

# Probing Element-Specific Charge Carrier Dynamics at Junctions

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Surface photoemission spectroscopy (PES) and transient absorption spectroscopy (TAS), utilizing femtosecond extreme-ultraviolet (XUV) laser pulses, are employed to investigate the electronic structure and ultrafast charge carrier dynamics in photovoltaic and photocatalytic junctions of several key types: p-n junctions (semiconductor-semiconductor), Schottky barriers (semiconductor-metal), and semiconductor-insulator-metal junctions. The laser-based XUV-PES and XUV-TAS methods monitor charge carrier dynamics with femtosecond time resolution, surface or interface sensitivity, and element and oxidation state specificity.

In recent examples, n-TiO<sub>2</sub> ultrathin films grown on a p-Si(100) substrate can form a heterostructure with a staggered type II band alignment, the alignment of which can be varied by the degree of oxidation of the titanium. The electronic structure of n-TiO<sub>2</sub>/p-Si(100) as well as ultrafast photoinduced electron migration from Si to TiO<sub>2</sub> are determined. Static photoemission is utilized to monitor the electronic structure of Zn clusters on p-Si(100) as a function of deposition. The transition from non-metallic to metallic Zn character is observed at about 0.16 ML of Zn coverage. Employing the pump-probe PES technique, the transfer of electrons to the Zn particles and a 3.5 ML metallic Zn film from Si are investigated, revealing Schottky barrier properties. Semiconducting Gallium Phosphide (GaP) has received considerable attention as a component in photocatalytic systems for water oxidation and carbon dioxide reduction due to its visible band gap (2.26 eV) and stability in reactive solutions. The electronic structure of a Zn/n-GaP Schottky junction serves as a model photocatalytic system for hole transfer. Experimental results indicate photoexcited holes transport from the GaP to the metal through the interface. Moreover, shifts in the energetic positions of the Fermi level and the Zn and Ga core levels are quantified by photoemission. The binding energy shift of the Zn core level follows the Fermi level temperature changes in time, providing a new marker for the ultrafast dynamics. Future studies will investigate the dependence of the direction and magnitude of carrier migration on band alignment by creating junctions in which metals are deposited on both n- and p-type versions of the same semiconductor. Finally, XUV TAS spectroscopy is used to observe charge transfer dynamics in a Ni/TiO<sub>2</sub>/Si photocatalyst junction structure. The element specificity of XUV transient absorption is used to monitor ballistic hole tunneling from the photoexcited Si through the TiO<sub>2</sub> insulator layer and into the Ni overlayer, followed by slower recombination by back diffusion of the holes, resulting in the subsequent relaxation and equilibration dynamics. All three layers are followed in time using time-resolved XUV transient absorption for the first time on a junction.

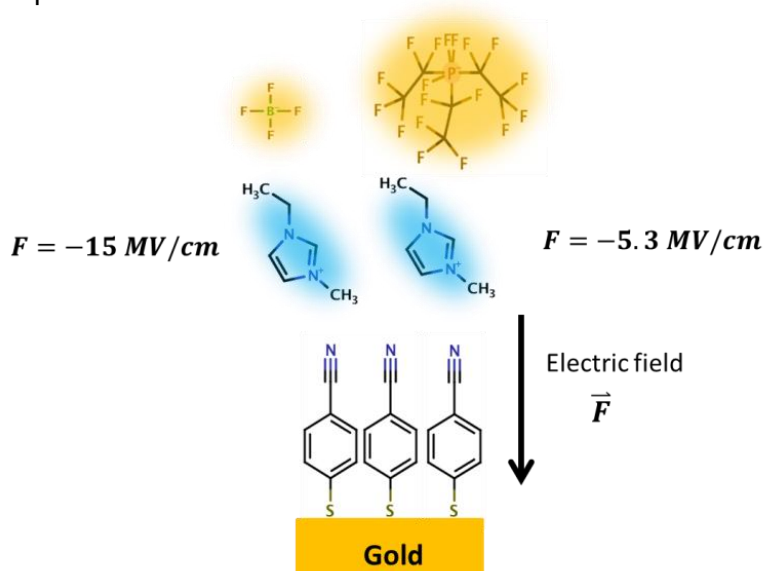
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# Local Electric Fields at the Interfaces of Ionic Liquids and Metals Measured by Stark Shift Spectroscopy

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Many applications of ionic liquids, especially those involving electrochemistry, require understanding and controlling local electric fields at the interfaces of ionic liquids with solids. However, the conventional understanding of ions near an interface in electrochemistry is based on dilute electrolytes and often does not apply to ionic liquids, not even approximately. Non-negligible ion sizes and hindered motion of molecules near the surface lead to non-trivial and unexpected behavior. Our approach to understanding the electric field at the interface is to measure the vibrational Stark shift of chromophores tethered at the interface using Sum Frequency Generation (SFG) spectroscopy. Since the Stark tuning properties of the probe molecule are reasonably well-known, the observed shifts can be related to the local electric fields. We will report results on vibrational Stark shift of benzonitriles tethered at the junction of gold and ionic liquids such as 1-Ethyl-3-methylimidazolium tetrafluoroborate (figure 1). We have previously developed an interfacial solvation theory as an extension of the Onsager solvation model that predicts the local electric fields influencing dipolar molecules at the interface. While the theory is successful in predicting the shifts for well-behaved dielectric solvents, our experimental Stark shifts for ionic liquids do not conform to this continuum theory. This work highlights the importance of discreteness and finite ion size in determining the local electric fields near the interface, and calls for more advanced theoretical descriptions of interfacial solvation by ionic liquids.



**Figure 1.** Interfacial electric field,  $F$ , at the junction of a metal and an ionic liquid is measured using vibrational Stark shift spectroscopy. The field strongly depends on the size of anions and does not conform to a continuum theory of local fields near the surface established by us earlier.

# Extraordinarily Slow Dynamics in Thin Films of a Room Temperature Ionic Liquid Investigated with Reflection Geometry 2D IR Spectroscopy

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The role that interfaces play in the dynamics of liquids is a fundamental scientific problem with vast importance in technological applications. From material science to biology, e. g., batteries to cell membranes, liquid properties at interfaces are frequently determinant in the nature of chemical processes. For most liquids, like water and benzene, the influence of an interface falls off on a  $\sim 1$  nm distance scale. Room temperature ionic liquids (RTILs) are a vast class of liquids composed of complex cations and anions that are liquid salts at room temperature. They are unusual liquids with properties that can be finely tuned by selecting the structure of the cation and anion. RTILs are being used or developed in applications such as batteries, CO<sub>2</sub> capture, and recently, liquids for biological processes. Here, it is shown quantitatively that the influence of an interface on RTIL properties is profoundly different from that observed in other classes of liquids. The dynamics of planar thin films of the room temperature ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BmimNTf<sub>2</sub>), were investigated using two-dimensional infrared spectroscopy (2D IR) with the CN stretch of SeCN<sup>-</sup> as the vibrational probe. The structural dynamics (spectral diffusion) of the thin films with controlled nanometer thicknesses were measured and compared to the dynamics of the bulk liquid. The samples were prepared by spin coating the RTIL, together with the vibrational probe, onto a surface functionalized with an ionic monolayer that mimics the structure of the BmimNTf<sub>2</sub>. Near-Brewster's angle reflection pump-probe geometry 2D IR facilitated the detection of the exceedingly small signals from the films, some of which were only 14 nm thick. Even in quarter micron (250 nm) thick films, the observed dynamics were much slower than those of the bulk liquid. The pulse shaping 2D IR spectrometer used in these experiments has tremendous advantages, but it has the limitation of not being able to reduce the amplitude of the local oscillator to enhance very weak signals. The third pulse in the 2D IR pulse sequence generates the collinear echo signal and serves as the local oscillator (LO) for heterodyne detection. Reducing the amplitude of pulse 3 reduces the LO but also reduces the signal the same amount, so there is no improvement. For thin films, the signal is emitted in the forward and reflection directions with the same amplitude. However, in reflection geometry using p-polarization for pulse 3, the reflection of pulse 3, which is the LO, can be made very small by bringing in the third pulse near Brewster's angle. Thus the sensitivity of non-collinear 2D IR is recovered while maintaining the advantages of a pulse shaping spectrometer. A new theoretical description of how the surface influence on the dynamics of liquids affects the 2D IR observables is presented. The 2D IR data are related to frequency-frequency correlation function (FFCF), which is modeled as a multi-exponential function for bulk liquids. The FFCF for BmimNTf<sub>2</sub> bulk liquid is well represented by a tri-exponential decay. The theory for films says that the time constants in the FFCF exponentials have an exponential dependence on the distance from the interface,  $r$ , a correlation length,  $l$ , and a time constants at the interface,  $\tau_0$ . The FFCF (observable) is the average over  $r$  from  $r = 0$  to half the thickness of the film,  $d/2$ , the mid-point between the two interfaces. For  $d \gg l$ , the bulk dynamics are recovered. For  $d < l$ , the observed dynamics slow dramatically. Using the theory, the data for several thicknesses are fit simultaneously, and a value of  $l = 20$  nm is obtained. The value of  $l$  for this system is a factor of 10 to 20 greater than for water.

## “Selective Triplet-Initiated Intermolecular [2+2] Cycloadditions Photocatalyzed by Visible-light-Absorbing Quantum Dots”

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Tetrasubstituted cyclobutyl structures are precursors to, or core components of, many important bioactive molecules, including prospective drugs. Light-driven [2+2] cycloaddition is the most direct strategy for construction of these structures. [2+2] photocycloadditions that proceed through the triplet excited state are advantageous because (i) their scope is not limited by the electrochemical potentials of the substrate, (ii) triplets have long enough lifetimes to mediate *intermolecular* cycloadditions, and (iii) triplets can be accessed using visible (as opposed to UV) light through excitation of a triplet sensitizer, such as a transition metal complex or organic chromophore, followed by triplet-triplet energy transfer (TT EnT). Synthetic applications of [2 + 2] photocycloadditions however also demand high selectivity, not only for specific coupling products, but also for particular stereo- and regioisomers of those products. Achieving selectivities for (i) a particular regioisomer of the coupled product, (ii) a particular diastereomer of the coupled product, and (iii) homo- vs. hetero-coupling within a mixture of reactive olefins still remains a challenge. Here, we discuss the use of colloidal CdSe quantum dots (QDs) as visible light absorbers, triplet exciton donors, and scaffolds to drive homo- (photodimerization) and hetero- (cross coupling) intermolecular [2+2] photocycloadditions of 4-vinylbenzoic acid derivatives, with (i) perfect and switchable regioselectivity and (ii) 97-98% diastereoselectivity for the previously minor *syn*-head-to-head (HH) or *syn*-head-to-tail (HT) configurations of the adducts. The diastomeric ratios (d.r.) we achieve are a factor of 5 - 10 higher than those reported with all other triplet sensitizers. Furthermore, the size-tunable triplet energy of the QD enables regioselective *hetero*-intermolecular couplings through selective sensitization of only one of the reagent olefins.

## Characterization of Heterogenized CO<sub>2</sub> Reduction Catalysis by Vibrational Sum-Frequency Spectroscopic, Electrochemical, and Theoretical Studies

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Rhenium (Re) and manganese (Mn) bipyridyl tricarbonyl complexes have attracted intense interest in recent years, due to their promising applications in photocatalytic and electrocatalytic CO<sub>2</sub> reduction in both homogeneous and heterogenized systems. So far, many efforts have been devoted to immobilize Re catalysts on solid surfaces for higher catalytic efficiency, reduced catalyst loading, and convenient product separation. However, in order for the heterogenized molecular catalysts to achieve the combination of the best aspects of homogeneous and heterogeneous catalysts, it is essential to understand fundamental physicochemical properties of such heterogeneous systems, such as surface-bound structures of Re/Mn catalysts, substrate-adsorbate interactions, and photo-induced or electric field-induced effects on Re/Mn catalysts. For example, the surface may act to (un)block substrates, (un)trap charges, (de)stabilize particular intermediates (and thus affect scaling relations) and shift potentials in different directions just as protein environments do. The close collaboration between the Lian, Batista, and Kubiak groups has resulted in an integrated approach to investigate the effect of the semiconductor or metal surface on the properties of the attached catalyst. Synthetic strategies to achieve stable and controlled attachment of Re/Mn molecular catalysts have been developed. Steady-state, time-resolved, and electrochemical vibrational sum frequency generation (SFG) spectroscopic studies have provided insight into the interfacial structures, ultrafast vibrational energy relaxation, and electric field effects on the Re/Mn catalysts, respectively. Various computational methods utilizing density functional theory (DFT) have been developed and applied to determine the molecular orientation by direct comparison to spectroscopy, unravel vibrational energy relaxation mechanisms, and quantify the interfacial electric field strength of the Re/Mn catalyst systems. The talk will focus on recent progress on determining the surface-bound structures of Re catalysts on semiconductor and Au surfaces by combining vibrational SFG measurements and first principles theoretical methods. The effects of the crystal facet, length of anchoring ligands, and doping of the semiconductor on the bound structures of Re catalysts and of the substrate itself will be discussed, as well as the vibrational relaxation (VR) dynamics of Re catalysts covalently adsorbed on semiconductor and metal surfaces, the role of electron-hole-pair (EHP) induced coupling on the VR of Re catalyst bound on Au, and the interfacial electric field experienced by the catalytically active site of the Re/Mn catalyst bound on Au electrode as probed by the combination of electrochemical SFG and the DFT study of the Stark tuning of the CO stretching modes of these catalysts.

## **Photo/Electro-Catalytic Fuel Production from First Principles**

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Electrochemically based water splitting to produce sustainable hydrogen remains impractical because of the dearth of inexpensive electrocatalysts that can efficiently carry out the more difficult half-reaction of water oxidation. Even more difficult is carbon dioxide reduction to useful products. I will discuss structural and mechanistic characterization of (photo-)electrocatalysis at complex semiconductor electrodes, as derived from quantum mechanics calculations. High fidelity modeling of the water-semiconductor interface is crucial. I will present my group's recent work identifying the most probable active crystal facets and key surface species involved in water oxidation at doped NiOOH electrodes, along with our latest findings related to photo-electro-reduction of carbon dioxide at functionalized compound semiconductor electrodes.

## Abstract

### MURI on Molecular Level Studies of Solid-Liquid Interfaces in Electrochemical Processes

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The efficient interconversion of electrical and chemical energy requires functional electrodes that are able to catalyze complex multi-electron energy conversion reactions. The electrodes in energy conversion devices must, therefore, serve not merely as inert sources or sinks of electrons but rather as active players that bind reactants, stabilize key intermediates, and enable inner-sphere electron transfer reactions. Despite its fundamental and technological importance, a molecular-level mechanistic understanding of the factors that drive efficient multi-electron inner-sphere electrocatalysis remains elusive, impeding systematic progress toward innovative and more efficient energy conversion technologies. This critical knowledge gap arises because the current-voltage response of an electrode provides little information about the complex array of elementary surface processes that underpin near all energy conversion reactions. Addressing this longstanding grand challenge requires multi-faceted methodologies that go beyond classical current-voltage measurements and combine *operando* probes and atomistic simulations to develop multiscale models of critical inner-sphere electron transfer reactions.

This MURI program is a multidisciplinary effort aimed at developing a molecular-level understanding of the fundamental processes that drive complex electrochemical reactions. It contains five closely integrated Thrusts, ranging from the development of enabling multimodal experimental and theoretical/computational platforms, *in situ* probes of interfacial structure and dynamics in model systems, to the application of these tools to complexes catalytic reactions. This talk will report on some of the progress so far. The development of a multimodal electrochemical platform is well under way, integrating *in situ* vibrational spectroscopy and mass spectrometry with electrochemistry measurements. The team is developing a new I-V simulation package that enables the integration of state-of-art theory and modelling results. Combined 2D-SFG, vibrational Stark effect spectroscopy, and atomistic simulation studies are being carried out to provide atomistic level insight of adsorbate/solvent/ion dynamics at the electrode/liquid interface. Significant progress has also been made in combined experimental and computational studies of proton-coupled electron transfer at electrode/liquid interfaces.

## Ultrafast Spectroscopy for Molecular Polariton and Atomic Specific Charge Dynamics

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In this talk, I will present recent research progress of two projects: (1) optical nonlinearity and dynamics of molecular vibrational polaritons, and (2) a compact table-top UV pump EUV probe spectrometer for element specific charge dynamics in solids.

1. Molecular vibrational polaritons, hybrid half-light, half-matter quasiparticles, enabled by Fabry-Perot microcavities, are studied using ultrafast coherent 2D IR spectroscopy. Molecular vibrational-polaritons are anticipated to open opportunities for new photonic and molecular phenomena, which hinge on fundamental understanding of physical properties of molecular vibrational polaritons. Using 2D IR spectroscopy to study vibrational-polaritons, we obtained a few results that are related to the delocalized and hybridized nature of polaritons: 1. A macroscopic dependent optical nonlinearity of polaritons. 2. Cavity-enabled intermolecular energy transfer and inter-cavity interactions. 3. Dynamics of optical dark states in molecular polaritons in cavities. These results will have significant implications in novel infrared photonic devices, lasing, molecular quantum simulation, as well as new chemistry by tailoring potential energy landscapes.
2. Element-specificity is important in understanding excited electronic state dynamics. Recent surge in table-top high harmonic generation (HHG) based EUV/soft X-ray sources provides an opportunity to follow element specific dynamics in regular research labs, complementary to the large national facilities. My group developed a compact ultrafast table-top UV pump EUV probe spectrometer and demonstrated proof-of-principle capability on following ultrafast charge dynamics of solid-state materials.



## Generalized Einstein Relations Indicate Static Disorder in Perovskite Nanoplatelets

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### ABSTRACT

The Einstein relations between rate constants for absorption, stimulated emission and spontaneous emission in line spectra are well-known fundamental concepts of spectroscopy. The Strickler-Berg and van Roosbroek-Shockley relations provide model-specific extensions to estimate radiative lifetimes from the broad-band spectra of molecules in solution and semiconductors, respectively. Generalized Einstein relations can be derived for broad-band spectra of homogeneous samples after each electronic band reaches internal thermal quasi-equilibrium. They provide a way to measure the chemical potential of excited states, but the requirement for a homogeneous sample has prevented their application. By using femtosecond two-dimensional Fourier transform spectroscopy to remove the inhomogeneity from static disorder, we have applied the Generalized Einstein relationships to determine the standard chemical potential for creation of an exciton in colloidal lead sulfide quantum dots. Testing the Generalized Einstein relationship between the shape of the homogeneous absorption and emission spectra (which has no free parameters), we found that if thermal quasi-equilibrium is established, the Generalized Einstein relationships provide an extremely simple route for determining static disorder from steady state absorption and emission spectra.

Prior studies of CdSe nanoplatelets have reported that linewidths in single nanoplatelet electronic spectra are slightly *wider* than the ensemble linewidths, which has been used to argue that nanoplatelet spectra are homogeneously broadened. We have synthesized perovskite nanoplatelets using the procedure developed by Tisdale's group. We have used the Generalized Einstein relations to determine the static disorder of colloidal perovskite nanoplatelets under a variety of synthesis conditions. The origin of static disorder in perovskite nanoplatelets is not yet clear, but it contributes about half of the linewidth under published synthetic conditions. Crucially for our purposes, this implies that the dynamical linewidth is narrow enough that it could support energy transfer through nonadiabatic vibrational-electronic resonance. We are currently exploring the coupling between stacked nanoplatelets.

## Project Abstract

### “Artificial Atoms, Molecules, and Solids: Multiple Functions and Emergent Properties”

Program Officer: Dr. Michael R. Berman, AFSOR/RTB2

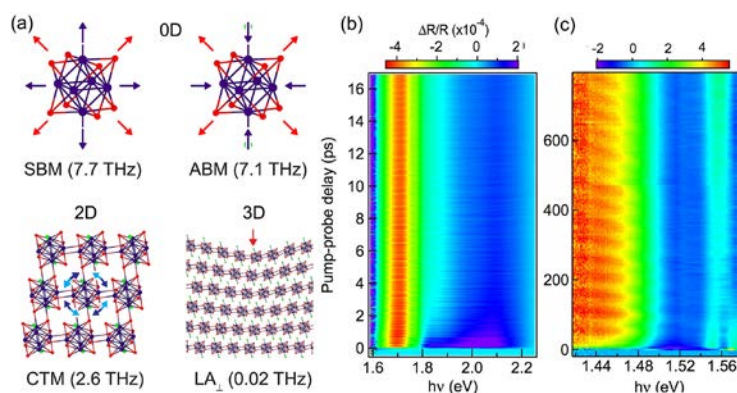
PI: Colin Nuckolls

Co-PIs: Xiaoyang Zhu, Michael Steigerwald, Xavier Roy

This project focuses on a new type of nanoscale building block, a superatom or nanoscale atom, and their assembly into functional materials. The superatoms are used in the design, synthesis, and characterization of a new generation of multi-functional materials, and in particular, to tackle the challenge of directing charge/energy flow. In this presentation, we will report our efforts in understanding phonon dynamics and electron phonon coupling in such hierarchical solids.

The coupling of phonons to electrons, excitons and other phonons plays a defining role in material properties, including charge and energy transport, light emission, and superconductivity. In atomic solids, phonons are delocalized over the three-dimensional (3D) lattice and are determined by bonding and crystal symmetry. In molecular materials, by contrast, localized molecular vibrations locally couple to electrons to produce, for example, high temperature superconductivity, as in  $A_3C_{60}$ . Here we expand the phonon space by combining localized 0D phonon manifolds in the hierarchical superatomic semiconductor of  $Re_6Se_8Cl_2$ . Its structure consists of  $Re_6Se_8$  superatoms covalently linked into 2D sheets that are stacked into a van der Waals lattice. Using transient reflectance spectroscopy, we identify three types of coherent phonons produced by optical excitation: localized 0D breathing modes of isolated superatom, 2D synchronized twisting of superatoms in each layer, and 3D acoustic interlayer deformation. The presence of local phonon modes in an extended crystal opens the door to controlling material properties from hierarchical phonon engineering.

In addition to the hierarchical phonons, we report how highly anisotropic phonons can be obtained in superatomic solids for potential applications in directional energy transport. We will also report the development of a new tool, Fourier-transform coherent phonon spectroscopy (FT-CPS), to specifically probe polaronic states resulting from strong electron-phonon coupling.



**Fig. 1. Hierarchical phonons in the 2D superatomic semiconductor:  $Re_6Se_8Cl_2$ .** (a) Schematic illustration of the 0D symmetric and anti-symmetric breathing modes (SBM and ABM) of the each superatom, the 2D LO phonon mode, and the 3D acoustic mode. The 2D pseudo-color plots show transient reflectance spectra of coherent phonons probed above bandgap (b) and below bandgap (c) following bandgap electronic transition. The former shows the 0D and 2D coherent phonon oscillations and the latter the 3D acoustic mode.

# **Many-Body Molecular Dynamics Simulations of Ionic Systems: From Clusters to Bulk and Interfaces**

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Two of the most challenging problems at the intersection of electronic structure theory and molecular dynamics simulations are the accurate representation of intermolecular interactions and the development of reduced-scaling algorithms applicable to large systems. To some extent, these two problems are antithetical, since the accurate calculation of non-covalent interactions typically requires correlated, post-Hartree-Fock methods whose computational scaling with respect to system size precludes the application of these methods to large systems. I will describe our many-body molecular dynamics (MB-MD) methodology that overcomes these limitations and enables computer simulations from the gas to the condensed phase, with chemical and spectroscopic accuracy. MB-MD is a unified molecular dynamics framework that combines many-body representations for potential energy, dipole moment, and polarizability surfaces that are derived entirely from correlated electronic structure data-driven approaches, with quantum dynamics methods that explicitly account for nuclear quantum effects. I will discuss the accuracy and predictive ability of the MB-MD methodology in the context of molecular modeling of ionic systems, from gas-phase clusters to bulk solutions and interfaces, with a particular focus on the relationships between many-body effects, structural and dynamical properties, and vibrational spectra.

# Conformational Motions and Electrostatics Facilitate Proton-Coupled Electron Transfer in BLUF Photoreceptor Proteins

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Photoreceptor proteins allow the control of biological processes by light absorption and play a central role in the field of optogenetics, where light is used to manipulate cells in living tissue, such as neurons, with high spatial and temporal resolution. In particular, blue light using flavin (BLUF) photoreceptor proteins have been shown to be critical for many physiologically important processes. Moreover, due to their modular architecture, the BLUF domain may be fused to the effector domains of various other proteins, allowing photocontrol of a variety of other processes. Thus, understanding the fundamental principles underlying BLUF photoreceptors is important for engineering novel systems that use light as a tool to achieve noninvasive control of biological processes with high spatiotemporal resolution. In the BLUF protein, photoexcitation of a flavin chromophore induces proton-coupled electron transfer (PCET), as well as local conformational changes that subsequently propagate to distal parts of the protein and drive other chemical and physical changes. BLUF proteins also serve as a prototype for understanding the fundamental principles underlying photoinduced PCET.

In the Slr1694 BLUF photoreceptor, experiments indicate that photoexcitation to a locally excited state within the flavin instigates electron transfer from a tyrosine to the flavin, followed by proton transfer from this tyrosine to the flavin via an intervening glutamine residue. Free energy simulations of the entire solvated system show that photoexcitation to the locally excited state of the flavin induces formation of the proton relay from tyrosine to glutamine to the flavin if it is not already formed. Electrostatically embedded time-dependent density functional theory (TDDFT) and complete active space self-consistent-field (CASSCF) calculations indicate that formation of the proton relay reduces the energy gap between the locally excited state and the charge transfer state associated with electron transfer from the tyrosine to the flavin. Although the charge transfer state is higher in energy than the locally excited state prior to photoexcitation, the protein environment can reorganize in a manner that stabilizes the charge transfer state, enabling a transition from the locally excited state to the charge transfer state. An electrostatic analysis identified motions of individual residues, such as a nearby arginine, that stabilize electron transfer from the tyrosine to the flavin. The conformational changes associated with rearrangements of hydrogen-bonding networks within the active site and movement of charged residues surrounding the active site alter the electrostatic environment in a manner that facilitates photoinduced PCET within the BLUF photocycle. These calculations provide fundamental insights into the roles of conformational changes and electrostatics in photoreceptor proteins.

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## CRYPTOCHROME-BASED MAGNETIC SENSING

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Although it has been known for half a century that night-migratory songbirds can detect the direction of the Earth's magnetic field for the purposes of orientation and navigation, the primary sensory mechanisms responsible for this remarkable feat are still obscure. The leading hypothesis centres on the quantum mechanical properties of short lived chemical intermediates known as radical pairs — in particular the radical pairs that are formed when a cryptochrome protein, located in the birds' retinas, is excited with blue light [1].

In this talk, I will outline how the quantum spin dynamics of radical pairs in non-equilibrium spin states could lead to changes in the yield of a signalling state of the protein even though the interaction with the geomagnetic field is six orders of magnitude smaller than the thermal energy,  $k_B T$ . I will then present some of the experimental and theoretical evidence for the cryptochrome hypothesis, comment on the extent to which cryptochromes are fit-for-purpose as magnetoreceptors, and discuss the possibilities for the construction of magnetic sensing devices inspired by the biophysics of avian magnetoreception.

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**Studies of metal oxide clusters and transient species with slow electron velocity-map imaging of cryogenically-cooled anions (cryo-SEVI)**

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Photodetachment of mass-selected negative ions provides a novel and unique means to investigate clusters, free radicals, and transition states for benchmark chemical reactions. The development of cryo-SEVI in our laboratory (slow electron velocity-map imaging of cryogenically-cooled anions) enables anion photoelectron spectroscopy with a resolution as high as  $1\text{-}2\text{ cm}^{-1}$ , an improvement of approximately two orders of magnitude relative to conventional methodology. One can then obtain well-resolved spectra of bare and complexed metal oxide clusters, which are powerful model systems for understanding key catalytic processes. Examples of recent work will be presented, including cryo-SEVI spectra of aluminum oxide clusters and the nitrate anion. Future directions involving a dual ion-trap modification and the addition of an infrared laser for pre-excitation of the anions will be discussed.

## **Abstract**

The kinetics of low-energy (thermal) systems are sensitive to details of the potential surface. Ion-molecule reactions often form sufficiently long-lived intermediates such that the assumptions of statistical theory are met and statistical theory can be used to extract quantitative energetic and qualitative mechanistic information from kinetics measurements. Computational requirements for this approach are modest compared to quasi-classical trajectory or related approaches allowing for rapid analysis of smaller systems and the possibility of treating larger systems. We report results for a range of systems involving 3<sup>rd</sup> row transition metals for catalytic cycles including activation of methane and oxidation of CO by N<sub>2</sub>O. Results include energetics of rate-limiting transition states, generally to an accuracy of 10-20 kJ mol<sup>-1</sup>, and where applicable the efficacy of intersystem crossings and the contribution (or lack thereof) of ‘two-state reactivity’ to the reactions. Analogous results for mixed-metal species also show the importance of considering multiple possible binding sites (including non-reactive sites). Efforts on larger systems including Al<sub>n</sub><sup>+</sup> + O<sub>2</sub> (n = 2 – 30) are in-progress and are summarized. Separately, we present an update on Air Force efforts to exploit chemical release of atomized lanthanide metals to create artificial ionosphere.

## **Chemi-ionization Reactions of the Lanthanides and Their Potential as Catalysts: Guided Ion Beam and Theoretical Studies**

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The Air Force is interested in the possibility of using the lanthanide chemi-ionization (CI) reaction,  $\text{Ln} + \text{O} \rightarrow \text{LnO}^+ + \text{e}^-$ , in the ionosphere to mediate scintillation effects that can disrupt telecommunications. For this use, the CI reaction must be exothermic but the favorability of the CI reaction exhibits an inverse correlation with the ease of lanthanide vaporization; thus, accurate thermochemistry for the CI reactions is critically needed. To this effect, we have examined the oxidation reactions of  $\text{Sm}^+$ ,  $\text{Gd}^+$ , and  $\text{Nd}^+$  to establish benchmark thermochemistry for the CI reactions, as well as several ancillary processes observed. Our results on these systems will be reviewed but lead to CI exothermicities of  $0.07 \pm 0.08$ ,  $1.54 \pm 0.10$ , and  $1.76 \pm 0.10$  eV, respectively. The former value has been used to help explain atmospheric release experiments. In addition, these results have shown that lanthanides may be interesting catalytic metals because the f-orbitals are potentially both sources and sinks for electron density. In our explorations of the oxidation chemistry of  $\text{Sm}^+$ , it became evident that some reactions exhibited distinct limitations on their efficiency, even when exothermic. Oxidation of  $\text{Sm}^+$  by  $\text{CO}_2$  and  $\text{COS}$  are two such examples, yet no restrictions are observed for sulfidation of  $\text{Sm}^+$  by  $\text{COS}$  or oxidation of  $\text{Gd}^+$  or  $\text{Nd}^+$  by  $\text{CO}_2$  (although these three systems do exhibit more efficient reactivity at higher collision energies). To understand these interesting observations, the potential energy surfaces (PES) for these reactions have been explored experimentally as well as theoretically. Quantitative agreement between experimental thermochemistry and theory requires the use of all-electron basis sets and corrections for spin-orbit effects. Operative effects include a tendency to conserve spin (interesting behavior for such heavy metals), avoided crossings between surfaces corresponding to different electronic configurations (of the same spin), and more facile activation of the S-CO bond (than the O-CS bond) because it is weaker and sulfur can bind effectively at more varied angles.



## Density Matrix Renormalization Group Pair-Density Functional Theory for Excited States and Transition-Metal Compounds

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Our latest progress in combining density matrix renormalization group (DMRG) with pair-density functional theory (PDFT) as a new way to calculate correlation energy will be discussed. We applied this new approach, called DMRG-PDFT, to study singlet–triplet gaps in polyacenes and polyacetylenes that require active spaces larger than the feasibility limit of the conventional complete active-space self-consistent field method. We will report also other ongoing applications of the method.

# Nonequilibrium Dissociation in Hypersonic Flows using Computational Chemistry

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Within the high-temperature shock layer that surrounds a high-speed vehicle, molecules undergo rapid rotational and vibrational excitation; ultimately dissociating into reactive atomic species that destroy the vehicle's heat shield. Modeling such high-speed flows is challenging because of strong thermochemical nonequilibrium involving molecular internal energy distributions that are non-Boltzmann. Dissociation rates at extreme temperatures are typically extrapolated from empirical relations based on few experimental measurements obtained for a limited range of conditions. However, during the past decade, computational chemistry has been used to investigate these processes from first-principles. The talk will summarize this effort with a focus on recent results for oxygen dissociation.

Specifically, the talk will describe a new method that combines rigorous statistical techniques from the Direct Simulation Monte Carlo (DSMC) method while integrating all atomic interactions directly on an *ab-initio* potential energy surface (PES). This numerical method, referred to as direct molecular simulation (DMS), is an accurate and efficient alternative to full state-resolved and master-equation analysis. Simulation results will be presented using potential energy surfaces, recently developed in the Truhlar group at the University of Minnesota, that govern collision dynamics for oxygen and nitrogen dissociation in the ground electronic state. Simulation results will be compared to experimental shock-tube data.

Finally, new continuum-level models, formulated based on the *ab-initio* results, will be presented. Such models can be used directly in large-scale computational fluid dynamics (CFD) simulations of full vehicle geometries at flight conditions.

## Studies of Dynamic Material Interfaces in Extreme Environments

Steven J. Sibener, The James Franck Institute and Department of Chemistry, The University of Chicago

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 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.

We will report at this year's meeting on several achievements: (i) Our newest scattering instrument is now fully operational, combining in one facility both reactive scattering and time-sequenced STM/AFM visualization of reacting surfaces [1-3]. We are studying presently the erosion and ablation of graphite when exposed to energy selected beams of molecular oxygen, observing reaction probabilities and morphological evolution of the reacting HOPG (basal plane) [2,3]. We have found that different oxidation conditions produce morphologically distinct etching features: Anisotropic channels, circular pits, and hexagonal pits, and that the reaction mechanism is beam-energy dependent and non-Arrhenius with respect to surface temperature. The combination of STM imaging and beam scattering connects time-evolving kinetics with nanoscopic morphology, helping to elucidate the mechanism of etching for this model aerospace material. In support of aerothermodynamic calculations, we have conducted scattering experiments with O<sub>2</sub> and N<sub>2</sub> where we monitor velocity and angle distributions for energy transfer for basal plane HOPG; this done in conjunction with MD simulations from the Hase group [4]. Results for O<sub>2</sub>/HOPG scattering indicate excellent agreement across a range of collision energies [4], validating the use of MD predicted outcomes as input to fluid dynamics simulations. (ii) We have extended our studies of energetic interactions of neutral species into crystalline, amorphous, and porous ice, with present focus on CH<sub>4</sub> [5]. Interactions with ice are important for understanding gas-surface energy & momentum exchange in high velocity gas flows, and for trace gas collection. (iii) We have demonstrated a new method for the separation of isotopes in space and time by gas-surface atomic diffraction [6a,b], initially demonstrated for <sup>20</sup>Ne and <sup>22</sup>Ne. This new method will be explored with other isotopes and isotopologues.

### Selected Recent Publications

1. Temporally and Spatially Resolved Oxidation of Si(111)-(7×7) using Kinetic Energy Controlled Supersonic Beams in Combination with Scanning Tunneling Microscopy, Bryan Wiggins, L. Gaby Avila-Bront, Ross Edel, and S. J. Sibener, *J. Phys. Chem. C* **120**, 8191-8197 (2016).
2. Atomically-resolved Oxidative Erosion and Ablation of Basal Plane HOPG Graphite Using Supersonic Beams of O<sub>2</sub> with Scanning Tunneling Microscopy Visualization, Ross Edel, Tim Grabnic, and S. J. Sibener, *J. Phys. Chem. C* **122**, 14706-14713 (2018).
3. Exploratory Direct Dynamics Simulations of <sup>3</sup>O<sub>2</sub> Reaction with Graphene at High Temperatures, Seenivasan Hariharan, Moumita Majumder, K. D. Gibson, S. J. Sibener, and William L. Hase, *J. Phys. Chem. C* **122**, 29368-29379 (2018).
4. Chemical Dynamics Simulations and Scattering Experiments for O<sub>2</sub> Collisions with Graphite, Moumita Majumder, K. D. Gibson, S. J. Sibener, and William L. Hase, *J. Phys. Chem. C* **122**, 16048-16059 (2018).
5. Sticking Probability of High-Energy Methane on Ice, Rebecca S. Thompson, Michelle R. Brann, and S. J. Sibener, manuscript in preparation.
6. (a) Separation of Isotopes in Space and Time by Gas-Surface Atomic Diffraction, Kevin J. Nihill, Jacob D. Graham, and S. J. Sibener, *Phys. Rev. Lett.* **119**, 176001/1-5 (2017). (b) APS Viewpoint: Atom Scattering Picks Out the Heavyweights, October 23, 2017, *Physics* **10**, 116. <https://physics.aps.org/articles/v10/116>.

# **Chemical Dynamics Simulations of Energy Transfer and Chemical Reaction in Collisions of $^3\text{O}_2$ with Graphite and of Gas-Phase Intermolecular Energy**

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Collisions of  $^3\text{O}_2$  with a graphite surface were simulated to study attributes of energy transfer in ablation. The simulation results were compared with experiments by the Sibener Research Group, and performed versus collision energy, incident polar angle, and surface temperature. For higher collisional energies of 7.4 and 15 kcal/mol, direct scattering of  $^3\text{O}_2$  from the surface dominates. However, for the lowest collision energy, conventional physisorption/desorption and trapping on the surface dominate. For all the scattering conditions considered experimentally, the relationship between the average final translational energy and average scattering angle for the  $\text{O}_2$  molecules found from the simulations is in excellent agreement with experiment. This experimental validation of simulation is important as it indicates that collisional energy-transfer predictions for this system can be reliably used in assessing interfacial energy flow in a variety of technological applications, including high-performance flight systems.

Direct chemical dynamics simulations were performed at high temperatures of reaction between  $^3\text{O}_2$  and graphene containing varied number of defects. Collisions on graphene with one, two, three, and four vacancies (1C-, 2C-, 3C-, and 4C-vacant graphene) showed no reaction. On the other hand,  $^3\text{O}_2$  dissociative chemisorption was observed for collisions on four- (with a different morphology), five- and six-vacant graphene (4C-2-, 5C- and 6C-vacant graphene). The enhanced reactivity with collision energy agrees with experiments by the Sibener Research Group.

Ion are important for plasmas around fast moving vehicles in the lower atmosphere. To assist in studies by the Viggiano and Troe research groups of ion-molecule kinetics, energy transfer dynamics was simulated for collisions of He and  $\text{N}_2$  with the propylbenzene cation. If time permits these simulation results will be presented, along with a study of intermolecular energy transfer in a mixed bath.

## Antenna-Reactors for Plasmonic Photocatalysis

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Metals can support surface plasmons, the collective oscillations of their conduction electrons. The nonradiative decay of surface plasmons results in the generation of hot electrons and holes within the metal; charge transfer of these hot carriers between the metal and adsorbate molecules can induce chemical transformations. Processes such as carrier-induced desorption can also be important in plasmonic photocatalytic processes. Since metallic nanoparticles provide direct optical excitation of surface plasmons and the ability to tune the plasmon energies through control of nanoparticle geometry, they are ideal structures for the controlled generation of hot carriers for photocatalysis.

We have applied this discovery to design a new type of photocatalyst using a modular approach, combining a metallic nanoparticle with a good plasmonic response as an “antenna”, coupled to a catalytically active but poorly optically absorbing metal nanoparticle, as a “reactor”, situated within the antenna nanoparticle’s fringing field. We have demonstrated this “antenna-reactor” concept to control the reactivity of the catalytic “reactor” particle, as well as control the selectivity of chemical reaction outcomes. We have also examined ways to distinguish the role of hot carrier-induced processes from thermal effects in plasmonic photocatalysis, and have shown how illumination can effectively lower the reaction barrier, changing the rate-limiting step in chemical reactions. [1-10]

\*with co-authors Emily A. Carter, Peter Nordlander, Philip Christopher, Henry Everitt, and respective research groups.

1. Hossein Robatjazi et al., “Plasmon-induced selective CO<sub>2</sub> conversion on earth-abundant Al-Cu<sub>2</sub>O antenna-reactor nanoparticles”, *Nature Communications* 8, 27 (2017).
2. Kun Li et al., “Balancing near-field enhancement, absorption, and scattering for effective antenna-reactor plasmonic photocatalysis”, *Nano Letters* 17, 3710-7 (2017).
3. Dayne F. Swearer et al., “Transition Metal Decorated Aluminum Nanocrystals”, *ACS Nano* 11, 10281-10288 (2017).
4. Dayne F. Swearer et al., “Plasmonic Photocatalysis with Aluminum Nanocrystals Probed by Terahertz Rotational Spectroscopy”, *ACS Photonics* 5, 3097–3106 (2018).
5. Linan Zhou et al., “Quantifying Hot carrier and Thermal Contributions in Plasmonic Photocatalysis”, *Science* 362, 69–72 (2018).
6. Hossein Robatjazi et al., “Metal-organic frameworks tailor the properties of aluminum nanocrystals”, *Science Advances* 5, Eaav5340 (2019).
7. Linan Zhou et al., “Light-driven methane dry reforming with single atomic site antenna-reactor plasmonic photocatalysts”, in revision.
8. Dayne Swearer et al., “Controlling N<sub>2</sub>O Decomposition Pathways by Antenna-Reactor Photocatalyst Design”, submitted.
9. Minghe Lou et al., “Quantitative Analysis of Gas Phase Molecular Constituents Using Frequency-modulated Rotational Spectroscopy”, *Reviews of Scientific Instruments*, submitted.
10. Lin Yuan et al., “Photocatalytic Hydrogenation of Graphene using Pd Nanocones”, submitted.

## Molecular-orbital-based machine learning for electronic structure

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Recent interest in the use of machine learning (ML) for electronic structure has focused on models that are formulated in terms of atom- and geometry-specific features, such as atom-types and bonding connectivities. The advantage of this approach is that it can yield excellent accuracy with computational cost that is comparable to classical force fields. However, a disadvantage of this approach is that building a ML model to describe a diverse set of elements and chemistries, such as those of interest for AFOSR applications to alkali metal tetrahydroborate materials for high-hydrogen-content fuels and propellants, requires training with respect to a number of features that grows quickly with the number of atom- and bond-types, and also requires vast amounts of reference data for the selection and training of those features; these issues have hindered the degree of chemical transferability of existing ML models for electronic structure.

In the presented work [1,2], we focus on the goal of using ML to describe the post-Hartree-Fock (HF) correlation energy. Assuming willingness to incur the cost of a HF self-consistent field (SCF) calculation, we aim to describe the correlation energy associated with perturbation theory, coupled-cluster theory, or other post-HF methods. Our approach focuses on training not with respect to atom-based features, but instead using features based on the HF molecular orbitals, which have no explicit dependence on the underlying atom-types and may thus be expected to provide greater chemical transferability. Indeed, numerical results indicate that molecular-orbital-based machine learning (MOB-ML) yields striking accuracy and transferability across chemical systems at low computational cost.

[1] "Transferability in machine learning for electronic structure via the molecular orbital basis." M. Welborn, L. Cheng, and T. F. Miller III, *J. Chem. Theory Comput.*, 14, 4772 (2018).

[2] "A universal density matrix functional from molecular orbital-based machine learning: Transferability across organic molecules." L. Cheng, M. Welborn, A. S. Christensen, and T. F. Miller III, *J. Chem. Phys.*, 150, 131103 (2019).

## Electronic Structure and Nonadiabatic Dynamics for Reactions Near Surfaces and Gas-Metal Scattering

Joseph Subotnik, University of Pennsylvania

In this talk, I will go over some of the primary steps that we have taken towards a comprehensive, but accessible, framework for modeling processes at metal surface, where the applicability of the Born-Oppenheimer approximation is very unclear. I will highlight both (i) our work in dynamics which has already resulted a new and powerful surface hopping framework for quantifying electron transfer as well as (ii) our work in electronic structure as far as calculating the electronic friction tensor which is still in progress (but which has the potential to open up new ab initio approaches for modeling complicated electron transfer processes). Finally, I will highlight a series of open questions, with both practical and theoretical value for the molecular dynamics community.

## Toward Ab Initio Molecular Dynamics on Many Electronic States

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Ab initio molecular dynamics methods enable the simulation of chemical reactions without prior knowledge of the potential energy surface or reaction coordinate. Many methods exist for modeling dynamics on the ground electronic state or on a few low-lying excited electronic states, but most of these become impractical for systems with dense manifolds of electronic states, such as those that arise upon high energy excitation. Ehrenfest molecular dynamics, on the other hand, does not require explicit knowledge of the electronic eigenspectrum, and therefore is a practical tool for modeling dynamics on many states. However, Ehrenfest suffers from well-known issues with overcoherence. We propose a novel variant of Ehrenfest molecular dynamics that incorporates decoherence. This method is based on two key ideas. First, decoherence times are inherently state-pairwise quantities, and must be treated as such to achieve accurate simulation of dynamics on many electronic states. Second, the history of the electronic wave function can be used to compute approximate eigenstates, so that the full eigenspectrum of the electronic Hamiltonian need not be computed. We will demonstrate the accuracy of this method by application to several model potentials. To provide on-the-fly electronic structure calculations for our simulations, we have developed graphics processing unit accelerated time-dependent complete active space configuration interaction (TD-CASCI) and multireference configuration interaction singles (TD-MRCIS) tools. Akin to time-independent direct configuration interaction methods, our algorithm does not require formation or storage of any data structures with the full dimension of the Hamiltonian, enabling the use of large configuration spaces. These tools have been applied to predict electronic dynamics in large, strongly correlated molecules (up to decacene;  $C_{42}H_{24}$ ).



# Modular Path Integral Methodology for Quantum Dynamics of Extended Systems

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Feynman's path integral formulation of quantum dynamics offers an attractive, fully quantum mechanical alternative to the traditional Schrödinger approach which does not require evaluation and storage of multidimensional wavefunctions. Unfortunately, the number of terms required to converge the path sum appears astronomical.

By taking advantage of the spatial locality of interactions (spin-spin, bond stretching/bending/torsional or exciton coupling) characterizing many extended systems (spin arrays, long organic molecules or molecular aggregates), Feynman's path sum can be disentangled and evaluated via sequential linking of the quantum paths representing adjacent "modules". The modular decomposition of the path integral (MPI) circumvents the exponential scaling of conventional quantum mechanical methods without introducing any approximations, and leads to a robust methodology characterized by linear or sublinear scaling with system size. Thus, the MPI decomposition offers a highly accurate and versatile approach to many processes of interest, including intramolecular energy flow, exciton-vibration dynamics and quantum phase transitions.

The MPI methodology for Frenkel exciton dynamics will be described in detail, with applications to poly(p-phenylene) and poly(p-phenylene-vinylene).

## Plume Chemistry in the Space Environment

Dr. Christopher Annesley

Thruster plumes undergo a series of reactions as they propagate through the space environment. We are conducting a series of investigations to better understand these changes to the chemical makeup of the plume. The primary method of chemical change we are studying is the effect of UV and VUV light. Water fluorescence from photodissociation after irradiation by Lyman- $\alpha$  has been a primary target in the laboratory. We have shown that water has a lower fluorescent yield than anticipated by previous Rydberg tagging techniques. This is due to the Rydberg tagging experiments detecting all OH(A) population, including a significant fraction that is not fluorescent due to being predissociative, therefore not as emissive. Also, by conducting this study with room temperature emission data, jet cooled emission data and a thorough evaluation of the literature, we have shown that there is a temperature dependence to the quantum yield of fluorescence after excitation by Lyman- $\alpha$  where molecular beam conditions are about 15% more fluorescent. (J. Phys. Chem. A 2018, 122, 5602) Among modern thruster designs, fluorocarbon fuels are finding use in pulsed plasma and cold gas thrusters. Their radical production in the space environment and eventual fluorescence is attractive for possible detection. We have shown that fluorescent products, CF<sub>2</sub> and CF, are produced from various fluorocarbon molecules by an electric discharge, and can be detected by laser induced fluorescence.

In order to improve electrospray thruster plume models, a better understanding the decomposition of ionic liquid clusters is needed. Our work using CID on alkylammonium and alkylhydrazinium nitrate clusters has shown that different hydrogen transfers can take place, creating a greater variety of chemical species in the electrospray thruster plume than expected. The products of an IL cluster dissociation was expected to be dominated by ion pair loss, but our work shows that the dissociation products includes significant production of nitric acid as well as ammonia or hydrazine based molecules. (J. Phys. Chem. A 2018, 122, 1960, ) Additionally, our work on alkylammoniums shows that cluster size affects the ratio of the loss channels. Here, we have shown that larger clusters will become dominated by ion pair loss. (cite) This work is being followed up with ion-trap based thermal dissociation experiments of various ionic liquid clusters.

Ionic liquid ion pairs provide an important testbed to begin to understand the decomposition of ionic liquids in the space environment upon irradiation with ultraviolet photons as would be provided by the sun. To this end, we have expanded our previous work on multiphoton photoionization of ionic liquid ion pairs (J. Phys. Chem. A 2013, 117, 12419) into multiple single photon steps. This allows us to better recover true absorption spectra of ionic liquid ion pairs. This spectrum is now true representation of the photodissociation process by removing any distortions caused by scanning the ionization photon at the same time. This work shows that the photodissociation-ionization two-laser spectra create a faithful reproduction of high quality literature spectra of common ionic liquids. Further, this work provides significant confidence that the ion pairs dissociate through electron transfer, and separate into the neutral radical species. (Booth, Annesley In Preparation) Additionally, we are able to obtain the onset wavelengths of the photodissociations and have determined the IPs of the neutralized-cation radicals. Specifically, we have determined that 1-ethyl-3-methylimidazolium radical has an IP of  $3.95 \pm 0.10$ . This shows that the solar photodissociation and ionization processes will be important for how the plume evolves in the space environment, and allow for its modeling.