

**A Bath Model for Simulating Gas Phase Intermolecular Energy Transfer:
N₂ + C₁₀H₈ (Azulene), N₂ + C₆H₆, and a Mixed Bath + C₆H₆ Collisions**

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Chemical dynamics simulations are used to study relaxation of a vibrationally excited molecule in a collision bath. Energy transfer from the “hot” molecule is investigated versus bath density (pressure) and number of bath molecules. For the large bath limit there is no heating of the bath. As the hot molecule is relaxed, its average energy is determined versus time, i.e. $\langle E(t) \rangle$. For a large bath and low pressures, the simulations are in the fixed temperature, independent collision regime and the simulation results may be compared with gas phase experiments of collision energy transfer. The derivative $d[\langle E(t) \rangle]/dt$ divided by the collision frequency ω of the bath gives the average energy transferred from the hot molecule per collision $\langle \Delta E_c \rangle$. *Ab initio* calculations are performed to determine accurate intermolecular potentials for the bath molecules and the bath molecules interacting with the vibrationally excited molecule. Simulations of N₂ + C₁₀H₈, N₂ + C₆H₆, and N₂/C₆H₆ + C₆H₆ low pressure, gas phase collision energy transfer give results in excellent agreement with experiment. The latter simulation involves energy transfer for a mixed bath, which may be easily studied by our bath model. Energy transfer from the hot molecule to rotation and translation of the N₂ bath is in accord with the equipartition model, with no transfer to N₂ vibration. This research is part of a collaboration with Simon North, Diego Donzis, and Rodney Bowersox at Texas A&M University, supported by AFOSR.

Spectroscopic Studies of Imidazolium-based Ionic Liquids and their Deuterated Analogs

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Ionic liquids (ILs) have been shown to be extremely useful in areas ranging from chemical synthesis to energetic materials. Furthermore, ILs are thought to be a potential replacement for hydrazine as satellite propellants because a subset are hypergolic with nitric acid. While ILs are useful, however, there is a lack of understanding of the microscopic origins for their macroscopic properties (e.g. viscosity). An example of this is that [emim][tf2N] is three times less viscous than its methylated counterpart [emmim][tf2N] and there is some discord regarding the reason. We have investigated the molecular properties of [emim][tf2N] and its methylated and deuterated analogs using UV and IR spectroscopy in the gas phase. UV data show that the photophysics of [emmim][tf2N] is different than [emim][tf2N] in that there is a lack of evidence for the existence of a charge transfer (CT) state (as was seen in [emim][tf2N]). Upon deuteration, the IR spectrum of [emim][tf2n] undergoes major changes in the ring C-H stretching region and provides evidence for multiple conformations of the [emim][tf2N] ion pairs. In addition, we have investigated the effect that the alkyl side chain length has on the conformational space available to the ion pairs in imidazolium-based ILs. Examples of these ILs include [mmim][tf2n], where the ethyl side chain in [emim][tf2n] has been replaced by a methyl group, and [bmim][tf2n], where it has been replaced by a butyl group.

Abstract – AFOSR Molecular Dynamics Program Review 2016

Evaluation of the exothermicity of the chemi-ionization reactions of the lanthanides

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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. Initial trials with samarium did not meet pre-launch expectations and hence a reevaluation of the thermochemistry of this reaction was needed. Using a guided ion beam tandem mass spectrometer (GIBMS) at the University of Utah, we measured a precise value for the bond energy of SmO^+ as 5.73 ± 0.07 eV. Combined with the established Sm ionization energy (IE), this value indicates an exothermicity of CI of 0.08 ± 0.07 eV, ~ 0.2 eV smaller than previous determinations. The accuracy of this result was confirmed by independent measurements of IE(SmO) at Emory University, also about 0.2 eV higher than the literature value. This much lower exothermicity enables accurate modeling of the atmospheric Sm release experiments in the thermosphere. Continued work has focused on similar studies with gadolinium (Gd) and holmium (Ho). Studies of the reaction of Gd^+ with CO, GdO^+ with CO, and GdO^+ with Xe provide consistent thermochemistry with an average GdO^+ bond energy of 7.63 ± 0.12 eV, in agreement but more precise than literature values. Combined with IE(Gd), this demonstrates that the exothermicity of CI with Gd is 1.48 ± 0.12 eV. Unfortunately, Gd has a boiling point that is 1100 K higher than Sm, making it more difficult to vaporize. In contrast, Ho has a boiling point 700 K higher than Sm; however, the literature thermochemistry indicates that the exothermicity of CI is only 0.15 eV, making it marginally useful. In such a case, reassessment of the thermochemistry is imperative. Ongoing studies are evaluating the bond energy of HoO^+ and a reassessment of the CI exothermicity for this metal should be available at the time of the Annual Meeting.

Understanding Electron Dynamics in Mixed Metal Oxide Catalysts Showing High Selectivity for Photo-Electrochemical CO₂ Reduction to Acetate

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Abstract:

We have prepared a novel mixed transition metal oxide catalyst for photo-electrochemical CO₂ reduction. Electrochemical studies show that this catalyst displays selective photocurrent meaning that it is photoactive in CO₂-saturated aqueous electrolyte but produces no photocurrent in argon-purged electrolyte, indicating that charge transfer from the catalyst surface to CO₂ is strongly preferred over proton reduction. Reaction studies show that this photo-electrocatalyst is also highly efficient for C–C bond coupling, producing acetate from CO₂ with greater than 60% Faradaic efficiency. XPS and SEM/EDAX spectroscopy provide important insights into the mechanism of selectivity and efficiency in this catalyst system. To better understand the photo-physics of this material leading to highly selective charge transfer to CO₂ and subsequent C–C bond coupling, we are investigating this system using ultrafast soft x-ray transient absorption spectroscopy at the metal M edges of this mixed metal oxide system. This experiment, which utilizes a tabletop high harmonic generation soft x-ray light source with femtosecond time resolution, promises to reveal the element-specific electron dynamics leading to efficient charge separation and injection during the photo-electrocatalytic reduction of CO₂ to acetate.

Electrostatics and orientation of interfacial water at charged surfaces

Alex Benderskii and Steve Cronin (USC)

AFOSR Contractors Meeting,

Molecular orientation is an important ingredient in our understanding of the structure and dynamics of hydrogen bonds at aqueous interfaces. Surface electrostatics play important role in determining the orientation of the water dipoles in systems such as electrode surfaces, surfactants, and biomembranes. Here we describe the spectroscopic probes of the molecular orientation utilizing the vibrational modes of the water molecule observed using the surface-selective nonlinear technique of sum frequency generation (SFG). We investigate the orientation of the interfacial waters as a function of surface charge for the case of ionic surfactant monolayers at the air/water interface, and water at the surface of single-layer graphene electrodes. We will present a new design of the electrochemical cell utilizing a single-layer transparent graphene electrode supported on CaF_2 substrate, which allows spectroscopic measurements while continuously varying the electrode potential in a wide range. The flip-flop behavior of the water is observed as a function of the applied voltage. Interestingly, both “free OD” and “Hydrogen-bonded OD” spectral features are observed at the graphene/water interface, and their orientational response to the applied potential is markedly different. This indicates restructuring of the interfacial water hydrogen-bonding network as the electrode potential is changed.

Ab Initio Studies on the Synthesis of Energetic Core-shell Nanoclusters

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Abstract

The identification and development of novel energetic materials for munitions, chemical propulsion, and other applications is an essential need of the United States Air Force. Nanomaterials are becoming an increasingly utilized to obtain increased performance, specifically the burn rates of high energy density materials, by decreasing the reaction domain. This can be done efficiently by constructing a core-shell nanoparticle in which the fuel and oxidizer reside in the same nanoparticle. There are currently a number of experimental efforts to synthesize and characterize core-shell nanoparticles. Presented here are modelling efforts to further understand in general the chemical nature of two model systems via ab initio methods, specifically structures and energetics involved in the formation of Cu/Mg and Si/Al core-shell nanoclusters. The most recent theoretical efforts of the Cu/Mg system 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-pwCVTZ) is used for magnesium and a comparable pseudo-potential basis set (aug-cc-pVTZ-PP) for copper. Si/Al nanoclusters are investigated to probe the formation of the potential “magic cluster” of SiAl₁₂, an isoelectronic alternative to Al₁₃⁺. “Magic clusters” are metal clusters with high symmetry and a closed electronic shell, that have been found to be inert to oxidation. MP2 methods are being employed alongside MCSCF methods in dealing with the some of the unique electronic properties associated with the formation of these clusters.

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Experimental Investigations of the Catalytic Decomposition of Ionic Liquid Monopropellants

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ABSTRACT

Next-generation monopropellants are being developed by the Air Force and NASA to reduce the toxicity of the fuels, and ionic liquids are promising replacements for the toxic hydrazine-based fuels currently in use. In order to develop chemical kinetics models for combustion of ionic liquid-based monopropellants, identification of the initial steps in the catalytic decomposition of components is needed, but is currently not well understood. This investigation includes two mass spectrometric techniques: 1) tunable vacuum ultraviolet photoionization aerosol TOF-MS and 2) nanotip ambient ionization MS, where HEHN is introduced onto a heated iridium catalytic surface and the products are probed mass spectrometrically. The products can be identified by their mass, their ionization potential and their collision-induced fragmentation patterns. The products and possible reaction mechanisms will be discussed.

Enhanced Photocatalysis on TiO₂-Passivated III-V Compounds for Water Splitting and CO₂ Reduction

Profs. Steve Cronin and Alex Benderskii (USC)

We report enhanced photocatalysis for H₂ evolution and CO₂ reduction using TiO₂-passivated InP and GaAs photocathodes.¹⁻³ The TiO₂ layer makes the InP semiconductor photochemically stable. This represents a major step forward in photocatalysis, which has typically been limited to metal oxide materials. In addition to making these surfaces stable, the TiO₂ film, deposited by atomic layer deposition (ALD), also provides a substantial enhancement in the efficiency of H₂ evolution. We find that passivating GaAs with just a few nm of TiO₂ produces a shift in the onset potential of H₂ evolution by +0.35 V at 1 mA/cm₂ and enhances the photocurrent by 32-fold over bare GaAs (at 0 V vs. RHE). Here, thinner TiO₂ films produce a larger enhancement than thicker films, which correlates with the higher density of O-vacancies (i.e., Ti³⁺ surface states) observed in these thinner films using X-ray photoemission spectroscopy (XPS). While TiO₂ films 1-5nm thick produce large enhancements, no enhancement is observed for TiO₂ thicknesses above 10 nm, which are crystalline and, therefore, considerably more insulating than thinner amorphous TiO₂ films.

We also report photocatalytic CO₂ reduction with water to produce methanol using TiO₂-passivated InP nanopillar photocathodes under visible wavelength illumination.² Again, the TiO₂ passivation layer provides a stable photocatalytic surface and substantial enhancement in the photoconversion efficiency and selectivity through the introduction of O-vacancies associated with the nonstoichiometric growth of TiO₂ by ALD. Plane wave-density functional theory (PW-DFT) calculations confirm the role of oxygen vacancies in the TiO₂ surface, which serve as catalytically active sites in the CO₂ reduction process. PW-DFT shows that CO₂ binds stably to these oxygen vacancies and CO₂ gains an electron (−0.897e) spontaneously from the TiO₂ support. The TiO₂ film increases the Faraday efficiency of methanol production by a factor 5.7X under an applied potential of −0.6 V vs NHE, which is 1.3 V below the E^0 (CO₂/CO₂[−]) = −1.9 eV standard redox potential.

In order to further understand the strong dependence of these photocatalysts on TiO₂ thickness over the range of 0–15 nm, we performed cross-sectional high resolution transmission electron microscopy (HRTEM) of GaAs/TiO₂ heterojunctions.³ Thinner films (1–10 nm) are amorphous and show enhanced catalytic performance with respect to bare GaAs. HRTEM images and electron energy loss spectroscopy (EELS) maps show that the native oxide of GaAs is removed by the TiCl₄ ALD precursor, which is corrosive. Thicker TiO₂ films (15 nm) are crystalline and have poor charge transfer due to their insulating nature, while thinner amorphous TiO₂ films are conducting.

References:

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Charge & Molecular Dynamics of Catalysis at Solid-Liquid Interfaces

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The aim of my AFOSR YIP proposal was to detect spectroscopically the initial photo-excited states of the water oxidation reaction, through *in-situ* experiments of a photo-electrochemical cell using ultrafast optical and mid to far IR spectroscopy. This means that the water oxidation reaction was investigated spectroscopically while the reaction occurred and from the point of charge transfer at the interface. Since the last AFOSR meeting, the identification of the oxyl radical (Ti-O^\bullet) through its sub-surface vibration by ultrafast mid-infrared spectroscopy and theory of the n-SrTiO₃/aqueous interface has been confirmed and a publication is in-press (Nature Chemistry, 2016). Intriguingly, once decoupled from the rest of the lattice oxygen, the sub-surface vibration couples to reactant dynamics (in particular, water librations), as shown by Fano lineshapes. Such a coupling to reactant dynamics is canonically anticipated of a catalytic intermediate, but had yet to be observed. Through these Fano lineshapes, we can then probe how water librations contribute to the activation barrier for bond formation. The sub-surface vibration is also coupled to electron (plasma) dynamics in the solid, which demonstrates the extent to which it is truly interfacial. Altogether, three handles for tracking nascent catalytic intermediates within the catalytic cycle have been demonstrated: the sub-surface vibration itself and its coupling to solvent and electron dynamics.

Recently, my lab has made progress in connecting the dynamics of radical formation across the solid-liquid interface. Nascent catalytic intermediates appear as localized charge at the solid-liquid interface, creating “mid-gap” states in semiconductors. While the mid-infrared probe provides molecular definition, the optical spectroscopy provides a definitive formation time because it directly tracks the dynamics of charge localization. Identifying which catalytic intermediate maps to a particular mid-gap state is a long standing goal. The formation times of two, distinct surface hole radicals at the n-SrTiO₃/aqueous interface have been isolated by an ultraviolet probe. Both radicals have in-plane optical transitions to the conduction band edge, with theory currently in progress.

Finally, the effect of these reaction intermediates on interfacial charge carriers was directly measured by applying transient optical diffraction spectroscopy to GaN/aqueous interfaces of different reactivity (Chemical Physics Letters (Frontiers), 649, 1, 2016). When reaction intermediates are created by charge transfer between n-GaN and an aqueous electrolyte at equilibrium, the diffusion coefficient for interfacial charge carriers increases markedly (>2). In other words, reaction intermediates open a new current pathway, demonstrating the inter-dependence of surface reactivity and interfacial charge transport for the first time. To what extent this inter-dependence determines steady state product evolution can now be investigated at semiconductor/aqueous interfaces under reaction conditions.

Microplasma Arrays for Energetic Oxygen Chemistry and Optically Pumped Rare Gas Lasers

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We are investigating applications of microwave microplasmas for generation of metastables and energetic molecules in a discharge-flow reactor at pressures up to 1 atm. The microplasmas are produced by compact linear arrays of micro-discharges at powers <30 W and frequencies of ~900 MHz. This micro-discharge approach provides enabling technology for efficient production of long-lived energy carriers at atmospheric pressure, opening the door to a wide variety of applications. The array design uses a set of parallel linear quarter-wave microstrip resonators deposited on a ceramic substrate, with a small (25-100 μm) gap to ground where the micro-discharge occurs. The microwave power, generated by a compact solid-state power amplifier and frequency generator, ignites and sustains a continuous-wave, spatially homogeneous column of micro-discharges at pressures from a few Torr up to 1 atm. For single arrays of micro-discharges, only a small fraction of the gas flow is processed by the active discharge. We have recently investigated dual overlapping arrays to increase the gas processing efficiency.

Energetic species of interest include O_3 , $\text{O}_2(a^1\Delta_g)$, $\text{Ar}(3p^54s)$ metastables, and excited states of N_2 . Using the dual-array microplasma at atmospheric pressure, we have measured the concentrations and flow rates of O_3 and $\text{O}_2(a^1\Delta_g)$ in the effluents of micro-discharges for O_2/He and $\text{O}_2/\text{N}_2/\text{He}$ gas mixtures. The results indicate faster-than-expected post-discharge quenching of $\text{O}_2(a^1\Delta_g)$, likely by vibrationally excited $\text{O}_3(v)$, and effective removal of O and O_3 by NO which enhances $\text{O}_2(a^1\Delta_g)$ production when N_2 is added to the discharge.

We have also used this approach to demonstrate a new class of optically pumped microplasma rare-gas lasers. We have observed efficient production of $\text{Ar}(1s_5)$ metastables for Ar/He mixtures at 200-760 Torr, and continuous-wave optical gain and lasing at 1 atm on the $2p_{10} \rightarrow 1s_5$ transition at 912.3 nm through optical excitation of $\text{Ar}(1s_5 \rightarrow 2p_9)$ at 811.5 nm. The lasing state is populated by energy transfer from optically excited $2p_9$ to $2p_{10}$ in collisions with He atoms. Through analysis with a steady-state kinetics model, together with discharge temperatures estimated from line-broadening theory, the observed optical gains are in excellent agreement with recently measured rate coefficients for the energy transfer reactions at elevated temperatures. Experiments using the overlapping dual-array micro-discharge flow reactor demonstrate greatly increased gain volumes, and post-discharge $\text{Ar}(1s_5)$ lifetimes limited by collisional quenching.

This research is supported by the Air Force Research Laboratory/AFMC, the High Energy Laser Joint Technology Office, and AFOSR.

Photobasicity: Thermodynamics, Kinetics, and Possible Applications

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Coupling of electron and proton motion is of central importance in a wide range of chemical phenomena, including natural and artificial light harvesting, enzymatic reactions, and synthetic organic chemistry. A contemporary challenge is to measure, explain, and ultimately control such coupled motion of charges in the excited states. Photoacids are the prime example of coupling between light excitation and release of protons from a molecule and have been studied for decades. Here we present a systematic study of photobasicity which is the inverse of this effect.

We present results for a series of 5-substituted quinolines, where the substituent's electron-withdrawing capability (Hammett parameter) varies from -0.7 to +0.7. The ground and excited state proton transfer drives are evaluated from Förster cycle analysis. Our work has two central findings. First, the free energy for protonation in the excited state follows a linear relationship with respect to the Hammett parameter of the substituent. While such a linear relationship is expected in the ground state, our work shows that the idea behind the Hammett equation also holds for the excited state. Secondly, we find that the excited state is about 5 times more sensitive to the electron-withdrawing capability of the substituents compared to the ground state. This is justified based on the increased polarizability of the excited state electronic charge density.

We also present results on ultrafast kinetics of proton removal from water by the quinoline photobase using broadband pump-probe experiments. We find that the proton removal time from water near neutral pH is about 20-30 ps. Finally we suggest approaches to use this proton removal drive in the excited state as a functional unit of water oxidation catalysts.

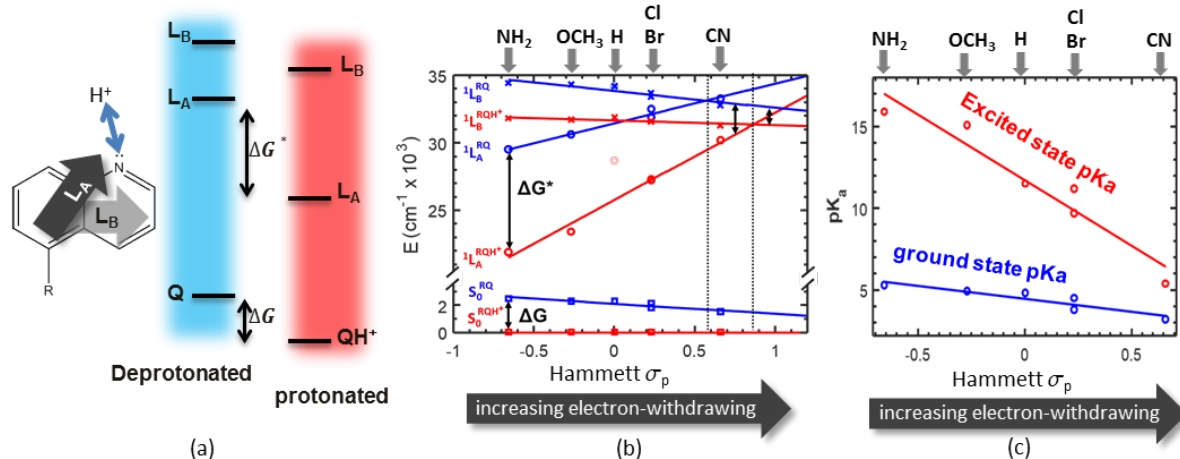


Figure 1. Summary of our recent experimental work on the effect of polarization of electronic charge density on the excited state pK_a of quinolines. (a) Both the ground and the excited states of quinoline are affected by protonation of nitrogen. The excited state L_A is more susceptible to protonation than L_B due to the orientation of its dipole towards the protonation site. (b) The relative energies are found from Förster analysis of the absorption and emission spectra as a function of the electron-withdrawing strength of the substituent R. (c) It is found that the excited state, due to its larger polarizability, is more sensitive to the electron-withdrawing strength of the substituent than the ground state.

Quantifying Ligand Exchange Processes at CdSe Nanocrystal Surfaces

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Controlled and selective functionalization of nanocrystals requires exquisite control over surface chemistry. 'Native' ligands employed in the synthesis of nanocrystals can be exchanged for other coordinating ligands which may vary in the identity of their surface anchoring group and chain length. Coordinating ligands may also incorporate functional groups which can influence solubility, incorporate electron transfer partners, or integrate a receptor site. Increasingly, the extent of ligand exchange must be controlled in order to limit the number of functional groups per nanocrystal. In order to learn how native ligands can be selectively displaced, ^1H NMR has been employed to quantify ligand displacement equilibria of oleate-capped CdSe nanocrystals (zinc blende). After rigorous post-synthesis cleaning, ^1H NMR spectra reveal exclusively surface-bound oleate ligands, as indicated by a broad signal for the *cis*-vinylene protons, and no free oleic acid. Ligand exchange reactions have been carried out with carboxylic acid-, phosphonic acid- and thiol-terminated ligands that incorporate a terminal alkene group. The vinylic protons of the native and the exchange ligands provides distinct NMR handles for the bound and free forms of both these ligands, from which binding equilibrium constants are calculated. Further, these methods differentiate between direct ligand displacement processes and the binding of an incoming ligand to open coordination sites. Quantitative information about ligand exchange processes determined in this work will guide the selective functionalization of semiconductor nanocrystals.

Concepts and Materials for Sub-Nano Chemistry

FA9550-15-1-0088

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We have developed new technology to produce ultrasmall sub-nano particles, also known as clusters. These cluster systems have been well-studied in the gas phase, but we now isolate them for the first time as materials. The objective of our research is to discover new sub-nanometer cluster systems and to evaluate their potential for materials with specific catalytic, electronic, magnetic, and optical properties. We focus on ligand-coated metal and metal-oxide particles, usually containing fewer than 30 atoms. These species are produced in the gas phase using the laser ablation method. Fundamental measurements use molecular beams, mass spectrometry, infrared laser spectroscopy, and computational chemistry to investigate the surface-ligand interactions and their dependence on the metal electronic structure. Synthetic measurements use a new flowtube reactor, applying insight gained about surface interactions, to ligand-coat the ultrasmall metal particles and to collect them in solution. These materials are investigated with laser desorption mass spectrometry, optical spectroscopy, and computational chemistry, as well as measurements of electrochemistry, catalysis, or magnetism. The fundamental and synthetic studies complement each other, providing unanticipated discoveries and improved understanding of metal particle chemistry in the sub-nanometer size range.

In recent progress, gas phase experiments have investigated cerium oxide clusters and their photodissociation pathways. The CeO_2 stoichiometry of the bulk is prominent in even the smallest nanoclusters. Synthetic experiments have explored the production of vanadium carbide systems, known from the gas phase to form "met-cars" cage and nanocrystal structures. An accidental oxygen leak proved fortuitous, leading to the discovery of new vanadium oxy-carbide nanorod and "nanostar" structures, with 30-50 nm dimensions. Characterization of these new systems is in progress. In a final area, a new collaboration has been initiated with the group of Tobias Lau at the BESSY synchrotron light source in Berlin. In this work, cobalt cluster ions have been produced, trapped in a cryogenic ion trap, and studied with X-ray absorption spectroscopy and X-ray magnetic circular dichroism (XMCD). The latter measurement provides both the orbital and spin components of the cluster magnetic moment. Coating these clusters with benzene ligands is found to totally quench the strong magnetic moment of the cobalt cluster.

Time-resolved surface-enhanced Raman studies of plasmon-driven photochemistry

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Hot electrons generated through plasmonic excitations in metal nanoparticles show great promise for driving energetically demanding chemical reactions with light. However, the lifetime, yield, and mechanism of action of plasmon-generated hot electrons involved in a given photocatalytic process are not well understood. Critical insight into these unknown parameters can be gained from a real-time, molecular view of plasmon-driven chemical processes. Here we use ultrafast surface-enhanced Raman scattering (SERS) as a direct probe of plasmon-molecule interactions during the plasmon-catalyzed dimerization of 4-nitrobenzenethiol to p,p'-dimercaptoazobenzene. With ultrafast SERS measurements, probing of molecular reporters in plasmonic hot spots reveals transient Fano resonances, which we attribute to near-field coupling of Stokes-shifted photons to hot electron-driven metal photoluminescence. The lifetime of these Raman features is in agreement with estimates for hot electron lifetimes. Surprisingly, we find that hot spots which yield more photoluminescence are also much more likely to drive the photochemical reaction, which indirectly proves that plasmon-generated hot electrons are responsible for driving photochemistry. Additionally, we have examined the role of the plasmon electric field dependence in driving this photoreaction. Unexpectedly, we find no correlation of increased reaction rate or yield with higher field enhancement. Our work identifies several factors which are critical in determining the overall efficiency of a plasmon-driven process, and should help in the rational design of plasmonic photocatalytic systems.

Metal-Promoted H-ZSM-5 for Endothermic Reforming of Alkanes

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ABSTRACT

A significant challenge in the design of future hypersonic aircraft is engine cooling and it has been proposed that the fuel be used as a coolant. The amount of energy that can be taken up by the thermal heat capacity of the fuel is limited but additional heat can be removed if the fuel is reformed via endothermic reactions prior to entering the combustion chamber. Although the reactions one would like to carry out are similar to the dehydrogenation reactions that occur in commercially practiced, naphtha reforming, the conditions for fuel reforming in the aircraft application are much more difficult. Endothermic fuel reforming must take place at high pressures in order to keep the fuel at liquid-like densities. Furthermore, with naphtha reforming H_2 is co-fed with the hydrocarbon to prevent catalyst coking on the Pt-based catalysts; this cannot be done in an aircraft application.

We have studied the addition of Zn to H-ZSM-5 zeolites for this application. Temperature-Programmed-Desorption/Thermogravimetric-Analysis measurements with 2-propanamine on two H(Zn)-ZSM-5 samples showed that each Zn cation displaces one Brønsted-acid site. Although rates for n-hexane conversion at 633 and 823 K and at a pressure of 137 bar also decreased linearly with the loss of Brønsted sites, Zn promotion greatly increased the production of H_2 and the formation of small aromatic molecules. FTIR of adsorbed acetonitrile- d_3 and calorimetric measurements of adsorbed CO at 195 K indicate that the exchanged Zn cations form Lewis-acid centers. A model in which the Zn cations, acting as Lewis-acid centers, polarize intermediates formed at Brønsted sites is presented as a way of understanding the observations.

Plasmon-mode-specific electronic dynamics and energy localization studied using single-nanoparticle interferometric nonlinear optical imaging.

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Plasmonic nanoparticle assemblies offer unique opportunities for controlling energy at the nanoscale. Here, we describe experimental outcomes in three key areas critical to understanding nanoscale-structure-specific light-matter interactions: 1) selective amplification of specific light polarization states; 2) structure-dependent plasmon coherence times; and 3) plasmon-mode-specific spatial localization of electromagnetic energy to nanoscale volumes. Interferometric single-particle second harmonic generation (SHG) and two-photon photoluminescence (TPPL) imaging techniques developed in our lab provide high spatial accuracy and precision along with femtosecond time resolution for examining nanoparticle assemblies. Femtosecond time-resolution is achieved by employing a sequence of phase-locked laser pulses to examine the nanostructures. These imaging methods have been employed to quantify plasmon coherence times for assemblies of nanospheres and nanorods. Determination of plasmon coherence times provides a quantitative measurement of mode-specific quality factors, which are important for assessing the efficiency of nanostructures for using electromagnetic energy. Based on our coherence data, one-dimensional nanorods are promising building blocks of nanoparticle networks for using electromagnetic energy at the nanoscale. The effectiveness of the nanorods results from the inherent length-to-diameter aspect-ratio-dependent tunability of the longitudinal plasmon resonance (LSPR) frequency. The LSPR of high aspect ratio nanorods can be energetically decoupled from interband relaxation channels, which are a major source plasmon decoherence, thus explaining the experimental results. Indeed, preliminary interferometric nonlinear optical studies of nanorod trimers indicate the plasmon coherence time can be increased by approximately 100% for nanoparticle networks of specific symmetries.

Surface Chemistry and Microplasma Studies of Reactive Processes at Plasma-Surface Interfaces

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Our studies are measuring elementary processes in reactive catalytic plasmas for CO₂-CH₄ dry reforming as an exemplary application of nonequilibrium microplasmas. Experiments are underway on several important species in these plasmas, including atoms, ions, and electrons, and how they affect surface chemistry on Ni(110), which is a reactive surface of nickel catalysts used for reforming. One component of our work has been to investigate the formation and reactivity of bulk (subsurface, absorbed) hydrogen that can be formed from incident hydrogen ions on Ni(110). The H⁺ ion energy affects the distribution and desorption temperature of bulk hydrogen, as revealed by temperature programmed desorption (TPD). Bulk hydrogen is more reactive than surface-bound adsorbed hydrogen, and we have explored the chemistry of bulk hydrogen with adsorbed CO. We find that the desorption temperatures of the products, formaldehyde and methanol, are also dependent on the ion energy used to synthesize the bulk hydrogen. Similarly, bulk hydrogen has been shown to be the reactive species in the hydrogenation of ethylene. Hydrogenation with surface hydrogen is 10x less efficient. We have also investigated the reaction of 50 eV H⁺ ions with adsorbed CO₂ to produce H₂O and CO. Incident low energy H⁺ ions are unique in their ability to generate these products. The secondary electron emission (SEE) from Ni(110) has also been examined for 50 eV to 3 keV electrons impacting at 0 to 50°. The emission yield for clean Ni(110) was determined to be independent of temperature, but dependent on impact angle, and the emission yield for hydrogen-exposed Ni(110) at 300 K was found to be equal to that for clean Ni(110). These surface chemistry studies are closely aligned with theory/modeling research by the group of George Schatz at Northwestern University.

The plasma physics and modeling component has been focused on the design and characterization of a microdischarge cell that can be used inside an environmental scanning electron microscope (ESEM) for in-situ characterization of reactive plasma-surface interactions. The discharge was characterized in two configurations: micro hollow cathode (MHC) and micro hollow anode (MHA). The electrical and optical emission spectroscopy (OES) data demonstrated that MHC and MHA plasmas are non-equilibrium: $T_e > T_{gas}$. The MHA can potentially offer a better controllability of the electron energy distribution function, which could be an advantage for fuel reforming and other microplasma applications. The microdischarge cell is currently being mounted within an ESEM and we expect to obtain images and data shortly from the first experiments.

Ultrafast charge carrier dynamics at type II heterojunctions: Nanoparticles and ultrathin semiconductor films on p-Si(100)

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Time resolution, surface sensitivity and element specificity are technical ingredients required to investigate ultrafast photoinduced processes and charge localization at semiconductor surfaces. All these requirements are fulfilled by an experimental apparatus that consists of a tunable femtosecond high harmonics extreme ultraviolet (XUV) source, a pump-probe setup, a photoelectron spectrometer, and an ultra-high vacuum surface science chamber for surface preparation and investigation.

n-TiO₂ films grown on p-Si form a type II heterojunction that allows a selective separation of charges. Due to the small difference between the conduction band minima of p-Si and n-TiO₂, the photogenerated electrons in Si can easily migrate to TiO₂. However, the large difference between the valence band maxima of these semiconductors prevents the migration of holes from p-Si to n-TiO₂. XUV photoemission spectroscopy is employed to investigate the electronic structure of defect-rich and defect poor ultrathin TiO₂ films prepared on a p-Si(100) substrate.¹ The concentration of oxygen vacancies and consequently the degree of n-type doping of TiO₂ is tuned by controlling the oxygen background pressure during the TiO₂ formation. Furthermore, by means of a pump-probe technique in conjunction with photoemission spectroscopy, the ultrafast transfer of electrons excited in p-Si(100) by a near IR-pump laser pulse is observed in the defect-rich TiO₂ layer by monitoring the shift of the photoemission spectra due to the transient charging of the TiO₂ surface. The injection of the electrons from p-Si(100) into the TiO₂ layer occurs with a time constant of 450 fs and is followed by charge carrier recombination, which is affected by the oxygen defects. No charge transfer is observed when defect-poor TiO₂ films are prepared on the p-Si(100) substrate. This may be attributed to a change in the energy band alignment at the TiO₂/Si(100) interface that reduces the built-in potential across the heterojunction and consequently reduces the driving force responsible for the injection of electrons into the TiO₂ layer.

A type-II heterostructure that permits a selective separation of charges can be also formed when n-ZnO is deposited on p-Si(100). The ZnO is produced via Zn atom evaporation on the p-Si(100) substrate followed by in-situ oxidation. Previous investigations in the literature show that clusters, nanorows, and ultrathin films of ZnO can be synthesized by controlling the amount of Zn evaporated on the Si(100) substrate prior to oxidation. The evolution of the ZnO electronic structure as a function of the ZnO particle size as well as the ultrafast charge carrier investigations at the interface between ZnO nanoparticles and p-Si(100) will be presented.

¹M. E. Vaida, and S. R. Leone, "Femtosecond extreme ultraviolet photoemission spectroscopy: observation of ultrafast charge transfer at the n-TiO₂/p-Si(100) interface with controlled TiO₂ oxygen vacancies," J. Phys. Chem. C **120**, 2769 (2016).

Cold Controlled Reactions between Molecular Ions and Molecular Radicals

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JILA and the Physics Department, University of Colorado

Radicals and ions frequently play an important role in gaseous media such as the Interstellar Medium (ISM), the upper atmosphere, flames, plasmas, discharges etc. Reactions involving such species often dominate the chemistry in these regions. Although collisions in the ISM between ions and radicals are very rare events, the long timescales involved mean such reactions make important contributions to the pathways for assembly and destruction of complex chemical species. Unfortunately, experimental measurements of the rates and particularly the dynamics of reactions *between* ions and radicals are very few and far between. This is simply a consequence of the typical low densities of such species formed under normal laboratory conditions. In addition, most radical beam sources are not “clean” and contain a variety of other species and a range of quantum states making precise determination of reaction dynamics challenging. Our system overcomes some of these challenges by using trapped molecular ions and Stark decelerated neutral radicals. We are exploring simple chemical reactions between cold, trapped molecular ions and the neutral free radicals NO, OH, NH, and CH.

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.

The Role of Hot Electrons in the Photoluminescence of Plasmonic Nano-Structures

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Abstract

Plasmons are able to efficiently generate hot electrons, important for photocatalytic applications. Photoluminescence (PL) of gold nanostructures is thought to involve hot electrons as intermediates. Understanding the mechanism of PL can potentially give us a way to follow the fate of hot electrons. Therefore, to investigate the PL mechanism we studied the one-photon photoluminescence of strongly coupled 50 nm Au nanosphere dimers, the simplest plasmonic molecule. We observed emission from coupled plasmonic modes as revealed by single-particle PL spectra in comparison to correlated dark-field scattering (DFS) spectra shown in Figure 1. The single DFS peak of the monomer, centered at 546 nm, is the typical dipolar plasmon mode (Figure 1A). In contrast, the DFS spectrum of the AuNS dimer (Figure 1B) shows two maxima as a result of near-field capacitive coupling: a longitudinal polarized resonance at 650 nm and a much weaker transverse polarized resonance mode at 545 nm. For the dimer coupled PL modes are also observed. The PL quantum yield of the dimers is found to be similar to the constituent monomers (Figure 1C), suggesting that the increased local electric field of the dimer plays a minor role. Furthermore, the PL emission from these particles was constant without any photoblinking or photobleaching observed (Figure 1D). Both observations are in contradiction to several proposed mechanisms, including emission from surface ligands and intrinsic small clusters. Aided by electromagnetic simulations of scattering and absorption spectra, we conclude that our data is instead consistent with a multi-step mechanism that involves the emission due to radiative decay of surface plasmons generated from excited electron-hole pairs following interband absorption [1]. This mechanism is further confirmed via excitation wavelength dependent PL quantum yield measurements in combination with detailed theoretical calculations. In contrast, plasmonic aluminum nanoparticles have a much weaker PL that appears to originate from hot electrons trapped in their aluminum oxide shell.

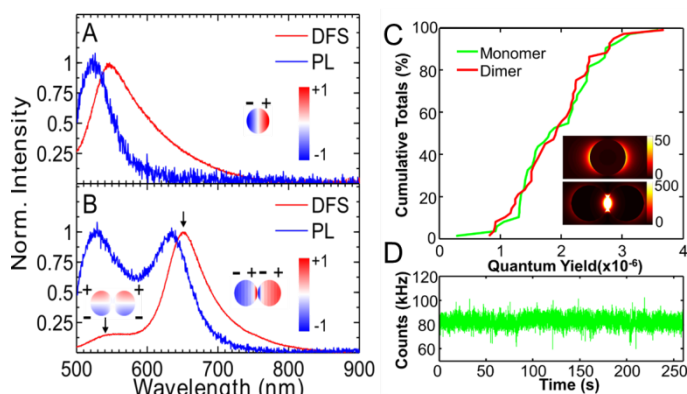


Figure 1: Representative single-particle DFS (red) and PL (blue, 488 nm excitation) spectra of an AuNS monomer (A) and an AuNS dimer (B). Charge distributions simulated at the DFS resonance maxima are included as insets to identify the plasmon modes supported by these nanostructures. (C) Cumulative distributions of the measured quantum yields of monomers (green) and dimers (red). Inset: Electromagnetic field enhancements for a monomer and a dimer calculated at 550 nm and 640 nm, respectively. (D) Photon count rate versus time for PL from an AuNS monomer.

[1] D. Huang, C. P. Byers, L.-Y. Wang, A. Hoggard, B. Hoener, S. Dominguez-Medina, S. Chen, W.-S. Chang, C. F. Landes, S. Link, *Photoluminescence of a Plasmonic Molecule*. ACS Nano 9, 7072 (2015).

Fundamental Interactions in Hypersonic Flows: Oxidation of Carbon at High Temperatures

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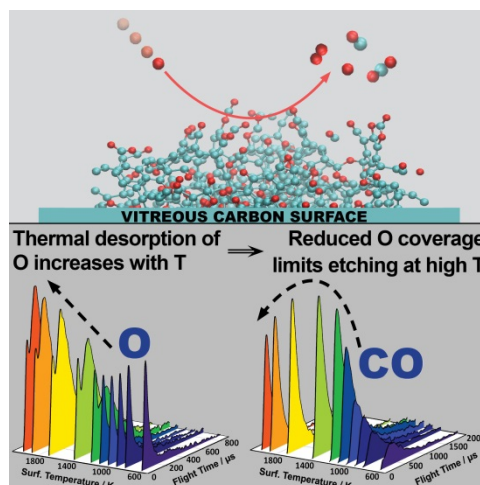
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Gas-surface interactions at high temperatures are of great importance to atmospheric re-entry of spacecraft. Hypersonic flows generate the most extreme thermal conditions experienced by any flight vehicle. For a flight vehicle to survive in this environment, it requires a thermal protection system (TPS) composed of materials that can function at extreme temperatures under harsh oxidizing conditions. Most TPS materials are based on carbon, either in pure form or in a composite. During atmospheric re-entry, these materials are exposed to partially oxidized air at temperatures that can exceed 2000 K. The fundamental reactive and non-reactive dynamics between carbon and atomic or molecular oxygen strongly impact the thermal load on these TPS materials, but they have not been studied in extreme environments such as re-entry.

Hyperthermal interactions of ground-state atomic oxygen, $O(^3P)$, with highly oriented pyrolytic carbon (HOPG) and vitreous (or glassy) carbon surfaces were investigated with a broad range of surface temperatures from 600 K to approximately 2200 K. Beams of 5 eV O atoms were directed at surfaces, and angular and translational energy distributions were obtained for inelastically and reactively scattered products using a rotatable mass spectrometer detector. Inelastically scattered O atoms exhibited both thermal and non-thermal components. The inelastic scattering from HOPG showed mostly nonthermal (impulsive) scattering with very sharp and superspecular angular distributions. In contrast, thermal scattering was much more important on the vitreous carbon and carbon preform surfaces and the angular distributions for impulsive scattering were broader. Surprisingly, an increasing fraction of thermally desorbed O atoms was observed on all surfaces the temperature was increased. Also, for all surfaces, CO and CO_2 were produced at lower temperatures, and CO_2 disappeared above 1100 K. The primary reaction product (CO) was formed through direct (nonthermal) and indirect (thermal) mechanisms, where the thermally desorbed products apparently needed to surmount a barrier before desorbing. The flux of CO reached a maximum at surface temperatures between 1200 and 1900 K, depending on heating rate, and decreased with increasing temperature. Similar non-Arrhenius behavior was observed decades ago in the oxidation of carbon with thermal O and O_2 , but we have explained it for the first time. The increasing thermal desorption of O atoms with temperature signifies a decrease in surface oxygen coverage, and with fewer reagent O atoms to react with carbon the reactivity of the carbon surface is limited even though the surface is being constantly bombarded with highly reactive (hyperthermal) O atoms. Another important result from these molecular beam experiments is that the key reactions that remove carbon from the surface occur mainly in thermal equilibrium with the surface regardless of the kinetic energy of the incident oxygen atoms, suggesting that the incident beam may be treated simply as a supply of oxygen atoms on the surface. The molecular-level scattering dynamics from the experiments have been used in DSMC models by collaborators to simulate the convection and diffusion of reactants toward the surface microstructure and the transport of surface reaction products away from the microstructure.



Liquid Microjet Studies of Non-Maxwellian Helium Evaporation and Prospects for Exploring the “Explosive” Evaporation of Complex Fuel Mixtures

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Abstract

Jet fuels contain an enormous variety of linear and cyclic alkanes and aromatic molecules, with oxygenated and metal species added to improve performance. These components have widely varying vapor pressures and will evaporate from fuel droplets at different rates. This rapid, non-equilibrium evaporation remains mysterious at the atomic scale: do fuel molecules evaporate quickly but quiescently, or do high vapor pressure components “explode” from the droplet, carrying longer-chain hydrocarbons with them into the gas phase? This behavior dictates the atomization of the liquid fuel droplets, a requirement before gas-phase combustion can begin.

The poster will review our previous studies of the vacuum-liquid interfaces of jet fuel and its components by monitoring the evaporation of helium atoms dissolved in liquid fuel microjets. Experiments and theory reveal that the He atoms emerge at non-Maxwellian velocities as they are accelerated by collisions with solvent molecules in the interfacial region that expel the interloping He atom. Together with surface tension measurements, these studies provide insight into mechanisms by which solutes evaporate from complex fuel mixtures such as Jet A and JP-8.

We also propose experiments to investigate the rapid disintegration of fuel droplets, including hydrocarbon liquids containing water as an immiscible “detonator” in water-in-fuel emulsions. We will monitor the explosive boiling of this immiscible water and fuel mixture by preparing microemulsions in a liquid microjet in vacuum and detecting the rapidly vaporizing water and hydrocarbon components by a mass spectrometer. The detection of long-chain hydrocarbons will reveal how the shattering of the emulsified droplet by rapid water vaporization can propel low-vapor pressure hydrocarbons into the gas phase.

Atomically Precise Nanostructures for Tunable Optical Response

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We report on the optical properties of atomically precise nanoclusters (NCs). Specifically, the $\text{Ag}_{12}(\text{SR})_6(\text{CF}_3\text{CO}_2)_6(\text{CH}_3\text{CN})_6$ (R = methyl naphthalene) NC was shown to exhibit dual fluorescence when in crystal form, breaking the well-known Kasha rule, where fluorescence is observed only from the first excited state. Stabilization of a higher energy excited state by an excimer-like complex in this case has been proposed. In this work, the structure was modeled by a dimer formed by π -stacking of aromatic groups bonded to the sulfur atoms. Following TDDFT calculations to predict absorption spectra of isolated models of the system, calculations for the dimer indicated that the π -bonded structure may have low-intensity, lower energy excited states in the range of 1.5 – 2.5 eV, in agreement with the measured absorption spectrum. Calculations of the two-photon absorption (TPA) cross-section for an isolated NC indicated two off-resonance peaks of over 100 GM in the visible spectrum. While some materials have significantly larger TPA cross-sections, such TPA cross-sections far off-resonance may be useful. Calculations for the dimer suggest significant resonance enhancement of TPA from the low-energy states.

In addition, TPA spectra for molecular neutral, cation, and anion cadmium chalcogenide nonstoichiometric NCs $[\text{Cd}_n\text{E}'_m(\text{ER})_m]$, $\text{E} = \text{S}$ and Se , $\text{R} = \text{hydrogen, methyl, phenyl, para-nitrophenyl, para-cyanophenyl}$ were investigated. Ligands and solvent were previously found to have a large influence on the color and intensity of the electronic absorption spectra of these materials. Effects of ligand and solvent were generally reduced with an increasing NC size. Blue-shifts were observed for the first electronic transition with reduced size for both CdS and the CdSe series. However, due to weakly absorbing and forbidden transitions underlying the one-photon absorption spectra, more care is needed in interpreting the quantum confinement from the NCs' lowest-energy absorption bands. Following careful benchmarking, we demonstrate that electron withdrawing ligands induce large enhancement in the TPA cross-section.

Many-body Potentials for Molecular Simulations From the Gas to the Condensed Phase

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Two of the most challenging problems at the intersection of electronic structure theory and computer 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 to large systems. Here, I will describe our many-body molecular dynamics (MB-MD) methodology that has been shown to enable computer simulations with chemical and spectroscopic accuracy. Specific focus will be on the modeling of aqueous systems from the gas to the condensed phase.

$$E_N = \sum_i V^{1B}(i) \quad \text{1-body}$$

$$+ \sum_{i < j} V^{2B}(i, j) \quad \text{2-body}$$

$$+ \sum_{i < j < k} V^{3B}(i, j, k) \quad \text{3-body}$$

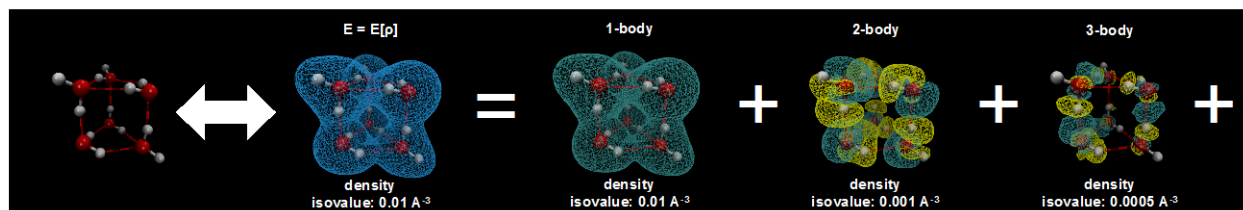
$$+ \dots$$

$$+ V^{NB}(1, \dots, N) \quad \text{N-body}$$

explicit 1Bterm
+
N-body polarization
+
explicit 2B and 3B terms
from CCSD(T)/CBS

dimer

bulk



Following Energy Relaxation within Plasmonic Metal Oxide Nanocrystals

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Transparent semiconducting metal oxide nanocrystals (TCOs) have recently emerged as a tunable platform for the development of infrared plasmonic structures. In contrast to noble metal nanoparticles that are rendered plasmonic due to their high free carrier densities, TCOs need to be doped to display plasmonic behavior. However, by selectively controlling their dopant concentration, the plasmonic resonances of TCOs can be tuned throughout the near- and mid-infrared. Moreover, altering the free carrier population of TCOs through either photoexcitation or electrical charge injection can allow dynamic modulation of their plasmonic absorption bands, making TCOs promising materials for infrared optical switches and electrically gated optical filters. In addition, tuning the plasmonic features of these materials into the mid-infrared can bring them into resonance with the vibrations of surface adsorbates, potentially allowing TCOs to be used for molecular sensing and imaging. However, designing TCO-based applications requires a detailed understanding of how the carrier concentration and spatial location of dopants within these materials impacts their optical properties and the dissipation of plasmonic excitations. We report the results of a series of transient absorption measurements carried out on a model TCO system, Sb-doped In_2O_3 (ITO) nanocrystals. The localized surface plasmon resonance (LSPR) of these materials can be tuned throughout the near-infrared by both altering their level of Sb inclusion and the spatial location of these dopants within the particles. We find that photoexcitation of the ITO LSPR leads to a photobleach that rapidly recovers over sub-picosecond timescales that can largely be modeled by a dual-temperature model for metallic relaxation. The influence of the spatial distribution of dopants within ITO nanoparticles on the relaxation rate of the ITO LSPR and resulting hot electron distribution will be discussed. In addition, groundwork experiments will be described that examine how bandgap excitation of ITO nanoparticles influences their plasmon resonance frequency.

Structural and Theoretical Study of Salts of the $[\text{B}_9\text{H}_{14}]^-$ Ion: Isolation of Multiple Isomers and Implications for Energy Storage

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Boranes and boron hydrides are known for their molecular structures and chemical reactivity, with $[\text{B}_9\text{H}_{14}]^-$, notable for its ease of isolation, unusual structure, and tautomerization. Recently, ionic liquids (ILs, molten salts at unusually low, often near-ambient temperatures) have been explored as low-volatility, liquid-state fuels and hydrogen storage materials. Incorporation of boranes into ILs as ions or functional groups has been investigating for making energetic materials. ILs have also been used as solvents that facilitate unusual reactions of boranes. We have recently investigated the use of boron(0) nanoparticles and *nido*-decaborane ($\text{B}_{10}\text{H}_{14}$) to increase energy density and reduce the ignition delay of hypergolic ILs. We found that $\text{B}_{10}\text{H}_{14}$ reacted with the ILs to form hypergolic boron hydride ions as $[\text{B}_9\text{H}_{14}]^-$ and thus set out to isolate salts of this anion with 1-ethyl-3-methylimidazolium ($[\text{C}_2\text{mim}]^+$) and *N*-butyl-*N*-methylpyrrolidinium ($[\text{C}_4\text{mpyr}]^+$). We observed that these salts not only added energetic density to hypergolic ILs but also induced hypergolicity in nonhypergolic liquids. This work led to our present interest in the implications of IL-borane interactions on the energetic performance and structures of boranes or boron hydrides isolated from ILs. Here we report our theoretical investigation of the energetics of reactions of $\text{B}_{10}\text{H}_{14}$ and $[\text{B}_9\text{H}_{14}]^-$ and the results of structural characterization of both $[\text{C}_2\text{mim}][\text{B}_9\text{H}_{14}]$ and $[\text{C}_4\text{mpyr}][\text{B}_9\text{H}_{14}]$ (**Figure 1**). The crystal structures provide the first unambiguous structural characterization of the {2xμH, 3x endo} isomer. The possibility of $[\text{B}_9\text{H}_{14}]^-$ stabilization by a salt matrix and its consequent chemical activation for energy release motivate our further development of ILs containing $[\text{B}_9\text{H}_{14}]^-$ or other boron hydrides as energetic materials and, possibly, hydrogen storage. (We thank our collaborator in this study, Prof. D. Dixon, The University of Alabama.)



Figure 1: 50% probability ellipsoid plot of asymmetric unit in $[\text{C}_2\text{mim}][\text{B}_9\text{H}_{14}]$ (left) and $[\text{C}_4\text{mpyr}][\text{B}_9\text{H}_{14}]$ (right). Dashed lines indicate shortest contacts between ions.

Acknowledgment. This work was supported by the U. S. Air Force Office of Scientific Research under AFOSR Awards No. FA9550-10-1-0521 and FA9550-14-1-0306 (Iowa State University subcontract 421-21-06A).

Fundamental studies of reactive processes at plasma-surface interfaces

George Schatz, Kelsey Stocker, Alona Furmanchuk, Wei Lin, Andrew Sirjoosingh, Department of Chemistry, Northwestern University, Evanston IL 60208

The theory/modeling component of this BRI project has been aimed at understanding what happens when species produced when CH_4/CO_2 gas mixtures (species of importance in dry reforming) are exposed to a plasma, and then interact with catalytic Ni nanoparticles. Some of these species and reactions are also being studied in the Koel group experimental work at Princeton, but the theory effort has been broader with the idea that theory might identify processes of sufficient interest to warrant subsequent experimental studies. Four general directions of the theory work have been considered. First we have used electronic structure theory and molecular dynamics to perform studies of the interaction of plasma species (H, CH_3 , CH_2 , CH, and CO) with Ni(110) including sticking probabilities, desorption, subsequent dissociation and reaction on the surface, and comparisons of the results with those for CH_4 and CO_2 interacting with Ni(110). Second, electronic structure theory has been used to characterize subsurface hydrogen atoms on Ni(110) and their reactions with surface adsorbed CO_2 . In the third, the interaction of atomic and molecular ions such as CO_2^+ as well as neutrals like C, O, CO and CO_2 with charged Ni(111) has been characterized, and in the fourth, the distribution and intensity of secondary electrons produced after impact of >100 eV electrons with Ni(110) surfaces have been characterized.

Sodium borohydride amine complexes: A simple way to organic borohydride salts

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Sodium borohydride is one of the most common reducing agents. It can also be used to produce a variety of other borohydride salts via simple metathesis reactions. The biggest problem for those reactions is the limited choice of suitable solvents. Literature procedures in acetonitrile have been reported to only result heavily halide contaminated samples. Procedures in CH_2Cl_2 delivered similar poor results (halide contamination of 22.5%). So far only a co-solvent procedure utilizing liquid ammonia and CH_2Cl_2 at 200K delivered analytical pure heterocyclic borohydride salts, as well as a patent procedure which relies on a phase separation of a highly basic water layer and the organic borohydride layer. Clearly, not all organic borohydrides will survive those conditions. Here we report a different method for the preparation of heterocyclic borohydride salts, which takes advantage of the well-established coordination chemistry between NaBH_4 and amines. The coordination complexes have completely different solvent characteristics than the parent compounds. This allowed us to run a much simpler metathesis in a single solvent at room temperature. The synthesis of the complex as well as results on some salts obtained by metathesis is presented.

Evolving the Selected Ion Flow Tube (SIFT) to

Meet Next Generation Air Force Needs

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Air Force Research Laboratory, Space Vehicles Directorate (RVBXT) Kirtland AFB, NM

The selected ion flow tube has long been employed to address a wide array of Air Force needs. The precision with which the temperature and pressure dependence of thermalized ion molecule reactions can be studied by the SIFT is truly unparalleled. One of the key advantages of the experiment, the large number of collisions ensuring thermalizing, also results in significant ion loss, limiting study to that of ionic systems with bright sources. This poster will highlight our group's efforts to minimize this hindrance, thereby greatly increasing the systems available for study by this instrument. These efforts are motivated by employment of two new ion sources, an electrospray ionization and a laser vaporization cluster source, towards addressing Air Force needs in fuel production catalysis and energy dense combustion additives. While these sources are necessary to produce the ions of interest for these needs, they produce much smaller signals than typical for this instrument. Upgrades to ion injection, transport, and detection will offer orders of magnitude increase in sensitivity. Details of upgrades will be presented, including replacing static ion optics with RF rectilinear ion guides allowing for less sensitivity to pressure and thus larger injection apertures, improved ion focusing thru an octopole ion guide, and employing time-of-flight over quadrupole mass detection. A replacement for the Venturi ion injection system is on order.

Matthew Sheldon, Texas A&M University

Hot Electron Enhanced Thermionic Emission (HEETE) Converters for All-Metal Optical Power Generation

We report on our initial studies of photo-induced charge transport from metal nanostructures. In particular, we outline how the remarkable thermal and optical energy concentration provided by plasmonic resonances can enable a new thermodynamic power cycle whereby photo-excited ‘hot’ electrons and resonant photothermal heating provides a dual excitation mechanism for electron emission. Because this process is closely related to purely thermionic emission, we label an optical power-converting device based on this mechanism a Hot Electron Enhanced Thermionic Emission (HEETE) converter. The strong enhancement of both thermal and optical energy channels, in addition to newly identified phenomena for optically induced rectification of electron transport, may enable a significantly more efficient strategy for optical power conversion, and one that can theoretically out-perform traditional semiconductor-based solar cells.

Our work emphasizes theoretical and experimental development of refined models for electronic distributions in metals, specifically when characteristic structural features are smaller than the mean free path of excited carriers. We focus on the coupling between electronic structure and photonic structure that can impart resonant photo-excitation in the metal, and thereby modify the relative excited state population, by analogy to a conventional semiconductor optical band gap. Our experiments are guided by several recent reports that show rectified current from plasmonic nano-junctions under no external bias due to photon-assisted tunneling, as well as our recent work identifying a thermodynamic basis for induced photovoltages mediated via the plasmoelectric effect.

Studies of Dynamic Material Interfaces in Extreme Environments

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The scattering of atomic and molecular beams from well-characterized surfaces is an incisive method for studying the dynamics of gas-surface interactions, providing precise information on energy and momentum transfer as well as complex reaction mechanisms. Scanning probe measurements provide a powerful complement to scattering data as SPM measurements give a direct route to the visualization and spectroscopic characterization of interfacial atomic and nanosystems. This AFOSR program is examining critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme 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. One focus is on interfacial behavior at high temperatures, involving ablative systems and superalloys. Related to this are oxidation studies using supersonic and hypersonic gas flows of atomic and molecular oxidants. A key feature of our activities is to systematically map out site-specific reactivity and morphology changes on the atomic/nano/meso/micro length-scales to accompany our precision measurements of interfacial chemical kinetics, revealing new details of interfacial time evolution such as the key roles that grain boundaries and defects play in materials change. Complementing these high temperature investigations are studies of dynamic materials performance at extremely low temperature, such as the intercalation of molecular species into ice and embedding into passivating coatings with concomitant consequences for changes in gas-surface energy and momentum transfer associated with high-velocity gas-surface collisions. Experiments are complemented by commensurate theory and numerical simulations.

We will report at this year's meeting report 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. Our first manuscript on the oxidation of Si(1x1)-(7x7) was just accepted for publication [1]. (ii) We will also report on the dynamical properties of a new, relatively redox stable methylated interface that is of importance to next-gen electrochemical energy systems (1x1) methyl-terminated Ge(111) [2,3]. (iii) We have extended our studies of energetic embedding of neutral species into ice to include molecular species, most recent CO₂ [4], demonstrating that this is a general mechanism for gas-surface interactions, and that it is a significant new channel by which incident species can be trapped under conditions where they would otherwise not be bound stably as surface adsorbates. This is an important new mechanism for understanding energy & momentum exchange in high velocity gas flows and trace gas collection and concentration.

Selected Recent Publications

1. Temporally and Spatially Resolved Oxidation of Si(111)-(7x7) 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.*, Accepted for Publication (2016).
2. Atomic Surface Structure of CH₃-Ge(111) Characterized by Helium Atom Diffraction and Density Functional Theory" Zachary M. Hund, Kevin J. Nihill, Davide Campi, Keith T. Wong, Nathan S. Lewis, M. Bernasconi, G. Benedek, and S. J. Sibener *J. Phys. Chem. C* **119**, 18458-18466 (2015).
3. Vibrational Dynamics and Band Structure of Methyl-Terminated Ge(111), Zachary M. Hund, Kevin J. Nihill, Davide Campi, Keith T. Wong, Nathan S. Lewis, M. Bernasconi, G. Benedek, and S. J. Sibener, *J. Chem. Phys.*, **143**, 124705/1-10 (2015).
4. Capture of Hyperthermal CO₂ by Amorphous Water Ice *via* Molecular Embedding, Grant G. Langlois, Wenxin Li, K. D. Gibson, and S. J. Sibener, Invited Feature Article for the Special Issue: "Dynamics of Molecular Collisions XXV – Fifty Years of Chemical Reaction Dynamics", *J. Phys. Chem. A*, **119**, 12238-12244 (2015).

VUV PHOTODISSOCIATION AND EMISSION OF THRUSTER PLUME SPECIES.

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During the STS-63 Space Shuttle mission, spectra of the molecular beam jets produced by the shuttle engine exhaust revealed fluorescence near 310 nm. Largely attributed to OH(A \rightarrow X) emission, this fluorescence could only be accounted for by including the photodissociation pathway leading from water excited by 121.6 nm light to excited OH radicals as a source of fluorescence. Here, molecular photodissociation processes from vacuum ultraviolet light excitation are investigated to properly model thruster plume emissions. OH radical emission is produced by seeding water into a jet expansion and exciting the sample with various vacuum ultraviolet wavelengths. Analysis of the emission provides insight into temperature and excitation wavelength dependence on the photodissociation process. Further experiments are planned for other plume species such as ammonia.

POSTER ABSTRACT:

Spatial and Spectral Control of Excitons within Quantum Dot-Molecule Assemblies via Coupled Energy Transfer Processes

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This work aims to obtain a mechanistic understanding of space-separated coupled energy transfer (ET) processes within excitonic materials – specifically, assemblies of semiconductor nanocrystals (quantum dots, QDs) and organic molecules – and to use this understanding to design systems into which we control the spatial and spectral distribution of excitons within the system as a function of time. Space-separated coupled ET is energy transfer involving two or more QDs or molecular chromophores in which the number of excitons increases by multiplicative downconversion (“quantum cutting”), or decreases by upconversion (“energy pooling”). **This work has two main goals: (i)** to use new spectroscopic and theoretical approaches – specifically two-dimensional electronic spectroscopy and real-time quantum mechanics coupled to molecular dynamics – to measure and predictively model the rates of space-separated coupled energy transfer processes in solution-phase and thin-film assemblies of QDs and organic ligands; **(ii)** to use our mechanistic understanding of space-separated coupled ET processes to design assembly architectures and chemistries to achieve previously unrealized coupled ET schemes, for example: the splitting of a high-energy exciton into two or more excitons of different energies, or the pooling of broadband absorption into a single high-energy chromophore.

Exciton conversion and splitting occurs readily in organic systems, particularly those comprising polyacene and perylene motifs. One of these mechanisms, singlet fission, the process through which a photogenerated singlet exciton can split into two lower energy triplet excitons, can proceed efficiently through a space-separated mechanism wherein the donor and two acceptors are different molecules. We show this using a **newly developed theoretical framework** based on perturbation theory, as well as time-dependent density functional theory calculations involving donor-acceptor-acceptor molecular clusters. This process, termed space-separated singlet fission (SSSF), is governed by coupling strengths of several meV. TDDFT calculations on donor-acceptor-acceptor supermolecules reveal excited states consistent with SSSF in energetic, spatial, and spin characteristics. Furthermore, at small inter-chromophore distances ($<5 \text{ \AA}$) these supermolecular calculations predict that generating two triplets through SSSF can carry a lower energy cost than the production of two isolated triplets.

We are **developing novel spectroscopic methods** to track energy exchange between different thermal reservoirs in hybrid organic-inorganic nanostructured materials. Specifically, we are using a 5th-order vibrational-electronic coherent spectroscopy built on a single-shot photon echo technique that reveals couplings between electronic, vibrational, and lattice reservoirs. In collaboration with the Weiss group, we are interested in studying coherent energy exchange between quantum-confined excitons, lattice phonons, and vibrational modes of surface-bound ligands shortly after photo-excitation.

We have **demonstrated fast energy transfer in the near-infrared in new QD-QD and QD-molecule complexes** that assemble through metal-coordination chemistry, electrostatics, and covalent bonds, and to tune the yield of energy transfer with pH. Sub-nanosecond energy transfer occurs from a PbS QDs to an adsorbed molecular J-aggregate, and between PbS QDs linked by divalent ions. We observe a $>80\%$ quantum yield of energy transfer in covalently linked assemblies of PbS QDs.

