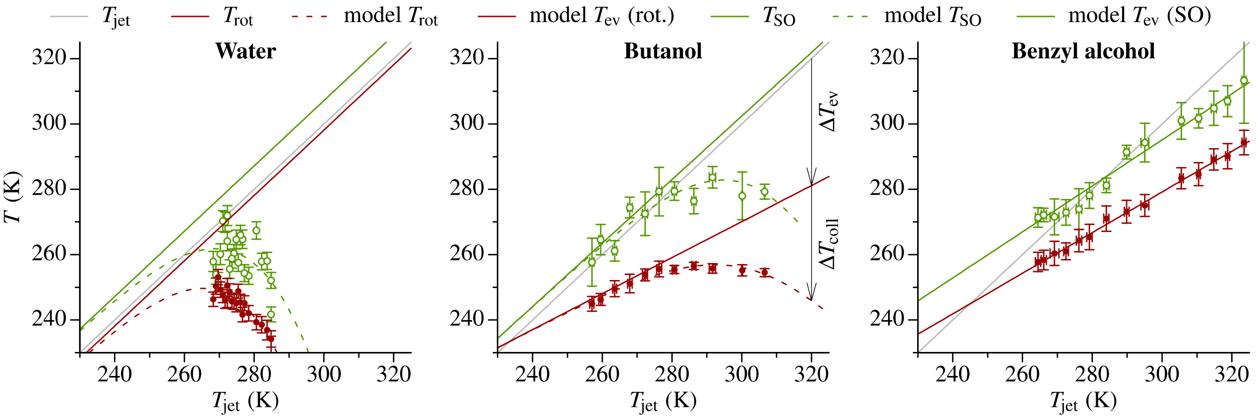
ABSTRACT

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



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

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Poster A17

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

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ABSTRACT

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

Poster A5

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

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ABSTRACT

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

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Poster A22

Novel Method of Learning Potential Energy Surfaces of Dense Manifold of Electronic States

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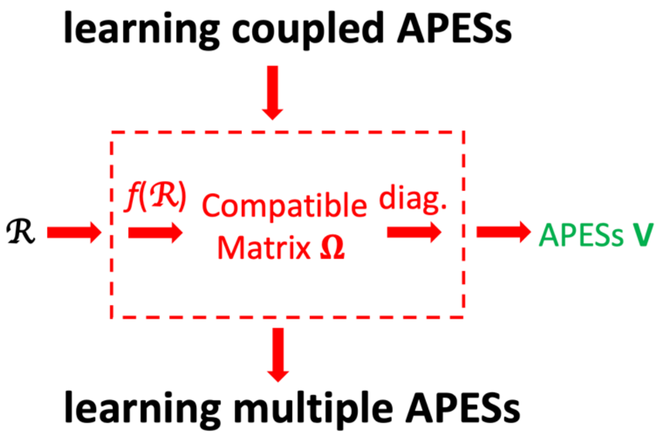
ABSTRACT

Machine learning potentials are very useful in simulating the dynamics of molecules and materials. Especially, with the analytical form of the potential energy surfaces (PESs), one can perform much longer simulation time, larger ensemble, and higher accuracy to study the detailed dynamical behavior as compared to direct dynamics – which computes the electronic structure on-the-fly. Many of the existing methodologies for machine learning potentials are focused on ground state PES, while to study the nonadiabatic behavior, one is required to have a multi-state PESs, and sometimes the PESs of dense manifold of electronic states. Traditionally, learning multi-state PESs is achieved by first transforming the learning target from adiabatic representation, i.e. adiabatic PESs, to a diabatic representation.[1] This transformation is critical in the sense that one does not need to learn nonadiabatic coupling vectors – which is a $3N_{\mathrm{atoms}}$ vector – explicitly, instead, one learns a diabatic potential energy matrix (DPEM). The DPEM is an N_{state} by N_{state} matrix whose off-diagonal elements are called diabatic couplings which couple different diabatic states. However, the traditional process of transforming from adiabatic representation to diabatic representation – which is called diabatization – often requires intensive human effort. To resolve this difficulty, we have recently developed a new method named diabatization by deep neural network[2] which discovers the diabatic representation on-the-fly during the learning process, and it is discovered semi-automatically by neural network. To achieve the complete autonomous learning procedure, we have further developed the compatible basis and compatibilization which fully automatize the learning process. And I will illustrate the compatibilization by deep neural network method and its application in automatic learning of PESs of dense manifold of electronic states.



learning coupled APESs

$\mathcal{R}$ → $f(\mathcal{R})$ → Compatible Matrix $\mathbf{\Omega}$ → diag. → APESs $\mathbf{V}$

learning multiple APESs

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Poster B1

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

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ABSTRACT

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

$$Li_2\,(A\,^1\boldsymbol{\Sigma}_u^+)(v_i,j_i) + X \;\text{->}\; Li_2\,(A\,^1\boldsymbol{\Sigma}_u^+)(v_f,j_f) + X$$

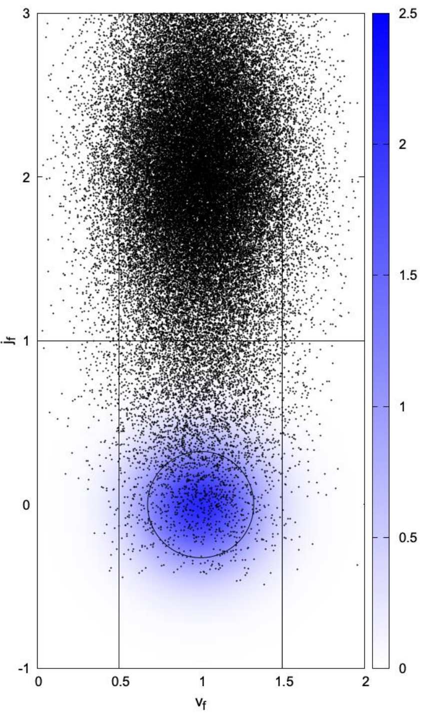
with X=Li or a rare gas. Collisions may be rotationally inelastic, rovibrationally inelastic, or reactive. The purpose of this work is to maximize the accuracy of measured and computed rate constants. Our twin goals are to

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

In pursuit of these goals, we are

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

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



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

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[2] See *e.g.* Bañares, L. *et al., J. Chem. Phys.* **118,** 565 (2003).

Poster B22

Evaluation of the Endothermic Europium Chemi-ionization Reaction and Europium Oxide Bond Energies

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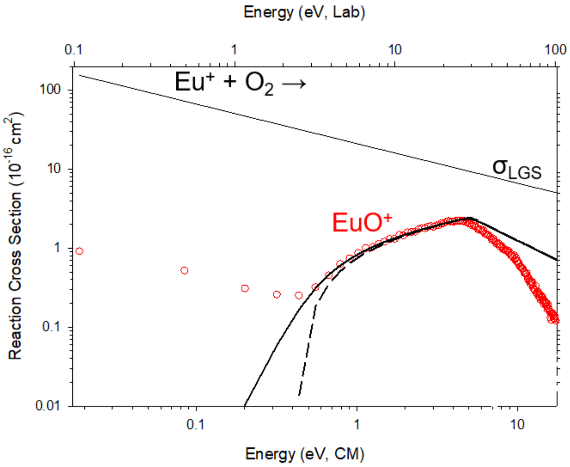
ABSTRACT

The endothermicity of the chemi-ionization reaction, Eu + O → $EuO^+ + e^-$, has been evaluated using guided ion beam tandem mass spectrometry and found to be 1.04 ± 0.08 eV. A beam of Eu^+ was reacted with O_2 and N_2O, and the cross section for formation of the product EuO^+ was determined as a function of the kinetic energy of the reactants. Modeling of the cross section curves yielded a 0 K bond dissociation energy for EuO^+ of 4.63 ± 0.08 eV. The endothermicity of the chemi-ionization reaction was found by combining this value with the literature value for the ionization energy of the Eu neutral (5.67 eV)[1] and a thermodynamic cycle. Using the literature bond dissociation energy[2] of EuO^+, 4.29 ± 0.81 eV, the endothermicity of the chemi-ionization reaction was determined to be 1.38 ± 0.81 eV. The exothermic tail that can be seen between 0 and 0.3 eV (CM) has been attributed to an excited state of Eu^+ and is 0.7% of the Langevin–Gioumousis–Stevenson (LGS) model collision limit as shown by the LGS cross section curve. Future work will include the removal of the excited state reactants through thermalization via secondary gas introduction in the ion source flow tube.



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Poster A8

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

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ABSTRACT

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

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

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

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

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

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Poster B17

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

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ABSTRACT

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

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

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

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

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

Poster A11

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

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

ABSTRACT

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

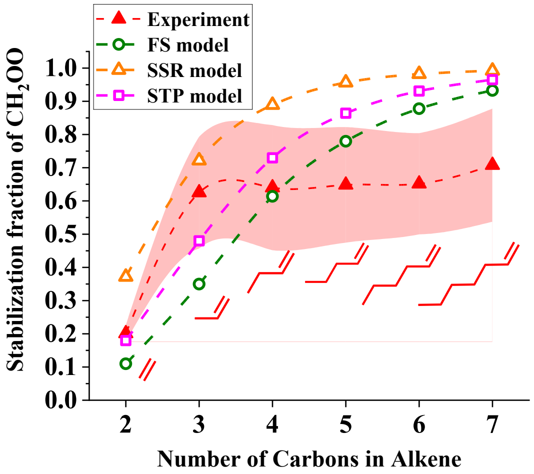

Figure 1 Nascent stabilization fractions of CH_2OO in ozonolysis of 1-alkenes compared to statistical models.

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Poster B16

SchrödingerNet: A Universal Neural Network Solver for The Schrödinger Equation

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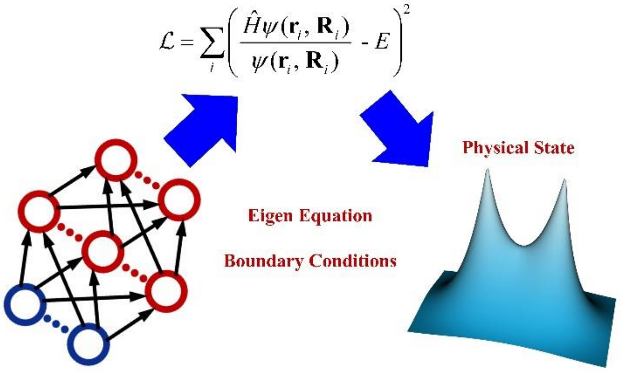
ABSTRACT

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



$$\mathcal{L} = \sum_i \left(\frac{\hat{H}\psi(\mathbf{r}_i, \mathbf{R}_i)}{\psi(\mathbf{r}_i, \mathbf{R}_i)} - E \right)^2$$

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[2] Pfau, D.; Spencer, J. S.; Matthews, A. G. D. G.; Foulkes, W. M. C., Ab initio solution of the many-electron Schrödinger equation with deep neural networks. Phys. Rev. Res. 2, 033429, 2020.
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