

Nanochemical Strategies for Propulsion Enhancement

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Hypersonic flight will require substantial cooling of engine and other vehicle components by the fuel,¹⁻⁵ exceeding the amount of cooling possible from just the fuel heat capacity. Substantial additional cooling can be achieved by using thermal energy absorbed by the fuel to drive endothermic reactions, such as dehydrogenation and cracking. Not only do such reactions absorb heat, but the heat is stored as changes in the fuel composition, adding to the energy release in subsequent combustion. The difficulty is that thermal reactions tend to form coke precursors such as alkynes and aromatics, leading to carbon deposition and eventual fuel system clogging. The authors listed above are a team focusing on developing novel strategies for using catalysts to enhance endothermic reactions at lower temperatures and to drive desired reactions selectively – both tending to reduce coking tendency.

After a brief overview of the team's work, this talk will focus on recent fundamental work by the groups of Alexandrova and Anderson seeking to understand the effects of boron doping to modify the selectivity and stability of Pt_n/alumina and Pt_n/SiO₂ model catalysts. Experimentally, boron is added to size-selected Pt_n catalysts by exposure to diborane, leaving boron selectively bound to the Pt clusters. The presence of boron results in substantial reduction in the binding energy of ethylene to the platinum, which is desirable from the perspective of preventing production of alkynes, which go on to form coke with high probability. As expected, boron doping also reduces the reactivity toward dehydrogenation. The effects of Pt_n size are significant. A variety of chemical, scattering, and spectroscopic methods are used to probe the nature of the boron-Pt binding, and the distributions of binding sites available for probe molecules such as ethylene and CO. DFT calculations by the Alexandrova group are focused on understanding the structures and energetics for Pt_n deposited on alumina and other supports, and the effects of boron doping. They show that boron tends to act as an anchor for the Pt particles, and also modifies their affinities for carbon. The calculations explore the thermally accessible range structures that should be present under high temperature reaction conditions, and the mechanisms for diborane decomposition on Pt.

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Theoretical studies of nanocluster formation

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Abstract

In support of ongoing Superfluid Helium Droplet Assembly (SHeDA) experiments at AFRL/RWME (PI Mike Lindsay, Eglin AFB) targeting the synthesis and characterization of novel core-shell nanoclusters, high level quantum chemical calculations have been performed to predict the structures, stabilities, and reaction pathways of the atomic stepwise formation of these systems. Presented here are modelling efforts to further understand the chemical nature of such systems via electronic structure methods, specifically structures and energetics involved in the formation of Cu/Mg core-shell nanoclusters and interactions at the Cu-Mg interface. Recent theoretical efforts have focused on exploring an intriguing result from helium droplet experiments in which copper appears to displace the magnesium at the core of a composite cluster, despite magnesium being the initially condensed species within the droplet. DFT methods (B3PW91) are employed using a hybrid basis set, in which a core-valence polarized basis set (aug-cc-p ω CVTZ) is used for magnesium and a comparable pseudo-potential basis set (aug-cc-pVTZ-PP) for copper. Furthermore, the potential energy surfaces of SiAl_n cluster formation via stepwise atomic addition reactions (SiAl_n + Al \rightarrow SiAl_{n+1}) have been computed using single reference (ZAPT) and multireference (MRMP2) second order perturbation theory methods in combination with the augmented correlation-consistent polarized valence triple zeta basis set (aug-cc-pVTZ.) The objective of these computations is to determine if reaction barriers to the stepwise formation of SiAl_n clusters are present, which could inhibit the formation of these clusters under the extremely low temperatures present within the helium droplet environment.

Toward the Development of Aluminum Cluster-Containing Materials for Propulsion Applications

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Results will be presented from our studies of several topics. (1) By interacting aluminum hydride cluster anions with a variety of different ligands in a collision cell, we have prepared several low oxidation state, ligated aluminum cluster anions, recorded their mass spectra, measured their mass-selected photoelectron spectra, and in conjunction with calculations extracted their geometric structures. (2) We have found that the Al_3H_8 moiety within $\text{Li}_2\text{Al}_3\text{H}_8$ forms an aluminum-to-aluminum chain, and that it also mimics the propane molecule. (3) We have prepared and characterized the tetra-coordinated aluminum cluster anion, $\text{AlCp}^*\text{ClH}_2^-$, which like other tetra-coordinated aluminum anions, may be promising as an anionic component of ionic liquids. (4) We have studied CO_2 activation and hydrogenation by PtH_n^- . (5) We have shown that PdH_3^- consists of a PdH^- moiety, whose Pd end is η^2 ligated by a H_2 molecule. These and other topics from our AFOSR-related work will be discussed.

Probing Pyrolysis in the Condensed Phase: One and Two Component Fluid Compositions

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This talk will cover our most recent efforts to probe pyrolysis reactions in model fluids using Suzie-Q—our supersonic molecular beam quadrupole mass spectrometer. The instrument consists of a home-designed high-temperature, high-pressure reactor configured with a 10 μm hole for fluid expansion and formation of a molecular beam. The reactor can be actively heated in a controlled manner up to ~ 1000 $^{\circ}\text{C}$, and the pressure maintained at a constant value up to ~ 1000 psi. The fluid that expands from the reactor into a first stage vacuum chamber is skimmed to create a molecular beam, which then is ionized and sampled via a quadrupole mass spectrometer. The mass spectral data obtained is viewed as a representation of the contents of the reactor at a given temperature and pressure. By ramping the temperature of the reactor continuously higher, we can observe the process of pyrolysis impacting the molecules making up the fluid. Data for one-component fluids (hexane, benzene, and toluene) have been collected in detail and is used to represent baseline behaviors for perturbation experiments. Two-component fluids consisting of hexane-benzene, hexane-toluene, and toluene-benzene, have been studied to examine the sensitivity of the pyrolysis process to bimolecular interactions that are present in condensed phase media (supercritical fluids). The data will be discussed within the context of solute-solvent interaction and the presence of a solvent shell.

Mechanistic Insights into CO₂ Reduction on Semiconductor Photoelectrodes

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Someday the world's liquid fuels will come from sustainable sources and low-energy processing. We are far from that day. While that fact is unfortunate, it opens up exciting opportunities for researchers from many different fields to work together to realize that vision. I will report on some of my research group's contributions toward this goal as manifested within a recently concluded DoD-MURI project (AFOSR Award No. FA9550-10-1-0572). Within this MURI project, we worked jointly with experimentalists to understand both electrochemical and photoelectrochemical reduction of carbon dioxide to fuel precursors. Because of time constraints, the talk today will only cover the latter effort. (For those interested in our joint work with the Kubiak and Nilsson groups clarifying mechanisms behind homogenous electrochemical reduction of CO₂ by Mn and Re complexes, please see Ref. 1.) Our photoelectrochemical studies were inspired by observations that illuminating semiconductor electrodes (first GaP,² then CdTe³ and CuInS₂⁴) with visible light in the presence of an aromatic amine co-catalyst in acidified aqueous solution selectively turns CO₂ into methanol, albeit at very poor overall efficiencies. The selectivity towards methanol is not understood nor is the low efficiency. It seemed clear that revealing aspects of the mechanism at the atomic scale could help to determine the origins of selectivity and low activity, with the hope that such understanding would point the way toward improving activity while retaining selectivity. We therefore embarked on a series of first-principles quantum mechanics calculations using both periodic slab and embedded cluster models to understand the roles of the semiconductor and the co-catalyst, the nature of the electrode/electrolyte interface, and the thermodynamics and kinetics associated with various potential photoelectrochemical catalytic pathways. This talk will briefly summarize our past work in this area⁵ as well as present our latest unpublished work that, e.g., explains observed differences in activity for different electrode surfaces as well as presenting a new possible mechanism for the catalysis observed.

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Impact of surface chemistry of semiconductor nanocrystals on their photophysics and photochemistry

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Semiconductor nanocrystals are remarkably tunable light absorbers that, when coupled with redox catalysts, can drive multi-electron photochemical redox reactions. Excited state dynamics of nanocrystals have a profound impact on the overall photochemical reactions. This presentation will focus on excited state processes with direct relevance to photochemistry.

Surface-capping ligands play a governing role in coupling of nanocrystals with redox catalysts. Ultra-short surface capping ligands, such as S^{2-} , Se^{2-} , and Te^{2-} strongly impact both the electronic structure and the excited state relaxation dynamics. While they enable faster charge transfer than organic ligands, they also can dramatically decrease excited state lifetimes, resulting in competing effects on efficiency of charge transfer. In case of S^{2-} in particular, the enhancement of electron transfer rate is a stronger effect than lifetime shortening, resulting in orders of magnitude higher electron transfer rates when compared to organic ligands and, consequently, enhanced rates of photochemical H_2 generation.

Photochemical oxidation driven by photoexcited holes in nanocrystals is complicated by the fact that hole trapping on the nanocrystal surfaces can be remarkably fast and efficient. As a result, trapped, rather than delocalized, holes are often the photochemically active carriers in nanocrystals. This presentation will address the dynamics of the trapped holes and their relevance to oxidation photochemistry.

Plasmon-induced Hot Carrier 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. 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 recently shown that room temperature dissociation of H₂ at Au nanoparticle surfaces- an “impossible reaction”- can be driven by hot electron injection into the LUMO level of the molecule. [1-3]

In a device geometry where we were able to distinguish between “hot” carriers due to plasmon decay and “cold” carriers resulting from direct excitation of electrons, we found that the generation rate of hot carriers is proportional to the local electromagnetic field within the plasmon-excited metal.[4] 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.[5] We will show how this “antenna-reactor” concept can be realized to control the reactivity of the catalytic “reactor” particle, as well as control the selectivity of chemical reaction outcomes. When the antenna-reactor complexes are fabricated as size-controlled, well-oriented structures, they reveal a different behavior for hot carriers and carriers generated by interband transitions in the antenna metal.

*with co-authors Emily A. Carter, Peter Nordlander, and respective research groups.

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Dynamics of Electron Emission into Water

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Electrons emitted into water have the ability to induce a range of novel chemical transformations. The formation of solvated electrons is also accompanied by the formation of H atoms, O_2^- (superoxide radical), OH, and other high-energy reactive species. We have been investigating alternative routes to emission of electrons into water in the “pre-plasma” regime as an energy-efficient way to produce highly reactive species in water. Two routes have been investigated. First, we can generate solvated electrons by direct electron emission from diamond’s conduction band into electrolyte solutions using nitrogen-doped diamond thin films. A second approach has led to the creation of a novel three-terminal device loosely described as a “water transistor”. In this device, electrons can be emitted directly into water at variable energies. Preliminary experiments have been performed primarily by examining formation of hydroxyl radicals using APF (aminophenylfluorescein), which converts to fluorescein in the presence of OH. Our experiments thus far show clear formation of hydroxyl radicals, demonstrating proof-of-concept of the water transistor. Other modifications are being made to this structure to improve its performance and to extend it to the creation of other reaction products. This talk will summarize our research to date and point to new directions for creating reactive species by direct electron ejection into aqueous solutions.

Nonadiabatic Dynamics of Photoinduced Proton-Coupled Electron Transfer

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Photoinduced proton-coupled electron transfer (PCET) plays an essential role in a wide range of energy conversion processes. Experiments on a phenol-amine complex in solution have provided evidence of an electron-proton transfer (EPT) excited state characterized by both intramolecular electron transfer and proton transfer from the phenol to the amine. Quantum mechanical/molecular mechanical nonadiabatic dynamics simulations were used to investigate the relaxation pathways following photoexcitation of this complex. The potential energy surface was generated on-the-fly with a semiempirical multiconfigurational method for the solute and a molecular mechanical force field for the explicit solvent molecules. The transferring hydrogen nucleus was represented as a quantum mechanical wavefunction, and surface hopping trajectories were propagated on the adiabatic electron-proton vibronic surfaces. The simulated relaxation times are qualitatively consistent with experimental measurements. The simulations illustrate that the proton transfers from the phenol to the amine on the EPT state and then transfers back to the phenol rapidly upon decay to the ground state. These calculations augment the original interpretation of the experimental data by providing evidence of proton transfer on the EPT state prior to decay to the ground state. The roles of solvent dynamics and vibrational relaxation in facilitating both proton transfer and decay to the ground state are also elucidated. The hydrogen/deuterium isotope effect is predicted to be negligible, indicating that the absence of an isotope effect does not imply the absence of proton transfer in these processes. The fundamental insights obtained from these simulations are relevant to other photoinduced PCET processes.

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Structure and Reactivity of Transient Species in Water Splitting and CO₂ Reduction Using Cryogenic Ion Spectroscopy

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We describe a powerful new way to study capture and structurally characterize a CO₂ molecule in the active site of a homogeneous reduction catalyst. These results were obtained with a custom built instrument that exploits electrospray ionization as a way to extract catalysts from solution into the gas phase, where the key reactions are carried out in cryogenically cooled ion traps. The structures of reaction intermediates are determined using vibrational predissociation of weakly bound mass “tags” such as rare gases, CO₂ or H₂. In this approach, we first expose the highly reactive metal center by fragmenting a stable, bimetallic Ni(I) precursor compound after extracting it into the gas phase. The CO₂ substrate molecule is then coordinated directly to the metal atom at low pressure by condensation in a temperature-controlled ion trap. The critical role of the Ni(I) oxidation state was established by carrying out measurements with both Ni(I) and Ni(II) in the same ligand environment. The degree of activation was determined by the shift in the vibrational bands of the attached CO₂ molecule, which reveal the intramolecular distortion and excess charge on the substrate. Furthermore, local attachment motif to the Ni center was found to be an asymmetric, η²-C,O type of coordination. We will also discuss studies that are underway designed to characterize the hydride addition step in a diiron system derived from the nitrogenase enzyme. Both these studies are carried out in close collaboration with synthesis groups (Krüger in Germany and Holland at Yale). Advances in instrument performance are a central theme of this program, and we therefore also carried out several experiments on model systems to establish the accuracy with which we can control the temperature of the reacting ions as well as guide theoretical innovations required to analyze the spectroscopic data obtained by the new methods.

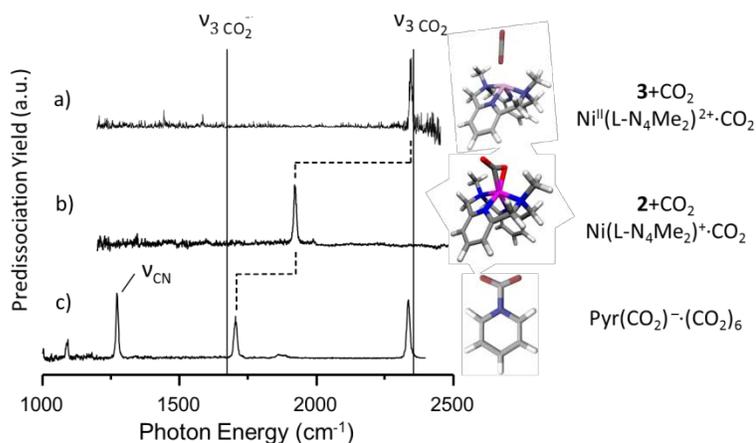


Figure: CO₂ predissociation spectra of a) the Ni(II) species, b) the Ni(I) species and c) a fully activated CO₂ on pyridine. The vertical lines indicate the positions of the asymmetric stretches for the neutral and radical anion of CO₂.¹

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Can Vibronic Resonances Control Energy Transfer?

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ABSTRACT

Photosynthetic antennas have the highest known quantum efficiency for energy transfer. Recently, we made a theoretical discovery that electronic energy transfer in some photosynthetic antenna proteins exploits non-adiabatic dynamics arising from vibrational-electronic resonances in which the adiabatic electronic energy gap between donor and acceptor matches the frequency of a vibrational mode that is weakly distorted by electronic excitation. This suggests vibrational-electronic resonance might be exploited to control energy transfer pathways in a multi-chromophore system by tuning the electronic energies for selective resonance between the donor and a desired acceptor. In photosynthesis, the protein tunes the electronic excitation energies of otherwise identical donor and acceptor pigments so that their common vibrational frequency matches their electronic energy gap. We have developed a framework for vibrational-electronic resonant energy transfer that is applicable to quantum confined materials with size-tunable electronic excitation energies; in these materials, the vibrational mode frequencies also change slightly with size. Such differences can actually promote energy transfer by prolonging the time that energy resides on the target acceptor. Vibrational-electronic resonance can also synchronize delivery of electronic excitations to the target for all input polarizations. Together, these might allow a simple excitation trapping mechanism that works on a single timescale. Finally, calculations indicate that selective tuning of non-adiabatic vibrational-electronic resonance can be used to direct energy transfer pathways so that they bypass one equally coupled chromophore in favor of another even under challenging conditions of similar excitation energies. The prospects for controlling energy transfer pathways in quantum confined materials seem bright.

Ultrafast Photoinduced Interfacial Proton-Coupled Electron Transfer

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Photoinduced proton-coupled electron transfer (PCET) is a fundamental process essential to many catalytic reactions, including electro- and photoelectron- catalytic CO₂ reduction to chemical fuels. Compared to its solution counterpart, interfacial PCET is much less well understood theoretically and more difficult to study experimentally. This talk will report our recent progresses on two selected projects that aim to advance understanding of these interfacial PCET through combined experimental and theoretical efforts.

In the first project, we study interfacial PCET process in CdSe quantum dot-bipyridine complexes, a mimic for interfacial PCET on semiconductor electrode surfaces. By transient absorption spectroscopy, we show that excitation of quantum dots leads to ultrafast generation of the doubly protonated bipyridine radical with transfer of both protons and electrons to bipyridine. Through studies of the dependence of PCET rate on isotope substitution, pH and bPYD concentration, the radical formation mechanism was identified to be a sequential interfacial electron and proton transfer (ET/PT) process with a rate limiting pH independent electron transfer step. Theoretical studies of the adsorption of [bPYDH]⁺ and methylviologen on QD surfaces revealed important effects of hydrogen bonding with the capping ligand (3-mercaptopropionic acid) on binding geometry and interfacial PCET. The mechanism of bPYD photo-reduction reported in this work may provide useful insights into the catalytic roles of pyridine and pyridine derivatives in the electrochemical and photoelectrochemical reduction of CO₂

In the second project, we develop in situ time-resolved vibrational sum-frequency generation (SFG) spectroscopy as a surface selective probe for a (sub)monolayer of adsorbates (molecular CO₂ reduction catalysts) on metal and semiconductor electrode surfaces. Our initial effort focus on strategies for covalent binding of molecular catalysts on electrode surfaces, characterization and control of their binding geometry, and investigation of interfacial solvation, energy relaxation and PCET dynamics.

Cluster Films by Helium Droplet Mediated Cluster Assembly: Growth and Characterization

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Over the past few years our laboratory has been investigating the use of the liquid helium droplet beam technique to generate of single component and composite nanoclusters at low temperature, deposit the clusters onto various substrates, and then investigate the stability, chemical, and physical properties of the subsequent cluster-based material. In this talk we discuss our progress in understanding the environment of the clusters prior to, during, and after collision of the doped droplet with a surface. To do this, we fabricate a range of clusters of varying sizes, examine them prior to deposition using mass spectrometry, then examine the properties of the resulting films using spectroscopic, conductivity, electron microscopy, and diffraction techniques. Materials to be discussed include pure magnesium, magnesium-perfluoropolyether composite, copper-magnesium core-shell, and gold nanoclusters.

Modeling Chemical Reactivity of Ionic Liquids in the Condensed Phase via Reactive Monte Carlo

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Previous work has demonstrated that many thermodynamic and transport properties of ionic liquids can be modeled accurately using condensed phase molecular dynamics and Monte Carlo simulations along with appropriately parameterized classical force fields. When reactivity is important, however, a quantum mechanical treatment is necessary. Because the solvation environment plays a major role in reactivity, simple gas phase models are inadequate. Given the very slow time scales associated with conformational motion in these liquids, a fully quantum mechanical treatment of reactivity in the liquid phase poses serious challenges. So-called “QM/MM” methods, where a portion of the system is treated quantum mechanically and the remaining part classically are promising, but this requires *a priori* knowledge of the quantum and classical regions of the system, which can be difficult to determine in liquid systems where reactions take place. Reactive force fields have also been considered, but again, time scale limitations pose serious problems for this method, as does the parameterization of the reactive potentials.

Here we describe the development and application of a reactive Monte Carlo (RxMC) method to seamlessly treat reactivity of ionic liquids in the condensed phase. In RxMC, ideal gas phase free energy differences between the reactants and products are obtained from thermophysical property tables (when the reaction is well studied) or by pre-computing them using highly accurate quantum mechanical methods (when the reaction is not well-studied). The condensed phase energetic interactions are modeled using classical potentials. Chemical “reactions” are modeled by transforming reactants into products (and vice versa) through stochastic moves. These reaction moves eliminate any activation barriers associated with transition states or molecular diffusion, thus achieving equilibrium concentrations in the condensed phase regardless of non-ideality or reaction rates.

We demonstrate the utility of the method for two systems. The first is the calculations of isotherms of CO₂ in ionic liquids designed to react with dissolved CO₂. To do this, we implement the RxMC method along with Gibbs ensemble Monte Carlo, so that reacted and dissolved CO₂ levels at a given pressure are self-consistently modeled. The second system we apply the method to is protic ionic liquids (PILs). PILs are a subset of ionic liquids that are prepared through the stoichiometric neutralization reaction of certain Brønsted acids and Brønsted bases. A key feature of PILs is that they have an available proton on the cation. The degree of dissociation of PILs is a major unknown of these materials. There is a correlation between proton transfer from the acid to the base and the pK_a difference between the acid and the base precursors, but these pK_a values are usually obtained from the aqueous phase, which are unreliable in the pure ionic liquid phase. Here we directly model the acid-base reaction in pure PILs using RxMC, and so estimate the degree of dissociation of these protic ionic liquids.

Velocity Map Photoelectron Imaging and Ultrafast Dynamics of Plasmonic Nanostructures

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The powerful combination of i) ultrafast lasers, ii) multiphoton photoemission, and iii) high numerical aperture in-vacuo objectives provides a remarkably flexible and sensitive experimental platform for exploring chemical physics of plasmonic materials on the nanoscale. This talk will provide an overview of recent progress in the group. 1) The first topic will be on exploiting novel high repetition rate (75 MHz) ultrafast OPO oscillators to probe plasmonic properties of isolated nanostructures via scanning photoemission imaging microscopy (SPIM). 2) Next, significant enhancement of these methods with velocity map imaging (VMI) of the ejected photoelectrons will be discussed, which provides detailed angle and energy resolved information on the optical, electronic, and Fermi level properties of single nanostructures. 3) Finally, we discuss very recent extensions of these capabilities to fs time resolved pump-probe measurements, which now provide information on fast relaxation dynamics and hot electron energy distributions in single plasmonic nanostructures of potential importance in photocatalysis applications.

Visible-Near IR Luminescence Resulting from Collisions of Xe Atoms at Relative Translational Energies in the 25–450 eV Range

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The Space Chemistry Lab has previously developed a Collisional Radiative Model (CRM) as a diagnostic tool for monitoring the performance characteristics of Xe-fueled Hall Effect thrusters (HET). This model employs emission excitation cross sections, determined in our lab, for chemi-luminescence resulting from collisions of the Xe^+ and Xe^{2+} ions generated in the engines with un-ionized fuel. The cross section measurements utilize a beam–cell configuration in which a mass and energy selected ion beam is passed through the target gas cell and the luminescence from collisions in the cell is coupled into a spectrometer via a fiber optic. Collisions of Xe^+ and Xe in the energy range relevant to HET and Xe ion thruster operation are dominated by a long-range charge transfer process in which there is negligible momentum transfer resulting, both in our experiment and in thruster plumes, in Xe atoms at velocities comparable to the accelerated ions.

In the present study, we determined the chemi-luminescence cross sections derived from Xe + Xe collisions in the range of relative translational energies of 25–450 eV, which spans the relevant thruster operation conditions. The experiments employ a modified version of the above beam–cell arrangement that involves an additional gas cell “upstream” from the luminescence target gas cell, along the ion beam. In the first of the cells the efficient, long-range $\text{Xe}^+ + \text{Xe}$ charge transfer process is exploited to produce an intense beam of neutral Xe at the velocity of the ion beam. The unaffected portion of the ion beam, as well as the thermal ions resulting from charge transfer, is deflected from the beam line and the resulting neutral beam continues to the luminescence cell. These measurements address the prospect of thruster plume processes involving the high velocity neutral species produced in the long-range charge transfer events. The neutral–neutral interactions result in emission excitation cross sections that are a substantial fraction of the corresponding ion–neutral channels, and confirm that the process giving rise to luminescence in both instances involves hard-sphere collisions that access the repulsive walls of the respective diatomic potentials. The present results also suggest that ion–neutral luminescence excitation may not occur exclusively as part of a small impact parameter charge transfer event. Comparison of the neutral–neutral and ion–neutral emission excitation cross sections also reveal instances of different relative intensities among the various emitting states.

The current edition of the CRM comprises ion–neutral cross sections for processes resulting in emission in the Near-IR range, from ~820–980 nm. In the present effort we have extended the emission excitation cross section determination for the ion–neutral process into the visible region down to ~460 nm, and have obtained neutral–neutral cross sections through the same visible–near-IR range. These results will allow refinement of the CRM to include neutral–neutral processes.

Nonequilibrium Dissociation Model from Direct Molecular Simulation

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Within the high-temperature shock layer that surrounds a high-speed vehicle, air molecules undergo rapid rotational and vibrational excitation; ultimately dissociating into reactive atomic species that destroy the vehicle's heat shield. Dissociation rates at extreme temperatures are typically extrapolated from empirical relations based on experimental measurements at lower temperatures, leading to large model uncertainty. Only recently has computational chemistry been used as a tool to determine such reaction rates, and only thermally averaged rates have been computed. However, such high-speed flows are in strong thermochemical nonequilibrium where molecular internal energy distributions are non-Boltzmann.

Although Molecular Dynamics (MD) can accurately model such non-equilibrium, the MD method is intractable for dilute gases due to the large mean-collision-times and the large number of atoms present in a real flow field. This 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.

DMS simulations for nitrogen dissociation, using a PES developed in the Truhlar group at the University of Minnesota, will be presented. The first key finding is that non-Boltzmann effects, specifically the depletion of high v -states due to preferential dissociation, reduces the overall dissociation rate by approximately a factor of 5. The second key finding is that the vibrational excitation rate for N_2 - N_2 collisions is in excellent agreement with experimental data and existing models, however, the rate for N - N_2 collisions (for which no experimental data exists) is found to be 10x faster than current models. This is due to N - N_2 exchange collisions, which enable multi-quantum jumps in vibrational energy level and therefore rapid excitation. Such fast vibrational excitation repopulates the high- v tails of the vibrational energy distribution and indirectly leads to faster dissociation due to the presence of N atoms in the system. These results are consistent with limited experimental data for high-temperature shock-layer dissociation but provide a much more detailed understanding of the coupling between internal energy and dissociation. New models formulated from these results will also be presented.

Advanced Electronic Structure Methods for Heavy-Element Chemistry

Toru Shiozaki

Department of Chemistry, Northwestern University

In the first part of the talk, to demonstrate what can be done with the state of the art for heavy-element chemistry and to highlight what the outstanding challenges are, I will present our computational work on the chemical bonding and potential energy surfaces of SmO and SmO⁻. This work is in collaboration with some of the groups in the AFOSR program (Prof. Neumark and Dr. Viggiano). I will then present the development of new-generation quantum chemical methods for open-shell heavy-element chemistry, which aims to advance the state of the art. The emphasis will be placed on electron correlation theories with non-perturbative treatments of the spin-orbit interaction¹ and those for molecular properties of open-shell species (including analytical nuclear gradients for on-the-fly dynamics).² All of the methods have been implemented in the BAGEL program package, which is specifically designed for modern parallel computer hardware. Future directions will be discussed.

Reference:

1. T. Shiozaki and W. Mizukami, *J. Chem. Theory Comput.* **11**, 4733-4739 (2015), "Relativistic internally contracted multireference electron correlation methods"
2. M. K. MacLeod and T. Shiozaki, *J. Chem. Phys.* **142**, 051103 (2015), "Communication: Automatic code generation enables nuclear gradient computations for fully internally contracted multireference theory"
3. BAGEL, Brilliantly Advanced General Electronic-structure Library. <http://www.nubakery.org> under the GNU General Public License.

Chemical releases, transition metal kinetics, and fundamental ion chemistry

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An overview of work ongoing in the Air Force Research Laboratory plasma chemistry group will be presented with emphasis on two projects. The AF aims to develop a method of elevating electron density below the peak of the ionosphere. Recent efforts have focused on doing so via spontaneous chemi-ionization of lanthanide metal atoms with ambient atomic oxygen at approximately 200 km. Experiments from sounding rockets using samarium in 2013 and 2015 have demonstrated capability, but characterization of the resulting electron cloud differs significantly from AFRL model predictions. Investigation of the relevant ion chemistry in collaboration with the Armentrout and Heaven groups determined that the literature exothermicity of the chemi-ionization of samarium was overstated, indicating that product SmO^+ may readily undergo dissociative recombination with electrons. Subsequent modeling showed that this process could explain observations in the field experiments of both 10x lower than expected electron density and of physical separation of species emitting in the blue from those emitting in the red. These results prompted a search for alternatives to Sm for future field efforts. To that end, the chemi-ionization kinetics of numerous rare earth metals were measured in the laboratory using a flow tube apparatus; several metals were found to chemi-ionize with near unit efficiency, as compared to ~3% efficiency for Sm. These results have prompted additional efforts with groups within the AFOSR molecular dynamics program (Neumark, Shiozaki) to determine the emission spectra of lanthanide oxides and their cations.

Gas phase studies of metal cation reactions can provide targeted information on the mechanism of catalytic activity. Low-lying excited electronic states present in iron cation compounds complicate both experiment and theory, but also offer access to otherwise inaccessible reaction pathways. For example, the reaction of $\text{Fe}(\text{CO})^+ + \text{N}_2\text{O}$ samples a common intermediate with $\text{FeO}^+ + \text{CO}$. Analysis of the temperature dependent kinetics of these reactions combined with quantum chemical calculations and statistical modeling offers insight into the “two-state reactivity”, including the time scale of spin-surface crossing. Separately, $\text{Fe}(\text{CO})^+$ reacts efficiently at 300 K with O_2 to yield FeO^+ , indicating a low-energy mechanism to dissociate O_2 and oxidize CO all at a single metal atom site.

The laboratory also has continued interest in fundamental ion chemistry. Recent investigations involve previously unstudied types of processes including reaction of ions with unstable polyatomic radicals, electron attachment to unstable species, and mutual neutralization of atomic species. A brief summary of these results will be shown.

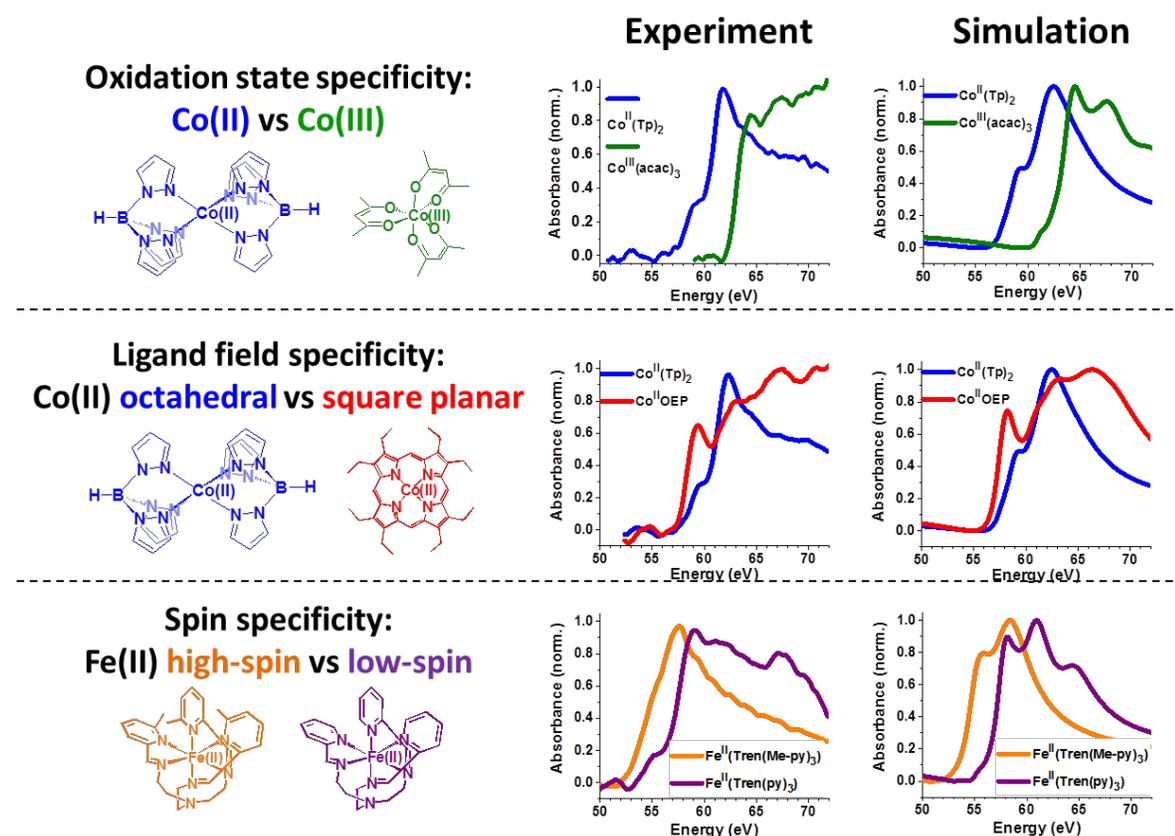
Title: A Surface Hopping Picture of Electrochemistry

Abstract: Electrochemistry is a very interesting but very complicated field of research. From an experimental point of view, the requirements for an electrochemical measurement are modest: a metal substrate, solvent with electrolytes, a reactive molecular species, and an applied voltage source. From a theoretical point of view, however, modeling electrochemical reactions is demanding: one must have a detailed understanding of *(i)* the nuclear motion at a surface, of *(ii)* the electronic dynamics within the metal substrate and within the adsorbed molecule, and of *(iii)* the electron-transfer dynamics between molecule and metal. Whereas in solution photoexcited molecules relax exclusively by exciting nuclear motion (yielding heat), at an electrochemical interface, by contrast, excited molecules can dissipate energy through either nuclear or electronic motion (in the metal). For this reason, computational progress has been slow, and there are few complete molecular models of electrochemical processes. In this talk, I will provide a very new perspective on electrochemistry -- a "surface hopping" picture -- that goes beyond Marcus theory and is applicable for inner, outer and photo-electrochemistry. I will also show how this perspective is very different from (and more general than) the usual approach for electrochemical dynamics based on so-called "electronic friction." Finally, after sketching how to derive dynamics, I will show how surface hopping can be used to simulate large-scale reactions.

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Tabletop M-edge XANES Spectroscopy of Molecular Transition Metal Complexes

High-harmonic extreme ultraviolet (XUV) spectroscopy has the potential to provide the elemental, oxidation-state, and spin-state specificity of core-level spectroscopy with the convenience and ultrafast time resolution of tabletop laser sources. We will show that M-edge spectroscopy of first-row transition metal complexes ($3p \rightarrow 3d$ excitation) is a sensitive probe of the electronic structure of molecular coordination complexes. Furthermore, this technique can be used to determine the relaxation dynamics of these molecules in the first few femtoseconds to nanoseconds after photoexcitation.

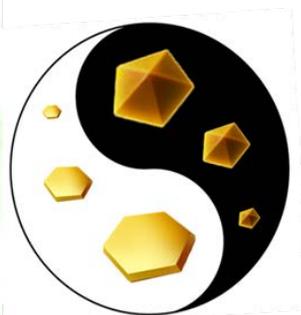
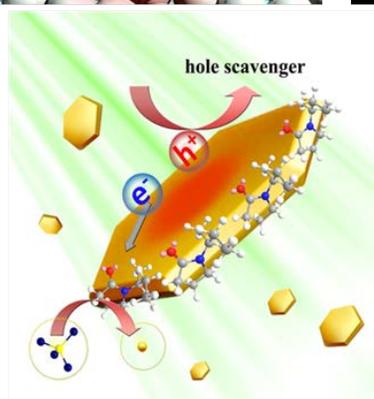
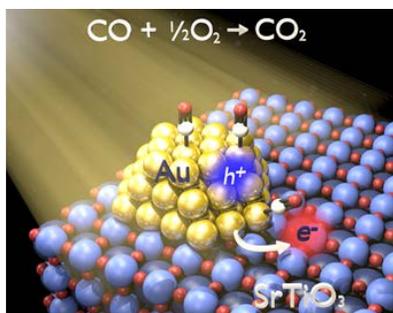
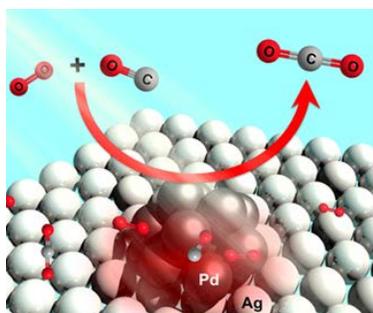


Elucidating the Specific Role of Metal SPR in Enhancing Surface Photochemistry

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Plasmonic metal nanoparticles (NPs) hold great promise as a means to dramatically improve the efficiency of solar energy conversion. Nevertheless, there is still no clear understanding of the exact mechanisms responsible for surface plasmon resonance (SPR)-enhanced photochemistry. Herein we carried out systematic studies to elucidate the specific role of the metal SPR in enhancing photocatalytic activity by examining SPR-induced photothermal effects and SPR-driven interfacial electron transfer (ET). We



demonstrated that a hybrid Pd/Ag nanostructure significantly boosts the carbon monoxide (CO) oxidation efficiency under low-power visible light irradiation and identified the Ag SPR-generated photothermal heating as the primary driving force. Meanwhile we showed that plasmon-mediated electron transfer (PMET) from the Au NPs to the strontium titanate

(SrTiO₃) support can be used to alter their electronic structures for improving CO oxidation activity. Furthermore, we illustrated the cooperative action of the metal SPR and surfactants in light-driven anisotropic growth of gold nanoprisms.

Improving the flow and measurement of energy transport in semiconducting carbon nanotube devices

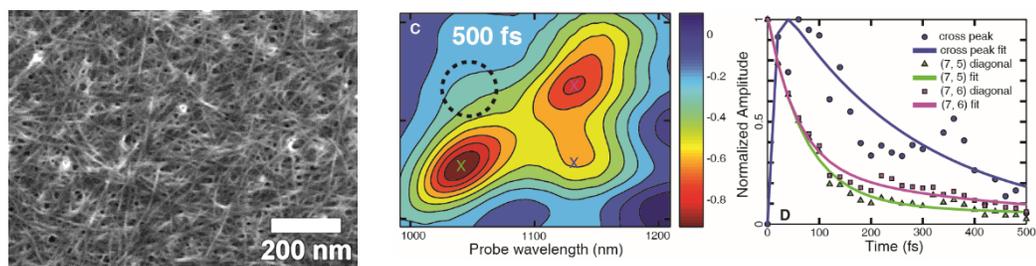
Martin T. Zanni, and Michael S. Arnold

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In this talk, we will present data showing sub-50 femtosecond energy transfer between semiconducting carbon nanotubes cast into thin films. In the last few years it has become possible to make films cast from purely semiconducting carbon nanotubes. These films are a new class of materials, because never before have macroscopic amounts of semiconducting carbon nanotube been purified from their metallic counterparts. These materials are exciting for applications in semiconductor electronics, because individual carbon nanotubes are well known to have very efficient energy transfer, which now might be utilized in devices. In this talk, we will present advances to a new variant of 2D optical spectroscopies, which we call 2D White-Light Spectroscopy, for time-resolving the energy transfer pathways in materials. We will also present data on films cast from bare nanotubes, in which we observe sub-50 fs transfer that rivals the intrinsic transfer rate of nanotubes. Moreover, energy transfer primarily occurs between parallel tubes, as expected for resonant energy transfer mechanisms. These results suggest that the photophysics and energy transfer properties of these thin films retain many of the most promising characteristics of carbon nanotubes that might be manipulated for new and improved devices.



(Left) Scanning Electron Microscope image of a mesoscale film made entirely from semiconducting carbon nanotubes. (Middle) 2D White-Light spectrum showing cross peaks that appear (Right) after only 30 fs, indicating ultrafast energy transport in the film.

Microdroplet Chemistry

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With AFOSR support, we have been studying chemical reactions in microdroplets and comparing the findings with the behavior of the same reaction in bulk solution. Our detection method has been a high-resolution mass spectrometer. Two different experimental setups are employed, one involving fusing together two streams of microdroplets (shown in Fig. 1, panel on the left), the other simply involving desorption electro spray ionization (shown in Fig. 1, panel on the right):

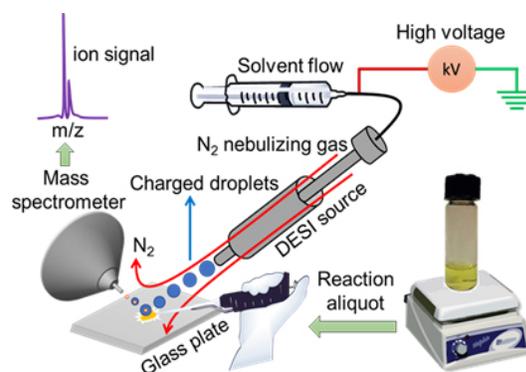
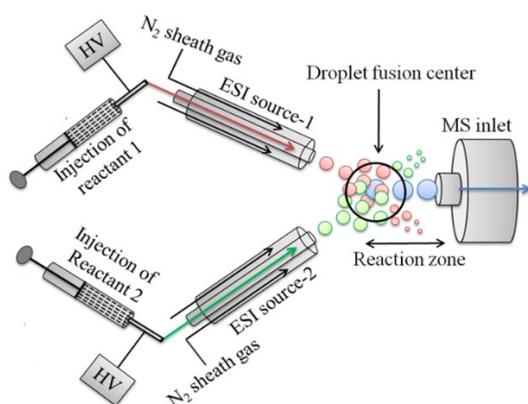


Figure 1. Two experimental setups used to investigate the chemistry occurring in microdroplets.



One significant advantage of investigating reactions in microdroplets is that this technique allows us to detect and identify fleeting intermediates in complex reactions. One example is our study of the conversion of C-H to C-Si bonds in methyl indole dissolved in tetrahydrofuran, catalyzed by potassium t-butoxide. Another special feature of microdroplet chemistry is that the rates of some reactions can be accelerated by a factor of 1000 or more. An example is the reduction of ascorbic acid by dichlorophenylindophenol. Some speculations will be presented to account for this marked rate enhancement.

Electron Dynamics in Super-Atom and Hybrid Semiconductors

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Traditionally, molecules and solids are built from atoms; this is the foundation for synthetic chemistry and materials science. The emergence of superatomic electronic properties in “artificial atoms” (AAs), clusters with atomic precision such as fullerenes and stoichiometric semiconductor nanocrystals, provides a new class of fundamental building units for the synthesis of molecules and solids. Assembling AAs into artificial molecules and solids allows the development of completely new families of materials whose physical and chemical properties derive from building blocks that are cluster extensions of the atomic periodic table. To realize this potential fully, the constituent “elements” must be defined at the atomic level of precision; control of these materials is obtained through management of the size and composition of these materials. Our efforts during the past year have been on the assembly of AAs into artificial molecules and two-dimensional (2D) solids. Using a variety of spectroscopic tools, we probe the electronic coupling between AA building blocks in both ground and excited states in time and energy domains. The important aspect of this project is that it enables us to target collective physical properties that are not a simple combination of the properties of the individual building blocks. In particular, the combination of hard and soft building blocks allows us to explore fundamentally new ways of achieving superior semiconductor properties. An excellent example comes from recent demonstrations of hybrid organic-inorganic perovskites. The room-temperature and solution synthesis of this class of hybrid materials means the unavoidable presence of a large density of defects. Yet, the materials behave in many ways as “defect-free” semiconductors, giving rise to exceptional optoelectronic properties. We find that the key to the success of this class of hybrid materials lies in the unique combination of hard and soft building blocks; the latter serves to protect charge carriers in the former via solvation or large polaron formation. Similar synergies may be designed into artificial semiconductors assembled from AA building blocks.