

Developing and Validating Sub-Nano Catalysts for Endothermic Cooling

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Abstract

The goal of this project is to develop sub-nano supported cluster catalysts that can selectively catalyze endothermic reactions of hydrocarbons, such as dehydrogenation or cracking, at temperatures below the onset of thermal pyrolysis, thereby enhancing endothermic cooling and reducing coking. In addition, the sub-nano cluster catalysts must be stable with respect to sintering/agglomeration at temperatures as high as ~ 700 K. The focus is on fundamental understanding of the factors that control activity, selectivity, and thermal stability, under both low pressure, surface science conditions, and at high (~ 1 - 2 atm) pressures using a new microreactor developed with DURIP support. Experiments and theory are tightly coupled, with theory used to predict promising catalyst candidates, which are tested with detailed experiments, which are then interpreted in light of more detailed theory for those systems with interesting and useful chemical and physical properties.

The experimental approach is two pronged. We use mass-selected deposition of atomically size-selected metal clusters, followed by post-deposition modification by self-limiting addition chemistry, to prepare size- and composition-selected sub-nano clusters (e.g. Pt_nSn_x , Pt_nGe_x) supported on oxides such as alumina or silica thin films. Surface science methods allow probing of adsorbate binding and reactivity properties and correlation with electronic properties measured by XPS/UPS. The newly constructed micro reactor system allows reactions of deposited clusters to be studied at pressures above 1 atm and temperatures to ~ 700 K. The micro reactor consists of a pair of oxide-coated silicon chips that are micro-machined to create a well defined reactor volume when the chips are assembled together in a fixture, which also provides heating for the cluster-containing areas of both chips. Gas exiting the micro reactor forms a supersonic expansion that is skimmed and passed through a mass spectrometer ionizer that can use both variable energy electron impact ionization (EI) and vacuum-ultraviolet photoionization (PI) to ionize with both standard (70 eV EI) fragmentation patterns, and soft ionize with little or no fragmentation. Product distributions are extracted from fitting mass spectra at different temperatures and ionization conditions to spectra for candidate molecules measured under the same conditions. The experimental work is currently focusing on butane and iso-butane decomposition as models for linear and branched alkane in fuels.

Theory is based on the paradigm of thermal grand canonical ensembles of catalysts states that develop in reaction conditions and provide numerous possible active sites and reaction rates. The theory is tightly coupled with the surface science experiments. The combination predicted and experimentally verified a new catalyst, oxide-supported PtGe cluster alloys, which are highly selective toward endothermic partial dehydrogenation of alkanes. These catalysts show a new effect of self-limiting poisoning by carbon, which promotes the selectivity and stability against sintering. In addition, collaboratively with the experiment, we showed that cluster sintering cannot be suppressed by size-selection, due to fluxionality and population of multitude of isomers at catalytic temperatures. However, sintering propensity is size-dependent, and there exist sinter-resistant “magic” cluster sizes at high temperatures, even when their thermal ensembles are large. Future work of the theory includes matching the experimental pressures of the micro reactor experiments, and studies of the reactivity, selectivity, and sintering of cluster catalysts under realistic pressures of gasses.

Lanthanide cation chemistry: Chemi-ionization reactions of dysprosium and periodic trends

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The reactivity of several lanthanide cations (Ln^+) have been evaluated using guided ion beam tandem mass spectrometry (GIBMS). This technique permits the measurement of the kinetic energy dependence of the reaction of interest, which can then be interpreted to yield thermodynamic and dynamic information. One focus has been the determination of the LnO^+ bond energies, which are useful in evaluating the chemi-ionization process, reaction 1.

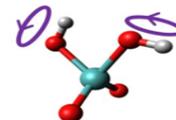


This reaction is of interest to the Air Force as a means to mitigate scintillation effects that disrupt radio wave communication. To date, this thermochemistry has been evaluated for six lanthanides with preliminary data available for another. The present poster features results for dysprosium (Dy). In addition, the poster will show the periodic trends in the LnO^+ bond energies evaluated to date and exhibit a predictive correlation found with the $\text{Ln}^{2+} + \text{O}^-$ asymptote.

Molecular Activation and Single Atom Catalysis: Surface and Gas-Phase Studies

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We have studied the activation and splitting of H₂O using both atomic and molecular anions. In the case of Ir⁻ + H₂O our combined mass spectral and anion photoelectron spectroscopic studies found [H-Ir-OH]⁻ and [H₂-Ir-O]⁻ activation intermediates as well as physisorbed Ir⁻(H₂O) species.¹ In the case of MoO₃⁻ + H₂O our photoelectron spectroscopic studies along with calculations by our computational collaborator, Evangelos Miliordos, found the activation intermediate, MoO₂(OH)₂⁻ as well as physisorbed MoO₃⁻(H₂O) species. Another system we have studied is ThO₂⁻ + H₂O, where we have seen clear photoelectron evidence of activation. Our other computational collaborator, Lan Cheng, is currently conducting calculations on this system. In studies that focused on the possibility of CO₂ activation, we have examined MoO₃⁻ + CO₂ and [Pt(La_xO_y)]⁻ + CO₂, where [Pt(La_xO_y)] is a cluster model of a single atom “catalyst”, SAC.



Given interest in reactions of iridium atoms, clusters, and iridium-containing small molecules with ionic liquid alternatives to hydrazine *propellants*, we have carried out two studies in the gas-phase. These focused on reactions of iridium-containing anions with hydroxylamine and with 2-hydroxyethylhydrazine (HEH).^{2,3} Additionally, three surface studies are close to coming on-line. We have generated [Ir(TiO₂)_n]⁻ and [Ir(ZrO₂)_n]⁻. Upon depositing mass-selected compositions of these cluster anions onto conductive substrates, they lose their charges to become iso-stoichiometric neutral cluster models of single atom “catalysts”, SAC. As microscopic mimics of iridium-encrusted metal oxide, hydrazine igniters, i.e., thrusters, these clusters will find themselves sitting (at sub-monolayer coverage) atop previously coated thin films of ionic liquid propellants, such as 2-hydroxyethylhydrazine nitrate (HEHN). Subsequent TPD/R and XPS studies will reveal their reaction products. In another surface study, neutral iridium clusters, Ir_n, will soon be deposited onto a layer of HEHN and then subjected to TPD/R and XPS for product evaluation.

The molecule, 1-propanamine is a candidate endothermic fuel for propelling *hypersonic* vehicles. In order to compare its dehydrogenation over bulk ZrO₂ powder catalyst with cluster models of a single atom “catalyst”, we co-deposited Pt₁Zr₂O₇ clusters and 1-propanamine. Upon conducting TPD/R and XPS studies, we found 1-propanamine to decompose into propionitrile and H₂, as in the bulk study. Interestingly, however, it exhibited no reactivity toward Zr₂O₇ alone.⁴

Acknowledgments: Our iridium-related work was done in collaboration with Steve Chambreau and Jerry Boatz at Edwards AFB. This work was performed under AFOSR FA9550-22-1-0271 (KHB).

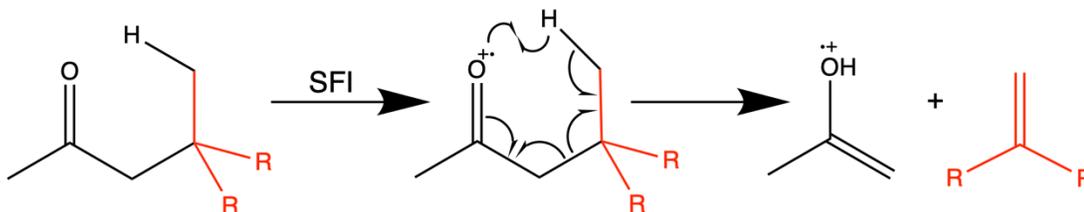
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Time-Resolved Dynamics of the McLafferty Rearrangement in Pentanone Cations

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Mass spectrometry, one of the most useful analytical tools in chemistry, remains a ‘black box,’ with molecules entering one end and fragment ions coming out the other end. Our goal is to determine the molecule-specific reaction mechanisms that lead to the fragmentation patterns used for molecular identification. We achieve ultrafast electron ionization by taking advantage of femtosecond strong-field ionization and electron rescattering. When such an event is followed by a weak probe pulse, one is able to track the time-dependent yield of tens of different product ions simultaneously. The focus of this work is the McLafferty rearrangement, where a ketone-containing molecule breaks the $\alpha - \beta$ bond following abstraction of the γ -hydrogen by the ketone oxygen. This rearrangement reaction is specific due to the low activation energy caused by the cyclic intermediate, as shown in the scheme below.



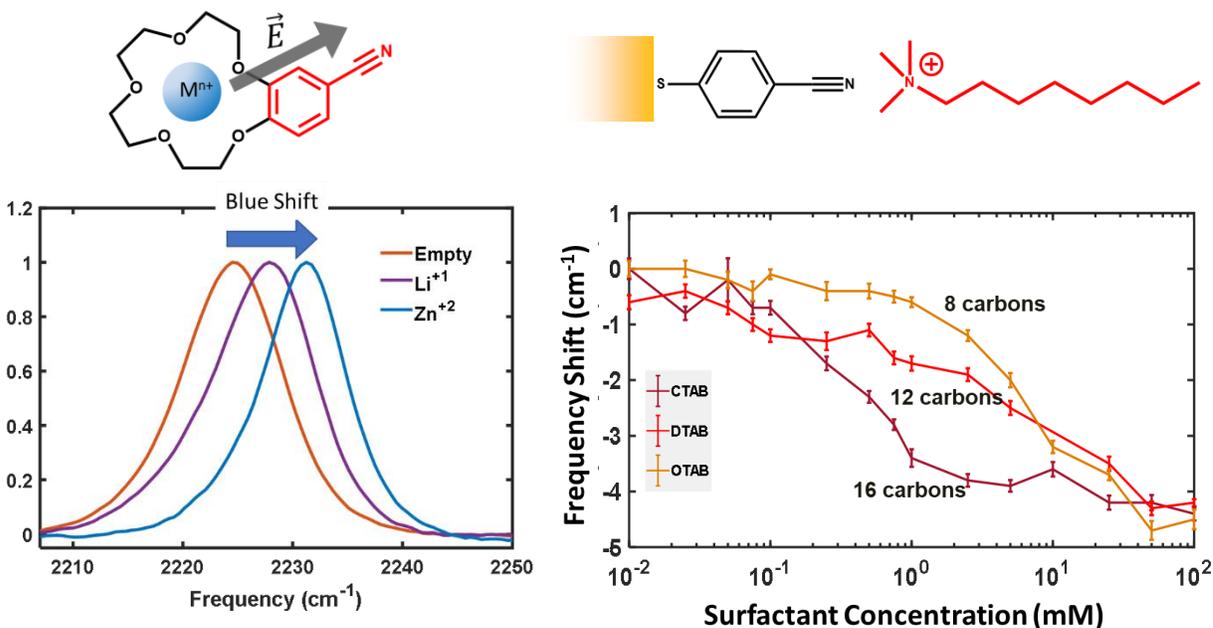
The McLafferty rearrangement mechanism is generally considered to proceed via a stepwise mechanism for most compounds. Following the McLafferty rearrangement of ionized 2-pentanone, 4-methyl-2-pentanone, and 4,4-dimethyl-2-pentanone, the acetone radical cation (shown in its more stable enol configuration) is formed. The reaction yield was tracked as a function of pump-probe delay for the three different reagents. We find product formation follows a fast timescale of ~ 325 fs, and a slow timescale of ~ 5 ps. The rate of proton transfer step depends on the distance between the γ -hydrogen and the oxygen atom, this distance is closest when the molecules attain a cyclic configuration. We propose that given a random distribution of distances, the fast timescale arises from molecules in the favorable cyclic configuration, while the longer timescales correspond to molecules that are far from such configuration. Therefore, proton transfer is delayed while the molecule exploring configuration space until the cyclic configuration is attained. This conclusion is consistent with the observed speedup of the slow dynamic component from 7.4 ps for 2-pentanone to 4.4 ps for 4,4-dimethyl-2-pentanone.

Soaps and Crowns: Electric Fields from Ionic Layers and Single Ions

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Controlling electric fields on the molecular scale to drive reactions is a challenge in modern chemistry. The challenge is to engineer the geometry of ions and solvent dipoles around a reactive site. Two approaches for creating such fields are using crown ethers for capturing and placing ions near a reactive site in the bulk, and surfactants for accumulating excess charge near an electrochemical interface. Here we use benzonitrile vibrational probes that are sensitive to the local electrostatics to estimate the polarizing influence of the ions in these scenarios. For the crown ether studies, we have further performed gas phase measurements of the ion-laden crowns to uniquely isolate the influence of the ion on the vibrational probe without the complicating influences of the solvent and counter ions. Our computational work further reveals the complexities of the local electric fields around the crown. These studies help with creating design rules for tailoring local electric fields with ions.



The Degradation of the 2-Hydroxyethylhydrazinium Nitrate Ionic Liquid System
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Recent experimental work has established that the 2-hydroxyethylhydrazinium nitrate ionic liquid degrades following the formation and loss of nitric acid. Current progress in the development of a reaction mechanism for this process is presented for systems containing n cations and $n - 1$ anions where $2 \leq n \leq 5$. Current results have been obtained utilizing a variety of techniques including Monte Carlo simulations involving Effective Fragment Potentials, as well as RHF, MP2, and DFT calculations.

Dehydrogenation of Cycloalkanes over SBA-15 Supported Pt for Endothermic Cooling

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Catalytic reforming of the fuel could provide a heat sink for engines in hypersonic aircraft, but the precious-metal catalysts that are active for these reactions tend to coke rapidly under the conditions of the fuel lines. However, recent research has shown that coking can be greatly suppressed when dehydrogenation reactions are performed at high pressures with the catalyst confined in small pores. In the present study, we examined dehydrogenation of cyclohexane, methylcyclohexane, and decalin over Pt supported on the mesoporous structure, SBA-15, at pressures between 1 and 60 bar and temperatures between 673 and 823 K. While the catalyst coked rapidly at lower pressures, high conversions with no deactivation were observed at pressures above 20 bar. Under a typical fuel-line condition of 823 K and 60 bar, the conversions of cyclohexane and methylcyclohexane were greater than 60% and the selectivities of cyclohexane to benzene and methylcyclohexane to toluene were greater than 95%, resulting in additional heat uptakes of ~1400 kJ/kg. The feasibility of using a mixture of cycloalkanes and paraffins as the endothermic fuel was also demonstrated.

Spectroscopy of Metal Oxide Space Clouds

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Communication with orbiting satellites and space vehicles is subject to interference resulting from the fluctuating electron densities encountered in the upper atmosphere. These uncontrolled signal modifications are also detrimental to targeting and GPS systems. It has been proposed that deliberate modification of high-altitude electron densities can be used to achieve temporary control of radio wave and microwave propagation. The chemi-ionization reactions $M + O \rightarrow MO^+ + e^-$ with $M=Sm$ or Nd are being evaluated for their ability to transiently increase the electron density via controlled, high-altitude release of the atomic metal vapors. Sounding rocket experiments have been conducted using both Sm and Nd (referred to as metal oxide space cloud (MOSC) measurements). These experiments were conducted under conditions where the cloud was subject to excitation by solar radiation. This resulted in visible-range fluorescence that was described as being pink for Sm , and green for Nd . Spectroscopic data were recorded for the Sm -release, and emission bands occurring in the red spectral range have been reliably assigned to neutral SmO . The degree of ionization achieved in the Sm MOSC experiments was below the expected result, and the question of whether SmO^+ was present could not be resolved. The only spectroscopic data available for the Nd -release was the color of the MOSC emission. Interpretations of the data obtained in the MOSC experiments have been limited to informed speculation due to the lack of definitive spectroscopic data for the monoxides and their singly charged cations.

Our recent efforts have focused on the spectroscopic characterizations of SmO and NdO over spectral ranges that are relevant to the MOSC projects. For SmO we have examined vibronic bands in the 645-670 nm wavelength range, where the field data show the most prominent molecular emission features. Rotationally resolved excitation spectra, dispersed fluorescence spectra and fluorescence decay lifetimes have been reported¹. The results are consistent with the assignment of a sub-set of the red-region bands to configurational transitions of the form $Sm^{2+}(4f^66s)O^{2-} \leftrightarrow Sm^{2+}(4f^55d)O^{2-}$. Analysis of the excited state hyperfine structure supports this configurational description¹.

The electronic spectrum of jet-cooled NdO has been examined using laser excitation and dispersed fluorescence techniques². Nine electronically excited states were characterized for the first time. Fluorescence decay measurements yielded radiative lifetimes that were indicative of fully allowed transitions. Dispersed fluorescence spectra, recorded using both visible and UV excitation wavelengths, were used in the process of establishing lower-energy state assignments. These spectra exhibited bands that were primarily in the red and blue spectral regions. The NdO emission spectrum was found to be surprisingly inactive in the green spectral range, casting doubt on the assumption that the green fluorescence of the Nd MOSC originated from neutral NdO .

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Ab-initio Quantum Electrodynamics Approaches to Investigate Polariton Photochemistry

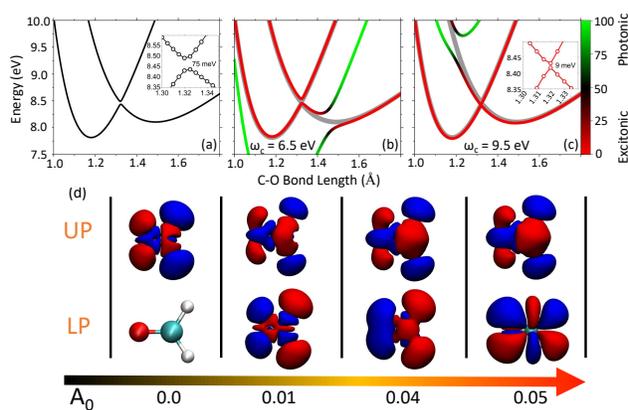
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Coupling electronic states with the quantized radiation field inside an optical cavity creates collective and delocalized excitations of light and matter, referred to as the upper and lower polariton states. These polariton states have delocalized excitations among the molecules and cavity mode, which have been shown to facilitate new chemical reactivities. Thus, polariton chemistry provides a new strategy to control chemical reactivities in a general way by tuning the fundamental properties of photons and provides a new paradigm for enabling chemical transformations that can profoundly impact catalysis, energy production, and the field of chemistry at large. Theoretical investigations play a crucial role in understanding the new principles in this emerging field. Simulating the time-dependent polariton quantum dynamics of such hybrid matter-field systems is a necessary and essential task, as these polariton photochemical reactions often involve a complex dynamical interplay among the electronic, nuclear, and photonic degrees of freedom (DOFs). However, accurately and efficiently simulating the polaritonic quantum dynamics remains a major challenge and is beyond the paradigm of photochemistry or quantum optics. We propose to develop a set of general and powerful theoretical and computational tools that enable direct ab-initio on-the-fly simulations of polariton photochemical processes based on the rigorous QED description of molecule-cavity interactions. Our proposed developments will be based on using rigorous quantum electrodynamics theory to describe many molecules coupled to the cavity, combined with the efficient and accurate polaritonic structure theory.

Here, we will two recent developments in our group.

(1) Develop Efficient Approaches for Computing ab-initio Polariton Eigenstates. We used rigorous, gauge invariant QED Hamiltonians that do not assume any unnecessary approximations to accurately compute polariton eigenenergy and eigenvector, by combing the electronic structure method of molecules and convenient basis for photonic mode. This approach will in principle, provide the exact form of the light-matter interactions. We will further assess the accuracy, strength, and limitation of this approach compared to the other available method based on variational principles.

(2) Developing On-the-fly Polaritonic Simulation Approaches. We developed on-the-fly quantum dynamics techniques to simulate the ab-initio polariton non-adiabatic dynamics in realistic molecule-cavity hybrid systems. We used machine learning models that provide accurate dipole vectors of the molecules, such that one can accurately describe the molecule-cavity interactions. This development was combined with our rigorous nuclear gradient for the molecule-cavity hybrid system beyond the commonly used Jaynes-Cummings model. We further propose to perform on-the-fly polaritonic electronic structure calculations to describe non-adiabatic transitions among the photon-matter entangled states.



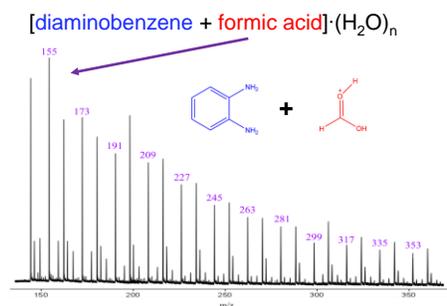
Capture and characterization of ionic reaction products generated in electrospray droplets with high resolution mass spectrometry and anharmonic analysis of cryogenic vibrational spectra

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Mass spectrometry is often used to characterize reactions that occur in ambient sprays (electrospray, nebulized neutrals, etc.) that are thought to be accelerated while reactants are confined in small droplets. We capture the ions generated by electrospray that have been invoked as markers for reactants, products and intermediates of reactions that take place during the complex series of events from micron-size droplets at one atmosphere pressure to the entrance aperture of a mass spectrometer where bare ions are transferred into high vacuum. Our measurements are carried out with similar instrumentation (in our case, a Thermo Fisher Velos Pro Orbitrap mass spectrometer) that is used in earlier reports of droplet accelerated chemistry. After being subjected to high resolution mass analysis (including measurements of ms-ms breakdown patterns), key ionic species are transferred to a custom built, cryogenic ion spectroscopy platform that yields vibrational spectra of cold ions using D₂ tagging. Vibrational spectra are obtained in an isomer-selective mode using two-color, IR-IR photobleaching. Species identification is carried out by comparing the observed band patterns with those displayed by candidate species that are typically available as pure compounds. These molecules are subjected to the same dissolution and ambient ionization protocol as that used in the reaction mixtures. This procedure is applied to several archetypal droplet-accelerated reactions including proton-catalyzed formation of benzimidazole from diaminobenzene and the Baeyer-Villiger oxidation reaction of 2-hydroxy-benzophenone. We also address the species at play in proton-catalyzed droplet reactions involving trace water and formic acid in a microhydration study of protonated formic acid. Specifically, analysis of the observed vibrational band patterns with anharmonic theory that explicitly treats nuclear quantum effects reveals how the excess proton is detached from the organic scaffold with increasing hydration.



Hydrogen bonding interactions on $(\text{EAN})_n:(1\text{-AT})_x$ DeEP revisited: Geometry optimization and quasiautomatic orbitals (QUAOs) bonding analysis

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The quasi-atomic orbital (QUAO) bonding and kinetic bond order (KBO) analyses are used to develop an understanding of the hydrogen bonding (H-bonding) interactions as a function of the cluster size for the Ethylammonium Nitrate (EAN) and 1-Amino-1,2,3-triazole (1-AT) deep eutectic mixture. Previous study of QUAO bonding and KBO analysis on EAN ionic liquids suggests that the H-bonds in the examined clusters follow the characteristic H-bonding three-center four electron interactions.

The strongest H-bonding interactions between the $(\text{EAN})_1:(1\text{-AT})_n$ and $(\text{EAN})_2:(1\text{-AT})_n$ ($n=1-5$) complexes are observed internally within EAN ion pair (i.e., between the ethylammonium cation $[\text{EA}]^+$ and the nitrate anion $[\text{NO}_3]^-$). The weakest H-bonding interactions occur between $[\text{NO}_3]^-$ and 1-AT. Consequently, the average strengths of the H-bonds within a given $(\text{EAN})_x:(1\text{-AT})_n$ complex decrease as more 1-AT molecules are introduced into the EAN monomer and EAN dimer. The QUAO bonding analysis suggests that 1-AT in $(\text{EAN})_x:(1\text{-AT})_n$ can act as both a hydrogen bond donor and a hydrogen bond acceptor simultaneously. Consequently, it is observed that two 1-AT molecules can form H-bonds to each other. Although the interaction between two 1-AT molecules as well as H-bonding interactions in $[\text{EA}]^+ : 1\text{-AT}$, $[\text{NO}_3]^- : 1\text{-AT}$ are weaker than the H-bonds in EAN, those weak H-bond networks with 1-AT could be important to form a stable deep eutectic propellant.

Energy Transfer and Spin-state Dynamics in Strained Metal Nanostructures

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Abstract. Electron dynamics of metals confined to the Ångstrom-length scale will be described. This presentation will focus on two types of metals: 1) 2-D crystalline films and 2) sub-nm 3-D nanoclusters. 2-D crystalline metal films are formed at high-energy silicon carbide surfaces and are passivated by bi-layer graphene. Templated by the silicon carbide lattice, the metals adopt highly strained and otherwise inaccessible lattices. This templating method results in the formation of highly strained, few-atomic layer films that exhibit structural ordering persistent on macroscopic length scales. As a result, the microscopic (i.e. Ångstrom-level) structure determines many of the macroscopic material properties. These include optical polarizabilities and electron-phonon scattering rates.^{1,2} In particular, ordering of silver atoms in one or two atomic layers at step edges controls multi-photon excitation pathways, which results in either enhanced light scattering or hot carrier generation. Thus, 2-D metals may provide opportunities for achieving microscopic control over interfacial energy transfer rates. 3-D sub-nanometer metals exhibit electronic, magnetic, and optical properties that are determined by atomic-level structure. Electronically excited metal clusters relax through a series of competitive internal conversion and intersystem crossing pathways, resulting in varying degrees of transient spin polarization. In particular, spin polarized emission for these systems can be modulated by metal-atom substitution and ligand exchange.^{3,4} The ability to control electron dynamics in both metal 2-D films and nanoclusters is expected to have impacts for metal-mediated catalysis, quantum information technologies, and energy management strategies for many other applications.

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Observing Water-Dependent Dynamics in Ionic Liquid Electrolytes Through the Lens of 2D IR Spectroscopy and Imaging

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A key goal of this project is to better understand the response of room temperature ionic liquids (RTILs) to external fields with particular attention paid to their dynamic behaviors near electrodes. RTILs have received much attention due to the ease of which they can be tuned to perform in many different applications ranging from using them as green solvent systems to the use of RTILs as electrolytes in electrochemical devices. In practice RTILs are hygroscopic and as such, the influence of water in RTILs must be understood. In the poster presented, I will discuss the effects of limited amounts (under 21.6% χ_{Water}) of water on 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) and 1-butyl-3-methylimidazolium dicyanamide (BmimDCA) room-temperature ionic liquid (RTIL) mixtures. The RTILs were characterized by tracking changes in the vibrational features observed in the linear infrared (IR) and two-dimensional infrared (2D IR) spectra of the dicyanamide anion (DCA). Peak shifts with increasing water suggest the formation of water associated and “dry” DCA populations. Further results showed clear differences in the dynamic behavior of these different populations of DCA at low (defined here as below 2.5% χ_{Water}), mid (defined here as between 2.5% χ_{Water} and 9.6% χ_{Water}), and high (defined here as between 11.6% χ_{Water} and 21.6% χ_{Water}) range water concentrations. Vibrational relaxation is accelerated with increasing water content for water-associated populations of DCA, indicating water facilitates population relaxation, possibly through the provision of additional bath modes. Conversely, spectral diffusion of water-associated populations slowed dramatically with increasing water, suggesting water drives the formation of distinct and non- or very slowly interchangeable local solvent environments. I will also discuss recent results acquired using linear IR and 2D IR microscopy to image the behavior of the RTIL electrolyte in a copper-based electrochemical cell.

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Carrier relaxation and displacive coherent phonon motion measured by XUV transient absorption spectroscopy

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The control of atomic motion in molecules and solids promises interesting applications, ranging from photocatalysis for efficient renewable energy sources to photo-assisted phase transitions for novel memory devices. In many solids, photoexcitation can lead to a large scale, coherent atomic motion through a process called Displacive Excitation of Coherent Phonons (DECP), wherein the excitation of carriers leads to a change in the potential energy surface of the lattice and a resultant movement of the atoms towards new energetically favorable positions. Although pioneering time-resolved experiments on prototypical materials exhibited the DECP effect, the Group V semimetals Bi and Sb, already showed a deviation from this model via the phase of the observed phonon oscillations [1]. This has led to sustained research efforts into the origins of these deviations. Recently, theoretical work has proposed that the deviation is due to highly-excited, optically polarized carriers of various excess energies. These lead to additional impulsive forces that act on the phonon motion, but quickly decay due to the momentum relaxation of carriers [2].

Using femtosecond extreme ultraviolet transient absorption spectroscopy, we have found strong evidence for these two mechanisms and this explanation for the departure from DECP. Measuring the coherent phonon motion in Sb through time-dependent changes in the core-level transient absorption gives spectroscopic insight into both the lattice and carrier dynamics. Applying a principal component analysis allows us to isolate the effect of highly-excited, optically polarized carriers of excess energy on the phonon motion. The results reveal the timescales of momentum-relaxation in the vicinity of the material's Fermi level. Typical for semimetals, the narrow density of states close to the Fermi level limits the relaxation rate compared to energetically higher regions. Most strikingly, the observed phase of the coherent phonon oscillation confirms the expected effect of transient impulsive forces. The results reveal a spectral dependence of the coherent phonon oscillation phase that follows the predicted momentum relaxation rate of optically polarized carriers. The more rapid is the carrier relaxation, the smaller is the impulsive force contribution to the phonon motion, and the closer the observed behavior is to the DECP model.

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Modeling Excited State Spin-Orbit Coupling using Time-Dependent Density Functional Theory
(FA9550-21-1-0344)

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Spin-orbit coupling (SOC) is the driving force behind many phenomena that have sparked the interest of chemists and physicists such as intersystem crossing, fine-structure splitting, and relativistic spectroscopies. Chemists have looked to take advantage of SOC to pursue new chemistry via spin-forbidden processes in addressing the world's technological needs. However, the investigation of SOC and its manifestation in chemical phenomena is not routinely pursued due to the high computational cost of current methods. Ironically, the prominence of SOC only increases with atomic number making it imperative for the study of heavy elements. In this work, we investigate the influences of SOC and its interplay with Jahn-Teller distortion in the $\text{Au}_{25}(\text{SR})_{18}$ nanocluster. We examine the evolution of the fingerprint region in the UV-Vis absorption spectrum with respect to oxidation state and characterize the features in the perspective of superatomic orbital excitations. Spectra were simulated through a variation treatment of SOC using the CRENBL relativistic effective core potential with two-component linear response time-dependent DFT (TDDFT). Also, we present a low-scaling perturbative treatment of SOC within a one-component closed-shell TDDFT framework (TDDFT-SO). We present benchmarks against exact two-component TDDFT (X2C-TDDFT) for atomic cases and a limiting case of the method. We also investigate the convergence behavior of the method with respect to the interaction space. Lastly, we reproduce the fingerprint UV-Vis absorption spectrum of the $\text{Au}_{25}(\text{SR})_{18}$ nanocluster with excellent agreement with experiment.

Benchmarking machine learning potentials to reproduce thermodynamic and transport properties of bulk liquids.

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Abstract

Classical Molecular Dynamics (MD) and Monte Carlo methods have proven to be extremely useful to provide a microscopic understanding of the thermodynamic and transport properties of bulk liquids. These simulations rely on simple algebraic functional forms (i.e., force fields) to describe the underlying potential energy that governs molecular interactions. A recurrent strategy to parametrize force fields relies on the use of experimental data, which might not be available for the system under study. An alternative parametrization strategy relies on the use of ab-initio quantum chemistry calculations, which do not require any pre-existing experimental measurements. Despite this clear advantage, quantum chemistry calculations can be prohibitively expensive, especially for large systems.

Recently, neural networks have raised a tremendous amount of interest due to their ability to reproduce highly complex and multi-dimensional potential energy functions with high accuracy. They have been proposed as surrogates to costly ab-initio molecular dynamics simulations, as they faithfully reproduce the underlying quantum mechanical energies and forces with less computational demands. Thus, longer time and length scales can be readily available.

We explore the ability of neural network force fields that use local descriptors to reproduce transport and thermodynamic properties of water as a model system. We trained deep potential force fields¹ of water using energies and forces from reference classical and ab-initio molecular dynamics simulations. Additionally, we explore a concurrent learning approach² to more efficiently train machine learning force fields. We show that the trained neural networks can reproduce the transport and thermodynamic properties of interest relative to the reference classical and ab-initio calculations.

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Abstract

Designing new quantum materials with long-lived electron spin states is in urgent need of a general theoretical formalism and computational technique to reliably predict spin relaxation and coherence times. We present a new, universal first-principles methodology based on density matrix dynamics (DMD) for open quantum systems to calculate the spin relaxation and decoherence time of solids with arbitrary spin mixing and crystal symmetry[1].

Through the complete theoretical descriptions of pump, probe and scattering processes including electron-phonon, electron-impurity and electron-electron scattering with spin-orbit coupling, our method can directly simulate the pump-probe measurements for coupled spin and electron dynamics and ultrafast Kerr rotation[2], and is applicable to any temperatures and doping levels, under external electric[3] and magnetic field[4]. Our ab initio predictions are in excellent agreement with experimental spin lifetime for a broad range of materials[1,2]. We then apply our method to investigate the condition of realizing spin-valley locking and long spin lifetime of 2D Dirac materials[3], as well as manipulation of spin-orbit fields and spin relaxation through substrate proximity effects[5]. We reveal the origin of substrate effects on spin and electron relaxation of 2D materials with strong spin-orbit coupling. We finally show how g factor fluctuations and nuclei spin lead to spin dephasing in halide perovskites under external magnetic field from our calculations[4].

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Ultrafast Dynamics of Strongly Correlated Metal Oxide Clusters

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Abstract:

A local rearrangement of 3d-electrons plays a crucial role in many properties of correlated transition metal oxide materials and supplies important information on their reactivity and magnetic interactions. Point defects, such as oxygen vacancies and their associated electrons, can lead to emergent phenomena that influence the lifetime of photoexcited states and therefore influence chemical reactivity. The ultrafast electronic relaxation dynamics of neutral metal oxide clusters were investigated with femtosecond pump-probe spectroscopy and supported by theoretical calculations to show that their excited state lifetimes are strongly dependent on the nature of the electronic transition.¹⁻⁴ We employ the atomic precision and tunability of gas phase clusters to stress that changes to the character of the orbital of the photoexcited electron leads to vastly different relaxation dynamics. I will present recent work on sub-nanometer clusters, where absorption of a UV (400 nm) photon initiates several relaxation processes. The simple picture of sequential oxidation of metal atoms reveals a linear tunability to the contributions of each relaxation component to the total transient signal. In particular, in chromium oxides a ~30 fs transient signal fraction grows linearly with oxidation, matching the amount of O to Cr charge transfer character of the photoexcitation and highlighting a gradual transition between semiconducting and metallic behavior at the molecular level. In contrast, the photoexcited lifetimes of nickel oxide exhibit a unique reliance on the nature of the atomic orbital contributions, providing new insights to the analogous band edge excitation dynamics of strongly correlated bulk-scale NiO material. Short lived dynamics in stoichiometric (NiO)_n clusters are attributed to excitation between Ni-3d and Ni-4s orbitals, where their strong exchange coupling produces metallic-like electron-electron scattering. Oxygen vacancies introduce 3d→4p transitions, which increases the lifetimes of the sub-picosecond transient by 20-60% and enables the formation of long-lived (lifetimes > 2.5 ps) states.

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Authors: George M. Elliott, Mark S. Gordon, Shinae Kim, and Megan Schlinsog

Iowa State University

Presenter: Megan Schlinsog

Presentation Type: Poster Presentation

Title: Recent developments in the QM-EFP method

Abstract:

The effective fragment potential method (EFP) is an ab initio force field method where each molecule is explicitly represented as rigid multipole potentials. It strikes a balance between the speed of traditional force field methods and the accuracy and transferability of having no fitted parameters. Because it is completely derived from quantum mechanics, it can interface naturally with fully quantum mechanical (QM) systems, resulting in the QM-EFP method. The QM-EFP method was developed to handle situations in which the geometry of a solvated molecule can change significantly during a molecular dynamics (MD) simulation and allows for a solute to be treated with a fully QM wavefunction while maintaining the efficiency of treating solvent molecules as EFPs. The QM-EFP method has undergone several recent developments to further expand its accuracy and range of applicability. These developments include the derivation of the charge transfer contribution to the energy expression, and the derivation of the gradient for the exchange-repulsion contribution to the energy expression. The charge transfer term is a purely quantum mechanical effect arising from short-range second order perturbation theory. The addition of charge transfer will allow QM-EFP to be more accurate for highly charged and ionic systems, which are of extreme interest to experimental chemists. The exchange-repulsion interaction in QM-EFP is a short-range, predominately repulsive interaction that arises due to the antisymmetric nature of the fermionic wavefunction. To accurately investigate reaction paths along a given potential energy surface (PES), the first derivative of the energy with respect to the nuclear coordinates is required. Given the importance of the exchange-repulsion term at short range, an analytic expression for its derivative provides a computationally efficient strategy in the development of QM-EFP optimization procedures. These developments will improve the accuracy of the QM-EFP method and allow it to be used on a wider variety of chemical systems, as well as enabling larger MD simulations which are able provide valuable chemical insights that would be unavailable with traditional force field methods.

Studies of Dynamic Materials in Extreme Environments

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The scattering of atomic and molecular beams from well-characterized surfaces is an incisive method for studying the dynamics of gas-surface interactions, providing precise information on energy and momentum transfer as well as complex reaction mechanisms. Scanning probe measurements provide a powerful complement to scattering data as SPM measurements give a direct route to the visualization and spectroscopic characterization of interfacial atomic and nanosystems. This AFOSR program is examining critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme terrestrial and space environments. Extreme conditions encompass high and low temperature regimes, high velocity gas flows, optical and charged particle illumination, and severe oxidative environments where interfacial aerodynamic performance (energy and momentum transfer characteristics), morphological change, and chemical stability need to be assessed and quantified. This effort is also focussed on the formation, collisional energy transfer, and reactivity of interfacial molecular ices in support of AFOSR fundamental science needs for materials and flight operations in arctic environments.

We will report at this year's meeting on several achievements: (i) Our newest scattering instrument that combines supersonic beam surface interactions with *in situ* STM visualization is now fully operational, examining N₂ dissociation on Ru to probe energy dissipation and non-adiabatic effects in reactive chemisorption. Initial results reveal fascinating single-molecule dissociation dynamics for this system [1]. New studies are probing the oxidation chemistry of graphene and moiré graphene structures on metals, revealing the site-specific and layer-specific chemistry of this new class of carbon-based materials. We are also examining the energetic gas-surface interactions with different structural ices and molecules to include embedding and capture into ice [2,3,4], now focusing on the preferential condensation of competing isotopologues under carefully chosen non-equilibrium gas-surface collision conditions [5] complemented by accurate MD simulations [6]. Such isotope selectivity during deposition and scattering may open new routes for *in-situ* isotopic materials engineering. Finally, we are examining the sticking and bonding of water and other molecules on hydrophilic vs. hydrophobic surfaces as a function of gas velocity and surface temperature. Such studies are revealing new details of ice formation in cold environments [7].

Selected Recent Publications

1. STM Visualization of N₂ Dissociative Chemisorption on Ru(0001) at High Impinging Kinetic Energies, Joshua Wagner, Tim Grabnic, and S. J. Sibener, *J. Phys. Chem. C*, **126**, 18333-18342 (2022).
2. Sticking Probability of High-Energy Methane on Crystalline, Amorphous, and Porous Amorphous Ice Films, Rebecca S. Thompson, M. R. Brann, and S. J. Sibener, *J. Phys. Chem. C* **123**, 17855-17863 (2019).
3. A New Method of Isotope Enrichment and Separation: Preferential Embedding of Heavier Isotopes of Xe into Amorphous Solid Water, K. D. Gibson and S. J. Sibener, *PCCP* **23**, 7902-7907 (2021).
4. Acetone-Water Interactions in Crystalline and Amorphous Ice Environments, Michelle R. Brann, Stephen P. Hansknecht, Mark Muir, and S. J. Sibener, *J. Phys. Chem. A*, **126**, 2729-2738 (2022).
5. Differential Condensation of Methane Isotopologues Leading to Isotopic Enrichment Under Non-equilibrium Gas-Surface Collision Conditions, Michelle R. Brann, Stephen P. Hansknecht, Xinyou Ma, and S. J. Sibener, Invited Submission to the Special Issue "Celebrating 125 Years of The Journal of Physical Chemistry", *J. Phys. Chem. A*, **125**, 9405-9413 (2021).
6. Isotopic Enrichment Resulting from Differential Condensation of Methane Isotopologues Involving Non-equilibrium Gas-Surface Collisions Modelled with Molecular Dynamics Simulations, Michelle R. Brann, Xinyou Ma, and S. J. Sibener, *J. Phys. Chem. C*, submitted (2023).
7. Initial Sticking of Water to Cold Hydrophobic and Hydrophilic Surfaces Under Non-equilibrium Supersonic Flow Conditions, K. D. Gibson and S. J. Sibener, in preparation (2023).

Activation of Methane by Zr^+ : A Deep-Dive into the Potential Surface via P- and T-Dependent Kinetics with Statistical Modeling

Brendan Sweeny, Tucker Lewis, Thomas Miller, Hua Guo, Shaun Ard, Nicholas Shuman, Albert Viggiano

The kinetics of $Zr^+ + CH_4$ are measured using a selected-ion flow tube apparatus over the temperature range 300–600 K and the pressure range 0.25–0.60 Torr. Measured rate constants are small, never exceeding 5% of the Langevin capture value. Both collisionally stabilized $ZrCH_4^+$ and bimolecular $ZrCH_2^+$ products are observed. A stochastic statistical modeling of the calculated reaction coordinate is used to fit the experimental results. The modeling indicates that an intersystem crossing from the entrance well, necessary for the bimolecular product to be formed, occurs faster than competing isomerization and dissociation processes. That sets an upper limit on the lifetime of the entrance complex to crossing of 10–11 s. The endothermicity of the bimolecular reaction is derived to be 0.09 ± 0.05 eV, in agreement with a literature value. The observed $ZrCH_4^+$ association product is determined to be primarily $HZrCH_3^+$, not $Zr^+(CH_4)$, indicating that bond activation has occurred at thermal energies. The energy of $HZrCH_3^+$ relative to separated reactants is determined to be -0.80 ± 0.25 eV. Inspection of the statistical modeling results under best-fit conditions reveals reaction dependences on impact parameter, translation energy, internal energy, and angular momentum. Reaction outcomes are heavily affected by angular momentum conservation. Additionally, product energy distributions are predicted.

Chiral Plasmonic Nanostructures Created by Circularly Polarized Light

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Abstract: Chirality is inherent in biological molecules such as DNA, amino acids and glucose. Compared to these natural products with chiral features, chiral plasmonic materials have advantages due to strong light matter interactions. Previous work done by the Tatsuma group has demonstrated the chiral growth of lead oxide on gold (Au) nanorods deposited on titania coated indium tin oxide (ITO), but their experiments were limited to circularly polarized 520 nm light^[1, 2]. Besterio *et al.* explained that the chiral photodeposition resulting from circular polarized light (CPL) occurs after high energy electrons or hot electrons are created inhomogenously across the nanocrystal's surface^[3]. The hot electrons are concentrated at the hot spots, i.e. the tips for plasmonic nanoparticles. Motivated by this work, we demonstrate chiral growth on Au bipyramids (AuBPs) deposited on titania coated ITO by CPL. Au BPs were selected as plasmonic substrates for their anisotropy and their long dephasing time. In this poster, we experimentally verify the mechanism by which CPL induces photodeposition on the Au BPs by showing the effect of wavelength and localized surface plasmon resonance position. This experimental verification of Govorov *et al.*'s calculations^[3] is new. This work provides insight into the synthesis and design of chiral materials with high dissymmetry ratios in the visible wavelengths.

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Ni Ingress and Egress in SrTiO₃ Single Crystals of Different Facets

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Metal-ion surface interactions and/or doping in host perovskite-oxides are techniques that are widely employed for electronic structure tuning purposes and in developing novel heterogeneous catalysts; albeit an in-depth understanding of the different elementary steps and factors involved in these processes is lacking. We use Atomic Force Microscopy (AFM), Scanning Transmission Electron Microscopy (STEM), and *ab initio* thermodynamics through density functional theory (DFT) to specifically investigate Ni surface adsorption, ingress, migration, segregation, and egress processes across different SrTiO₃ (STO) single-crystal facets and terminations, specifically the (001), (110), and the (111). Under oxidizing and reducing conditions at different temperatures, Ni egress is observed on (110) STO samples, but not the (001). DFT results demonstrate Ni to have a higher thermodynamic egress propensity, specifically through an oxygen-terminated (110) facet in comparison to other (001) terminations, whereas for the (111)-Ti terminated facet, Ni is likely to remain in the bulk post ingress. We suggest that the observed uniqueness of the (110) surface facet towards Ni egress is possibly a consequence of a surface phase transition. These results can help guide design interests with regards to Ni surface stabilization, ingress/egress suppression or facilitation in STO by elucidating the nuances involved across different facets.

Molecules in Optical Cavities: Precision Spectroscopy & Strong Light-Matter Interactions

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This poster will provide an overview of various projects we are embarking on in the Weichman Lab, which launched at Princeton Chemistry in July 2020.

Much of our recent work has focused on fundamental studies of chemistry under strong interactions with light engineered in optical cavities. Light-matter interactions are typically weak and can be treated perturbatively. This picture breaks down in the regime of strong coupling, where the rate of light-matter interaction competes with the dissipation of excitations. In this regime, superposition states with mixed light-matter character, dubbed *polaritons*, emerge. Polaritons inherit the coherent, wavelike nature of light while maintaining local molecular interactions and structure. Polaritonic molecules may therefore demonstrate distinct reactivity from their ordinary uncoupled counterparts, representing a rich sandbox for new chemistry. We are setting out to build a detailed picture of how molecular polaritons behave and react, using both precision and ultrafast spectroscopies to follow the dynamics of benchmark condensed-phase and gas-phase systems under strong light-matter coupling.

We are also developing cavity-enhanced spectroscopies to interrogate the quantum structure of unprecedentedly large and complex chemical species. In particular, we are harnessing direct frequency comb spectroscopy as a sensitive, broadband, and precision technique. Frequency combs are light sources consisting of thousands of evenly spaced, sharp frequency “teeth.” Cavity-enhanced frequency comb spectroscopy (CE-FCS) matches a comb’s evenly spaced spectral structure to the resonant modes of a high-finesse optical cavity. This method allows for simultaneous detection of absorption signal across the comb spectrum, extremely high frequency resolution, and high sensitivity as the cavity enhances the interaction length between light and sample. We are combining cryogenic buffer gas cooling of large molecules with CE-FCS in order to fully resolve the rovibrational structure of large, astrochemically-relevant molecules including fullerenes and polycyclic aromatic hydrocarbons. We are also harnessing comb spectroscopy to demonstrate make broadband single-particle optical measurements of atmospherically-relevant aerosol particles, in order to explore their absorption, scattering, photochemistry, and droplet nucleation and growth dynamics.

Ultrafast photophysics and device fabrication of carbon nanotube exciton-polariton microcavities

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Coupling between light and matter in an optical cavity creates hybrid states known as polaritons with properties that are not observed in purely molecular systems. We fabricate and investigate polariton microcavities and devices containing semiconducting single-walled carbon nanotubes (sSWCNTs), which are an ideal class of molecules to create polaritons with due to their strong and narrow absorption in the visible and the near-infrared. Applying ultrafast 2D white-light spectroscopy in a donor-acceptor sSWCNT polariton, we find that the interplay between light-matter coupling and molecular parameters, such as intermolecular coupling and disorder in the CNTs, enables a long-range energy transport process across several hundreds of nanometers. Furthermore, we find that long-range energy transport persists even in the presence of weak light-matter coupling. We will also present some recent results on the fabrication and optimization of sSWCNT photodetector devices in a polariton cavity.