

Probing and Manipulating the Photophysics of New Semiconducting Carbon Nanotube Films

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Semiconducting carbon nanotubes are strong optical absorbers that are distinguished in their ability to route energy in specified directions. Our research project is focused on (i) understanding how energy flow can be rationally directed using films and assemblies of nanotubes; (ii) developing new optical technologies including 2D white-light spectroscopy and microscopy for mapping and understanding energy flow in these materials; and, (iii) building new designs of phototransistors, photodetectors, and photovoltaics to test our concepts. Three recent advances will be presented.

First, we will report on how spectroscopy advances are guiding materials development towards improved films with controlled energy flow. For the first time, 2D white-light spectroscopy has made it possible to relate increased inter-nanotube energy transfer *between* nanotubes in assemblies (measured from cross-peaks in 2D spectra) to increased device efficiency (Fig. 1). Second, we will present an overview of our recent publication in *Nature Chemistry* (2019), in which we invented a new type of microscope – one that can measure 2D white-light spectra – and do so with sub-micron spatial resolution. Using this new microscope, we have measured energy flow and the spatial structures of photovoltaic materials made to increase photocurrent. Finally, we will report on a new type of phenomenon and device architecture we are exploring for promoting coupling and energy transfer over long distances – via carbon nanotube exciton-photon polaritons. We have shown that the electronic states of semiconducting carbon nanotubes placed between highly reflecting mirrors can strongly couple to the light field between the mirrors, significantly splitting the energy levels (by as much as 0.45 eV) and creating what is called a polariton that mixes electronic states across all the nanotubes between the mirrors. Our preliminary measurements characterize the coupling and relaxation pathways in these cavities and demonstrate that they can produce a photocurrent response.

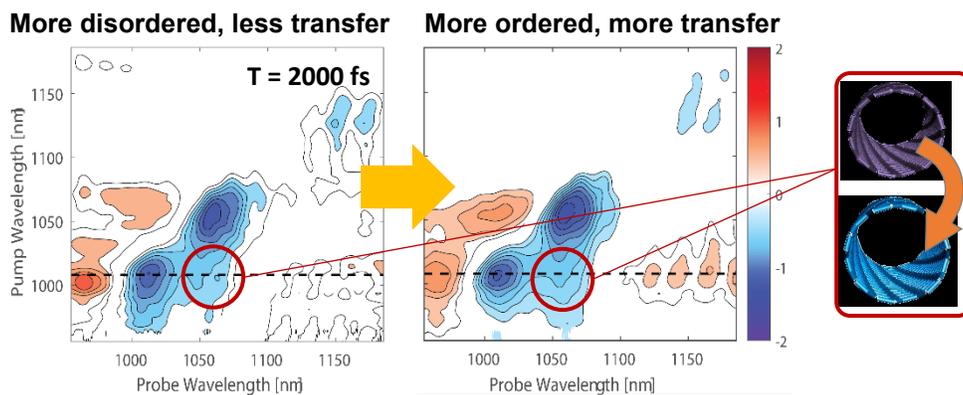


Figure 1. For the first time, 2D WL spectroscopy has made it possible to relate increased inter-nanotube energy transfer to increased device efficiency, showing the importance of inter-tube coupling in this energy harvesting/transport system.

Fe and Ni Molecular Photochemistry Revealed by Femtosecond M-edge XANES

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Catalyst development and optimization requires detailed understanding of transition states and reactive intermediates. We have developed M_{2,3}-edge XANES as an ultrafast probe of the electronic structure of transition metal complexes: the shape and position of the 3p→3d transition is specific to the element, oxidation state, spin state, and ligand-field. This talk will highlight the femtosecond dynamics of three systems: 1) An Fe(III) porphyrin that relaxes from an π-π* state to a ligand-to-metal charge state through ballistic expansion; 2) a Ni(II) porphyrin that undergoes intersystem crossing to a triplet (d,d) state in <100 fs; and 3) An Fe(II) polypyridyl complex that passes through a ³(d,d) state on the way to a metastable ⁵(d,d) state. In the latter case, we demonstrated that the ligand-field specificity of M-edge XANES allows us to fingerprint the specific vibrational mode that is activated upon formation of the ⁵(d,d) state. Progress on extension of this technique to [NiFe] hydrogenases and to the solution phase will also be discussed.

Molecular Level Studies of Solid-Liquid Interfaces in Electrochemical Processes

Tim Lian, Emory; Héctor D. Abruña, Cornell; Jahan Dawlaty, USC; Sharon Hammes-Schiffer, Yale; James M. Mayer, Yale; Joseph Subotnik, U Penn; Yogi Surendranath, MIT, and **Adam P. Willard**, MIT

The electric double-layer forms at the interface between an electrode and an electrolyte solution and sets the stage for a wide range of microscopic electrochemical processes. The structure of the double-layer is typically described using continuum level models, such as those derived from the pioneering efforts of Gouy, Chapman, and Stern. While continuum-based models provide an efficient and intuitive framework for studying and understanding the macroscopic behavior of electrochemical systems, they are inappropriate for modeling the time and length scales inherent to individual electrochemical reactions. Over these scales - generally nanoseconds and nanometers - the discrete molecular nature of the electrolyte is apparent. Here, I present the efforts of a MURI team focused on understanding the molecular properties of the double-layer and their influences on electrocatalysis. I will present project goals, recent progress, and future directions.

Control of the selectivity of alkane dehydrogenation for endothermic cooling on supported Pt cluster catalysts

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Through a combination of theory and experiment, we will show that supported size-selected Pt clusters exhibit size-dependent activity toward hydrocarbon dehydrogenation, and will explain the size-dependence through catalyst dynamics and thermally-accessible morphologies at reaction temperatures. Further, the most active Pt clusters quickly coke, and Pt clusters of all sizes also sinter on the support, losing active sites and catalytic activity. We will present several main group dopants (B, Sn, Si, Ge) that we developed for stabilizing the supported Pt cluster catalysts against sintering, and tuning their selectivity of dehydrogenation toward olefins. B and Sn are characterized also experimentally, and show no deactivation over several cycles of dehydrogenation. The four dopants alter the properties of Pt through principally different mechanisms. We will further show that catalyst stability is again a property of an ensemble of all thermally-accessible catalyst states at reaction temperatures. In fact, theory would not be able to predict or explain the beneficial effect of doping if just the global minimum structure would be considered. These simulations are enabled by new computational methods for global optimization and catalyst isomerization pathway exploration.

Vibrational Spectroscopy of Water at Graphene Electrode Surfaces

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Aqueous interfaces play a crucial role in areas ranging from life sciences, environmental chemistry, and oceanography, to heterogeneous catalysis, electrochemistry, and energy conversion applications. In particular, the solvation properties of interfacial water dictate the chemical equilibria and reaction rates. Our basic understanding of water as a dielectric medium (polar solvent) relies on the assumption of linear response, i.e. that an external perturbation (electric field) induces a linearly proportional response in the medium (in this case, polarization). Explicit in this assumption is its anti-symmetry with respect to the sign of the external field: the response must be of the same magnitude and opposite sign for positive vs. negative applied fields of a given strength. Here, we present surface-selective vibrational sum frequency generation (VSFG) spectroscopy of water (D_2O) near a monolayer graphene electrode, allowing us to study the response of water to an external electric field under controlled electrochemical conditions. The graphene Raman G-band frequency is used as an internal gauge of the surface charge density. VSFG spectra in the OD-stretch region show a pronounced asymmetry for positive vs. negative electrode charge. At negative charge (below $-5 \times 10^{12} e^-/cm^2$), a 2700 cm^{-1} peak corresponding to the “free” (non-hydrogen-bonded) OD groups pointing towards graphene surface is observed. At neutral or positive electrode potentials, the “free OD” peak is absent, and the spectra are dominated by the broad peaks of the hydrogen-bonded OD-stretch ($2300\text{--}2650\text{ cm}^{-1}$). Evolution of VSFG spectra as a function of the external electric field is connected to the linear susceptibility (and the dielectric constant) by the Miller’s rule. The observed deviation from the linear response to electric fields of the order of $\pm 3 \times 10^8\text{ V/m}$ therefore calls into question the validity of considering interfacial water as a simple dielectric medium.

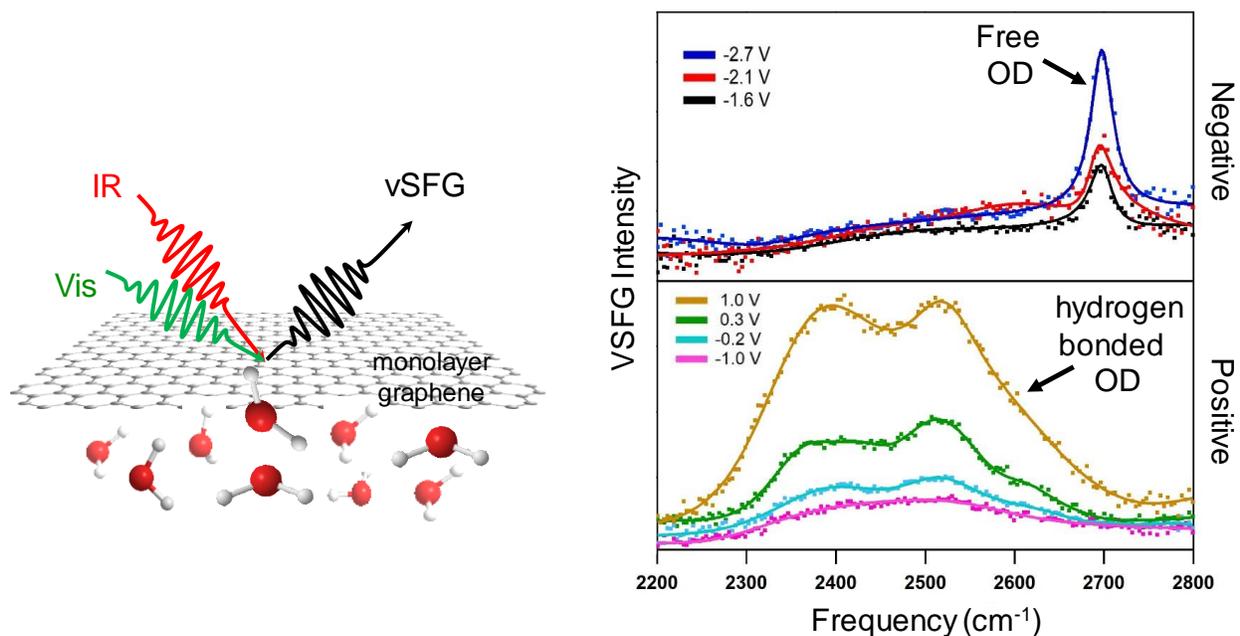


Figure 1. VSFG spectra of the OD-stretch of D_2O at the graphene electrode at different potentials vs. $Ag/AgCl$. The spectra were recorded using SSP polarization combination (IR, visible, SFG). Solid lines show the fit to the model with interfering surface and bulk contributions.

Playing with the DOLFIN

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DOLFIN – Direct Optical Lithography of Functional Inorganic Nanomaterials – is new concept for high-resolution patterning of colloidal nanocrystals and quantum dots (QDs) for electronic, optoelectronic and photonic devices. The intensive research efforts over two decades have led to an increased understanding of nanomaterials and their technological prospects, enabling a number of applications. The quantum-tuned nanomaterials have been successfully commercialized for displays and lighting, and are actively researched for lasing, sensing, electronics, photovoltaics and quantum information technologies. The transition from individual devices to electronic circuits, sensor arrays, and electroluminescent QD displays requires new methods for high-resolution and high-fidelity additive patterning of functional nanomaterials.

We introduced DOLFIN as photoresist-free method for high-resolution patterning of inorganic nanomaterials using photochemically active surface ligands. Next, we expanded DOLFIN versatility by designing photochemically active ligands for various photon energies including deep UV (DUV, 254 nm), near-UV (i-line, 365 nm), blue (h-line, 405 nm) and 450 nm light. We also developed a general approach for resist-free direct electron-beam lithography of functional inorganic nanomaterials (DELFIN) which enabled all-inorganic nanomaterials patterns with feature sizes down to 30 nm. We also developed surface ligands for heat-induced patterning of inorganic nanomaterials (HIPIN) and, most recently, focused on surface chemistries that efficiently preserved photo- and electroluminescent properties of different QDs. We demonstrated patterned QD LEDs with feature sizes down to $\sim 1.5 \mu\text{m}$ using red, green, and blue QD inks. In a parallel effort, we developed methods for patterning optically smooth layers of oxide nanocrystals for photonic components with full 2π phase control of visible light. Features with different thicknesses exhibit distinct structural colors, good optical transparency across a wide wavelength range ($0.3 - 10 \mu\text{m}$) and engineerable refractive indexes. The above examples demonstrate new prospective framework for additive device manufacturing.

Project Abstract

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

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PI: Colin Nuckolls

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This presentation will describe our research in creating electronic materials from molecular and superatomic building blocks. We are designing crystalline and self-assembled systems from these building blocks. We have created clusters of atoms that behave like the functional equivalent of atoms, but are on the nanoscale. These materials form solid solutions that show drastically enhanced electrical conductivity. Thin films of these materials have low thermal conductivity and point to a new direction to optimize thermoelectric materials. In addition, using these building blocks, we have made new materials with unusual magneto-optical properties.

Aluminum-based Bridged Superatomic Molecule: Unusual Nano p- n- junction with tunable Band gap, Adjustable Band alignment, and Effective Electron Hole separation

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Abstract

Electronic states in a confined nearly free electron gas are grouped into shells due to quantum confinement. Depending on the nature of metal, small compact clusters of metals therefore have electronic structure marked by gaps between filled and unfilled states. These features allow classification of clusters with well-defined valence as superatoms. By combining such clusters via organometallic bridges, it is possible to develop superatomic molecules where the quantum gaps can be used to create interfaces that resemble semiconducting pn- junctions. An unusual feature of such a junction is that the placement of electronic levels in individual clusters can be controlled by adding charge transfer ligands offering a nano device that unifies the three most important features of a pn-junction namely, controllable band gap energies, tunable placement of levels to assure desirable band alignment, and effective electron hole separation.

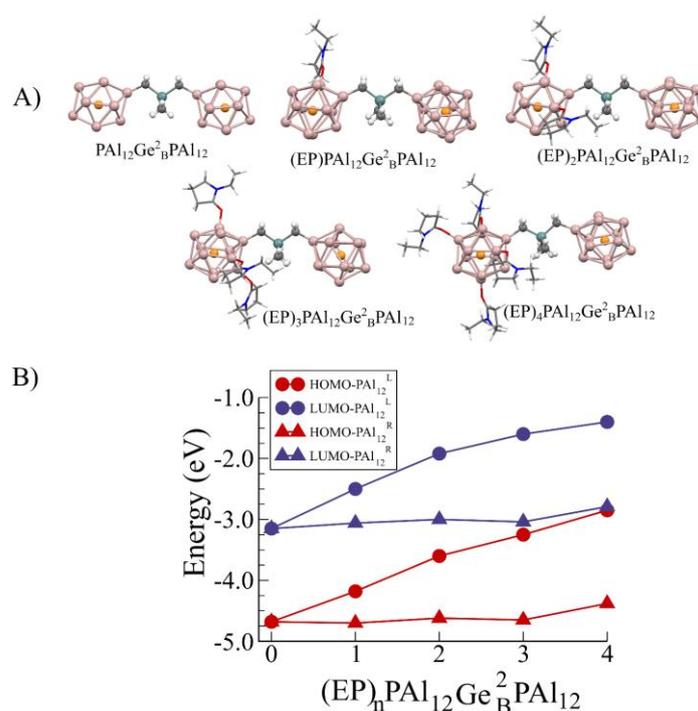


Figure: A) The structure of two PA₁₂ superatoms linked via an organometallic Ge(CH₂)(CH₃) linker with increasing number of EP ligands. B) The energy of the HOMO and LUMO of the left (L) and right hand (R) cluster as ligands are added.

In this talk I will demonstrate this intriguing possibility by considering a superatomic molecule formed by joining two aluminum based clusters linked by an organometallic bridge. I will show that the addition of ligands can induce a significant shift between the conduction and valence band edges across the inter-cluster interface. The band alignment is induced by the N-ethyl-2-pyrrolidone (EP) ligands, and the placement of the ligands strongly affects the direction of the dipole moment, including the case where the dipole moment is parallel to the cluster interface. This provides an alternative strategy for constructing nanometer-scale electronic interfaces. The semiconducting features in the PA₁₂ clusters emerge from the grouping of the quantum states in a confined nearly free electron gas that creates a substantial energy gap. An organometallic Ge(CH₃)₂(CH₂)₂ bridge links the clusters while maintaining the cluster's electronic shell structure. The amount of band shifting between the bridged clusters can be changed by controlling the number of ligands. Attaching multiple ligands can result in the valence band edge of one cluster being aligned with the conduction band edge of the other bridged cluster. Furthermore, the singly ligated bridged superatomic molecule is found to exhibit promising features to separate the electron-hole pairs for photovoltaic applications.

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DES and SILs: Improving Energetics by Applying Modern Concepts

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The theoretical performance (specific impulse) of propellant systems is a primary metric in propellant investigations. In publications of prospective propellant families the performance of specific propellant combinations is emphasized and compared to state-of-the-art alternatives. Since elements which are suitable for chemical propulsion are limited, the gains in raw performance have been relatively modest. Therefore, rather than chasing after totally new ingredients, per se, it might be time to reconsider how the present systems may be altered and improved. The best known examples of this thinking are the Energetic Ionic Liquids (ILs), which have been seen as the solution to some of the handling difficulties of the classical, neutral hydrazines with a toxicity closely related to their volatility. However, many energetic ILs of interest are expensive to make and additionally quite difficult to purify. Deep Eutectic Solvents (DES) and Solvated Ionic Liquids (SILs) could be improved hydrazine alternatives because of their properties and increased design tunability, but are accompanied by new challenges.

Molecular Simulation of Solid Propellants: Models for Ammonium Perchlorate and Hydroxyl-Terminated Polybutadiene

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Solid composite propellant formulations consisting of ammonium perchlorate (AP) and hydroxyl-terminated polybutadiene (HTPB) based polymeric binders have been utilized in the aerospace and defense industries for decades. While being easy to store and possessing near-instant readiness, AP-HTPB propellants are susceptible to aging and degradation over the course of decades. Once sufficiently aged, there is a significant risk of device failure upon use due to the formation of defects related to embrittlement of the polymeric binder over time. Despite the abundance of knowledge on these materials, the relationship between particular degradation mechanisms and the resulting material properties are not well understood. Furthermore, the majority of experimental investigations utilize accelerated aging techniques involving high temperatures, which may skew the resulting degradation products relative to that which occurs under ambient conditions. To simultaneously overcome the ambient condition timescale limitations and provide a direct comparison between degradation pathways and resulting material properties, we have been developing physics-based simulation models to investigate the aging of AP-HTPB propellants.

In this talk, we will report on our efforts at evaluating classical force fields for both AP and HTPB. We have used classical molecular dynamics (MD) simulations to compute the structural and dynamical behavior of the orthorhombic crystal phase AP, including density, lattice parameters, bulk modulus, IR spectrum and rotational dynamics. Results are generally in good agreement with available experimental data, although some improvements in the force field may be needed. We have also developed a fully atomistic model designed to reproduce the molecular weight and average functionality typical of commercial HTPB formulations. The structural and dynamical properties of HTPB were investigated utilizing MD simulations. Spatial conformations of the HTPB chains were characterized using the radius of gyration and end-to-end distance. HTPB chain dynamics were described by the end-to-end vector autocorrelation function. Terminal hydroxyl (OH) groups were found to associate in dynamic aggregates of various sizes. The distribution of the OH aggregate sizes and their relative stabilities were calculated. The significance of OH association in relation to curing reactions that take place when preparing this binder for use in propellant formulations is discussed.

Plasmonic Photocatalysis with Antenna-Reactor Particles

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

We have designed and demonstrated a new type of photocatalyst using a modular approach, combining a metallic nanoparticle with a good plasmonic response as an “antenna”, coupled to a catalytically active but poorly optically absorbing metal nanoparticle, as a “reactor”, situated within the antenna nanoparticle’s fringing field. We have demonstrated this antenna-reactor concept to control the reactivity of the catalytic reactor particle, as well as to control the selectivity of chemical reaction outcomes. We have extended the antenna-reactor concept to also include individual atomic reactive sites on plasmonic nanoparticle surfaces. We have examined ways to distinguish the role of hot carrier-induced processes from thermal effects in plasmonic photocatalysis, and have shown how illumination can effectively lower the reaction barrier, changing the rate-limiting step in chemical reactions. We have also shown that isolated reactive sites on antenna-reactor particles virtually eliminate the polymerization of carbon, a phenomenon known as coking that poisons conventional thermal catalysts, in the dry reforming of methane to produce Hydrogen.

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

Influencing the Nonlinear Optical and Electronic Properties of 2D Materials at the Atomic Level

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Correlative light and electron microscopy are employed to understand the interplay between 2D-material structure and their optical and electronic properties. Recent examples from our lab include understanding the nonlinear optical responses of 2D polar metals (2D-PMets) and the influence single-atom coordination on the electronic structure and relaxation dynamics of 2D semiconductors.

Nonlinear frequency mixing (e.g. harmonic generation) and polarization rotation of electromagnetic waves are the foundation of many important and emergent applications, which include laser technologies, optical switches, and frequency combs, among others.¹ The current state-of-the-art for second-order harmonic generation is achieved using a sequence of multiple quantum wells that are designed to resonantly enhance transitions at both fundamental and harmonic frequencies.² However, these systems are intrinsically limited to the mid infrared, precluding their operation at frequencies relevant for optical imaging and telecommunications. Therefore, new materials that can achieve large nonlinear optical responses over a broader range of frequencies are desired. Here, near-infrared-to-visible second harmonic generation for two-dimensional polar metals formed from gallium and indium is described. These systems exhibit the largest second-order susceptibilities ($\chi^{(2)}$) reported in the near infrared (approaching $10 \text{ nm}^2/\text{V}$).³ This extra-ordinary response results from the unique atomic-level interfacial structure and bonding properties of one-to-three-atom-thick crystalline metal films, that were formed by a process called confinement heteroepitaxy.⁴ Two-dimensional metals formed in this way grow epitaxial to a silicon carbide substrate and are passivated by bilayer graphene. A unique feature of these metals, revealed by cross-sectional electron microscopy, is that they adopt the hexagonal silicon carbide crystal structure. The bonding character of these heterostructures evolves from covalent at the silicon carbide interface to metallic within the metal films and to van der Waals at the metal/graphene interface. Consequentially, the out-of-plane metal-metal bond distances change by approximately ten percent (0.2 \AA) over a few atomic layers. This transformation in out-of-plane bonding results in $\chi^{(2)}$ -active symmetry breaking and the induction of an axial electrostatic dipole, which combine to yield the large observed second-order susceptibilities. Polarization-resolved second-harmonic imaging revealed periodic patterns in the nonlinear response, which resulted from distinct orientations of the crystalline metal atoms with respect to silicon carbide. The strong interplay between atomic-level structure and material nonlinear optical responses suggest that the photonic properties of metals can be tuned with atomic precision.

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Surface Plasmons for Inducing and Probing Surface Photochemistry

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Abstract: Mechanistic understanding of surface reactions is fundamental in heterogeneous catalysis that is important in chemical manufacturing and decontamination of exhausts. Unlike in solution, molecules adsorbed on metal surfaces can be considered dark as they don't fluoresce. Fortunately, localized surface plasmon resonances of metal nanoparticles brighten these adsorbates to the extent that single molecules can be detected using surface enhanced Raman spectroscopy. At the same time, surface plasmons can induce photochemistry at low incident photon flux comparable to that of solar radiation. In this talk, mechanistic insight obtained by combining the dual effects of surface plasmons will be discussed. The importance of plasmon-pumped adsorbate excitation in initiating surface chemical reaction will be underscored using N-demethylation of methylene blue as an example. In understanding the mechanism of the reaction, it is important to determine the electronic absorption band of the adsorbate. We determine the adsorbate electronic transition energy taking advantage of the molecule-plasmon excitation coupling that results in induced transparency at the absorption band of the molecule. The sharpening of cavity plasmon resonances as the gap length decreases to the quantum tunneling limit observed in gold nanorods coupled to gold film will be discussed. Finally, our recent progress in vibrational near-field vibrational imaging of surface ligands will be highlighted briefly.

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Trapped hole diffusion in semiconductor nanocrystals

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Semiconductor nanocrystals exhibit remarkable tunability in electronic structure and chemical properties that have over the years led to developments in fundamental science as well as a number of applications. One of the persistent and ubiquitous features of excited state dynamics in multiple nanocrystalline materials is the fast and efficient trapping of photoexcited holes to the particle surface. The transformation of a photoexcited hole from a delocalized carrier to one that is localized to a surface site impacts processes such as electron-hole recombination and charge transfer. We recently reported that the trapped photoexcited holes are mobile on surfaces of CdS and CdSe nanocrystals, undergoing random-walk diffusion by hopping between chalcogen sites on the particle surface.

This presentation will focus on our work in discovering and understanding the process of trapped hole diffusion through a combination of experimental measurements and theoretical insights. Specifically, experimental evidence for trapped hole diffusion in non-uniform nanorods of CdS and CdSe from transient absorption spectroscopy will be described. Temperature-dependent transient absorption measurements are consistent with a small polaron hopping description of trapped hole hopping close to room temperature, but not at low temperatures. Theory and calculations examining the mechanism of hole hopping as a function of temperature will be presented. Measurements of impacts of solvent and surface-capping ligand on trapped hole motion will also be discussed, as well as the evidence for diffusion-limited hole transfer.

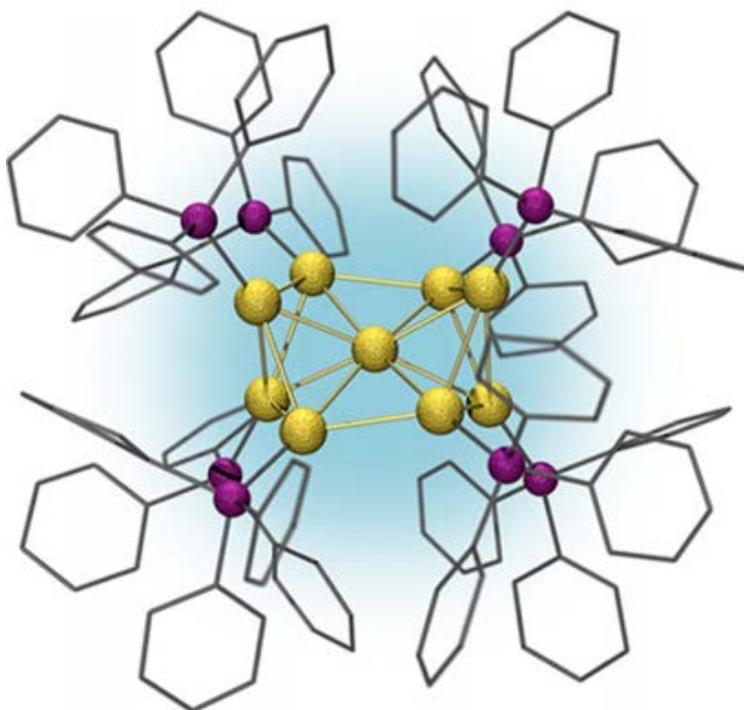
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Probing the Electronic Structure of Ligand-Protected Metal Nanoclusters Using Atomically-Precise Spectroscopic Methods

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Nanostructured particles hold much promise as “designer materials,” but full realization of this promise requires a detailed understanding of the geometric and electronic effects driving their behavior. While some smaller particles, often called nanoclusters, can be synthesized monodispersely and crystallized to determine their geometric structures, this is not generally true and no similarly powerful technique exists for the determination of their electronic structures. We have extended mass-selective absorption spectroscopy techniques to small ligand-protected metal nanoclusters synthesized using standard solution-phase protocols. These experiments reveal dramatically more information than do typical UV/Vis spectra in solution, near the limit of spectroscopic resolution. We find that subtle functionalization of the protecting ligands has a drastic impact on the cluster electronic structure, even for transitions between two nominally metal-based states, suggesting a route to control critical features of their electronic structure such as the HOMO-LUMO gap. Very subtle environmental effects, such as solvation by He or N₂, yield notable shifts to the spectra, suggesting that even weakly interacting ligands and solvents can have major impacts on electronic structure, and highlighting states with particularly high electronic density at labile surface sites. Taken together, these spectra provide the first experimental windows into using classic synthetic methods to tune the properties of these clusters for chemical and technological applications.



Molecular Reaction Imaging of Charge Generation, Transport, and Recombination in Ultrathin 2D Semiconductors

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Ultrathin photovoltaics made of transition metal dichalcogenides (TMDs) such as MoS₂ or WSe₂ have the potential to convert solar energy to electricity with high efficiency because all photo-generated carriers are produced at a charge-collecting interface. Solid-state monolayer photovoltaic devices typically require that charge carriers travel parallel to, instead of perpendicular to, the three atom-thick material towards charge-collecting contacts. Parallel charge transport across long distances decreases energy conversion efficiency. Here we show that liquid electrolytes provide a conformal electrical contact to monolayer semiconductors over large centimeter-square active areas and enable highly efficient extraction of photogenerated carriers. Efficient perpendicular charge transport is evidenced by high peak internal quantum efficiencies (IQE) of 44.2, 9.1, and 10.5% for 0.4 mm² MoS₂, WSe₂, and MoS₂/WSe₂ domains in a predominantly monolayer MoS₂/WSe₂ film. The monochromatic energy conversion efficiencies are competitive with state-of-the-art solid-state monolayer heterojunction photovoltaics. However, inefficient light absorption limits the overall power conversion efficiency to 0.19% for this planar geometry monolayer photovoltaic system. In addition, we investigated charge recombination and transport pathways in monolayer MoS₂/WS₂ photoelectrochemical cells by spatially resolving the net collection of carriers (i.e., the photocurrent) at the single nanosheet level. We discovered an excitation-wavelength-dependent recombination pathway that depends on the heterojunction stacking configuration and the carrier generation profile in the heterostructure. Photocurrent mapping measurements revealed that charge transport occurs parallel to the layers over micrometer-scale distances even though the indium tin oxide electrode and liquid electrolyte provide efficient charge extraction pathways via intimate electron- and hole-selective contacts. Our results reveal how composition heterogeneity influences the performance of bulk heterojunction electrodes made from randomly oriented nanosheets and provide critical insight into the design of efficient heterojunction photoelectrodes for solar energy conversion applications.

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Capture and characterization of small molecules activated by homogeneous catalysts using cryogenic ion chemistry and spectroscopy

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We exploit recent advances in the integration of high-resolution mass spectrometry with cryogenic ion chemistry and vibrational spectroscopy, developed under AFOSR support, to structurally characterize substrates bound to the active sites of homogeneous catalysts. We have focused on the reductive activation of CO₂ by Ni(I) cyclam because it is a prototypical system studied extensively in solution. Furthermore, fundamental characteristics of this system remain unresolved. These include the nature of the binding site and the degree of activation in the pre-reactive complex leading to CH or OH bond formation. Our years-long efforts to trap the key intermediates in this process have highlighted the challenges that must be overcome for the new methods to effectively engage “real” systems. Paramount among these is the ability to control the fragile oxidation state of the metal center and to establish whether widely used theoretical methods can accurately predict the strength of the local interactions in the isolated system, for which they are presumably ideally suited. We met these challenges by working in close collaboration with inorganic synthesis groups (Kruger, Kaiserslautern; Hazari, Yale). Our approach was to rationally generate the critical open coordination site on a Ni(I) metal center sequestered in two ligand structures that systematically tune the d-level splitting patterns by changing the coordination symmetry. The degree of activation was determined using temperature-programmed desorption of the substrate in combination with vibrational spectroscopy. Our results indicate that widely used computational methods are inconsistent, in some cases yielding textbook-like explanations for behavior while failing completely in other closely related systems. Finally, our AFOSR-sponsored instrument has been recently reconfigured to monitor the real-time kinetic behavior of isolated systems at elevated temperature. This capability provides an exquisite window on how large amplitude motions are incrementally activated with increasing temperature. As such, we have created “micro-reactors” that reveal how a dynamic equilibrium is sustained by the concerted motions of the solvent and the reactants.

Solvated Ion Cluster Dissociation Rates for Ionic Liquid Electro spray Propellants

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Electro spray thruster technology uses strong electric fields to generate thrust through the field-induced evaporation of a suitable propellant. Currently, the propellants of choice are typically ionic liquids which typically have high electrical conductivities, high windows of thermal stability and low vapor pressures. Mass spectrometry of prototype laboratory thrusters has found that emitted ionic liquid clusters can span bare cations or anions to solvated clusters of significant size and charge. Recent literature reports and measurements indicate that some of these emitted clusters appear to undergo in-flight fragmentation before detection by conventional mass spectrometers. It is hypothesized that the emission of these clusters from the liquid phase results in significant temperature increases in the gas-phase cluster, often with internal energies significantly greater than the binding energy of the cluster. These metastable clusters, given sufficient time, can fragment before detection by mass spectrometers and directly impact the determined thrust value of the propulsion system. In addition, depending on the location of break-up relative to the acceleration region of the thruster, some clusters can return to the spacecraft posing contamination concerns.

In the presentation today, I detail efforts underway at the Air Force Research Laboratory and collaborators to theoretically predict and experimentally measure the unimolecular dissociation rate constants for clusters of various ionic liquids. Specifically, we focus on clusters with atomic counts ranging from about 50 atoms to 500 atoms. In particular, I emphasize and detail the predictions and approaches made using gas-phase classical molecular dynamics simulations as they compare to the available experimental data.

Effects of Organic Moieties on the Optical Properties of Inorganic Frameworks

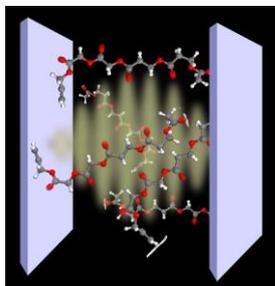
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In our effort to address requirements for specific optical responses of photonic materials, we discuss the computational prediction of linear and nonlinear optical absorption, as well as of emission characteristics of inorganic quantum dots (QDs) and two-dimensional (2D) materials. Although nonlinear optical absorption was previously demonstrated for colloidal QDs of II-VI semiconductors, CdSe 2D nanoplatelets have been drawing increased interest because of improved optoelectronic properties, including large two-photon absorption cross sections. However, the growth of these materials is still unresolved, and it was postulated that atomically precise nanoclusters, or so-called magic-size semiconductor clusters (MSCs), play a role in the growth mechanism. At the same time, MSCs were shown to undergo structural transformations in reversible isomerization reactions, with some determination of the structures. However, the structural features are not well defined. To accurately predict the properties of CdS MSCs with carboxylate ligands in comparison to experimental data, we discuss the development of an empirical potential using density functional theory (DFT) and neural networks, combined with a comprehensive structures search using genetic algorithms, molecular dynamics simulations and local optimizations. Our results for different core frameworks with carboxylate ligands of varying alkyl lengths demonstrated that MSCs with short alkyl chains are distorted from the symmetric inorganic framework. Interestingly, the calculated X-ray diffraction (XRD) and electronic absorption spectra for the $\text{Cd}_{44}\text{S}_{26}\text{X}_{36}$ (X=oleate ligand) cluster with a penta-supertetrahedral framework are in better agreement with experiment than the previously assumed $\text{Cd}_{37}\text{S}_{20}\text{X}_{34}$ structure. In addition, to discern fluorescence and phosphorescence emission characteristics of noble metal clusters, we describe the results for $\text{Au}_{25}(\text{SR})_{18}$, $\text{Au}_{38}(\text{SR})_{24}$ and $\text{Au}_{22}(\text{SR})_{18}$. Good agreement between calculated and measured absorption spectra, and with the experimental lowest energy emission values is indicated, verifying the accuracy of the theoretical methods employed. Our results for $\text{Au}_{25}(\text{SR})_{18}$ explain a newly observed feature in the absorption peak, also rationalizing the optical response in terms of the super-atom model. Analysis of the calculated absorption and emission characteristics, e.g. for the $\text{Au}_{25}(\text{SR})_{18}$ and $\text{Au}_{38}(\text{SR})_{24}$ clusters, provide an estimate of the spectral regions where fluorescence or phosphorescence are predicted to occur. Finally, to elucidate the role of the organic cation type in tuning the optical properties of 2D organic-inorganic halide perovskites (OIHPs), which are promising for nonlinear optical absorption applications, we report on a study in which we considered fourteen organic cations, ranging from aliphatic molecules to chromophores. We discuss the effects of the calculated structural distortion in the 2D OIHPs, which can be correlated to the band gaps in some cases. Band alignments indicate variability in the quantum-well types, modified for organic cations with functional groups. We report on calculated absorption spectra that demonstrate tunability in the optical response, including enhanced absorption.

Vibrational polaritons: reactivity and spectroscopy

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Strong coupling between photon modes in microcavities and ensembles of molecular vibrations in solution leads to vibrational polaritons, hybrid light-matter excitations. Vibrational polaritons open doors to room-temperature opportunities for the nontrivial control of physico-chemical properties of molecular assemblies. In this short talk, I will showcase some of these opportunities that we have been theoretically (and, together with our experimental collaborators in the Xiong group at UCSD) exploring in the past few years. I will briefly discuss a theoretical framework that explains how vibrational polaritons could catalyze thermally-activated reactions even in the absence of external photon pumping [1] and strategies to employ vibrational polaritons to induce strong nonlinear

optical properties [2], turn on artificial energy transfer pathways [3], and induce remote control of photoinduced chemical reactions [4]. If time permits, I will also describe how the strong coupling of circularly polarized light fields with vibronic transitions in anisotropically oriented molecular aggregates induces magnetic-like phenomena (e.g. Aharonov-Bohm effects) that can control energy transfer phenomena in the nanoscale [5].

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Abstract:

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Probing Carbon-Carbon Bond Breaking and Bond Formation as it Applies to Endothermic Fuels Development

At AFRL/RQTF, we are supporting the development of advanced thermal management systems for high-speed flight by studying the elementary chemical physics of neat fuel decomposition at extreme temperatures (200-1000 °C) and pressures (400-1000 psi) using *in situ* mass spectrometry. We have demonstrated that a neat supercritical fluid can be sampled by means of a supersonic expansion into the gas phase to provide a “snapshot” of the chemical speciation in solution using molecular beam mass spectrometry. For predominantly aliphatic fuels, we have observed light alkyl cracking intermediates, which are dependent on the fuel identity, at shorter residence times in the reactor ($t \approx 1$ s). These intermediates evolve into a final aromatic product distribution that is independent of the fuel identity as the temperature is further increased and the residence time simultaneously increases (> 30 s) as a result of coke formation on the nozzle. This result implies a transition between reactions under kinetic and thermodynamic control as the temperature and residence times increase. We have verified the presence of kinetic “bottle necks” during fuel pyrolysis (C2 and possibly C3 fragments) by tandem mass spectrometry in a triple quadrupole instrument. By performing collision-induced dissociation in this instrument, we have distinguished electron-impact fragments (@ 10 eV) from thermal cracking products via precursor scans and have deduced the structural identity of substituted aromatic products using product scans. These results will be presented and discussed within the context of advanced thermal management for high-speed flight.

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Watching solids and liquids through the ultrafast shock compression microscope

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We have developed a microscope that looks into solids and liquids as they are subjected to controlled high velocity impacts from laser-launched flyer plates. This convenient tabletop microscope set up allows us to perform well-characterized controlled shock experiments on tiny samples hundreds of shots per day. The flyer plates move a few kilometers per second, creating intense mechanical and thermal effects that can trigger new kinds of chemistry. One of these impacts can create pressures of 200,000 atm and temperatures of 4000K while compressing matter to half its density. In this talk, I will describe the shock compression microscope and the peripheral high-speed optical diagnostics that measure pressure, temperature, density and composition in real time. I will mention a few applications ongoing in my lab, such as studying the chemistry of extreme water, shock waves in biology and medicine and shock compression of molecular architectures designed to dissipate shock energy. Then I will discuss shock initiation and detonation of high explosives, including liquid explosives and plastic-bonded explosives. This shock compression microscope has many applications in chemistry, physics, materials science and biology and it lets us see right inside detonating high explosives with high time and space resolution.

Dana Dlott is the William H. and Janet G. Lycan Emeritus Professor of Chemistry and a Professor of Materials Research at the University of Illinois. He received a bachelor's degree from Columbia University and a Ph.D. from Stanford University under the supervision of Prof. Michael Fayer, using ultrafast laser spectroscopy to study electronic energy transfer in molecular materials. After he joined the Chemistry Department at the University of Illinois (in 1979) he began a research program to study vibrational relaxation in solids. About 30 years ago he began to study shock waves in solids. Dlott is a Fellow of the American Physical Society, the Optical Society of America and the American Association for the Advancement of Science. He has been recognized with the ACS award in Experimental Physical Chemistry and the Lippincott prize of the OSA for his work in ultrafast vibrational spectroscopy. He is a former Chair of the APS Topical Group on Shock Compression in Condensed Matter and the author of 325 scientific publications.