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Cluster Dynamics: Laying the Foundation for Tailoring the Design of Cluster Assembled Nanoscale Materials

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Nanoscale materials with selected electronic and geometric structures have broad applications of potential value to the Air Force extending from energetic materials to catalysts with large turnover rates and selectivity, to optical and electronic detection devices, and also ones with unique structural properties. Acquiring the ability to design and produce a range of materials with selected properties cannot be overestimated, and we are exploring prospects employing bottom up approaches. As the size of free-electron metals approach the molecular regime, their properties begin to differ significantly from those of the bulk.

During the course of studying the dynamics and structure of various clusters, a surprising finding in our laboratory led to the concept of superatoms whereby certain clusters were found to take on the properties of specific elements, and sometimes even ones with multiple functionality. The concept of superatoms takes advantage of isoelectronic characteristics of various combinations of atoms acquired via clustering. Through photoelectron studies employing velocity map imaging, and investigations of reactions, superatom concepts are being quantified. This talk will focus on recent advances in terms of the breadth of the systems identified as displaying properties of superatoms, and the size, complexity and range of the groups explored and found to mimic various elements. Findings related to s-, p-, and d-block elements, and quantification of s-p hybridization, will be discussed.

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Model Catalysts and Nanoparticles for Propulsion Applications

A. Size-selected model catalysts: Effects of catalyst support

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Monodisperse model Pd/metal oxide catalysts were prepared by deposition of size-selected Pd_n⁺ on single crystal or thin film metal oxide supports. The catalysts are probed by ion scattering, x-ray photoelectron spectroscopy, and mass spectrometry, with the goal of understanding the complex interplay between Pd cluster size, support, electronic structure, morphology, and activity. Results will be compared for Pd_n on TiO₂(110) and on three different thin film alumina supports. The size dependent pattern of activity is different on the different supports, and the different supports also result in different patterns of electron energy level shifts with Pd_n size. Results for mixed alumina/tantalum oxide supports are particularly interesting, showing high activity as oxidation catalysts, and correlation of activity with Pd 3d binding energy.

B. SAXS/PDF probing of catalyst nanoparticle growth in solution and in flames

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One strategy for introducing ignition catalysts into engines is to incorporate a catalyst precursor into the fuel. Ideally, the catalyst precursor might catalyze endothermic reactions in the fuel for cooling, and then become an ignition catalyst when injected into the combustor. Experiments will be described using X-ray scattering for *in situ* probing of the growth of Pd nanoparticles from Pd organometallic precursors, both in heated hydrocarbon solutions, and in flames.

C. Oxide-free, air-stable boron and aluminum nanoparticles for propulsion applications

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Boron and aluminum are of interest as additives to increase the energy density of liquid and solid propellants and explosives. Reducing the particle size to a few tens of nanometers has potential advantages in stabilizing particle suspensions, reducing ignition times, and increasing combustion efficiency. Both boron and aluminum are normally covered by a spontaneously formed native oxide layer a few nanometers thick. This oxide layer is undesirable for nanoscale fuel particles because it retards ignition, and makes up an increasing fraction of the particle mass as the size decreases. Methods for inexpensive and efficient production of unoxidized and air-stable B and Al nanoparticles, with good dispersion in liquid fuels, will be described. A fuel of particular interest is the hypergolic ionic liquid 1-methyl-4-amino-1,2,4-triazolium dicyanamide ([MAT][DCA]). We have showed that oxide-free boron nanoparticles can be capped with [MAT][DCA], rendering them air-stable and highly suspendible in the IL, and that boron loading does not impact the hypergolic ignition delay. X-ray photoemission, IR spectroscopy, zeta-potential, and theoretical studies have been used to examine the nature of the IL-boron bonding, indicating that interaction is primarily via the MAT cation.

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Neutral Cluster Heterogeneous Catalysis: New Systems, Supported Species, Mechanisms

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During the past few years we have expanded our studies of the catalytic behavior of neutral transition metal compound clusters to include new systems and mixed metal clusters or “supported catalysts”. We have focused attention on hydrocarbon reactions, CO oxidation, and ammonia synthesis. Following the model suggested by biological enzymes and industrial catalysts, we have studied the catalytic behavior of transition metal sulfides, V_mS_n and Fe_mS_n , with respect to hydrocarbon and CO reactions. V_mS_n clusters detected by time of flight mass spectrometry, display an incredibly rich array of species with up to 7 V atoms and up to 11 S atoms under our present growth conditions, as generated by laser ablation of the metal, reaction with CS_2 or H_2S in He, and supersonic expansion cooling. Clusters V_mS_n with $m = 1$ and $n = 1, 2, 3$ and $m = 2$ and $n = 1, 2, 3$, all add C_2H_4 readily, while V_1S_4 does not. Larger clusters also show selective activity with regard to unsaturated hydrocarbons: V_mS_n clusters do not react with saturated hydrocarbons at $T < 400$ K. With added H_2 to the reaction cell, the species $V_mS_nC_2H_{4,5,6}$ are observed: structures, potential energy surfaces (PESs), and thermodynamics are calculated for these reactions, and mechanisms for a complete catalytic cycle are presented. Odd H species can be derived from a multi cluster or multi site reaction. V_mO_n are unreactive with saturated hydrocarbons (at low T), but can remove H and H_2 from unsaturated hydrocarbons and cleave C=C bonds. The clusters $VO_3(V_2O_5)_x$ ($x=0,1,2,\dots$) are especially active species in this system. Again, cycles and PESs for the catalytic process are suggested. The Fe_mS_n neutral cluster series $m=2$ and $n=2-4$, $m=3$ and $n=3-5$, $m=4$ and $n=4-6$ are observed and all these clusters readily add up to three H atoms. Fe_mS_n species with one H atom are more active with C_3H_6 , C_2H_4 , and CO than are those with no or more H atoms attached. Clusters $m=2$ and $n=2,3$, and $m=4$ and $n=4,5$ are the most active neutral clusters for these reactions. Fe_3S_3 is inactive with respect to these processes. Calculations of PESs and catalytic cycles for these Fe_mS_n clusters are still in progress.

Ammonia synthesis is both important and expensive: new catalytic processes to generate NH_3 would certainly be welcomed. Synthesis of Co_mN_n can be done with N_2 , N_2O , or NO_x to generate a series of Co_mN_n neutral clusters. $Co_{6,7,8,9}N_{1,2,3}$ are especially active with H_2 at 300-400 K to yield $Co_7(NH_3)_{1,2}$ and $Co_{8,9}(NH_3)$. Additionally, Co_m clusters simply add NH_3 and do not dissociate it as occurs with NO_x , N_2 , and N_2O . Note too, that odd H is present in this system as well. Odd H in $Co_{7,8,9}(NH_3)$ probably comes from H_2 dissociation on two cobalt containing clusters, based on DFT calculations: for example, $2Co_7N + H_2 \rightarrow 2Co_7NH$. Both experimental observations and theoretical calculations suggest that ammonia generation requires two active sites: H_2 dissociation on these two active sites is the key step in formation of NH_3 . Clusters $Co_{7,8,9}N$ have high reactivity with H_2 for ammonia generation.

Finally, experiments with mixed metal systems, such as $M'_aM_bO_c$ and M''_aM_b , with $M' = Al, Si, Ti, Ce$, M'' , $M=Fe, V, Co$, are in progress and data will be presented for both distributions and reactions. $AlVO_4$ seems to be especially active with unsaturated hydrocarbons.

Ultrafast High Harmonic, Soft X-Ray Laser Probing of Molecular Dynamics

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High order harmonics generated with femtosecond laser pulses in rare gases are excellent laboratory table-top x-ray sources. Time-resolved photoelectron/photoion mass spectroscopies are developed by combining these vacuum ultraviolet or soft x-ray pulses with visible and ultraviolet pump pulses in a pump-probe configuration for probing photo-initiated dynamical processes of atoms and molecules on ultrafast time scales. In addition, synchrotron ionization mass spectrometry (tunable vacuum ultraviolet light from the Advanced Light Source) is an excellent method to probe the products of reaction dynamics. Goals of this research are to investigate photoionization and photodissociation dynamics of ionic liquids, as well as to explore hypergolic ionic liquid reaction dynamics. Isolated ion-pairs of ionic liquids are generated in a molecular beam or in the form of aerosols. Dynamics is monitored via soft ionization by mass spectrometry and time-sliced ion velocity map imaging. Recently the photodissociation dynamics of a room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)imide ([Emim]⁺[Tf₂N]⁻) is investigated. Ion velocity map images of intact cation and intact anion that are produced from photoexcitation of the isolated ion pairs at 54 nm in the gas phase reveal several dissociation pathways. The kinetic energy distribution of the intact cation has both slow ions arising from previously reported dissociative ionization and fast ions from ion-pair dissociation of the neutral isolated ionic liquid (positive and negative ion pairs). The intact anion shows complementary momentum to the fast intact cation, indicating that the dissociation arises from two-body dissociation of the neutral ion-pair. Observation of the ion-pair dissociation upon photoexcitation of the ionic liquid vapor not only reveals this previously unobserved photodissociation pathway, but it also provides direct evidence for the existence of the isolated ion-pairs in the gas phase. In collaboration with Steve Chambreau and Gammy Vaghjani of the Air Force Research Laboratory, investigations are performed at the Advanced Light Source to explore reaction dynamics and kinetics of hypergolic ionic liquids. Ionic liquid aerosol submicron particles, with diameters of ca. 180 nm, are used to study the heterogeneous reaction. Reaction of hypergolic ionic liquid, 1-butyl-3-methylimidazolium dicyanamide ([Bmim]⁺[Dca]⁻), with fuming nitric acid is investigated. Reaction intermediates, cyanoamine (42 amu/q) and isocyanourea (85 amu/q), are identified by photoionization efficiency measurements, i.e. product ions versus tunable vacuum ultraviolet photon energy. Reaction kinetics of these products is also measured by monitoring the product yields as a function of nitric acid exposure to the ionic liquid aerosols. The reaction step yielding cyanoamine is observed to be faster than the reaction step producing isocyanourea. These observations provide a detailed understanding of the early stages of the hypergolic ionic liquid reaction mechanisms.

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Size Matters: Photophysical Properties of Nanoclusters

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In our continuing interest in multi-photon absorption, calculation of the optical response for nanoclusters (NCs) by applying time-dependent density functional theory will be described. In order to discern NC structures that are based on well-validated methods, because of the lack of experimental characterization, ground and excited state benchmark calculations for small CdSe and ZnS NCs will be reported. In this context, the importance of long-range-corrected hybrid functional schemes for charge-transfer excitations will be discussed. Based on the results, morphologies of larger NCs were predicted and analyzed. In addition, effects of gold NCs were explored for attachment of the donor- π -acceptor dimethylamino nitrostilbene (DANS) chromophore. Our results demonstrate enhancement of the DANS chromophore's TPA cross-section, even by thiolated gold clusters as small as Au₂S.

Computationally Guided Materials Design via Coarse-Graining

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In complex condensed phase systems the effective interactions are manifest over multiple length scales, beginning at the scale of the electronic quantum mechanics and continuing on to the scale of molecular self-assembly and mesoscopic phenomena. An understanding of these various scales of interaction and their physical emergence can in principle be obtained through a renormalization approach that maps very high resolution structures into simpler ones that, in turn, inherit new effective interactions. An example of this renormalization scheme includes the mapping of forces between nuclei on a Born-Oppenheimer electronic surface onto simpler (sometimes called “molecular mechanics”) interaction potentials. Another example is seen in the rapidly advancing methodology of “coarse-graining”, in which molecular structures are projected onto simpler molecular-like entities that, again, exhibit effective interactions. Such effective interactions should in principle be rigorously derived from the underlying molecular-scale forces. The challenge is therefore to develop an overall systematic and practical approach that allows one to carry out such calculations both accurately and efficiently. In this talk such a methodology will be described that relies on variational methods to map complex atomistic-scale interactions onto new effective interactions, all within a proper statistical mechanical framework. The resulting theory and its associated computational algorithm can be utilized, e.g., to construct molecular mechanics potentials from electronic structure data, to coarse-grain complex systems into simpler ones, and to reveal the net effective interactions in a given system at a chosen level of detail. Considerable physical insight can be gained and the methodology also provides a means to assess the sensitivity of condensed phase thermodynamic and structural properties to key aspects of the underlying molecular forces.

A target of this research is to help design new catalysts, via coarse-graining methods, that can produce or utilize alternative fuels. The design principles for these catalysts are derived from insight gained into the key functional elements of natural enzymes, such as the hydrogenases that can reversibly produce or consume molecular hydrogen. The coarse-graining methods systematically eliminate the structural complexity of the enzymes and map them onto a simpler representation. In turn, we can understand the electrostatic contributions to the reactive pathways coming from these simpler coarse-grained models. This approach will allow us to better understand the effective interactions in the catalytic site of enzymes and to then help define biomimetic “catalytic clusters” that could be synthesized in the laboratory to mimic these interesting and important natural systems of relevance to alternative fuel production. If time allows new work will also be presented on how this approach can be generalized to explicitly model the underlying chemically reactive processes.

Using Vibrations to Probe and Control Photoisomerization in Liquids

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Dissociation and isomerization of electronically excited molecules are fundamental processes with wide-ranging practical consequences, and our previous studies have shown that initial vibrational excitation can profoundly influence these processes in isolated molecules. Excited-state reactions often involve conical intersections between electronic states, and it is possible to control the course of excited-state dissociation in isolated molecules using vibrational excitation to influence passage through the intersection. Because excited-state processes are important in more complex environments such as liquids, the interior of proteins, aerosols, or even solids, the goal here is to obtain comparable insights and influence over excited-state dynamics in a solutions and in solids

The three components of these condensed-phase experiments are preparing vibrationally excited molecules, promoting them to an electronically excited state, and observing their motion in the excited state. The key to altering excited-state nuclear motion and influencing dissociation or isomerization is to intercept vibrationally excited molecules as they evolve in their ground electronic state and to transfer them to an electronically excited state with selected nuclear motion. We have used this approach to study the excited-state isomerization of vibrationally excited stilbene in solution, a molecule that has a barrier to excited state isomerization that controls the isomerization dynamics. Isomerizations that occur more directly are better choices for exploring the role of vibrational excitation in the excited-state dynamics, and we have begun studying a molecule synthesized by a collaborator to have that property. One-photon excitation of this N-alkylated indanylidene pyrroline Schiff base leads to isomerization in less than 500 fs, a process we monitor by ultrafast transient absorption.

Identifying the influence that surroundings have on an initial photochemical event can potentially uncover pathways that are not obvious from gas-phase studies. The advantage of monitoring the initial event with good time resolution is that it permits identification of the promptly formed products that carry the subsequent chemistry. We have shown that it is possible to study excited species in liquids using ultrafast laser pulses to prepare vibrationally and electronically excited molecules and to probe both excited molecules and their reaction products. Most recently, we have developed a technique for observing ultrafast isomerization in a cryogenic matrix, a development that permits comparison of the excited-state dynamics in a liquid and a cryogenic solid. We have studied the isomerization of halomethanes, CHX_3 , induced by the interaction of the separating fragments with surrounding solvent molecules in either a liquid or a cryogenic solid. The departing halogen atom returns to bond weakly to the radical fragment, producing the corresponding iso-halomethane, $\text{CHX}_2\text{--X}$. We have probed this product using transient electronic absorption in a cryogenic matrix and using both electronic and broadband vibrational transient absorption in liquids. These experiments show that the timescales in the two environments are similar though not identical and that vibrational relaxation of the initially highly excited isomer is a key first step in stabilizing the isomer.

Nanoscale Dynamics and Spectroscopy in Extreme Environments

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Recent advances in two areas will be presented: 1) elucidation of structure-specific exciton dynamics for quantum-confined nanostructures and 2) the development of polarization-resolved single-particle spectroscopy techniques. In both cases, advanced spectroscopic techniques are used to examine the interplay between nanoparticle structure and optical properties.

Shape- and crystal structure-dependent exciton dynamics of semiconducting nanoparticles were investigated using time- and polarization-resolved magneto-photoluminescence spectroscopy. Experiments were performed at low temperature (<2 K) in magnetic fields up to 17.5 T to investigate spin-dependent radiative relaxation in CdSe quantum dots and nanorods. In contrast to 0-D quantum dots, one-dimensional CdSe nanorods displayed a high degree of spin polarization even at relatively low magnetic field strengths (2 T). The observed spin polarization, evident in intensity-integrated and wavelength-resolved photoluminescence and time-correlated single-photon counting measurements, resulted from spin-polarized excitons that were formed upon highly efficient mixing of “dark” and “bright” fine-structure states. The relative population of these fine-structures was dependent upon the strength of the applied magnetic field. These results demonstrate the potential use of particle shape and crystal structure, two key nanostructure design parameters, to control photoinduced nanoscale dynamics. I will also demonstrate the use of applied fields to optimize resonant energy transfer efficiency. The findings may impact significantly technologies such as solar-to-electric energy conversion, spintronics, and chemical lasers, which all employ the nanocrystal platform.

In addition, femtosecond laser-based second harmonic generation-detected circular dichroism (SHG-CD) spectroscopic probes have been developed with single-structure sensitivity to investigate nanoscale plasmonics. Because SHG is sensitive to local fields, the data enable determination of structure-dependent surface electric and magnetic fields. Recent results from both small and extended plasmon-supporting aggregates will be presented.

Nano-Scale Energetic Films by Superfluid Helium Droplet Assembly

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Since the pioneering work of the Toennies, Scoles, and Northby groups in the early 1990's, dozens of instruments around the world have been constructed to produce and study beams of superfluid helium nano-droplets. The technique has been exploited to shed light on a wide range of topics in chemical physics such as atomic scale manifestations of superfluidity, chemistry at ultra-low temperatures, and the assembly of exotic Van der Waals complexes to name a few. The helium droplet method has been considered for more applied use as a tool for isotope enrichment, low-fragmentation ionization mass spectrometry, and synthesizing/depositing core-shell spintronic nano-particles.¹⁻³ The helium droplet methodology is in the midst of transitioning from a cryogenic nano-scale matrix to a tool for performing fundamental research into synthesizing, characterizing, and manipulating material.

Our research group has been transitioning superfluid helium droplet assembly of clusters into a deposition tool that is capable of creating nano-structured films of composite metal-based energetic materials (EM). Such materials are ideal candidates to study propagation of reactions at small scale, and could be alternatives to organic based EM due to their higher energy densities. The helium droplet methodology provides a high level of control during the cluster formation process of these materials that opens up the possibility of overcoming issues of reaction-limiting effects such as the formation of oxide layers. This presentation will describe the following: foundational work to model the deposition of clusters by superfluid helium droplet assembly, our efforts to deposit magnesium with this method and the resulting efforts to demonstrate its final state on a surface, and our early efforts to create EM cluster-based films on a surface.

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Investigating Catalytic Processes using Mass Spectrometry

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Capturing Fleeting Intermediates

Identifying intermediates is essential to understanding chemical reactions. However, few analytical techniques can intercept transient species in solution because of their low concentrations, short lifetimes, concurrent side reactions, and the complexity of the reaction environment. The high speed, sensitivity, and chemical resolution of mass spectrometry (MS) make it one of the preferred methods for studying reactivity. Recently, the Zare laboratory demonstrated that desorption electrospray ionization (DESI)^[1] can intercept catalytic intermediates with millisecond time resolution.^[2] In DESI, primary microdroplets bombard a surface of interest, extracting physisorbed chemicals into secondary microdroplets (Fig. 1). The secondary microdroplets evaporate, producing unsolvated ions that enter the mass spectrometer. By placing reagents in the spray and on the surface, chemical reactions occurring in the secondary microdroplets can be analyzed in real time. Because of the short travel time from the surface to the mass spectrometer inlet, it is possible to intercept species formed during the first few milliseconds. DESI is an ambient ionization technique, so sample preparation is greatly simplified.

Using this approach, our lab is currently exploring the catalytic and degradation pathways of various transition metal complexes important for synthetic and energy transformations: (a) transfer hydrogenation, (b) C-H amination, and (c) water oxidation. A recent discovery^[3] is the detection of all the proposed major intermediates (**1-7** in Fig. 2) in C-H aminations catalyzed by the dirhodium tetracarboxylate complex $\text{Rh}_2(\text{esp})_2$ (**1**).^[4] Perhaps one of the most amazing results of this study is observation of the Rh-nitrene **6**, which has never been previously observed because it is postulated to have a half-life in the nano- to microsecond regime. These results highlight the remarkable power of DESI-MS to intercept fleeting intermediates in solution. We are also developing new mass spectrometric instrumentation to facilitate real-time reaction monitoring of air-sensitive catalysts and for probing reactivity in various gaseous environments. These technologies will significantly facilitate new discoveries in organometallic catalysis.

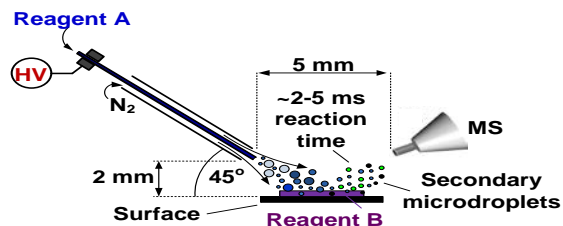


Fig. 1. Experimental setup that used DESI to intercept reaction intermediates in solution on the millisecond timescale.^[2] Velocity of the droplets exiting the sprayer = ~100 m/s; Velocity of the secondary microdroplets = 4 m/s.; Reaction time = ~2-5 ms.

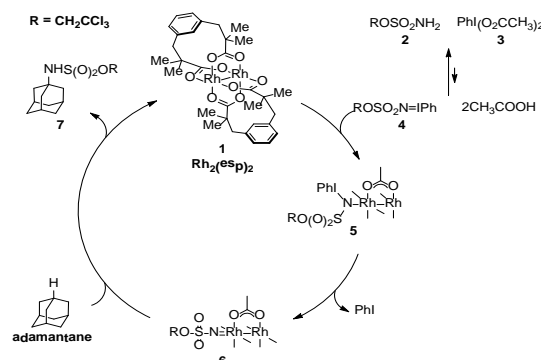


Fig. 2. Proposed mechanism for $\text{Rh}_2(\text{esp})_2$ -catalyzed C-H aminations.

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Photoinduced Proton-Coupled Electron Transfer Reactions: Electron-Proton Nonadiabaticity and Ultrafast Dynamics

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Proton-coupled electron transfer (PCET) reactions play an important role in a wide range of energy conversion processes. This talk will present theoretical approaches for describing electron-proton nonadiabatic effects and for simulating the ultrafast dynamics of photoinduced PCET. A brief summary of recent advances in the nuclear-electronic orbital (NEO) approach, which incorporates electron-proton nonadiabatic effects into quantum chemistry calculations, will be presented. The remainder of the talk will focus on simulating photoinduced PCET reactions with either a dielectric continuum or explicit solvent representation. In the dielectric continuum solvent representation, an ensemble of nonadiabatic surface hopping trajectories is propagated with Langevin dynamics on electron-proton vibronic free energy surfaces that depend on two collective solvent coordinates. In the explicit solvent representation, the surface hopping trajectories are propagated with Newtonian dynamics on multidimensional electron-proton potential energy surfaces that are calculated on-the-fly with a multistate empirical valence bond potential. Applications of these approaches to model systems illustrate both sequential and concerted mechanisms, as well as more complex branching processes involving a combination of sequential and concerted mechanisms. These calculations illustrate that the charge transfer dynamics, solvent dynamics, and vibrational relaxation processes are strongly coupled. Preliminary calculations of the experimentally studied photoinduced PCET reaction in the hydrogen-bonded adduct of *p*-nitrophenylphenol and *tert*-butylamine will also be presented. In this system, photoexcitation may induce a sequential reaction, in which intramolecular electron transfer within the *p*-nitrophenylphenol precedes intermolecular proton transfer from the phenol to the amine, or the corresponding concerted electron-proton transfer reaction. Understanding these types of photoinduced PCET processes is critical for the development of alternative, renewable energy sources such as solar cells.

How Changing the Number of Electrons Opens the Door to Routine, Multi-Reference Coupled-Cluster Applications

Rodney J. Bartlett, Ajith Perera, Victor Lotrich, Tom Watson

Quantum Theory Project

University of Florida

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Because of coupled-cluster's theory exponential ansatz, which has to be maintained to ensure its size-extensivity and rapid convergence to the exact solution, MR-CC formulations and implementations are difficult [1] unlike multi-reference CI. Doing MR-CC is like writing a sonnet while MR-CI is like free verse. This has led to several variants of MR-CC, which have some formal objections. These problems include one or more of the following for all variants, active orbital selection, Intruder states, no analytical forces, not size-extensive, fails to converge to full CI, not invariant to rotations among active orbitals, and does not reduce to the single reference CC result in the absence of multi-reference effects.

One unusually attractive potential solution we are proposing is to use the flexibility inherent in CC theory and in its equation-of-motion (EOM) extensions, to make such applications routine. This leads to a series of methods based upon multiply ionized (MI) or attached (MA) vacuum states, to ultimately describe the N-electron system in an unbiased, multi-reference way [2-3]. We report on this theory, its applications to many, illustrative MR problems including singlet-triplet splittings and potential energy surfaces.

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Charge & Field Effects in Clusters: Nanocatalysis, Water Nanodrops, Electrocrystalliation, and Proton-Coupled Electron Transfer in DNA

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When the scale of materials structures is reduced to the nanoscale, emergent physical and chemical behavior often occurs, that is not commonly expected, or deduced, from knowledge learned at larger sizes. Using computer-based simulations [1], often in conjunction with laboratory experiments, we highlight and illustrate such behavior in diverse emergent phenomena. In particular, we focus on mechanisms and effects of charging of clusters and the response of clusters to applied electric fields. Systems that we discuss include: (i) First-principles theoretical and laboratory experimental investigations of Charging effects in Nanocatalysis [2] and post-ionization proton-coupled-electron-transfer (PCET) reactions in DNA underlying oxidative reactions that lead to mutagenesis and malignancy [3]; (ii) Electric-field-induced shape transitions and electrocrystallization of dielectric nanodroplets [4, 5]; (iii) Theoretical and experimental studies of singly and doubly negatively charged water nanodroplets, with a focus on clusters with up to ~ 100 molecules, revealing interior, surface, and diffuse electron attachment modes, and the mechanism of hydrogen evolution dielectron reaction in $(\text{H}_2\text{O})_n^{-2}$ clusters with $n \geq 105$ molecules [6].

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Novel Catalytic Mechanisms for the Chemical Reduction of Carbon Dioxide to Energy-Dense Liquids (MURI)

Clifford Kubiak (UCSD), Andrew Bocarsly (Princeton), Emily Carter (Princeton),
Nathan Lewis (Caltech), Anders Nilsson (Stanford) and Jens Nørskov (Stanford)

Contract/Grant #: FA9550-10-1-0572

Results from the MURI on "Novel Catalytic Mechanisms for the Chemical Reduction of Carbon Dioxide to Energy-Dense Liquids" will be reviewed. We continue to examine aspects of the mechanisms of CO₂ reduction using heterogeneous and homogeneous catalysts through both experimental and advanced theoretical methods. In heterogeneous catalysis, particular attention has been paid to copper surfaces, which are known to be the only metal electrodes capable of producing hydrocarbons from CO₂. Recent theoretical investigations of CO₂ reduction at copper have focused on the C–C coupling step that ultimately produces ethylene. These computational studies have been coupled to high resolution X-ray spectroscopies at SLAC where EXAFS was applied to monolayer copper surfaces under electrochemical conditions to observe the nature of the catalytic intermediates and surface states during electrochemical reduction of CO₂ to hydrocarbons. Notably, it has been found that the substrate of the copper monolayer plays a non-innocent role. For example, a monolayer of Cu on Au leads to alloying of the two metals. These studies were also extended to the study of molecular catalysts for CO₂ reduction, and XANES and EXAFS experiments have been carried out on isolated intermediates for the homogeneous catalytic reduction of CO₂ by Re(L)(CO)₃X catalysts.

The electrochemical reduction of CO₂ to methanol is being investigated on several fronts, including organic, inorganic, and heterogeneous catalyst materials. At Cu₂O electrodes, it has been found that different results are observed depending on the method of generating the Cu₂O film. Our understanding of the pyridinium CO₂ reduction catalyst system has increased significantly over the past 12 months from new calculations that show that the pyridinium system previously reported by Bocarsly is not a purely homogeneous system. This highlights the importance of understanding the electrode-solution interface. Current efforts are focused on studying the interaction between the pyridinium catalyst and the Pt or GaP electrodes, which are known to be active systems for CO₂ reduction to methanol. Advances in modeling of the GaP surface under aqueous conditions have shown that water is cleaved at the GaP surface to make Ga–OH and P–H bonds. The interaction of pyridine and pyridinium with these surfaces is currently being explored. The versatility of the pyridinium system has also been expanded to other electrodes besides Pt, Pd, and GaP. It has been found that use of bipyridines and other nitrogen-containing heterocycles significantly affects product distributions.

Research on molecular catalysts based on Ni, Re, Cu, and Rh have identified an electronic structural basis for branching ratios for H⁺ vs. CO₂ reduction. Studies on the Ni(cyclam) catalyst show that it operates through a homogeneous catalytic mechanism at glassy carbon. This contradicts previous reports that the catalyst was only active when adsorbed on mercury. We have also reported a versatile new synthesis of "proton relay" P₂N₂ ligands which opens up the possibility for the preparation of new catalysts for the reduction of CO₂.

Ultrafast and Diffusion-Limited Charge Extraction from PbS Quantum Dots Gated by the Native Ligand Shell

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This talk describes ultrafast hole transfer and both ultrafast and microsecond-timescale electron transfer from photoexcited PbS quantum dots (QDs) to the coordinating photo-oxidant aminoferrocene and the non-coordinating photo-reductant benzoquinone, respectively. We show with this work that, while PbS QDs coated with an oleate ligand shell permit the coordinating molecule aminoferrocene to permeate this shell and participate in photoinduced hole transfer with the QD, PbS QDs coated with the tighter-binding thiolate monolayer do not participate in hole transfer (Figure 1). We also show that, because the lifetime of the excited states of PbS QDs is $> 1 \mu\text{s}$, we can observe both static and diffusion-limited electron-transfer quenching of the QD excited state by the weakly-adsorbing benzoquinone molecule (Figure 2) within a single QD-BQ sample. These results are important for photocatalytic systems incorporating PbS QDs and solution-phase redox-active substrates because they establish both the surface chemistries that will facilitate the exchange of charges with PbS QDs, and the range of timescales over which charge transfer processes can occur.

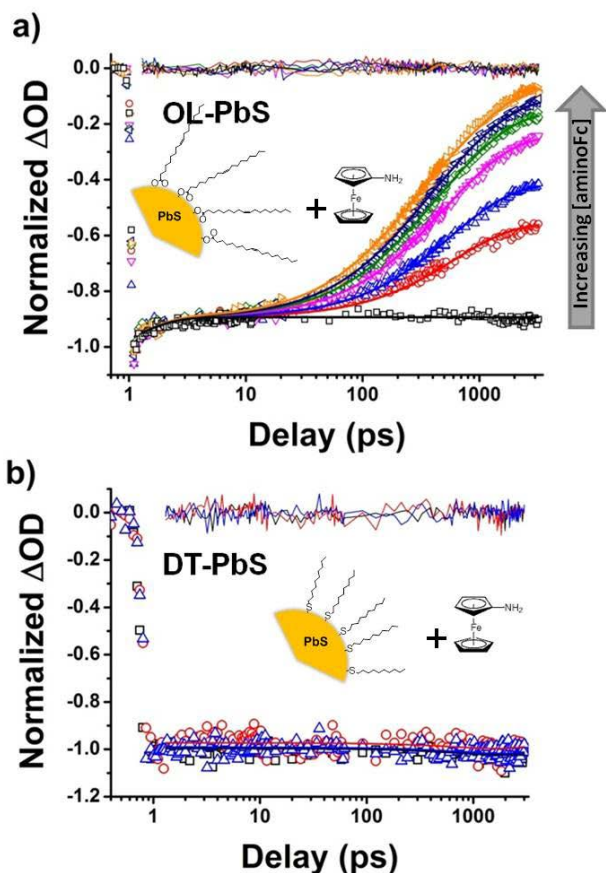


Figure 1. Normalized kinetic traces monitored at the peak of the ground state bleach of the QDs for **a)** OL-PbS QDs in toluene solutions containing AminoFc and **b)** DT-PbS QDs in toluene solutions containing AminoFc.

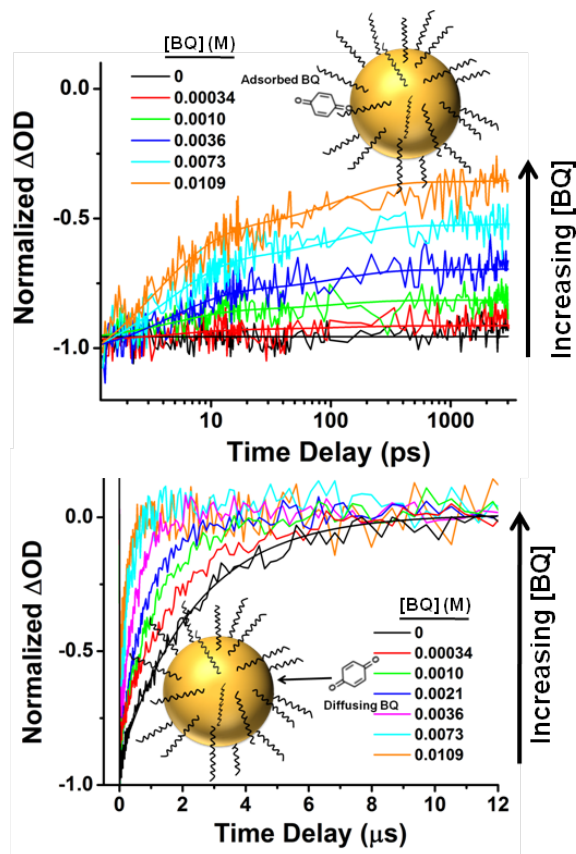


Figure 2. Normalized kinetic traces monitored at the peak of the ground state bleach of the QDs for OL-PbS QDs in toluene solutions containing BQ on the picoseconds timescale **(a)** and the microsecond timescale **(b)**.

Thermodynamics of Isolated Bi-Atomic Clusters

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Recent efforts have confirmed that atomic clusters with specific coordination and mixed occupancy of species are the fundamental structural units of nearly all metallic glasses. In this work, a quasi-chemical approach is used to determine the total energy of each possible bi-atomic configuration in a 12-fold coordinated (icosahedral) cluster containing Cu and Zr. This defines a configurational density of states from which the enthalpy, entropy, and free energy of Cu-Zr and other such isolated clusters can be determined via a statistical-mechanics-type analysis. Results of this analysis are contrasted with a parallel approach based on ab initio techniques to determine the total energy of each Cu-Zr cluster in the same ensemble configuration space. These results are then compared with known data to assess the efficacy of using such an analysis of bi-atomic clusters as a proxy for the thermodynamic properties of Cu-Zr-based metallic glasses.

Efficient Methods for Exploring Potential Energy Surfaces of Chemical Reactions and Discovery of Excited Roaming Pathways for NO₃ Photodissociation

Chirality Control in the Growth on Carbon Nanotubes

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1. We have recently developed the artificial force induced reaction (AFIR) method for those of type $A + B \rightarrow X (+ Y)$.¹ This method and the global reaction route mapping (GRRM) method for reaction pathways of type $A \rightarrow X (+ Y)$ can find not only all TS structures for a single PES but also minima and saddle points on the seam of crossing (MSXs)² including conical intersections. These methods have been applied successfully to organic multicomponent reactions, photodissociation reactions of aldehydes and ketones, and homogeneous catalytic reactions. Roaming mechanisms have recently been observed in several chemical reactions alongside trajectories that pass through a traditional transition state. Recently we showed using GRRM and AFIR that the visible light-induced reaction $\text{NO}_3 \rightarrow \text{NO} + \text{O}_2$ proceeds exclusively by roaming. High level ab initio calculations predict specific NO Λ doublet propensities (orientations of the unpaired electron with respect to the molecular rotation plane) for the two channels in this mechanism, which has recently been discerned experimentally by ion imaging.³

2. Controlling chirality is one of the largest problems in growing single walled carbon nanotube (SWCNT). In order to quantify the chirality of irregular growing SWCNT, we have recently developed the local chirality index (LOCI) based on orientation of individual hexagons.⁴ The distribution of LOCI of all hexagons as function of growth time provides information on how and when the chirality is maintained and lost. This method has been applied to quantum chemical molecular dynamics (QM/MD) simulation of SWCNT growth from a cycloparaphenylene template⁵ as well as coninued growth of zigzag and armchair SWCNT on transition metal cluster.⁶

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Structure-Property Relationships in Nanostructured Electrodes for Hybrid Photovoltaics and Batteries

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The development of low-cost, lightweight, and flexible energy harvesting and storage devices are an enabling technology for many different applications. The fabrication of highly efficient power conversion and energy storage devices with high power and energy density are highly dependent on the materials and device structures used to make up the active components. Some of the factors limiting the performance of organic and nanoparticle-hybrid devices include poor spectral response and restricted charge transport. These effects can result from poor light absorption, increased carrier recombination, low electronic charge carrier mobilities, relatively random thin film morphologies, and/or limited ionic intercalation and conduction pathways. Our efforts to address these issues for a variety of devices (including photovoltaics and battery electrode materials) include developing materials and fabrication methodologies that result in highly ordered structures to permit enhanced charge transport and developing unique device configurations to facilitate light absorption and charge transfer. This talk will provide an overview of current state-of-the-art for these devices, highlight current barriers to improved performance, and describe a number of specific approaches being investigated to address these issues.

A variety of different nanostructured electrode architectures are being developed and will be discussed. These include a nano-templating methodology based on porous anodic alumina in order to fabricate vertically aligned titania nanotubes of controllable shape and size and vertically aligned carbon nanotubes for use as either intercalation (in batteries) or charge collecting (in PVs) electrodes. In addition, efforts to understand and tune the device spectral response will be discussed. By utilizing an interfacial modification technique based on layer-by-layer deposition, nanoparticle surfaces have been functionalized with electronically active species and integrated into device structures. This technique is amenable to developing an 'energy cascade' device architecture commonly utilized in photosynthetic organisms. Finally, efforts focused on the development of nanostructured electrodes for high energy density and rate capability batteries will be described.

Extremes in Oxidizing Power, Acidity, and Basicity

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The first issue addressed is the production of extreme oxidants that would be useful for oxidation of normally inert substrates. DFT (PCM-M06-2X/cc-pVTZ//M06-2X/cc-pVTZ) calculations of redox potentials of ~20 halogenated CB_{11} anions in liquid SO_2 relative to $\text{CB}_{11}\text{Me}_{12}^-$ (1.16 V above Fc/Fc^+) have been performed. Since the already known radical $\text{HCB}_{11}\text{F}_5(\text{CF}_3)_6^-$ (calculated 3.0 V above $\text{CB}_{11}\text{Me}_{12}^-$) is strong enough to attack fluorocarbons, we started with an examination of $\text{HCB}_{11}\text{F}_{11}^-$, which is calculated to be 'only' 1.45 V above $\text{CB}_{11}\text{Me}_{12}^-$ and which would be easier to find inert solvents for. Surprisingly, $\text{HCB}_{11}\text{Cl}_{11}^-$ and $\text{HCB}_{11}\text{Br}_{11}^-$ are calculated to be stronger oxidants (1.65 V above $\text{CB}_{11}\text{Me}_{12}^-$), presumably due to less efficient π -donation from lone pairs. $\text{HCB}_{11}\text{I}_{11}^-$ is calculated to be only 0.65 V above $\text{CB}_{11}\text{Me}_{12}^-$ and has an electronic structure reminiscent of an antihydrogen atom: a negative charge delocalized on a central CB_{11} core is surrounded by a spherical sheet of positive charge delocalized over the overlapping iodine lone pairs.

The synthesis of $[\text{Cs}][\text{HCB}_{11}\text{F}_{11}]$ by direct fluorination of $[\text{Cs}][\text{CB}_{11}\text{H}_{12}]$ has been improved. However, all attempts at chemical oxidation to $\text{HCB}_{11}\text{F}_{11}^-$ have thus far been unsuccessful. In some cases (F_2 , XeF_2) there was no reaction, and in others (K_2NiF_6 , NiF_3^+ , AgF_2 , AgF_3) overoxidation to BF_4^- occurred. We have therefore turned to electrochemistry, which offers finer tuning. In liquid SO_2 , the oxidation of $\text{HCB}_{11}\text{X}_{11}^-$ is irreversible, at 1.44 (X=F), 1.24 (Cl), 1.4 (Br), and 0.63 (I) V above $\text{CB}_{11}\text{Me}_{12}^-$, and we believe that the radicals oxidize the solvent. In $(\text{CF}_3)_2\text{CHOH}$, the oxidation of $\text{HCB}_{11}\text{X}_{11}^-$ is reversible at 1.48 V above $\text{CB}_{11}\text{Me}_{12}^-$ when X=F, but remains irreversible for X=Cl, Br, or I (1.49, 1.54, or 0.87 V, respectively). Most recently, we have discovered a new solvent suitable for electrochemical oxidation of our anions that promises to be inert, 1,1,1,3,3-pentafluorobutane, and a preparative-scale electrochemistry apparatus is under construction.

Novel Catalytic Synthetic Methods for Main Group Materials and Reagents for Organic Synthesis Pls

R.G. Bergman, J. Arnold, F.D. Toste

The catalytic activation and selective functionalization of readily available small molecules (*e.g.* H_2 , O_2 , ethylene, silanes, boranes, *etc.*) has been a dominant driving force behind the development of organometallic chemistry and its application in the chemical industry. The study of organometallic reaction mechanisms has identified many key transformations in these metal catalyzed reactions. The data from these detailed studies have led to the development of new reaction types, complexes, and applications that have had a profound affect on our modern economy and life style. However, the vast majority of studies have focused on transformations that occur at the metal center (*e.g.* oxidative addition, reductive elimination, 1,2-insertion, sigma-bond metathesis, *etc.*). The study and development of transformations that occur at the ligand or in cooperation with a ligand are advantageous because they are particularly useful for forming carbon-heteroatom bonds. However this functionalization approach has been explored less extensively than those involving more traditional organometallic pathways. A particular example of this type of chemistry that we wish to explore is the [1,2]-addition of main group-hydrogen bonds (*e.g.* H_2 , BH , CH , SiH , NH , *etc.*) to metal-ligand multiple bonds (*e.g.* $L_nM=X$; $X=O$, S , NR), a relatively rare reaction, that we believe provides substantial potential for innovative research in both organic methods development and main group materials methods development. Towards these ends, we have embarked on a collaborative study with initial targets in the areas of novel bond activations with niobium and gold.

We will discuss the discovery of a Nb(III)-mediated catalytic hydrogenation of internal alkynes to Z-alkenes that has been found to proceed through an unprecedented mechanism. The mechanistic proposal involves initial reduction of the alkyne by the Nb(III) complex $(BDI)Nb(N^tBu)(CO)_2$ to provide a Nb(V) metallacyclopentene, itself capable of σ -bond metathesis reactivity with H_2 . The resulting alkenyl hydride species then undergoes reductive elimination to provide the Z-alkene product and regenerate a metal complex in the Nb(III) oxidation state. Support for the proposed mechanism is derived from *i*) the dependence of product selectivity on the relative concentrations of CO and H_2 , *ii*) the isolation of complexes closely related to those proposed to lie on the catalytic cycle, *iii*) H/D crossover experiments, and *iv*) DFT studies on multiple possible reaction pathways.

In addition, we have prepared the first terminal gold(I) amide and phosphide complexes and studied their reactivity toward an array of electrophiles and small molecules. These complexes illustrate an unexplored mode of reactivity for gold complexes in which a nucleophilic ligand is capable of forming C—N and C—P bonds. In addition, the potential for these complexes in catalysis is demonstrated through phosphine alkylation, the first example of C—P bond formation through homogeneous gold catalysis.

Polynitrogen and High-Nitrogen Chemistry

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Polynitrogen and high-nitrogen compounds are highly energetic and environmentally clean propellants and explosives. While most elements are known to occur in the form of different allotropes with very similar energies and high barriers toward their inter-conversion, no nitrogen allotropes of sufficient kinetic stability under normal conditions are known. This is due to the very high energy content of polynitrogen compounds, low activation energy barriers toward nitrogen elimination, and the lack of suitable preparative methods. However, there are a few candidates which have been predicted to possess sufficiently high activation energy barriers toward N_2 elimination. The foremost candidate in this respect is tetrahedral N_4 . Previous attempts at the Colorado School of Mines under DARPA sponsorship to isolate this molecule at low temperatures in a nitrogen matrix have been inconclusive because the observed 14/15 nitrogen isotope shifts deviated substantially from the theoretical predictions. Under an AFOSR program at USC the bulk syntheses of N_4 and other polynitrogen compounds are being pursued using low-temperature silent glow-discharge, quenching techniques, and detection by Raman spectroscopy.

In the area of high-nitrogen chemistry, numerous novel polyazide molecules and ions were synthesized and characterized. These include the binary Group 15 compounds $[Bi(N_3)_4]^-$, $[Bi(N_3)_5]^{2-}$, $[bipy-Bi(N_3)_5]^{2-}$, $[Bi(N_3)_6]^{3-}$, $bipy-As(N_3)_3$, $bipy-Sb(N_3)_3$, and $[(bipy)_2-Bi(N_3)_3]_2$ which have potential as lead-free, nontoxic primary explosives. With the tetraazido arsenite and antimonite anions, a set of highly unusual chemical cameleons was discovered. For five salts with the very similar cations $N(Me_4)^+$, $P(Ph_4)^+$, and PNP^+ , five different anion structures were found.

Theoretical Studies of Gas-Surface and Gas-Phase Dynamical Processes

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This abstract summarizes my AFOSR-sponsored theoretical studies of gas phase and gas/liquid dynamical processes (Grant FA9550-10-1-0205). The primary aim of this work is to understand dynamics under energetic conditions such as are important in plasmas, in high performance jet engines and in upper atmospheric collision processes.

A major result this year has been the development of a combined R-matrix method and trajectory-surface hopping (TSH) approach for simulating electron-impact dissociation (EID) of methane.¹ The R-matrix method is used to calculate inelastic electron scattering cross sections for collision energies ranging from threshold to 50 eV or higher, and for electronic states up to the ionization threshold of around 15 eV, and then the TSH calculations are used to determine product branching in the subsequent dissociation of the methane excited states. Vibrational averaging is done using the vibrational Wigner function approach based on the methane ground state. The UK molecular R-matrix code was used for these calculations, and most calculations using the highest level theory available, CAS-CI with cc-pVTZ basis functions, but this level of theory makes several eV errors in excited state energies, and some empirical shifting of excitation functions is needed to connect to experiment. The TSH calculations were performed using the NewtonX code, and a key simplification that we found is that the higher excited states of methane all undergo rapid internal conversion to the lowest excited singlet state or the lowest triplet state, so the branching is determined by dissociation on just two states. The resulting EID cross sections for CH₃ and CH₂ production show excellent agreement with some of the experiments, which makes it possible to resolve on-going confusion as to which experiment is correct. Moreover, the calculations show that the dominant product is CH₃, and that this arises because the largest electron-impact excitation cross sections are to triplet states, and the triplet states dissociate exclusively to CH₃ + H. Also, the new results have clarified branching to give the CH radical (important in soot formation) which we found comes only from singlet dissociation.

Another area of important progress this year has concerning the study of energy transfer in collisions of hyperthermal CO₂ with ionic liquid surfaces.² Here we developed a new code² (improving on past work that was useful for studying gas-liquid and gas-solid reactive collisions^{3,4}). With the newer code we studied the rotational excitation of CO₂ in collisions with the two ionic liquids [bmim][BF₄] and [bmim][Tf₂N], and we were able to use our results to interpret experiments due to Nesbitt's group. Nesbitt's group found that CO₂ collisions with these ionic liquids proceed via both impulsive scattering (IS) and trapping desorption (TD) mechanisms. The relative amounts of these mechanisms and the amount of rotational excitation from these mechanisms depend on ionic liquid, with [BF₄] leading to greater TD and less rotational excitation. Our QM/MM molecular dynamics calculations produced results which matched the observations accurately, and they demonstrated that the key factors for these results are the strength of the CO₂ interaction with the anion, and the position of the anion relative to the surface of the ionic liquid.

Other papers published this year relate to our studies of bimolecular reactions.^{5,6}

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2. QM/MM Studies of CO₂ Rotational Excitation in Collisions with Ionic Liquid Surfaces. X. Li, G.C. Schatz and D. J. Nesbitt, J. Phys. Chem. B, ASAP (2012).
3. Dynamic QM/MM: a hybrid approach to simulating gas-liquid interactions, Scott Yockel and George C. Schatz, Top. Curr. Chem, 307, 43-68 (2012)
4. Theoretical studies of the erosion of (100) and (111) diamond surfaces by hyperthermal O(3P), Jeffrey T. Paci, George C. Schatz and Timothy K. Minton, J. Phys. Chem. C, 115, 14770-14777 (2011).
5. O(³P) + CO₂ collisions at hyperthermal energies: dynamics of nonreactive scattering, oxygen isotope exchange, and oxygen-atom abstraction, L. Y. Yeung et al, J. Phys. Chem. A 116, 64-84 (2011)
6. Kinetics of the reaction of the heaviest hydrogen atom with H₂, the ⁴Heμ + H₂ → ⁴HeμH + H reaction: Experiments, accurate quantal calculations, and variational transition state theory, including kinetic isotope effects for a factor of 36.1 in isotopic mass, D. G. Fleming et al, J. Chem. Phys. 136, 184310 (2011)

Spectroscopy of Gas-Phase Ionic Liquids

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The Air Force is seeking new fuels to replace toxic hydrazines commonly used in satellite thrusters and to serve as the emitted material in electric propulsion systems. Ionic liquids (ILs) are viewed as potential candidates for both. However, finding the right cation-anion combination for each type of thruster, or for a dual-use thruster, is a difficult problem. The quantum-mechanical and other methods used to calculate IL properties are not yet accurate enough to be used predictively. We have begun a research program using gas-phase spectroscopy to explore the fundamental optical and structural properties of ionic liquid ions, neutral pairs, and ionic clusters in order to assess various computational methods. We present here our initial studies on the UV spectroscopy of [emim][Tf₂N] and discuss upcoming experiments using IR spectroscopy to determine ion pair conformations, providing the first direct test of various levels of computations. We will also discuss the new instrument we will be implementing later this year, which uses electrospray ionization to inject small ionic liquid clusters into a multistage mass spectrometer. The clusters will be trapped in a 22-pole ion trap and collisionally cooled for UV and IR spectroscopy.

Size and Composition Optimized Nanocatalysts for Propulsion Applications

Lead PI Lisa Pfefferle, ChE, Yale University, (speaker)
Maria Flytzani-Stephanopoulos, ChE, Tufts University
Raymond Gorte, ChE, University of Pennsylvania
Gary Haller, Chem/ChE, Yale University
Charles McEnally, ChE, Yale University
Matthew Neurock, ChE, University of Virginia
Stefan Vajda, Adjunct Professor, ChE, Yale University, (Argonne Ntl Lab)

We discuss the development of dispersible catalysts that actively carry out cracking and dehydrogenation of large alkanes and cycloalkanes. These reactions provide cooling but also change the chemical composition of the fuel either enhancing or inhibiting ignition. Our practical work on catalyst synthesis and fuel chemistry is complemented by detailed theoretical and experimental studies on the reactivity of size-selected clusters including studies of the role of size, composition and support interactions on the catalytic activity and selectivity. The links between theory, model catalyst and real catalyst tests are designed to elucidate the behavior of the nanoparticles, establish the study of support-catalyst interactions on a fundamental level to aid in the design of active and stable catalysts. Early in the project we have demonstrated a selectivity effect of Pt and Co particle size for dehydrogenation of cyclohexane and linear alkanes both experimentally and theoretically.

The focus of the talk will be a new acid catalyst based on sulfated zirconia grafted to multiwalled carbon nanotubes (MWNT). We used X-ray absorption techniques to show covalent bonding of the zirconia to the carbon in the MWNT indicating increased electronic coupling between components that are covalently bonded. We also showed that these catalysts are active for hydrocarbon cracking, and when doped with a precious metal catalyst component, can significantly accelerate fuel lean combustion. The catalyst without precious metal exhibits excellent activity for cracking cyclohexane at temperatures consistent with fuel preheating and represents a new paradigm in catalyst design and is inexpensive to fabricate.

We have also carried out density functional theory calculations to confirm that the ZrO_2 clusters are strongly anchored to the support via the formation of strong Zr-O-C bonds that likely form at edge or defect sites. The interaction between the non-defective closed CNT surfaces and ZrO_2 on the other-hand is very weak and thus unlikely. In order to establish a better understanding of the mechanism and the influence of the catalyst properties on the kinetics we examined the unimolecular cracking of n-butane over different acid catalysts with different degrees of Brønsted acidity. Theoretical results show that cracking proceeds via the formation of a carbenium ion transition state involving the deprotonation of the acid together with protonation and rupture of the C-C bond. The activation barriers were shown to be linearly related to the deprotonation energy, which is a direct measure of solid acid acidity. The theoretical results indicate that supported sulfated zirconias are stronger acids than tungstated zirconias and more comparable to the highly acidic heteropolyacids.

POSTERS

TDDFT Optical Absorption Characteristics Of Silver And Gold Nanoparticles: Effect Of Shape, Size, And Composition

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Department of Chemistry, Kansas State University, Manhattan, KS 66506

Silver and gold nanoparticles have many useful applications because of their plasmonic properties. In this research, time-dependent density functional theory (TDDFT) is employed to calculate the optical absorption of silver and gold nanoparticles with shapes ranging from nanowires to octahedra to icosahedra. We find that a linear combination of single-particle transitions that combine in-phase is responsible for the sharp absorption peaks displayed by many nanoparticles; the plasmon resonance is suggested to arise in part from this phenomenon. The absorption peaks shift as a function of the nanoparticle size. Gold nanoparticles display more prominent interband transitions than silver; for nanowires, this is directly related to the density of states for these systems.

Understanding Ultrafast Energy Transport in Carbon Nanotube Hybrid Materials for Next Generation Solar Cells

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Department of Materials Science and Engineering and Department of Chemistry
University of Wisconsin-Madison

The aim of this project is to develop the fundamental science behind a new and exciting class of materials based on carbon nanotube photoabsorbers that enable a new type of photovoltaic solar cell. Semiconducting carbon nanotubes are extremely promising materials for photovoltaics because of their strong optical absorptivity, ultrafast exciton and charge transport, chemical stability, and solution-processability. We have already demonstrated prototype devices exhibiting incident-photon to collected-electron conversion efficiency of 15% at 1.05 μm and 20% at 1.2 μm and monochromatic power conversion efficiency of 7% at 1.05 μm , which are 5-10x better than semiconducting polymers in this range. However, we know almost nothing about how these promising new devices operate.

A key aspect of understanding these materials is learning and controlling how energy is transferred among nanotubes. We are working to use state-of-the-art two-dimensional electronic (2D Elec) spectroscopy to identify hopping mechanisms, sample heterogeneity, and environment-induced correlations in these materials. Our ultimate goal is to study and design quantum coherences into nanotube-based materials and devices through bundled architectures, analogous to how bacteria and plants are now thought to foster ultrafast and efficient exciton transport. Thus, we will both understand and learn to manipulate energy and exciton transport in these new nanotube materials.

We have started by characterizing the dynamics of energy transfer among nanotubes in a weakly coupled regime because this regime is the basis for the prototype photovoltaic devices that have been tested so far. In these devices, efficient exciton hopping between nanotubes is critical for transporting the excitons to the heterojunction interface where they can separate into free electrons and holes (see Figure). At an average wall-to-wall inter-tube separation of approximately 8 Å, the nanotubes are sufficiently close to enable inter-tube energy transfer. We show that the energy transfer proceeds from large to small bandgap nanotubes with a characteristic time-constant of < 10 ps. Specifically, in a mixture of five discrete diameters of nanotubes, we observe that by exciting the E_{22} interband optical transitions of the (7, 5) and (7, 6) chiralities of semiconducting nanotubes, transient photobleaching of smaller bandgap (8, 6) and (8, 7) chirality nanotubes occurs within 10 ps. In contrast, if the nanotubes are not coupled, i.e. separated by at least 5 nm, no energy transfer is observed.

Current work on arranging nanotubes in physically coupled bundles in tailored environments will increase electronic coupling, leading to the potential for (i) delocalized excitonic states for ballistic energy transfer rather than slow hopping processes, (ii) quantum coherences that enable eigenstates to efficiently search for the charge dissociation site and (iii) dynamic disorder that helps overcome trap states.

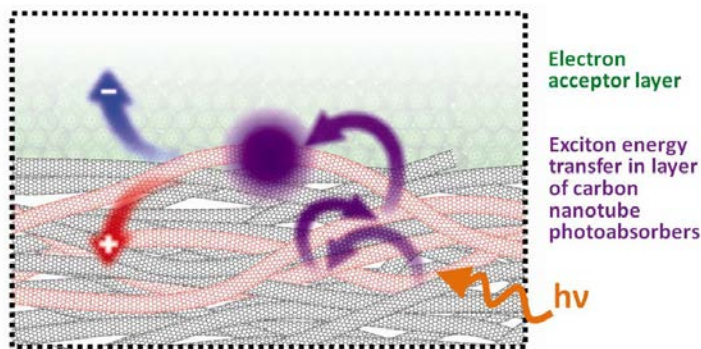


Figure. Schematic of exciton hopping between nanotubes. Excitons are photogenerated (orange arrow), the excitons hop / transfer between nanotubes (purple arrows), and then dissociate into free electrons and holes (blue and red arrows).

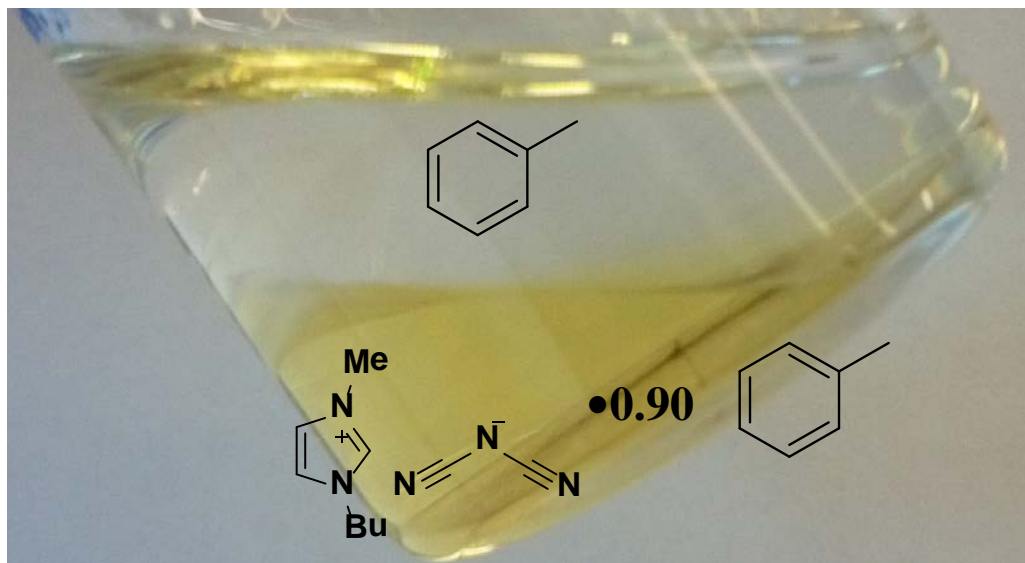
Energetic Ionic Liquid “Liquid Clathrates”

Preston A. Beasley,^a Parker. D. McCrary,^a O. Andreea Cojocaru,^a Tommy W. Hawkins,^b Stefan Schneider,^b and Robin D. Rogers^a

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Energetic Ionic Liquids (EILs) provide an interesting set of properties and are being studied for their potential ability to replace current state of the art energetic materials, but may lack key features such as low viscosity and high energy density. Liquid Clathrates, liquid inclusion compounds which form upon the interaction of aromatic molecules with certain salt moieties, have long been studied for their bonding features and application into solving separations problems. We are incorporating the ability of ILs to form stable liquid clathrates and the varied characteristics of aromatic molecular liquids to gain a higher level of understanding of the interaction between the aromatic and liquid clathrate and the electron density flow of the system.¹ This presentation will discuss the novel salts and their ‘liquid clathrate’ behavior and a spectroscopic insight into the correlation between the aromatic and the effect on the physical and chemical properties. This work is supported by the Air Force Office of Scientific Research under AFOSR Awards No. F49550-10-1-0521 (UA) and FA9300-06-C-0023 (AFRL).



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Transition Metal Promoted Acrylate Formation from CO₂ and Ethylene

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The functionalization of renewable small molecule resources by transition metals continues to expand the scope of commodity chemicals which may be produced from sustainable origins. Unfortunately, the synthetic utility of most methods is limited by the inability to catalytically eliminate the functionalized fragments from the metal center. This obstacle is pervasive in transition metal promoted efforts to utilize carbon dioxide as a feedstock for producing the chemical inputs of carbon based materials. Developing techniques to not only functionalize carbon dioxide, but also enhance the reductive removal of CO₂ containing products will drive metal mediated carbon dioxide activation toward more viable fixation techniques. Our investigations have included a series of low-valent molybdenum and tungsten complexes which successfully promote the reductive coupling of carbon dioxide and ethylene to metal bound acrylate products. Kinetic, isotopic labeling and structure-reactivity relationship studies have been used to explore the mechanistic pathways for formation of the metal acrylate hydride products from CO₂ and ethylene. In addition, factors influencing the coordination geometry of the metal-acrylate compound and techniques to mediate the reductive extrusion of acrylic products in route to a catalytic protocol have been investigated.

Titanium Aluminum Borohydride Nanoparticles as a Reactive Metal Fuel

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Albert Epshteyn, *NRL Chemistry Division, Materials Chemistry Branch, Naval Research Laboratory, Washington, DC 20375*

Reactive metal fuel nanoparticles are an attractive alternative to organic fuels and energetic materials, due to their higher energy density and favorable mechanical properties. It has been shown that the domain sizes of metal fuels, when reduced to the nanoscale, exhibit kinetics that may reasonably be expected to approach those of conventional molecular explosives. So far, however, the addition of reactive metal nanoparticles into explosive systems has had limited application, primarily due to the formation of oxide layers and due to their sensitivity to friction and electrostatic discharge stimuli. Investigations of reactive metal fuel nanoparticles, such as nanoaluminum, have been complicated by the fact that oxidation at the surface of the fuel particles is difficult to avoid. At the smallest domain sizes, where the kinetics should be most favorable, the oxide layer at the surface of the metal fuel particles takes up a significant portion of the volume, thereby introducing unacceptable amounts of inert material.

Recently, promising new mixed metal hydride nanopowders that are resistant to unintentional oxidation were produced at NRL. Gram quantities of these air stable titanium aluminum borohydride nanopowders have been produced for full energetic reactivity testing, and efforts are underway at AFRL/RW to evaluate their energy content, air stability, sensitivity, and reaction dynamics. The titanium aluminum boron hydride nanopowder materials were synthesized via a sonochemically mediated *in situ* complex hydride decomposition, which produced crystallite sizes of less than 20 nm. After a subsequent annealing, which also served as a purification step, these reactive metal fuel nanoparticles were mixed with various oxidizers and compared to the energy content of mixtures of nanoaluminum with the same oxidizer. The nanopowder's stability against aging when mixed with the different oxidizers was also studied. The composition, morphology, sensitivity and reactivity of these nano particles were analyzed using calorimetry, UV-VIS, FTIR, XRD, SEM, and other standard energetic materials characterization techniques.

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

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In this poster, we describe progress in two main arms of our program for exploring aluminum cluster-based materials for propulsion applications. These two parts of our research program relate to beam-oriented work for identifying and characterizing the properties of specific sub-units of promising cluster-assembled materials and to bulk material-oriented work for synthesizing small but macroscopic amounts of material. Under beam-oriented work, we report on our work involving polymers of aluminum hydrides and on our studies of sodium-aluminum, magnesium-aluminum, and boron-aluminum hydride clusters and their anion photoelectron spectra. Under bulk-oriented studies, we describe collaborative work with B. Eichhorn and H. Schnoeckel in which derivatives of aluminum hydride clusters (earlier discovered in our beam-oriented work) are synthesized. This work is conducted using our co-condensation generator for making the precursor compounds required for synthesizing these extraordinary materials. We also describe the development of a new apparatus for collecting and sequestering small but macroscopic amounts of aluminum hydride clusters themselves.

Positron Chemistry and Positron Annihilation Spectrometry Applications at AFIT: Positronium Annihilation Ratio (PsARS) of Ps Atoms in Electric Fields

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We are studying field effects at surfaces employing a PsARS system developed to efficiently measure the ratio of two to three photon positron annihilation events. It is known that application of electric fields (~ 200 V/cm) alters the bulk mechanism of thermalizing positrons in polymers and hydrocarbons without significantly changing the annihilation lifetime. An electric field decreases formation of o-Ps and increases the fraction of hyperthermal positrons that annihilate in the bulk material, interpreted as a shifted balance between field enhancement of positrons that escape out of the Ore gap before Ps formation and acceleration of mobile positrons into the Ore gap before annihilation. Positronium annihilation ratio spectrometry (PsARS), which measures the intensity ratio of 3-gamma to 2-gamma annihilation events, and positron annihilation lifetime spectrometry (PALS) are sensitive to the mechanism of positronium annihilation. Para-positronium (p-Ps), having zero spin, decays rapidly by even electron annihilation. Ortho-positronium (o-Ps), having unit spin, decays by odd-gamma annihilation, usually 3-gammas, or by electron pickoff yielding 2 gammas at a rate depending on the surrounding electron density. We are studying the mechanism of positronium atom annihilation at the surface of a polymer surface modified by gold nanoparticles that can condense an applied electric field. We have demonstrated that the PsARS ratio for Ps atom decay at surfaces can be altered by the electric field condition at the nanoparticle surface. Depending on localization surface of the surface field, we find that the 3-gamma/2-gamma PsARS ratio is increased or is decrease with increasing electric field. Statistically significant enhancement of positron lifetime corresponds to fields that increase 3-gamma/2-gamma PsARS ratio.

Work continues to design and build a state-of-the-art PAS laboratory at AFIT. A Surko-type slow positron beam line is being interfaced to a UHV chamber designed to accommodate a new version of our three-dimensional positron annihilation momentum spectrometry system (3DPAMS), which measures coincident Doppler broadening of annihilation radiation (CDBAR) and two-dimensional angular correlation of annihilation radiation (2D-ACAR) measurements, that we demonstrated in previous research. The system is designed with intent to measure electron-positron annihilation momenta for surface enhanced vibrational Feschbach resonance annihilation. Longer term, the system will be adapted to study selective positron stimulated fragmentation of adsorbates using mass spectrometry.

Ab Initio Study of the Stepwise Formation of Al₁₃⁻ and SiAl₁₂ Energetic Nanoclusters

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An essential need of the United States Air Force is the identification and development of novel energetic materials for use in munitions, rocket propulsion and other uses. This includes the improved performance, reduced sensitivity, and easement of environmental and toxicological hazards. Recently nanoparticles or metastable intermolecular composites (MICs) have been used in order to improve upon the performance, specifically the burn rates, of metal based materials (e.g. B, Al, and Mg). Nanoparticles increase the surface area of the reacting metal as well as decrease the reaction domain of the metal and the oxidizer. As anticipated, a decrease in size leads to an increase in performance, however, in the case of aluminum a limit as a naturally occurring oxide layer is formed on its surface. While this oxide layer is only several nanometers thick, when considering a MIC that has a radius of ~10 nm, a significant percentage of material is wasted, decreasing its performance. A solution to this problem can be found in what is commonly referred to as “magic clusters”, metal clusters with high symmetry and a closed electronic shell, that have been found to be inert to oxidation. Results from *ab initio* calculations on the formation of the Al₁₃⁻ and SiAl₁₂ “magic clusters” via a stepwise addition mechanism will be presented.

Gas-Phase Spectroscopy of Ionic Liquids

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The Air Force is seeking new fuels to replace toxic hydrazines commonly used in satellite thrusters and to serve as the emitted material in electric propulsion systems. Ionic liquids (ILs) are viewed as potential candidates for both. However, finding the ideal cation-anion pair is complicated by the sheer number of ILs. Predictive computations would allow for in silico testing, and would greatly increase the testing speed of new ILs. Unfortunately IL computations are not yet sufficiently accurate to be used predicatively. We present here initial studies on the UV spectroscopy of [emim][Tf₂N] ion pair. We report both the absorbance and the fragmentation of the ion pair under various experimental conditions. These studies suggest the presence of multiple conformations in the gas phase. Additionally these UV studies provide the background for future IR/UV double resonance spectroscopy.

Dramatic Increase of Fluorescence Efficiency of Metal Nanoparticles Induced by Thiol Adsorption

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A more than 2 orders of magnitude enhancement in photo-, in this case two-photon, excitation induced luminescence from colloidal Ag nanoparticles has been observed upon surface adsorption of ethanethiol. This dramatic increase in the luminescence intensity occurs with a notable time delay following the thiol adsorption onto the Ag particle surface. It is proposed that the formation of the strong S-Ag bond upon thiol adsorption eliminates the surface defects that quench excited carriers and increases luminescence efficiency. The time-lag can be explained by that the quenching cross section on surface per defect site is much larger than the initial surface area physically occupied by the defect site, or that it takes multiple adsorption of thiols to eliminate a surface defect. This model is consistent with the observation that a smaller increase but without time-lag in the luminescence from Au nanoparticles.

This work shows that a saturated coverage of thiol molecules, in particular ethanethiol, at the particle surface can dramatically improve the luminescence quantum efficiency of Ag nanoparticles. Thiol adsorption can also improve the luminescence intensity of other metal particles. This discovery points to an approach for improving the usage of nanoparticles as fluorescence agents in imaging and sensing devices. The time lag observed between the nonlinear and linear optical phenomena can be quantitatively accounted for by the model in which the initial quenching by surface defects is highly efficient. A substantial fraction of the defects has to be eliminated before the photo-excited electrons can survive the quenching. The interpretation of the luminescence enhancement through the elimination of surface defect sites also supports the proposed mechanism that luminescence blinking is caused by trapping of excited electrons by surface defects.

Laser-Driven Flyer Plates for Shock Compression Spectroscopy Research

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A laser-driven flyer plate system has been developed that launches and characterizes flyer plates at speeds up to 4.5 km/s. The shocks last for either 8 ns or 16 ns depending on the thickness of the flyer. This system has been coupled to real-time diagnostics in order to measure the properties of the flyer impact and shock propagation, and ultrafast and spectroscopic probes to study shock-induced chemistry of nanotechnology energetic materials and effects of microstructure.

Research supported by AFOSR via contract FA9550-09-1-0163 and ARO via contract W911NF-10-1-0072.

Light-Driven Electron Transfer and H₂ Production in Nanocrystal-Hydrogenase Complexes

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We have developed complexes of CdS nanocrystals and the enzyme hydrogenase that produce H₂ under visible illumination with quantum efficiencies of up to 20%. This hybrid material serves as a model system for bio-inspired integration of light absorption and catalysis. The nanocrystals serve as light harvesting elements, while the enzyme catalyzes H⁺ reduction. This presentation will describe the characterization of the mechanism of H₂ production and the factors that limit the efficiency and long-term stability of the hybrid system. The focus will be on the rates and efficiencies of the electron transfer steps that couple light absorption and catalysis, measured by transient absorption spectroscopy.

Synthesis and Isolation of Ligand-Coated Transition Metal Oxide Nanoclusters

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Transition metal oxide clusters have been produced in the gas phase and studied with mass spectrometry for many years. These species often exhibit magic number stoichiometries that are believed to correspond to especially stable clusters. To attempt isolation of these stable clusters, we have constructed a laser vaporization flow reactor (LVFR), consisting of a pulsed laser ablation source combined with a fast flowtube reactor for the production and isolation of ligand-coated metal clusters. The source includes high repetition rate laser vaporization with a 100 Hz KrF (248 nm) excimer laser, while cluster growth and passivation with ligands takes place in a flowtube with ligand addition via a vapor or nebulizer spray. An in-line, differentially-pumped time-of-flight mass spectrometer provides diagnostics of the cluster growth. Samples are isolated in a low temperature trap and then the resulting clusters are thawed and collected in a solution of excess ligand. These solutions are analyzed initially with laser desorption time-of-flight mass spectrometry using a MALDI-TOF instrument. In addition to mass spectrometry, infrared, Raman, UV-VIS absorption and emission, and density functional theory computations are employed to characterize these new cluster materials. Vanadium oxide nanoclusters coated with THF or acetonitrile ligands have been produced in the size range up to a mass of 2000-3000 amu.¹ Acetonitrile captures clusters having the same stoichiometries as gas phase magic numbered clusters (V_3O_6 , V_4O_9 , V_5O_{12}), while THF captures the same magic number core clusters, but with displacement of terminal oxygens. Cobalt oxide clusters have no magic numbers in the gas phase, but are captured with high selectivity by acetonitrile ligands, producing almost exclusively the $Co_4O_4(CH_3CN)_6$ cluster. Surface enhanced Raman spectroscopy on silver nanorod confirms that these species have a cubic structure. High level computational chemistry, done in collaboration with Truhlar and coworkers, find that these species have high-spin configurations. Chromium oxide clusters produce ligand-coated Cr_4O_{10} or Cr_6O_{14} clusters under different conditions.

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Low Oxidation State Aluminum Clusters

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We describe the use of a metal halide co-condensation reactor (MHCR) for the production of soluble AlX precursor solutions and their subsequent use in preparing low oxidation state Al clusters. The solutions have been employed to prepare the known compounds Al_4Cp_4 , $\text{Al}_2(\text{terp})_2\text{X}_2$ [where terp = the terphenyl ligand, X = Br/I] and the metalloid cluster $\text{Al}_{77}[\text{N}(\text{SiMe}_3)_2]_{20}^{2-}$ containing a nearly metallic Al core. In addition, we have prepared new paramagnetic $\text{Li}_2\text{Al}_3(\text{PR}_2)_6$ trinuclear clusters (R = Ph, cyclohexyl) containing mixed valent Al atoms (+1/+2) and Al-Al bond orders of 0.83. The compounds have been characterized by single crystal X-ray diffraction, epr, magnetic susceptibility (Evans method) Raman and NMR spectroscopy as well as DFT calculations. Both clusters show near perfect D_{3h} point symmetry despite being highly susceptible to first-order Jahn-Teller instabilities. The surprising structures are discussed in terms of sigma-delocalization (aromaticity) and Li-ion templation. This work is a collaborative effort involving scientists from Johns Hopkins University, Karlsruhe University and NSWC-Indian Head.

Modeling Magnesium Cluster-Based Thin Film Deposition by Helium Droplet Assembly

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Since the pioneering work of the Toennies, Scoles, and Northby groups in the early 1990's, dozens of instruments around the world have been constructed to produce and study beams of superfluid helium nano-droplets. The technique has been exploited to shed light on a wide range of topics in chemical physics such as atomic scale manifestations of superfluidity, chemistry at ultra-low temperatures, and the assembly of exotic Van der Waals complexes to name a few. The helium droplet method has been considered for more applied use as a tool for isotope enrichment,² low-fragmentation ionization mass spectrometry,³ and synthesizing/depositing core-shell spintronic nano-particles.⁴ Indeed, the helium droplet methodology is in the midst of transitioning from a novel cryogenic nano-scale matrix in which to perform fundamental research into a technology for synthesizing, characterizing, and manipulating material.

This presentation describes our efforts to model a user-friendly, broadly-tunable helium droplet cluster assembly process for the synthesis and deposition of composite nano-particles. In this effort hydrodynamic properties (thermal transport, mass flow, and jet divergence) were combined with previously reported theory and experiments on the droplet size distributions. These modeled helium droplets were then passed through a model region of magnesium vapor and an iterative, memory retaining Poissonian-like mechanism was implemented to describe dopant incorporation. Helium boil-off and its effects were tracked, and the mass transport of the beam was estimated, and shown to give excellent agreement with validation experiments we conducted. Preliminary optical, structural, and morphological studies of these magnesium cluster-based films are also presented.

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A Buffer Gas Cooled Photoablation Beam Source for Use in Chirped Pulse mm-Wave Spectroscopy of Material Ablated from Room Temperature Solids

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In the past few years we have developed the Chirped Pulse millimeter Wave (CPmmW) technique and are preparing to record pure electronic spectra of alkali earth atoms (Calcium, Barium) and alkali earth monohalide molecules (CaF, BaF, CaCl). The conventional source for such species is a supersonic jet coupled with laser ablation, which has many advantages, such as low translational and rotational temperatures, relatively small gas load, and production of a wide range of species. However, fast beam velocities, large shot-to-shot fluctuations, and relatively low number densities significantly degrade the resolution, signal to noise, and limit the applicability of CPmmW spectroscopy to problems such as superradiance and dipole-dipole interactions, which require a higher and more stable number density.

To overcome such difficulties, we have begun to construct a new molecular beam source that will provide higher and more stable number densities of interesting species with slower beam velocities. The new technique is known as buffer gas cooling or collisional cooling, and a schematic outline of the technique is shown in **Figure 1**.

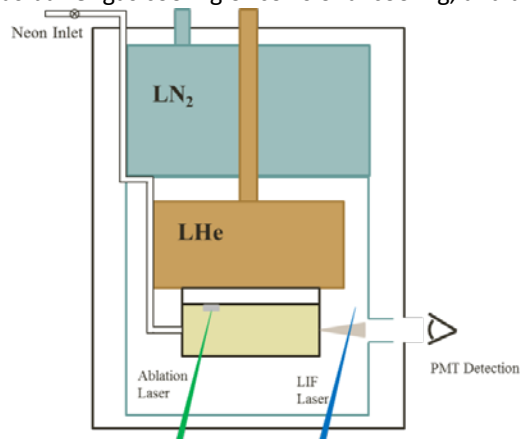


Figure 1: A schematic diagram of the buffer gas cooling process. The species of interest is formed in an ablation process that leaves the products at a range of temperatures in excess of 1000 K. The buffer gas (neon) is cooled to 20 K, just above its condensation point, and continuously flowed into and through the cooling cell at a rate of 20 standard cubic centimeters per minute (sccm). The species of interest is therefore introduced into the cooling cell in the presence of a large quantity of the buffer gas, and quickly thermalizes through soft collisions. The combined, now 20 K gas of both species is drawn out of the cell and into a detection zone. The probe laser for characterization of the beam is propagated through the radiation shield, and the fluorescence is detected with an external photomultiplier tube (PMT).

We have tested the buffer gas cooling scheme on a target of calcium atoms, using laser induced fluorescence on the 5p-4s atomic transition to measure the beam flux and temperature. Absolute numbers of atoms excited in each pulse were determined through comparison of the detected voltage from the PMT with known quantum efficiency and PMT gain curves. The results showed that at least 100x more atoms per pulse are entrained in the buffer gas cooled beam than in a typical supersonic expansion, see **Table 1**. In addition to this increase the number density, many of the advantageous qualities of supersonic expansions are retained, such as low translational and rotational temperatures. However, the shot-to-shot number density fluctuations are much smaller and the lab frame velocity of the beam is significantly slower, leading to significantly less longitudinal transient broadening and transverse Doppler broadening, which limit the resolution and sensitivity of the CPmmW spectrum. The characteristics of the buffer gas cooling method, and comparisons to other common methods for producing solid materials in the gas phase, are displayed in **Table 1**.

Table 1: Comparisons between three methods of creating gas phase samples from room temperature solid materials. All species-dependent values are calculated for the case of calcium atoms, or calcium monofluoride for molecular values (rotational temperature and particles/quantum state).

	Effusion-type Oven	Supersonic Expansion	Collisional Cooling
Beam Velocity	0.2 – 0.8 mm/ μ s	1 – 2 mm/ μ s	0.1 – 0.2 mm/ μ s
Translational Temperature	500 – 2000 K	1 – 5 K	5 – 10 K
Rotational Temperature	500 – 2000 K	1 – 5 K	5 – 10 K
Stability	~5%	~40%	~5%
Particles/Quantum State	$\sim 10^7$ - $\sim 10^8$	$\sim 10^8$	$\sim 10^9$ - $\sim 10^{10}$

Dynamics of Photochemical Reduction of CO₂ by Electron Photoemission

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We are exploring the dynamics of photochemical reduction of CO₂. Initial experiments have focused on

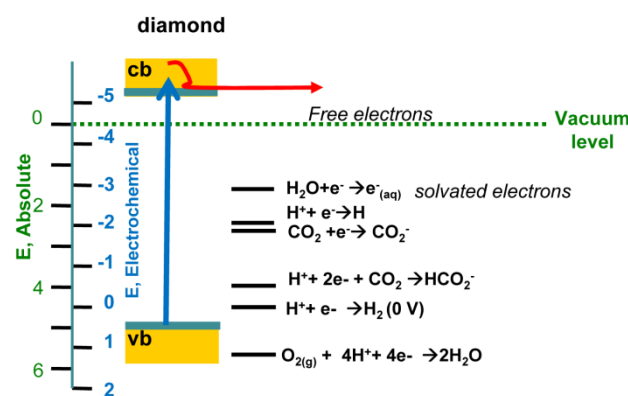


Fig. 1: Potential diagram showing relevant electrochemical processes. Energies are shown relative to vacuum (absolute energies) and also relative to the normal hydrogen electrode.

reduction of CO₂ by the novel process of electron photoemission at surface of diamond. Hydrogen-terminated diamond surfaces have the unusual property of negative electron affinity (NEA), in which the conduction band lies higher than the vacuum level. When excited with UV light, excitation of diamond leads to emission of electrons with little or no barrier. Valence-band photoemission experiments show that the electrons are ejected at the energy of the diamond conduction band, equivalent to a reduction potential of nearly -5V vs. the normal hydrogen electrode (NHE). The ejected electrons are capable of initiating

electrochemical reduction processes and/or forming solvated electrons. Of particular interest is that the conduction band of diamond and the energy of solvated electrons both lie above the potential needed to perform the direct 1-electron reduction of diamond via $\text{H}^+ + \text{e}^- + \text{CO}_2^- \rightarrow \text{HCO}_2^-$ instead of the more common 2-electron, proton-coupled electron transfer $\text{H}^+ + 2\text{e}^- + \text{CO}_2 \rightarrow \text{HCO}_2^-$

We are investigating the product distributions and dynamics of CO₂ reduction produced by electrons emitted from photo-illuminated diamond in CO₂-saturated water. Preliminary experiments have demonstrated CO₂ reduction, and ongoing experiments are characterizing the distribution of products. Thus far infrared absorption experiments have identified formation of CO, while gas chromatograph - mass spectroscopy (GC/MS) experiments have shown the presence of formic acid, acetaldehyde, and methanol. Current experiments are aimed at validating these results using isotopically labeled ¹³CO₂ and characterizing the time dependence of the production of the different products. Measurements using transient absorption spectroscopy have shown that excitation of diamond with UV light results in an increase in absorption arising from solvated electrons. The role of solvated electrons in inducing the reduction of CO₂ is being investigated.

Direct Dynamics Studies of Hypergolic Ignition of Ionic Liquids

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Room temperature ionic liquids exhibit hypergolic activity as liquid bipropellants.¹ Understanding the chemical pathways and reaction mechanisms associated with hypergolic ignition is important for designing new fuels. It has been proposed¹ that an important ignition step for the hypergolic ionic liquid bipropellant dicyanamide/nitric acid is the association of a proton with the 1,5-dinitrobiuret anion DNB⁻. In the work reported a quasiclassical direct dynamics simulation, at the DFT/M05-2X level of theory, was performed to study H⁺ + DNB⁻ association and the ensuing unimolecular decomposition of HDNB. This association step is 324 kcal/mol exothermic and forms a highly vibrationally excited HDNB molecule. The molecule decomposed by 19 different reaction paths. Some of these paths are the same as found in a direct dynamics simulation of the high temperature thermal decomposition of HDNB.² Simulations are also underway to study the association of hydrated protons H⁺(H₂O)_n with DNB⁻ to investigate the possibility that the presence of the water molecules affects the relative importance of the different decomposition pathways. The likelihood that the water molecules also react with H⁺ and DNB⁻ in forming reaction products is also considered.

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Gain and Lasing of Optically Pumped Metastable Rare Gas Atoms

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In recent years there have been concerted efforts to develop high energy diode-pumped alkali vapor lasers (DPAL). These hybrid gas phase / solid state laser systems offer possibilities for constructing high-powered lasers that have high beam quality. DPAL's utilize excitation of the alkali metal $^2P_{3/2} \leftarrow ^2S_{1/2}$ transition, followed by collisional relaxation and lasing on the $^2P_{1/2} \rightarrow ^2S_{1/2}$ line. Considerable progress has been made, but there are technical challenges associated with the reactivity of the metal atoms.

Rare gas atoms (Rg) excited to the $np^5(n+1)s \ ^3P_2$ configuration are metastable and have spectral properties that are closely similar to those of the alkali metals. In principle, optically pumped lasers could be constructed using excitation of the $np^5(n+1)p \leftarrow np^5(n+1)s$ transitions. We have recently demonstrated gain and lasing for optically pumped Ar*, Kr* and Xe*. Three-level lasing schemes were used, with He as the collisional energy transfer agent that established the population inversion. These laser systems have the advantage using inert reagents that are gases at room temperature, with excellent potential for closed-cycle operation.

Hardware-Accelerated Computation of Fixed-Centroid Path-Integral-Averaged Potentials of Mean Force

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Centroid molecular dynamics (MD) simulations [1-3] represent one popular and powerful method for incorporating some of the effects of quantum mechanics into classical molecular dynamics simulations. Centroid MD simulations originate in path integral (PI) formulations [4,5] of quantum statistical mechanics, and use the harmonic ring polymers that are familiar from PI studies to represent the particles of a many-body system. The physical extent of each ring polymer loosely represents the quantum mechanical delocalization of the corresponding particle in the underlying many-body system, and a particle's "position" is identified with the centroid of its ring polymer. The polymer centroids (and thus the particles in the underlying many-body system) move on an effective potential energy surface that is obtained by averaging the inter-particle forces over the spatial distribution functions of the polymer beads, subject to the constraint that each polymer's centroid remains fixed.

Most of the computational expense of a centroid MD simulation is associated with the calculation of the effective forces on the polymer centroids, and a variety of software-based approaches have been proposed to accelerate this task [3, 6-9]. Here, we explore the use of graphics processing units (GPUs) to accelerate the calculation of the effective inter-particle forces in helium nanodroplets, and compare the efficiency and accuracy of GPU-based approaches that use double-precision, single-precision, and integer [10] variables to represent the coordinates of the ring polymers' beads.

This work was partially supported by the U.S. Air Force Research Laboratory (contract FA8651-11-1-0005) and by the U.S. National Science Foundation (grants CHE-0840041 and CHE-0625598).

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Quantum Sized Metal Nanoclusters: The Case of Gold

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Ultrasmall metal nanoparticles exhibit distinct quantum size effects, and such effects fundamentally alter metal nanoparticles' electronic and optical properties. Controlling such nanoparticles with atomic precision, however, remains a major challenge, which significantly hampers the pursuit of fundamental science of this special class of nanomaterial as well as the development of their applications such as in catalysis. In our research, we chose thiolate-protected gold nanoparticles (referred to as $\text{Au}_n(\text{SR})_m$ nanoclusters, SR=thiolate) as a model system to develop solution phase synthesis of atomically precise gold nanoclusters that are composed of dozens to hundreds of gold atoms. We will present a recently developed size-focusing methodology for synthesizing molecular purity gold nanoclusters with precise size control at the atomic level. Such quantum sized $\text{Au}_n(\text{SR})_m$ nanoclusters exhibit interesting electronic and optical properties that are fundamentally different than their larger counterparts—plasmonic Au nanocrystals. A few representative, size-specific $\text{Au}_n(\text{SR})_m$ nanoclusters will be discussed in detail. Unlike *fcc* Au nanocrystals that possess translational symmetry in the metal core, small $\text{Au}_n(\text{SR})_m$ nanoclusters do not adopt *fcc* structure; indeed, new types of non-crystallographic structures have been discovered in X-ray crystallographic analyses on $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and other sized nanoclusters. Experiment and theory have revealed quantized electronic structure (e.g. electron energy gap) in nanoclusters and even intrinsic magnetism in certain sizes. The transition from the discrete electronic state to metallic state is expected to occur with increasing size (*n* above a few hundreds). The $\text{Au}_n(\text{SR})_m$ nanoclusters have also been found to be excellent catalysts for some selective oxidation and hydrogenation processes. Correlation of $\text{Au}_n(\text{SR})_m$ catalytic properties with crystal structures will ultimately offer fundamental understanding on nanogold catalysis.

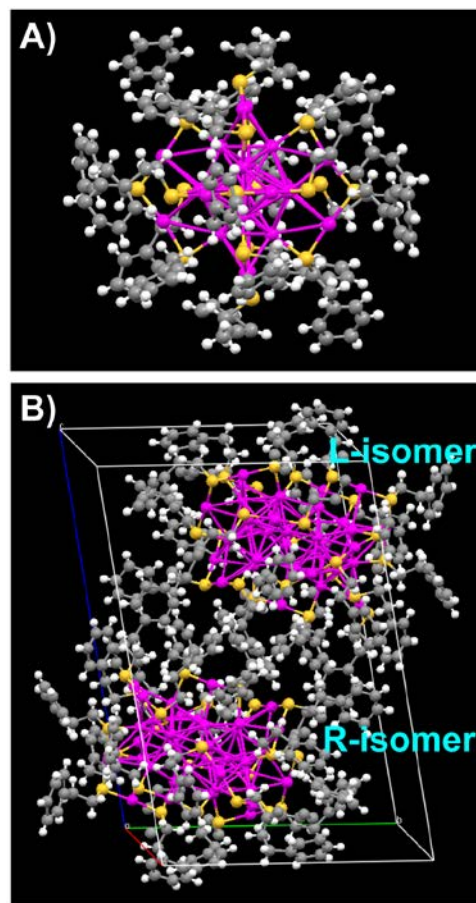


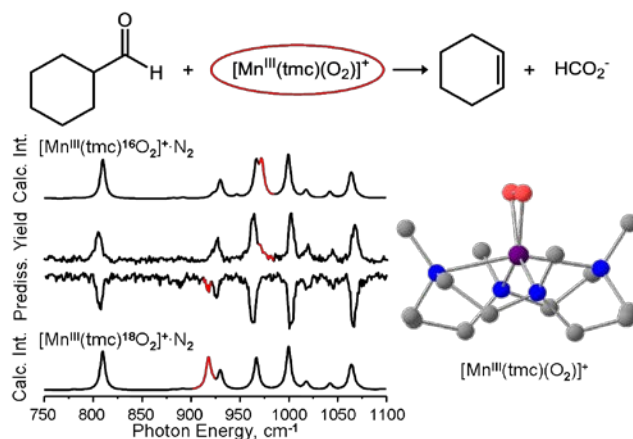
Figure 1. Crystal structures of (A) $\text{Au}_{25}(\text{SR})_{18}$ and (B) chiral $\text{Au}_{38}(\text{SR})_{24}$ nanoclusters, where, $\text{R}=\text{CH}_2\text{CH}_2\text{Ph}$.

Optimizing Catalysts for Solar Fuel Production: Spectroscopic Characterization of the Key Reaction Intermediates

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We are characterizing catalytic reaction intermediates by combining electrospray ionization (ESI) with cryogenic mass spectrometry. This technique uses a cold (10-30K) ion trap to rapidly cool reaction partners and freeze the intermediates into well-defined structures. After mass-selection, these species occur as isomers at a particular mass, and we isolate the spectra of each using a photochemical hole burning scheme involving three stages of mass selection and two independently tunable pulsed infrared lasers. We first demonstrated this methodology on a biomimetic peptide catalyst for stereoselective bromination,¹ and have focused our recent efforts on the isolation of organometallic intermediates involved in CO₂ activation and water splitting. We will describe two approaches to manipulate the oxidation states of the metal centers, one involving coupling an electrochemical cell to the ion source and another where highly labile compounds are created by collisional break-up after suitable precursors have been extracted from solution. The latter method is used to isolate an Mn(III)-O₂ compound used extensively as the active species in aldehyde deformylation, and its structure is illustrated in the figure. The vibrational predissociation of the 25K ion was obtained using weakly bound N₂ molecules for the messenger “tags,” and bands due to the O-O stretch (highlighted in red) were identified by following the evolution of the band pattern upon incorporation of ¹⁸O₂. We will discuss plans for the next year to isolate CO₂ activation catalysts based on Ni(II) compounds, as well as report progress on the next-generation experimental platform based on a 7 tesla FT-ICR.

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25K predissociation spectra of $[\text{Mn}^{\text{III}}(\text{tmc})\text{O}_2]^+$ (tmc=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane) using N₂ tagging, where the O-O stretch is identified by following band shifts in the ¹⁸O₂ isotopomer. Top and bottom traces correspond to the calculated spectra for the structure in the inset for normal and heavy oxygen.

Untangling the Energetics and Dynamics of Elementary Reactions of the Boron Monoxide Radical ($^{11}\text{BO}; X^2\Sigma^+$)

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The primary objectives of this project are to experimentally explore the energetics, dynamics, and potential energy surfaces (PESs) of elementary reactions of ground state boron monoxide radicals ($^{11}\text{BO}; X^2\Sigma^+$) with key unsaturated hydrocarbons such as acetylene and ethylene under single collision conditions. The experiments employ a hydrocarbon-free crossed molecular beams machine with ultra-sensitive detection schemes incorporating a universal, rotatable angular resolved time-of-flight (TOF) mass spectrometric detector with electron impact ionization as well as laser induced fluorescence (LIF) detection. By conducting state-of-the-art crossed molecular beam experiments and combining these results with electronic structure calculations, we extract the chemical dynamics, reaction mechanisms, products, intermediates, energetics, branching ratios, and enthalpies of formation of small carbon-, hydrogen-, oxygen-, and boron-bearing (CHOB) molecules. Besides the basic scientific interest from the physical chemistry community (reaction dynamics) to unravel the chemical dynamics of hitherto poorly explored boron monoxide radical reactions, the proposed studies are also of fundamental interest to the fields of boron combustion chemistry, boron-based chemical propulsion systems, and to the physical-organic chemistry community to advance insights into basic chemical structure and chemical bonding of carbon-, hydrogen-, oxygen-, and boron-bearing molecules.

The reaction dynamics of boronmonoxide ($\text{BO}; X^2\Sigma^+$) with acetylene ($\text{C}_2\text{H}_2; X^1\Sigma_g^+$) were investigated under single collision conditions at a collision energy of 13 kJ mol^{-1} employing the crossed molecular beam technique. The reaction was found to have no entrance barrier and proceeded via indirect scattering dynamics initiated by an addition of the boron monoxide radical with its boron atom to the carbon-carbon triple bond forming the $\text{O}^{11}\text{BHCCH}$ intermediate. The latter decomposed via hydrogen atom emission to form the linear O^{11}BCCH product through a tight exit transition state. The experimentally observed sideways scattering suggests that the hydrogen atom leaves perpendicularly to the rotational plane of the decomposing complex and almost parallel to the total angular momentum vector. The overall reaction to form the linear ethynylboronmonoxide (HCCBO) plus atomic hydrogen from the separated reactants was determined to be exoergic by of 62 kJmol^{-1} . Secondly, the reaction dynamics of the boron monoxide radical ($^{11}\text{BO}; X^2\Sigma^+$) with ethylene ($\text{C}_2\text{H}_4; X^1\text{A}_g$) were probed at a nominal collision energy of 12 kJ mol^{-1} employing the crossed molecular beam technique. The reaction is governed by indirect scattering dynamics with the boron monoxide radical attacking the carbon-carbon double bond of the ethylene molecule without entrance barrier with the boron atom. This addition leads to a doublet radical intermediate ($\text{O}^{11}\text{BH}_2\text{CCH}_2$), which either undergoes unimolecular decomposition through hydrogen atom emission from the C1 atom via a tight transition state located about 13 kJmol^{-1} above the separated products or isomerizes via a hydrogen shift to the $\text{O}^{11}\text{BHCCH}_3$ radical, which also can lose a hydrogen atom from the C1 atom. Both processes lead eventually to the formation of the vinylboronmonoxide molecule ($\text{C}_2\text{H}_3\text{BO}$). The overall reaction was determined to be exoergic by about 40 kJmol^{-1} . Note that the abstraction reactions leading to HBO plus ethynyl (CCH) and vinyl (C_2H_3) are endoergic by ~ 90 and $\sim 100 \text{ kJmol}^{-1}$ and hence not open under our experimental conditions.

Towards Aluminum Cluster Based Nano-Energetic Materials

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In our search for energetic aluminum cluster based nanoenergetic materials, we will present our recent findings along two potential directions. First, it will be shown how stable aluminum based cluster motifs can be formed by adding ligands to Al_{13} and Al_{14} clusters. The studies based on adding I ligands show how one can control the reactivity of aluminum clusters with oxygen, that is governed by electronic shells, as well as with water/methanol where the reactivity is governed by complementary active sites. It will be shown that the addition of I at selective sites can induce such pairs of active sites. In this regards, our work also has potential for making nanocatalysts that can break strong polar covalent bonds. We will also present our recent findings on Al_nMg clusters that indicate how new composite building blocks for nanoenergetic materials may be formed in mixed clusters. Since Mg is a divalent atom while aluminum is trivalent, the composite clusters have the potential of forming stable multiple anionic species. The second direction refers to the formation and properties of the actual nanoenergetic materials based on these building blocks. To this end, we will present our latest investigations on the nanoenergetic materials composed of aluminum clusters and cryptated K atoms. We will present our results on the atomic structure, stability, electronic structure, and other properties of the new cluster assembled nanoscale material.

We gratefully acknowledge financial support from Air Force Office of Scientific Research through FA9550-09-1-0371 and FA9550-08-1-0400 MURI grant.

Condensed Phase Simulations Using a General Chemical Dynamics Program VENUS

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VENUS¹ is a general chemical dynamics computer program (<http://cdssim.chem.ttu.edu>) that can perform simulations to study unimolecular dynamics, bimolecular reactions and gas-surface collisions. In this program, the potential and gradient information for describing potential energy surface of the chemical system is obtained using the built-in molecular mechanical (MM) functions or by performing quantum mechanical (QM) calculations using electronic structure programs such as NWChem, MOPAC etc. The latter kind of simulations is called as direct dynamics simulation.² These versions of VENUS are capable of studying chemical systems in a gas-phase environment. In this work, we present a new version of VENUS capable of performing QM/MM direct dynamics simulations in a condensed phase.^{3,4} This new version of VENUS, allows a user to perform simulations in a condensed phase by choosing a solvent, such as argon, dichloromethane, chloroform etc., and by specifying the simulation conditions such as density, temperature and pressure. The user also has an option of plugging in different force field parameters, such as those available in the literature or those developed in the Hase Research Group, to describe the interactions between the solvent and the chemical system. QM calculations for the reactive system are performed using an electronic structure program whereas MM potentials are used to represent the solvent and their interactions with the reactive system.

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Adapting GAMESS towards a Hybrid CPU/GPU Future

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The CPU based General Atomic and Molecular Structure System (GAMESS) quantum chemistry code is accelerated using general purpose graphical processing units (GPGPU). The acceleration strategy, preliminary performance results, and development roadmap of the accelerate code is presented.

Assembly of Carbon Clusters in Helium Droplets using Long-Pulse Laser Vaporization

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Carbon-metal cluster materials exhibit interesting chemical properties due to charge exchange between metal centers and the carbon lattice. The structure, energy levels, and electron distribution are sensitive to the identity of the metal and the size of the cluster. Consequently, mixed carbon-metal materials offer the possibility of novel and potentially tunable chemistry for catalysis and photochemistry. Indeed, with our collaborators we recently produced and studied metal-coated carbon dots with photocatalytic properties applicable to CO₂ conversion and H₂O splitting¹. A bottom-up understanding of the chemistry, starting with small clusters and working upwards, would greatly aid efforts to optimize photocatalytic activity in these materials. In such studies, control over the size and structure of the carbon-metal clusters is of course highly desirable.

We intend to use helium droplet beam methods, which can assemble clusters from a wide variety of species with extraordinary control over size and structure, to produce and study novel carbon-metal clusters. As a first step in this direction, we have assembled pure carbon clusters in helium droplets using long-pulse laser vaporization of graphite. Using this method we are able to assemble carbon clusters ranging from C₂-C₉. Although our results are preliminary, the droplet size dependence of the C_n signals suggests that pre-existing clusters (especially C₂, C₃) are being captured by the droplets and used to assemble larger clusters. In future work, we will add metal heteroatoms to the carbon clusters, ultimately attaching reactants such as CO₂ and H₂O in order to study photochemical reactions.

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Pyrolysis of Gas Phase and Supercritical Fluid Hydrocarbons in a Molecular Beam Mass Spectrometer

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To understand thermally-stressed fuels, a robust understanding of chemical dynamics in hydrocarbons at elevated temperatures must be developed. Currently there is a fundamental disconnect between models developed from extensive gas-phase pyrolysis studies and what is observed under supercritical fluid conditions. Previous supercritical investigations that examined the state of samples before and after thermal stressing have identified differences between the final products of gas-phase and supercritical pyrolysis, but direct observation of important chemical processes occurring under supercritical conditions has proven exceedingly difficult. Yet the ability to do so, and to make comparisons with the analogous processes found in gas-phase dynamics would greatly advance our understanding of hydrocarbon pyrolysis.

Our approach is to obtain direct observations of the pyrolytic chemistry occurring in hydrocarbons as a function of fluid property (temperature, pressure, and density) using a supersonic molecular beam mass spectrometer to expand and isolate the species present, including radical transients. Briefly, samples are taken to pyrolytic temperatures and the nascent chemistry is quenched by the expansion of the fluid into a vacuum. Modular sources are used to probe pyrolysis in both gas-phase and supercritical fluids flows. For gas-phase measurements, we sample the output of an effusive flow tube. For supercritical fluid experiments, the flow is supersonically expanded from a pinhole nozzle. The expansion is skimmed to form a molecular beam which is ionized downstream by electron ionization and detected by a quadrupole mass spectrometer. The incident electron energies can be adjusted to either selectively ionize low energy species such as radicals or set to a higher energy in order to ionize all species.

Our initial studies have focused on the gas-phase pyrolysis of *n*-hexane and branched isomers at temperatures up to 1000° C. In agreement with earlier reports, we observe methane, ethene, propene, and butene products. However, the relative concentrations are somewhat different than those obtained in earlier investigations using residence times several orders of magnitude larger. We are able to influence the extent of reaction using a simple method we have developed to control the residence time inside the pyrolysis tube. We have also studied the pyrolysis of *n*-hexane in the presence of AgBN and PdBN-based catalysts. We observe pyrolysis onset at temperatures several hundred Kelvin below those necessary in the absence of the catalysts. We find that the pyrolysis products observed at these lower temperatures in the catalyzed systems are different from those measured at higher temperatures in either the catalyzed or un-catalyzed systems.

First Principles Evaluation of Optical, Transport, and Catalytic Properties of Pure and Doped Hematite for Photocatalytic Water Splitting

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Photoelectrochemical cells (PECs) have the potential to generate fuel from sunlight-driven electrochemical reactions. Among the many candidates for photoanode materials, hematite (α -Fe₂O₃) stands out as being low-cost, abundant, non-toxic, and it has a nearly optimal band gap for solar energy absorption. However, hematite in its pure form suffers from several drawbacks, including high electron-hole recombination rate, low electron/hole conductivity, and large reaction overpotentials. The first problem may be overcome by nanostructuring, so we focus on the latter two challenges in our work. Our strategy is to characterize pure hematite's properties first and then to evaluate whether various dopants can improve conductivity and reactivity. This poster presents our research studying the optical, transport, and catalytic properties of hematite, with the aim to develop practical photoanodes with high efficiency. We used embedded correlated wavefunction methods to characterize the optical excited states of hematite [1] and various versions of the GW approximation to investigate the photoemission/ inverse photoemission gap of hematite [2]. Electron and hole transport in pure or doped hematite were studied within electrostatically embedded unrestricted Hartree-Fock (UHF) theory and the small polaron model [3, 4]. We also used our new first principles scheme [5] to evaluate absolute valence and conduction band edge positions for comparison with relevant fuel-producing redox reaction free energies, which allows us to evaluate the thermodynamic propensity for these redox reactions to occur under illumination. Finally, water oxidation catalyzed by a hematite surface was studied with *ab initio* DFT+U theory to elucidate detailed reaction mechanisms and energetics [6]. The reaction energetics on pure or doped hematite surfaces were analyzed using the typical volcano plot employed in catalysis. We found several dopants that may improve conductivity without introducing traps and also dopants that provide optimal binding strengths for adsorbed intermediates that should reduce the overpotential of hematite photoanodes.

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Physical and Chemical Properties of Iodine Oxide Films

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Architectural features in the micron and nanometer regime influence many properties observed for the combustion efficiency of binary and monomolecular composed energetic materials. Solid state reaction rates for such systems, which can be inferred from the burn-rate, is a key indicator for the performance of a potential system, and has been traditionally performed on loose powders, pressed pellets, and laminates with mixed results. More recently films have been explored as an alternative material form for testing performance at smaller scales and have demonstrated similarly high burn rates as those observed in loose powder tests. In general there are many methods available to produce films, and these established techniques may provide a new means of controlling or modifying the physical properties of the metal-oxidizer systems.

In this study, films of HI_3O_8 (a hydrated form of I_2O_5) were investigated for their potential as an oxide matrix for future inclusion/blending with fuels (Al, Mg, etc). Recrystallization of HI_3O_8 in various alcohol/ketone/ester blends using ultrasound will be presented and discussed. Furthermore, utilizing the aforementioned suspensions, the effects of relative humidity (RH) and spin coating rate on the film properties are investigated and reported. Sonication of HI_3O_8 in alcohol blends is an effective method for decreasing the particle size and improving the uniformity of the particle morphology, which is desirable for blending purposes. However, UV-visible spectroscopy and gravimetric evidence suggests that minor side reactions are occurring between the alcohol and iodine oxide species thus forming iodine (I_2) which has been showed to lower the pH ($\sim 7 \rightarrow 4$) of alcohol/water mixtures. Powder X-ray Diffraction (PXRD), Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), IR and Raman spectroscopy show that the deposited films are of equal or higher purity than that of the starting material. PXRD results suggest that films generated from increasing the spin rate are more inclined to align their crystal lattice planes normal to the substrate surface. Scanning Electron Microscopy (SEM) images showed that layering of individual oxide coatings can be influenced by the spin rate. Adsorption of H_2O vapor by the particles are most prominent with smaller particles (few microns), which are highly susceptible to deliquescence. Particle structure due to RH and/or spin coating rate was observed and showed that smaller particles are more susceptible to undergo morphological changes into specific crystallites given certain conditions (particle \rightarrow rods, plates, etc). Ultimately, these oxide films generated with the above mentioned processes provide an alternate route to engineer unique structural motifs for future sub-gram scale energetic materials.

Molecular Simulations of Ionic Liquids: Melting Points, Charge Distributions and Interfacial Transport

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We report the results of recent molecular simulation studies directed at predicting melting points and interfacial gas transport for ionic liquids. We computed melting points and liquid dynamics for a series of alkyl-imidazolium PF₆ ionic liquids. Experimentally it has been observed that the substitution of a methyl group for a hydrogen at the C2 cation ring position leads to an increase in both the melting point and the viscosity, contrary to arguments that had been made regarding associations between the ions. The simulations are consistent with experimental trends and show that the origin of the effect is entropic. This suggests that configurational entropy is a key quantity for controlling the properties of ionic liquids.

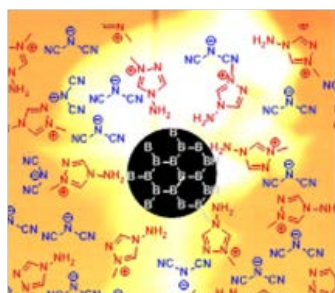
We also present the results of a study on effective ways to estimate partial charges for classical force fields. It is known that the physical properties obtained from molecular simulations of ionic liquids depend sensitively on the quality of the intermolecular potential (force field) used to describe interactions in the system. Simple fixed charge models are desirable because they enable long simulations of large systems to be carried out, though the neglect of polarizability has been shown to lead to incorrect dynamics and other properties. We show that this limitation in fixed charge models can be overcome by using ab initio molecular dynamics of the condensed phase to derive effective charge distributions. By performing these calculations on a crystalline phase, accurate estimates can be obtained in a fraction of the time required when the liquid phase is used. We compare five different charge assignment procedures and make recommendations for the best way to determine partial charges. By using the approach, the dynamics and thermodynamics of the condensed phase is accurately computed.

Finally, results of interfacial simulations of ionic liquids and carbon dioxide / water mixtures are presented. We compute the interfacial structure of the ionic liquid as well as the water and carbon dioxide molecules. We find that CO₂ prefers to sit at the outer hydrophobic region of the interface, while water goes to the inner hydrophilic and high charge density layer. The CO₂ potential of mean force for interfacial crossing is computed and we find a barrier for crossing the interface, which is consistent with dynamical trajectories from the simulations as well as recent experimental work.

Controlling the Properties of Energetic Ionic Liquids (EILs) by Stabilizing Reactive Nanomaterials

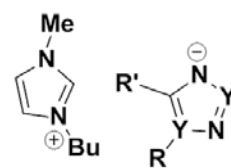
Parker, D. McCrary,^a Preston A. Beasley,^a O. Andreea Cojocaru,^a Steven P. Kelley,^a Spencer A. Alaniz,^a Tommy W. Hawkins,^c Stefan Schneider,^c Jerry A. Boatz,^c Jesus Paulo L. Perez,^b Brandon W. McMahon,^b Scott L. Anderson,^b Mark Pfeil,^d Steven F. Son,^d and Robin D. Rogers^a

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Energetic ionic liquids (EILs, salts which melt below 100 °C with potential as energetic materials) have been reported as hypergolic, indicating they spontaneously ignite on contact with a variety of oxidizers, but many challenges still remain to their practical use such as low density and relatively low heats of combustion when compared to the current state of the art hypergols, such as hydrazine. One approach that can be taken to improve EIL performance is to introduce an additive which does not interfere with the desired IL traits such as low or negligible vapor pressure. Boron nanoparticles have been shown to provide an increased energetic performance when milled in a hypergolic IL, 1-methyl-4-amino-1,2,4-triazolium dicyanamide ([MAT][DCA]) based on surface interactions with the cation.⁵

While initial reports determined that the stability of the nanoparticle dispersion in EILs were insufficient for practical use, chemically designing the IL to interact with the surface of nanoparticles *via* coordination would allow the ability to alter the strength of such an interaction through control of the structure of the IL. Initially, we investigated the stabilizing features of functionalized Azolium Azolate based EILs to coordinate and stabilize Ti(0) nanoparticles.⁶ We will present the use of nanoparticles as energetic additives to EILs and our current efforts to increase the stability of these dispersions through coordination to the surface of B and Ti nanoparticles.



R = -NH₂, -NO₂, or -CN
R' = -NH₂, -NO₂, or -CN
Y = N or CH

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Iron Catalyzed Oxidation Reactions: Temperature Dependent Kinetics

Joshua J. Melko, Shaun Ard, Nicholas S. Shuman, Albert A. Viggiano

Oxidation of Fe^+ by N_2O , followed by oxidation of C-H and C-C bonds by FeO^+ , forms an efficient catalytic cycle for C-H and C-C bond activation.¹ The various reactions involved in these cycles have received significant study; however, the temperature dependent kinetics of these reactions have been only minimally explored.^{2,3} Experimental temperature dependent kinetic data offer a means to test subtle aspects of theoretical models, and provide a clearer understanding of these reactions under conditions in which they are typically employed. Here, we present the temperature dependent kinetics from 230 K to 700 K, including reaction rate constants and product branching ratios, for the oxidation of Fe^+ by N_2O , the iron catalyzed oxidation reactions of CO, CH_4 , C_2H_4 , and C_2H_6 , as well as for various side reactions involving Fe^+ .

In contrast to prior results, the formation of FeO^+ from Fe^+ and N_2O shows a flat temperature dependence; no prior evidence of an inefficient (1% of collisions lead to reaction) ion-molecule reaction with a flat temperature dependence over such a wide temperature range exists, and attempts to understand this unusual mechanism through statistical modeling are underway. The oxidation reactions of methane, CD_4 , and CH_2D_2 to methanol show a pronounced isotope effect favoring $-\text{OH}$ production. All three reactions show similar temperature dependencies in both their rate constants and product branching ratios, with undesirable side-products increasing significantly as the temperature approaches 700 K, suggesting the catalytic efficiency is higher at lower temperatures. The oxidation of CO to CO_2 by FeO^+ proceeds efficiently at room temperature with the rate constant varying as $1/T$. Finally, we detail reactions of FeO^+ with ethane and ethene, providing temperature dependent rate constants and branching ratios that reveal how the competing pathways within their respective catalytic cycles change with temperature.

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Molecular Beam Studies of Jet Fuel Surrogates using Liquid Microjets

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Our motivation is to explore the heating, evaporation, and aging of volatile fuel droplets, which ultimately evaporate into a gaseous mixture at pressures and temperatures up to 30 atm and 2000 K in the combustion region of a jet engine. This complex kerosene fuel mixture is modeled as pure dodecane ($C_{12}H_{26}$) in our initial experiments. At 298 K, dodecane has a vapor pressure of 0.1 Torr and a mean free path of ~ 0.1 mm; this small distance makes it difficult to investigate gas-liquid interactions in vacuum because of frequent gas-gas collisions above a surface that is wider than the mean free path. Gas-liquid scattering experiments based on narrow diameter liquid jets offer the opportunity to explore collisions and reactions at the surface of volatile liquids with reduced interference from collisions in the gas phase.

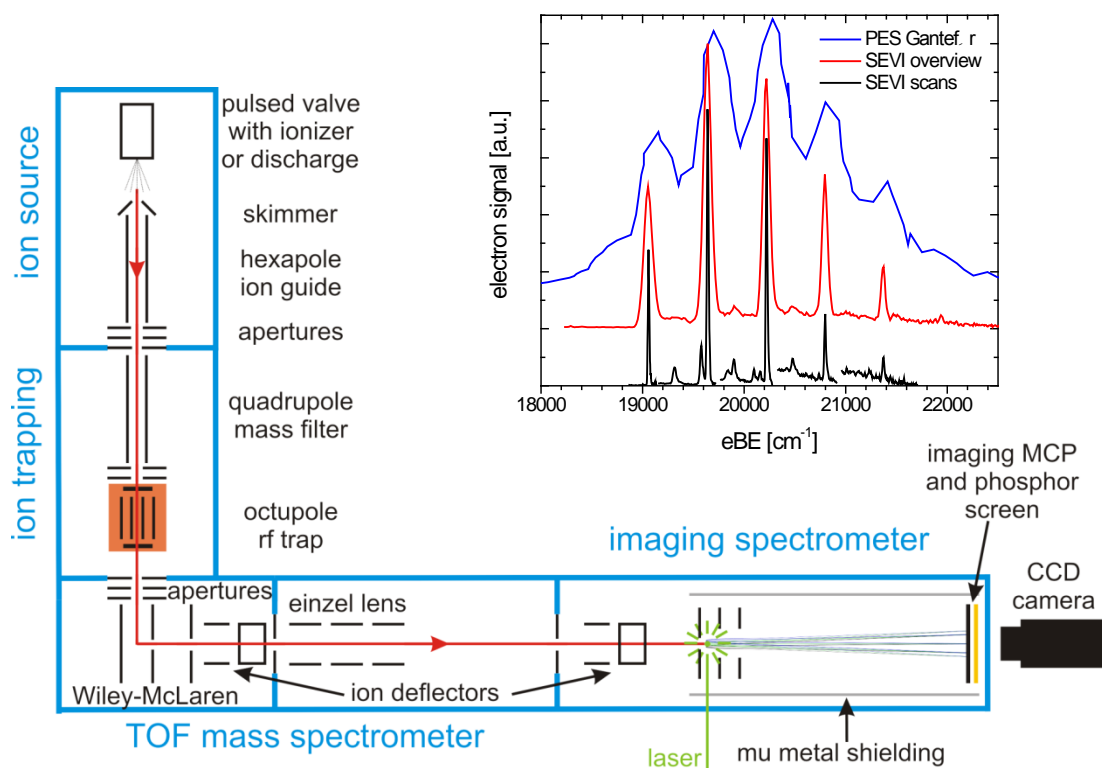
Investigations of oxygen molecule collisions with 0.04 mm diameter jets of dodecane and squalane ($C_{30}H_{62}$, $P_{\text{vap}} < 10^{-8}$ Torr) were carried out at low ($E_{\text{inc}} = 6$ kJ/mol $= 2.5RT_{\text{liquid}}$) and high ($E_{\text{inc}} = 30$ kJ/mol $= 15RT_{\text{liquid}} \sim RT_{\text{combustion}}$) incident energies. At low energy, O_2 molecules exit from the surface in a Maxwellian distribution at T_{liquid} , implying extensive exchange with surface hydrocarbon molecules. This energy transfer remains large even at $E_{\text{inc}} = 30$ kJ/mol, where O_2 molecules transfer 2/3 of their energy to the surface molecules. The similar O_2 energy transfers for dodecane and squalane suggest that chain length does not alter the rate of gas-liquid energy transfer. These results imply that gas-liquid collisions between hot gases and cold fuel droplets within the combustion region will not limit the rate of fuel droplet heating and vaporization.

Liquid microjet experiments also provide a means to monitor solute and solvent evaporation. We have monitored gas evaporation from dodecane, squalane, ethylene glycol, and even liquid water. These studies show that the solvents and most gases (O_2 , H_2O , Ar) evaporate in a Maxwellian distribution of velocities, whereas helium atoms evaporate at average energies up to 40% higher. This remarkable observation will be discussed in terms of He atoms squeezing between hydrocarbon chains and being swatted by surface groups into vacuum.

New Insights into Catalytic Sites: Characterization of Spectroscopy and Reactivity of Metal Oxide Clusters with Anion Slow Electron Velocity-Map Imaging

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Our primary focus during the past year has been to incorporate ion trapping and cooling into our anion slow electron velocity-map imaging (SEVI) instrument, with the goal obtaining high resolution photodetachment spectra of mass-selected transition metal oxide clusters that play a key role in catalysis. The current instrument is shown below. Mass-selected negative ions are introduced into an octopole rf trap cooled to temperatures as low as 5 K. The ions are cooled by collisions with low pressure He buffer gas and are then injected into the photoelectron imaging section of the instrument. The goal of trapping and cooling is reduce spectral congestion from vibrational hot bands and rotational contours, allowing us to take full advantage of the high resolution capabilities of SEVI. First results (shown below) have been obtained for the S_3^- anion. We continue to measure infrared spectra of atmospherically important anions in collaboration with Knut Asmis in Berlin. Spectra have recently been obtained for mixed sulfuric acid/nitric acid anion clusters such as $H_2SO_4(HSO_4^-)HNO_3$. The spectra reveal the charge carrier in these species, which have been implicated in aerosol formation.



Optical Emission Spectra of the Iodine Hall Thruster

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The performance and plasma characteristics of Hall effect thrusters (HETs), such as charge species densities and electron temperatures, are traditionally measured by various plasma probes. However, the plasma-probe diagnostics can be strongly affected by the local environment of the plasma especially in the region of high temperature such as the HET discharge region. Optical plasma diagnostics avoid these problems and are therefore an alternative to probe measurements.

Plasma generated by HETs produces optical emissions due to collisional excitation of propellant gas by electrons and ionized propellant ions. In the xenon-propelled HETs, the prominent near-infrared emission lines were observed. Passive optical dispersed detection of these lines provides a non-intrusive method to assess electron temperatures and ion charge state distributions.[1,2] Karabadzhak, Chiu, and Dressler developed a collisional radiative model for HET xenon plasma diagnostics based on experimental and theoretical emission excitation cross sections and they showed that ratio of the 823 to 828 nm line intensities is sensitive to the plasma electron temperature.[1,2]

The idea of using iodine as an alternative propellant for HETs was proposed a decade ago [3,4] but the testing has only been carried out recently at Busek Co, Inc. Using a 200 Watt (BHT-200) iodine Hall thruster, Szabo et al [5] demonstrated that the efficiency of iodine thrusters is similar to that of xenon HETs, but with added benefits of iodine being a low cost propellant with three times the storable density of xenon. The iodine HETs are also thought to have higher thrust to power ratio. In the present work, we report the results of a series of optical emission spectral measurements for the iodine BHT-200 thruster carried out in the Busek facility. The emission spectra were measured along the thrust axis of the BHT-200 by viewing with a spectrometer perpendicular to this axis. This orthogonal arrangement allows spectra to be taken at various locations in the plume region. Figure 1 shows emission spectra taken at three positions along the central axis of the plume in the visible to near-infrared spectral range. The bottom panel shows the emission spectra taken along the axis of the nose cone while the middle and top panel represent the emissions observed at a distance of 1" and 2" downstream from the nose cone, respectively. The BHT-200 thruster operating conditions employed are with 250 V anode potential, 0.78 A anode current, 0.8 A keeper current, and mass flow rates of iodine vapor at 0.8-1.0 mg/s. The analysis of emission spectral lines identifies that the main excited species observed are iodine atoms (I^*), iodine ions (I^+), xenon atoms (Xe^*), and xenon ions (Xe^+). The presence of xenon species is due to the use of xenon gas feed in the cathode and is consistent with the observation that the xenon emission intensities were found to increase in the cathode vicinity. Interestingly, no detectable excited I_2 or I_2^+ species were observed. Comparison of optical emission results to that of probe measurements will be discussed.

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Dynamics of Alkali Atom Excitation and Population Inversion in Optically Pumped Rare-Gas Exciplex Systems

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Diode-pumped alkali laser (DPAL) technology offers an attractive means of converting high-power diode laser energy into high-beam-quality gas phase laser output by single-photon pumping of the D-lines of Cs, Rb, and K. The exciplex effect, based on weak attractive forces between alkali atoms and polarizable rare gas atoms (Ar, Kr, Xe), provides an approach to lasing via broadband excitation of the upper electronic states of the alkali atoms (XPAL). The weakly bound exciplex collision pairs are optically excited to upper electronic molecular states which rapidly dissociate to produce electronically excited alkali atoms. The single-photon exciplex absorption, $X^2\Sigma_{1/2}^+ \rightarrow B^2\Sigma_{1/2}^+$, produces excitation and inversion on the D₂ alkali atom transition, $^2P_{3/2} \rightarrow ^2S_{1/2}$. In the presence of a collisional spin-orbit transfer agent such as ethane, the alkali D₁ transition, $^2P_{1/2} \rightarrow ^2S_{1/2}$, can also be excited. In addition, we observe multi-quantum excitation through the exciplex leading to excitation of blue-emitting and infrared-emitting states of the alkali atom; these transitions are also laser candidates.

Optical gain is a fundamental measure of the lasing potential of a medium, independent of the details of the resonator design. In the case of DPAL and XPAL systems, which must operate at elevated pressures and optically thick conditions, measurements of spatial and spectral distributions of the gain and loss provide key information on the complex dynamics of the optically pumped medium. We have developed approaches for measuring spectrally and spatially resolved gain, and have applied them to observations of D₁ excitation in Cs-exciplex mixtures pumped on the D₂ line by a continuous-wave Ti:sapphire laser at low to moderate pump power densities. The results provide insights into the population inversion dynamics as well as the effects of radiative transfer within the medium for the DPAL case. We are also investigating exciplex excitation at high pump powers relevant to XPAL using a pulsed dye laser. We will discuss recent preliminary results from gain measurements in pulsed excitation of the exciplex near threshold.

Generation of Energetic Species by RF Microplasma Arrays

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We present preliminary results from the first implementation of a prototype single-board RF micro-discharge, linear array device in a discharge-flow reactor for quantitative determinations of ozone and singlet-oxygen production from microplasmas in O₂ and air at 1 atm. The ultimate objective is to develop compact, portable low-power micro-discharge based systems to generate energetic species for atmospheric-pressure applications including decontamination and disinfection. The technology uses application of low DC voltages (20-30 V) and low applied powers (~25 W) at ~1 GHz frequencies, across small gaps in arrays of resonators to ignite and sustain highly energetic microplasmas at elevated pressures. A set of 15-resonator micro-discharge assemblies was designed, fabricated, and tested in static and flowing environments for O₂, air, and Ar flows at pressures of 20 Torr to 1 atm. O₃ production was measured by UV absorption spectrometry, and O₂(a¹Δ_g) ("singlet-oxygen") concentrations were determined by absolute near-infrared emission spectroscopy. Near-infrared emission spectra from an argon plasma were also recorded, and showed extensive excitation of the Ar(I) 3p⁵4p – 3p⁵4s emission system near 12 eV. The experimental measurements are guided by kinetics modeling of the chemistry within and downstream of the active discharge. The data demonstrate the potential of this novel low-power, high-field, CW micro-discharge approach for high-efficiency generation of a variety of energy-carrier species including ozone, metastable singlet molecular oxygen, and metastable argon atoms.

Magnesium-Perfluoropolyether Reactions Studied by TPD/TPR

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Exothermic reactions between metals and fluorinated polymers are found in a variety of energetic materials, including reactive binder systems and the magnesium-Teflon-Viton incendiary composition. This poster describes the reactions between a high molecular weight perfluoropolyether, Fomblin 140/13, and magnesium in a variety of morphologies including micron-scale powders, micro laminates, and nano-scale particles. Using Temperature Programmed Desorption (TPD) and Temperature Programmed Reaction (TPR), we have found that the magnesium-perfluoropolyether interaction is characterized by: 1) competition between Fomblin decomposition vs. desorption and 2) magnesium passivation by the formation of magnesium fluoride.

High molecular weight Fomblin (6800 amu average) undergoes a competitive reaction/desorption process with desorption occurring at 550 K and decomposition at 610 K. Decomposition becomes more favorable relative to desorption at higher heating rates and higher coverages. Perfluoropolyethers produce several characteristic ions in the mass spectrometer, but the CF_3^+ ion is the most abundant ion observed during both the molecular desorption and decomposition. Two ions with masses of 235 and 285 amu, corresponding to whole Fomblin monomers, are observed in relatively high concentrations during desorption and low concentrations during decomposition.

The reaction between magnesium and Fomblin begins at 200 K with a reaction that produces CO as its only gas phase product. Another reaction begins at 400 K, producing CF_3 , CO, and C_2F_5 . We believe that these reactions form a passivating layer of magnesium fluoride that protects the remaining metal until the substrate reaches the magnesium sublimation temperature near 700 K. The majority of the reaction seems to take place between 750 K and 800 K, with the desorption of CF_3 , Mg, CO, C_2F_5 , and CO_2 .

The thin-film magnesium/Fomblin reactions are compared with DSC/TGA results from samples prepared with micron-sized magnesium powders and TPD/TPR results from samples prepared with nanometer-sized magnesium clusters.

Thermal Electron Attachment to Fluorocarbon Radicals: Experiment and Kinetic Modeling

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Most plasma environments contain populations of short-lived species such as radicals, the chemistry of which can have significant effects on the overall chemistry of the system. However, few experimental measurements of the kinetics of electron attachment to radicals exist due to the inherent difficulties of working with transient species. Calculations from first principles have been attempted, but they are both exceptionally arduous and, because electron attachment is so sensitive to the specifics of the potential surface, their accuracy has not been established. Electron attachment to small fluorocarbon radicals is particularly important, as the data are needed for predictive modeling of plasma etching of semiconductor materials, a key process in the industrial fabrication of microelectronics. We have recently developed a novel flowing afterglow technique to measure several types of otherwise difficult to study plasma processes, including thermal electron attachment to radicals. Variable Electron and Neutral Density Attachment Mass Spectrometry (VENDAMS) exploits dissociative electron attachment in a weakly ionized plasma as a radical source. Here, we apply VENDAMS to a series of halofluorocarbon precursors in order to measure the kinetics of thermal electron attachment to fluorocarbon radicals. Results are presented for CF_2 , CF_3 , C_2F_5 , CF_3 , 1- C_3F_7 , 2- C_3F_7 , and C_3F_5 from 300 K to 600 K. Both the magnitude and the temperature dependences of rate coefficients as well as product branching between associative and dissociative attachment are highly system specific; however, thermal attachment to all species is inefficient, never exceeding 5% of the collision rate. The data are analyzed using a kinetic modeling approach. Barrier heights between the neutral and anion surfaces are extracted and shown to be significantly higher than those obtained with a simple Arrhenius equation fit to the data. The inefficiency in attachment in all cases is only reproduced by assuming a more significant deviation from extended Vogt-Wannier theory at higher collision energies than has been observed for any other systems, and may indicate large cross-sections for electron scattering to these species. Finally, the kinetic modeling, along with complimentary data from electron beam measurements, is used to extrapolate the electron attachment rate coefficients to temperature and pressure regimes inaccessible to the experiment, including to non-thermal plasma conditions most relevant to plasma etching.

Precision Gas-Surface Scattering and Imaging Studies of Complex Interfaces

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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 the energy and momentum exchange mechanisms which govern such encounters. They also serve as precision tools for examining the properties of clean, adsorbate decorated, and thin-film covered interfaces. One strategic objective of this AFOSR program is to extend, quite significantly, the scope and precision of such scattering studies to include complex interfaces, encompassing crystalline, glassy, structurally-dynamic, and amorphous materials, as well as those having aligned structural elements. We also seek to improve understanding of interfacial condensation and reactivity. Scanning probe imaging is being used to augment the scattering data, helping to visualize local events on atomic and nano length scales.

We report on several accomplishments that occurred during the past grant period: (i) building upon our initial studies of collisional energy transfer at polymeric interfaces as a function of composition (PMMA, PS, PB), molecular weight, thickness & nanoconfinement, temperature, and annealing, we have examined the surface dynamical properties of PET polymer thin films in their glassy vs. crystalline phases, and have elucidated for the first time clear changes in the energy accommodation characteristics due to such polymer structural changes [1]; (ii) helium atom scattering has been used to measure the surface structure and vibrational dynamics of (1x1) CH₃- and CD₃-terminated Si(111). The high quality of the observed diffraction patterns indicate a high degree of long-range ordering for this novel, atmospherically stable, and technologically interesting interface, while inelastic measurements have quantified the lateral and perpendicular displacements – with energy accommodation being dominated by local Si-CH₃ librations [2]; (iii) we are studying gas-surface collisions at higher energies with organic films that lead to molecular penetration and trapping/incorporation into such films. Such non-dissociative deposition experiments, which are dominated by dynamical factors, allow creation of new types of multi-component nanoscale materials [3,4]; (iv) we have extended our scattering experiments to the hyperthermal regime, and have initiated neutral scattering experiments to explore sputtering induced by neutral atom bombardment [5]. These results suggest that sputtering of surfaces with neutrals might be useful as a non-charging and non-chemically-destructive adjunct to ion-induced sputtering and SIMS for compositional depth profiling and trace analysis; (v) we have initiated experiments involving thin polymer film reactivity, examining reactions of O(³P) with PMMA including synergistic photochemical processes [6]; fast oxygen ion reactions with hydrocarbon surfaces are also being examined [7].

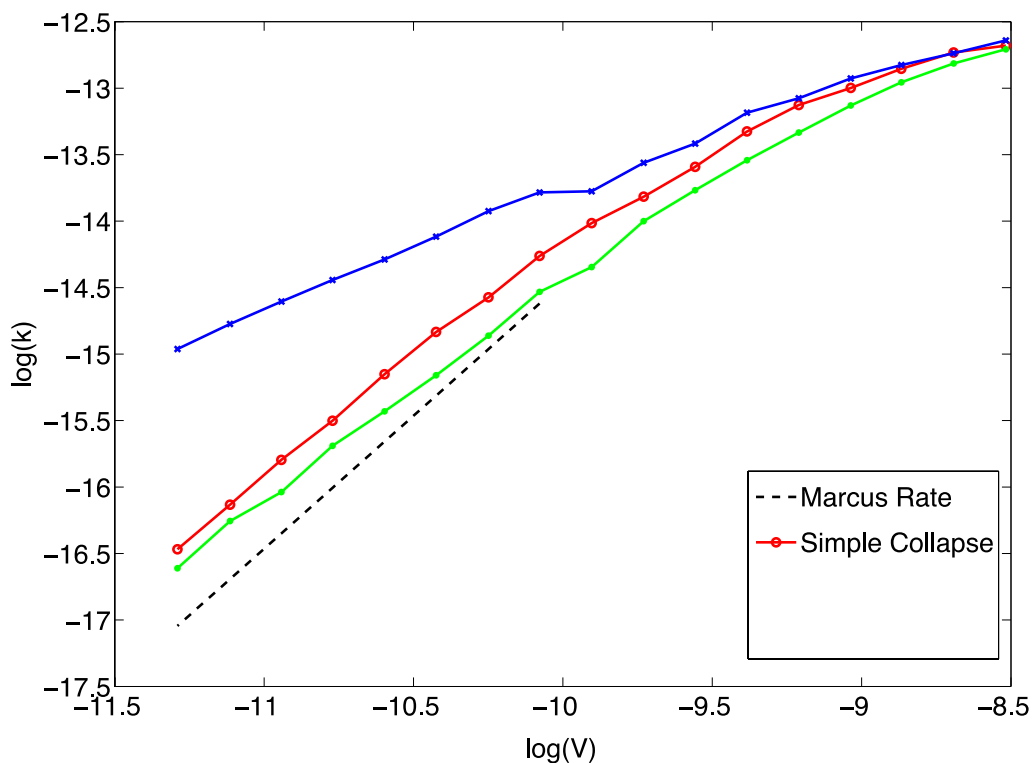
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Standard Surface Hopping Predicts the Incorrect Scaling for Marcus's Electron Transfer Rate: Why Decoherence Saves the Day

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Tully's fewest-switches surface hopping (FSSH) algorithm is probably the most popular modern approach for modeling photo-excited nonadiabatic dynamics, and yet we know that the FSSH model has one large shortcoming, its failure to treat decoherence correctly. We have shown previously that FSSH's overcoherence problem is manifested at long times if nuclei visit regions of derivative coupling more than once. In this poster, we will show a very troubling ramification of this same problem. Our focus is the spin-boson model for the case of a small diabatic coupling parameter (V), where nuclei should cross a region of nonadiabatic coupling repeatedly before an electron is transferred. Using FSSH dynamics, we calculate the transition rates between diabatic surfaces— ideally, FSSH should yield the celebrated Marcus rates for electron transfer. Instead, we show that FSSH yields an incorrect scaling with diabatic coupling ($\sim V$). To recover the correct scaling ($\sim V^2$), we must modify FSSH to include decoherence events, thus proving the absolute need for decoherence when modeling electron-transfer dynamics and highlighting the strengths of our new (decoherence-included) augmented FSSH (A-FSSH) approach.



Dynamics of Collisions of OH with Fluorinated Surfaces

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We present a theoretical study of the dynamics of collisions of the hydroxyl radical with fluorinated self-assembled monolayers and liquids. Classical trajectories are propagated using an intermolecular potential energy surface derived from high-quality *ab initio* calculations to determine the amount of gas/surface energy transfer and the mechanistic aspects of the collisions. Special attention is given to understanding energy transfer in a state-to-state manner by initiating the collisions with OH in specific rovibrational states. This work is motivated by recent experiments in the McKendrick group in which the rotational distribution of photoinduced OH were measured after collision with a variety of liquids. The calculated OH rotational distributions are in excellent agreement with the measurements, which lends confidence to the accuracy of the simulations. The calculations show subtle differences between the dynamics of OH scattering from an atomically flat perfluorooctanethiol self-assembled monolayer and the rougher surface of liquid perfluorooctane. The major differences between these two surfaces are clearly noticed in an analysis of the mechanism on the collisions, which shows that the roughness of the liquid surface results in an enhanced number of interactions with the colliding OH molecules. An isotopic calculation in which the mass of fluorine atoms is set to 1.008 amu produces OH rotational distributions that are in good agreement with measurements of OH scattering from an alkane surface (squalane), suggesting that kinematic factors play a major role in determining energy transfer in inelastic collisions of OH with organic surfaces.

Dynamics of OH Reactions with Alkenes and Alkanes

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We present a theoretical study of the reactions of OH with alkenes and alkanes, which play an important role in atmosphere, using electronic structure calculations and direct dynamics simulations. High-accuracy calculations of the potential energy surface at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVDZ level have been carried out to characterize representative regions of the potential energy surface of various reaction pathways, including OH-addition and H-abstraction in the reactions with alkenes, and H-abstraction in the reaction with alkanes. These *ab initio* calculations have been subsequently employed to derive an improved set of parameters for the MSINDO or AM1 semiempirical Hamiltonian, which are specific to the OH + alkenes and alkanes family of reactions, specifically. The specific-reaction-parameter (SRP) Hamiltonian has been used to perform a quasi classical-trajectory study of OH+C₂H₄, C₃H₆, CH₄ reactions. The trajectory calculations reveal that whereas the OH-addition is the dominant channel for both OH+C₂H₄ and OH + C₃H₆ reactions, the H-abstraction channel becomes more competitive for OH + C₃H₆. Analysis of simulation results suggests a tendency of sequential decrease and increase of cross sections as the initial collision energy increases for addition and abstraction, respectively. The results of trajectories propagated with the SRP Hamiltonian agree with the experiment and recent theoretical studies. It is also noticed that the damped dispersion correction of the original MSINDO is necessary in cases where long-range correlation effects become important.

Volatilization Mechanism of 1-Ethyl-3-Methylimidazolium Bromide Ionic Liquid

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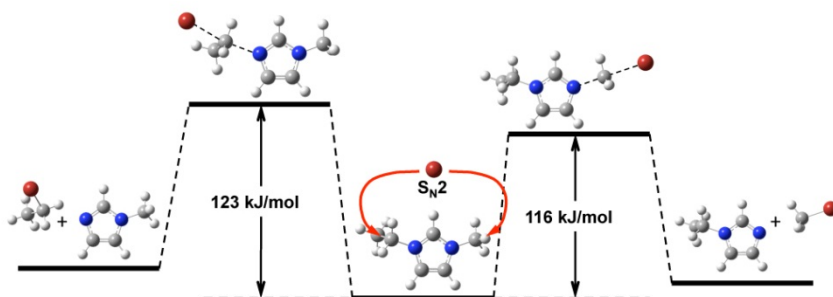
Although molten salts, more recently known as ionic liquids (ILs), have been known for almost a century (for instance, ethylammonium nitrate, mp =12 °C, was discovered in 1914),¹ the rapid development of ionic liquid chemistry has only occurred within the last decade. In 2000, only 217 papers were published on the subject, whereas in 2010, over 6,000 papers appeared in the literature.² The number of possible ILs has been estimated at 10^{18} .³ Detailed studies of ILs offer insight into new and more complex fundamental chemistry, as well as allow for an assessment for their potential application in emerging technologies such as in solar cells, fuel electrolytes, bio- or nano-catalysts, high-energy-density propellants, and green solvents.

In order to better understand the volatilization process for ILs, the vapor evolved from heating the ionic liquid 1-ethyl-3-methylimidazolium bromide (EMIM⁺Br⁻) was analyzed via tunable vacuum ultraviolet photoionization time of flight mass spectrometry (VUV-PI-TOFMS) and thermal gravimetric analysis mass spectrometry (TGA-MS). For this ionic liquid, the experimental results indicate that vaporization takes place via the evolution of alkyl bromides and alkylimidazoles, presumably through alkyl abstraction via an S_N2 type mechanism, and that vaporization of intact ion pairs or the formation of carbenes is negligible.

Activation enthalpies for the formation of the methyl and ethyl bromides were evaluated experimentally, $\Delta H^\ddagger(\text{CH}_3\text{Br}) = 116.1 \pm 6.6$ kJ/mol and $\Delta H^\ddagger(\text{CH}_3\text{CH}_2\text{Br}) = 122.9 \pm 7.2$ kJ/mol, and the results are found to be in agreement with calculated values for the S_N2 reactions. Comparisons of product photoionization efficiency (PIE) curves with literature data are in good agreement, and *ab initio* thermodynamics calculations are presented as further evidence for the proposed thermal decomposition mechanism. Estimates for the enthalpy of vaporization of 1-ethyl-3-methylimidazolium bromide and, by comparison, 1-butyl-3-methylimidazolium bromide (BMIM⁺Br⁻) from molecular dynamics calculations and their gas phase enthalpies of formation obtained by G4 calculations yield estimates for the ionic liquids' enthalpies of formation in the liquid phase: $\Delta H_{\text{vap}}(298 \text{ K})$ (EMIM⁺Br⁻) = 168 ± 20 kJ/mol, $\Delta H_{\text{f, gas}}(298 \text{ K})$ (EMIM⁺Br⁻) = 38.4 ± 10 kJ/mol, $\Delta H_{\text{f, liq}}(298 \text{ K})$ (EMIM⁺Br⁻) = -130 ± 22 kJ/mol, $\Delta H_{\text{f, gas}}(298 \text{ K})$ (BMIM⁺Br⁻) = -5.6 ± 10 kJ/mol, and $\Delta H_{\text{f, liq}}(298 \text{ K})$ (BMIM⁺Br⁻) = -180 ± 20 kJ/mol.

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S_N2 reaction energetics involved in the heating of the ionic liquid, 1-ethyl-3-methylimidazolium bromide (EMIM⁺Br⁻)

Platinum and Cobalt (Oxide) Cluster Based Dehydrogenation Catalysts

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Particle composition and size which primarily determine catalytic performance, as well as sufficient lifetime during operation are parameters that form a considerable challenge on the way of the identification of optimized catalysts. Prerequisites for such studies are catalysts prepared with well defined size/composition and *in situ* characterization of the catalysts under working conditions.

The dehydrogenation of cyclohexane (C₆H₁₂) and cyclohexene (C₆H₁₀) - as model jet fuel surrogates - was studied on Pt- and Co(Ox)-based nanocatalysts. The small Pt nanoparticles were prepared on multiwalled carbon nanotubes of three kinds: as purchased (Pt-NT), functionalized by treatment with nitric acid (Pt-NO) and obtained after high-temperature annealing of the functionalized nanotubes (Pt-HT). The sub-nm size CoOx clusters were prepared by deposition of a narrow distribution of cluster sizes from cluster beams supported on various oxide surfaces and nanocrystalline diamond. The performance of the nanocatalysts and their *in situ* characterization was studied using a GISAXS/GIXAS/TPRx cell of own design.

The catalysts performance was monitored by temperature programmed reaction (TPRx), particle size with *in situ* grazing-incidence small angle X-ray scattering (GISAXS) and their oxidation state by X-ray absorption (GIXAS) characterization. The Pt-based catalysts were studied in the absence of oxygen, the Co-based catalysts under oxygen rich and oxygen poor conditions. A strong dependence of the catalytic performance on the size of the particles as well as on the composition and functionalization of the support was observed.

Figure 1a and 1b show temperature dependent line cut (horizontal) profiles of oxidized Co clusters supported on MgO and Al₂O₃, respectively. There is no change observed in the GISAXS pattern of alumina (nor the UNCD and ZnO, not shown) supported clusters, thus providing evidence of the sintering-resistance of clusters with cyclohexene on these supports. The resulting particle size and distribution is shown in Figure 1c. At room temperature, GISAXS data are represented by a dominant substrate scattering induced by surface roughness, with a little contribution from cobalt clusters. This confirms that the clusters are of subnanometer size as-prepared. The most significant change in the GISAXS pattern is observed at 300 °C, reflecting the formation of a nanostructure with a main size of about 2.3 nm and about 1 nm size distribution. As shown in Figure 1c, the main particle size drops to about 0.6 nm with a broad size distribution when the sample is cooled down to room temperature, thus indicative of a highly flexibly evolving particle assembly which adopts its size and morphology to promote the reaction path.

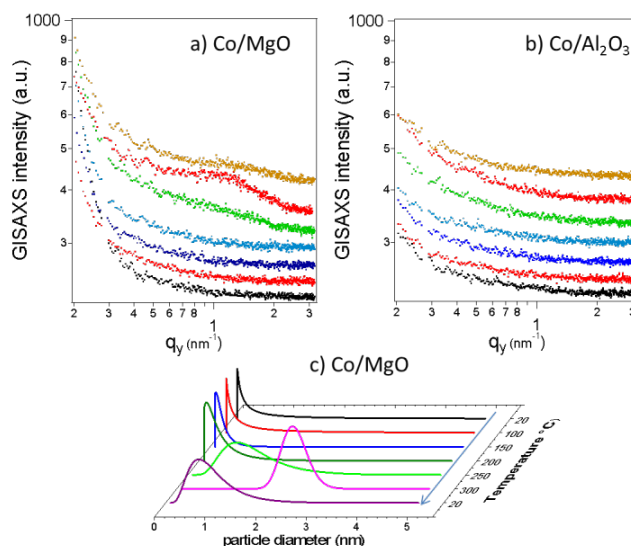


Figure 1. GISAXS intensity (horizontal line cut) change during the heating cycle, from the bottom 20, 100, 150, 200, 250, 300 and 20 °C (after reaction) respectively for (a) MgO-supported and (b) Al₂O₃ supported cobalt clusters; the spectra are offset for clarity. (c) evolution of particle/nanoassembly size distribution of the magnesia-supported clusters during the reaction. Cyclohexene (0.4%) in He at total pressure of 800 torr.

"Oxidative Dehydrogenation of Cyclohexene on Size Selected Subnanometer Cobalt Clusters: Improved Catalytic Performance via Evolution of Cluster-Assembled Nanostructures", S. Lee, M. Di Vece, B. Lee, S. Seifert, R. E. Winans and S. Vajda, *Phys. Chem. Chem. Phys.*, invited paper, on-line, DOI: 10.1039/c2cp40162b

"Support-Dependent Performance of Size-Selected Subnanometer Cobalt Cluster-Based Catalysts in the Dehydrogenation of Cyclohexene" S. Lee, M. Di Vece, B. Lee, S. Seifert, R. E. Winans and S. Vajda, *Chem. Cat. Chem.*, invited paper, submitted

Parallel Implementation of Coupled Cluster Methods with Application to Excited State Energies and Geometries of Nucleobases and Their Complexes

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Benchmark accuracy for molecular systems is critical for the development of less expensive, but thorough, methods to enable the accurate theoretical treatment of large, chemically relevant molecules. In particular, no biological molecules are more important than DNA and RNA strands, which through the nucleobase pair and sugar network and the influence of hydration remain highly protected against the absorption of harmful high energy ultra-violet (UV) photons. Currently, no applicable theory is sufficiently accurate to characterize the correct energies, orderings, and geometries of the excited states generated by UV radiation. Therefore, an accurate description of the excited states of nucleobases, Watson-Crick pairs, nucleosides, and hydrated complexes is needed, such that lower level methods can be parameterized to allow extended calculations on the DNA and RNA strands.

In this vein, we have implemented coupled cluster (CC) methods, and the equation of motion extensions (EOM-CC) to include full single and double substitutions as well as perturbative triples corrections (CCSD(T) and EOM-CCSD(T)) in an efficient massively parallelizable way in ACESIII. These methods are considered “gold standard”, capable of chemical accuracy (within 1 kcal mol⁻¹ in error), but need to be implemented in such a way that allows the data to be distributed over $O(10,000)$ to $O(100,000)$ compute cores.

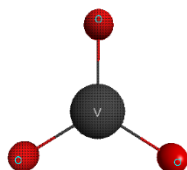
We present the design philosophy of the ACESIII program package that is capable of performing these types of calculations in an efficient “black-box” manner. EOM-CCSD(T) benchmark results are shown for various nucleobases and their complexes, with the largest basis sets reaching 577 basis functions parallelized over 1024 processors. Performance numbers are shown for EOM-CCSD for a base-pair complex with over 1,000 basis functions parallelized over 60,000 processors.

Optimized excited state geometries are illustrated with the recently implemented EOM-CCSD gradients, which shows great scaling performance. This opens the door for a detailed characterization of excited state potential energy surfaces.

Bonding in Transition Metal Oxides. The Jahn-Teller Effect and Unexpected Bonding Paradigms

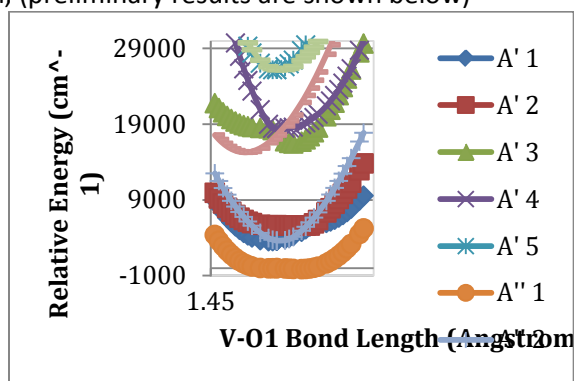
Liza Moon Young Lee and David R. Yarkony
Department of Chemistry, Johns Hopkins University

Recent density functional based descriptions of vanadium trioxide



suggest dramatically different equilibrium structures for the ground electronic state. Two recent studies using the BPW91 functional found the ground state of VO_3 to be a $^2\text{A}_2$ state with C_{3v} symmetry.^{1,2} This result is supported by a quantum Monte Carlo calculation.³ A third study, based on the B1LYP functional, found a $^2\text{A}''$ ground state having C_s symmetry⁴ consistent with earlier results of Davidson.⁵ The electron photodetachment spectrum of VO_3^- has been recorded by Wu and Wang.⁶ Peaks assigned to three electronic states were reported at electron binding energies of 4.36, 4.95 and 5.15 eV.

We are in the process of developing an SA-MCSCF/MRCI description of VO_3 to understand and resolve these discrepancies. Following our determination of the coupled state representation of the electronic states in question, (preliminary results are shown below)



a coupled diabatic state representation of these states and their interactions will be determined and used to simulate the measured photoelectron spectrum of VO_3^- . The simulated photoelectron spectrum will allow us to validate our electronic structure results.

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Molecular Conformations and Dynamics on Surfaces of Gold Nanoparticles Probed with Multiple-Mode Multiple-Dimensional Infrared Spectroscopy

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Knowledge about molecular conformations and nuclear and electronic motions on surfaces of metal nanomaterials, is critical for many applications but extremely difficult to obtain. We demonstrate that valuable information of this sort can be determined using multiple-mode multiple-dimensional vibrational spectroscopy. A model compound, 4-mercaptophenol, on the surface of 3.5nm gold nanoparticles demonstrates the method. Its 3D molecular conformations and vibrational dynamics on the particle surfaces were determined with the method. The experimental results imply that on the particle surfaces, the ligand molecules can't form energy-optimized hydrogen bonds because of the surface geometry constraint. The conclusion is supported with experiments on the ligand molecules in the crystalline phase and in a dilute solution. Our experiments also showed that the effect of the particle surface non-adiabatic electron/vibration coupling does not play a significant role in the vibrational relaxation of high frequency modes ($>1000\text{ cm}^{-1}$) about 3 Angstrom away from the surface. Simple theoretical calculations support this observation. The method holds promise as a general tool for the studies of molecular structures and dynamics on the surfaces of nanomaterials. The capability of resolving 3D molecular conformations on nanomaterials surfaces is expected to be helpful for understanding specific intermolecular interactions and conformation-selective reactions (e.g. chirality selectivity) on the surfaces of these materials.

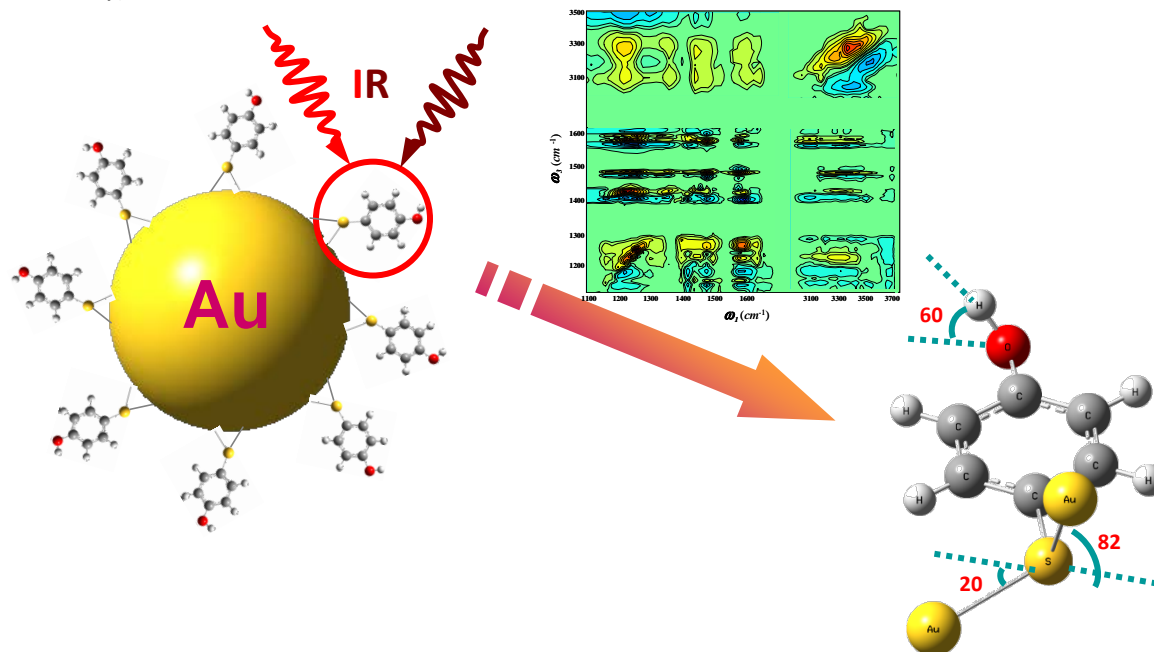


Figure 1. Schematic representation of resolving 3D molecular conformations on nanoparticle surface with the multiple-mode 2D IR method

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