

The search for blends: The physics behind electron and hole acceptor materials for CNT photovoltaics

Michael S. Arnold¹, Martin T. Zanni²,

¹Department of Materials Science and Eng., University of Wisconsin-Madison, Madison, WI 53706

²Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706

Semiconducting single-walled carbon nanotubes (s-SWCNTs) are promising materials for solar energy conversion and photodetectors. A critical step in utilizing s-SWCNTs for photovoltaics is dissociating the excitons into charges using acceptors. Fullerenes and their derivatives are acceptors that effectively dissociate excitons into positive and negative charges by forming heterojunctions with s-SWCNTs with favorable energetic offsets. However, the limited tunability of energy levels and poor compatibility of fullerene derivatives with s-SWCNTs have been a major obstacle for further improving the device performance in nanotube/acceptor blends. Here, we investigate the exciton dissociating capability of a series of non-fullerene acceptors (NFAs) by measuring the internal quantum efficiency (IQE) for exciton dissociation and charge transfer in bilayer s-SWCNT/NFA devices. A maximum IQE of ~50% is achieved with a (6,5) s-SWCNT/indacenodithiophene-based acceptor heterojunction, and a trend is determined based on Marcus electron transfer theory that predicts IQE as a function of energy levels measured via electrochemical redox measurements. The flow and transfer of excitons between coupled nanotubes is another important process in s-SWCNT/acceptor heterojunctions that affects device performance and is being characterized from cross-peaks in two-dimensional white-light spectroscopy measurements. Our results indicates that non-fullerene acceptors with larger (deeper) electron affinities could potentially replace traditional fullerene acceptors and achieve high quantum efficiency in s-SWCNT photovoltaic devices.

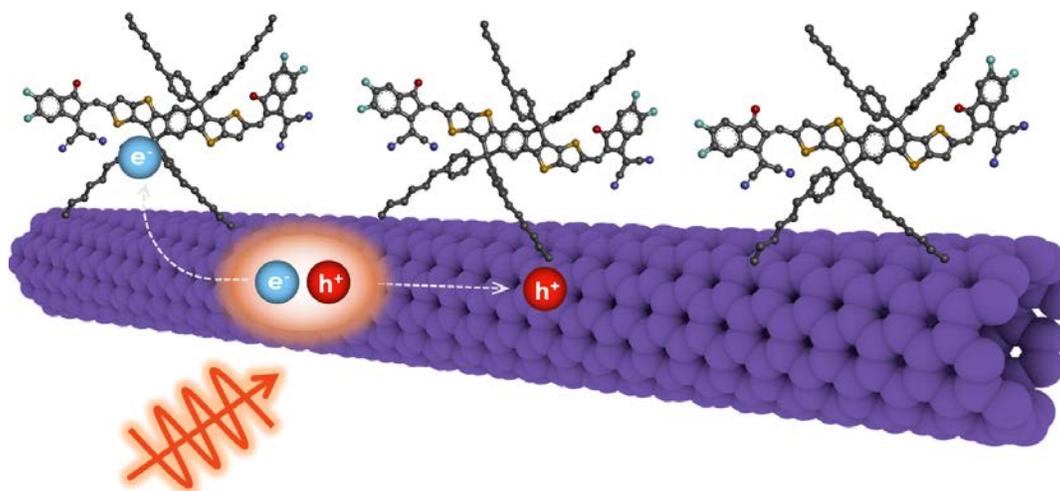


Figure 1. Schematic diagram depicting exciton dissociation and photoexcited electron transfer from a type-sorted semiconducting carbon nanotube to an indacenodithiophene-based electron acceptor.

Isolation of reactive intermediates in proton-coupled electron transfer with Cryogenic Ion Chemistry and Spectroscopy

Mark A. Johnson
Yale University

Proton-coupled electron transfer (PCET) is a fundamental process that mediates charge translocation in the catalytic activation and transformation of small molecules like CO₂ and H₂O. A primary goal of our program is to capture and characterize intermediates that are often invoked to explain the mechanism of these reactions, but are only indirectly evidenced by analysis of the overall solution kinetics. One such reaction that is of particular interest here is the case where two protons and two electrons are transferred in a system based on a Ru compound reacting with quinone derivatives leading to the formation of the hydroquinones. In this case, the reaction is observed to proceed directly from Ru(II) to Ru(IV), indicating that two hydrogen atoms are transferred in the PCET process. This suggests formation of a strongly bound complex such that both transfers occur either in a concerted fashion or sequentially while the reactants are in close proximity. In our approach, we use ambient mass spectrometry to force the complex formation, and analyze its structure using cryogenic ion vibrational spectroscopy. This is accomplished using a custom built instrument that integrates a commercial mass spectrometer (Thermo Velos Orbitrap) with a triple focusing photofragmentation mass spectrometer, a technology enabled by DURIP support from AFOSR in 2018. Using this capability, we successfully captured the intermediate complex and determined its docking arrangement by analyzing the vibrational spectrum at 10 K. This complex is observed to adopt an entrance channel arrangement in which the key H-atoms on the ligand are attached to the C=O groups that will ultimately accept them. We have also explored how this docking geometry evolves with other reaction partners, including anions like PF₆⁻, and followed their reaction chemistry using uv photoexcitation as well as collisional heating. We will also discuss the performance of this new instrument in other contexts, such as in the structural characterization of breakdown products from biopolymers that are generated in the course of peptide sequencing. Most recently, we have characterized the products resulting from divalent metal ion-mediated decarboxylation of carbohydrates. The latter processes are relevant to the reaction pathways leading to the activation of CO₂ in mimics of photosynthesis.

What did the metals know, and when did they know it?

Femtosecond M-edge XANES reveals short-lived states in transition metal complexes

Josh Vura-Weis

University of Illinois at Urbana/Champaign, 600 S Mathews Ave, Urbana, IL USA

e-mail: vuraweis@illinois.edu

X-ray absorption near edge spectroscopy (XANES or NEXAFS) is a powerful technique for electronic structure determination. However, widespread use of femtosecond XANES is limited by the need for scarce free-electron laser beamtime. We have developed $M_{2,3}$ -edge XANES, corresponding to $3p \rightarrow 3d$ transitions, as a reliable technique for measuring the electronic structure of first-row transition metal coordination complexes. The tabletop high-harmonic source provides femtosecond time resolution and 24/7 accessibility. In this poster, we will present the photophysics of three transition metal complexes relevant to photocatalysis: Iron(III) tetraphenyl porphyrin chloride, which relaxes through a ligand-to-metal charge transfer state; Nickel (II) octaethylporphyrin, which relaxes through a $^3(d,d)$ state; and a heterobimetallic CoMn complex which undergoes metal-to-metal charge transfer. Progress on solution-phase XANES will also be presented.

Electron-Phonon Coupling at Molecularly Functionalized Hematite Surfaces Probed by XUV Reflection-Absorption Spectroscopy

L. Robert Baker
Department of Chemistry and Biochemistry
The Ohio State University
Email: baker.2364@osu.edu

Direct observation of charge transfer and trapping at interfaces is necessary to provide understanding of the materials properties that determine electronic decoherence and charge trapping and transport at interfaces. This understanding is required to design materials for efficient energy conversion as well as charge and spin-based information processing. To enable these studies, we have constructed an ultrafast extreme ultraviolet (XUV) light source based on high harmonic generation. Reflection-absorption (RA) spectroscopy using this source combines the benefits of x-ray absorption, such as element and oxidation state specificity, with surface sensitivity and ultrafast time resolution, having a measured probe depth of only a few nm and an instrument response less than 100 fs.^{1, 2} Utilizing XUV-RA spectroscopy, we investigate the dynamics of small polaron formation at functionalized surfaces and the molecular properties of the interface, which mediate these dynamics. We have shown that in photoexcited α -Fe₂O₃, surface electron trapping is correlated with small polaron formation³, suggesting that small polarons rather than surface defects represent the primary driving force for electron localization to the surface. Further we find that the kinetics of small polaron formation at the surface differ significantly from the same process in bulk.⁴ These experimental observations are consistent with theoretical treatments of small polaron formation, which conclude that “the properties of polarons near surfaces are significantly different from bulk behavior” and that “interpretation of data from surface spectroscopies in terms of bulk quantities is generally not warranted.”⁵ To better understand the properties of a surface, which mediate electron-phonon coupling, we now functionalize α -Fe₂O₃ surfaces via covalent attachment of small molecules having tunable redox potentials and dipole moments. The coverage, orientation, and stability of these molecular layers is characterized using SFG vibrational spectroscopy and XPS measurements. Ultrafast XUV spectroscopy of these systems reveals that the molecular overlayer modulates the kinetics of small polaron formation at the α -Fe₂O₃ substrate. We consider the significance of these results in terms of both electron-phonon coupling as well as electron transport at the molecule-semiconductor interface.

References

1. Biswas, S., Husek, J. & Baker, L.R. Elucidating ultrafast electron dynamics at surfaces using extreme ultraviolet (XUV) reflection-absorption spectroscopy. *Chemical Communications* **54**, 4216-4230 (2018).
2. Cirri, A., Husek, J., Biswas, S. & Baker, L.R. Achieving Surface Sensitivity in Ultrafast XUV Spectroscopy: M_{2,3}-Edge Reflection-Absorption of Transition Metal Oxides. *The Journal of Physical Chemistry C* **121**, 15861-15869 (2017).
3. Husek, J., Cirri, A., Biswas, S. & Baker, L.R. Surface electron dynamics in hematite (α -Fe₂O₃): correlation between ultrafast surface electron trapping and small polaron formation. *Chemical Science* **8**, 8170-8178 (2017).
4. Carneiro, L.M. et al. Excitation-wavelength-dependent small polaron trapping of photoexcited carriers in α -Fe₂O₃. *Nature Materials* **16**, 819 (2017).
5. Goodvin, G.L., Covaci, L. & Berciu, M. Holstein Polarons Near Surfaces. *Physical Review Letters* **103**, 176402 (2009).

Direct Optical Lithography of Functional Inorganic Nanomaterials (DOLFIN) Enabled by Novel Surface Chemistry

Dmitri V. Talapin

Department of Chemistry and James Franck Institute, University of Chicago, Chicago IL 60637, USA

In recent years, solution-processed colloidal nanocrystals and quantum dots (QDs) have emerged as a versatile platform for building electronic and optoelectronic devices. These materials enable non-epitaxial deposition and low-temperature processing of light-emitting diodes, field effect transistors, near- and mid-infrared photodetectors, and solar cells. The transition from individual devices to the level of electronic circuits, sensor arrays, and electrically driven QD displays requires development of material-adapted patterning methods, which was lagging behind. The lack of efficient methods for high-resolution and high-fidelity additive patterning of solution-processed electronic materials slows the transition from individual proof-of-concept devices to real-world applications.

We introduce a new method for Direct Optical Lithography of Functional Inorganic Nanomaterials (DOLFIN), which uses inorganic nanomaterials with photochemically active surface ligands. This process combines multiple benefits of photolithography and is tailored toward efficient patterning of inorganic nanomaterials without diluting or contaminating them with organic photoresists and other byproducts. The range of materials that can be patterned using this new technique includes metals, semiconductors, oxides, as well as magnetic or rare earth compositions. Almost any inorganic nanomaterial can be converted into a photosensitive ink that can be directly patterned using DOLFIN. The ultimate lateral resolution of DOLFIN can extend down to about 30 nm and possibly below. No organic impurities are present in the patterned layers, which helps achieve good electronic and optical properties. The conductivity, carrier mobility, dielectric, and luminescence properties of optically patterned layers are on par with the properties of state-of-the-art solution-processed materials. The ability to directly pattern all-inorganic layers using a light exposure dose comparable to that of organic photoresists provides an alternate route for additive device manufacturing.

Energy transfer in inter-dimensional metals

Kenneth L. Knappenberger, Jr.
Department of Chemistry
The Pennsylvania State University, University Park, PA 16802

Recent advances in understanding energy transfer in a comprehensive range of metals spanning quantum-metal clusters, 3-D plasmonic colloids, and 2-D layers will be described. Using a process known as confinement heteroepitaxy, non-traditional plasmonic metals can be formed and kept stable for several months. A unique feature of metals formed in this manner is the ability to generate materials that support both classical plasmon modes (in-plane) and discrete quantum excitations (out of plane). This multifaceted behavior results because the heteroepitaxy process generates 2-D metal films while confining axial growth to a few atomic layers, and hence, yielding inter-dimensional materials. As a result, both the quantum and classical aspects of these systems can be leveraged for tailoring material properties. In particular, inter-dimensional group III metals (e.g. Ga and In) show extraordinary optical and electronic properties. In the case of gallium and indium, we observe nonlinear χ^2 values that are 10^3 larger than values typical for colloidal 3-D gold, and approximately 500x larger than for industrial standards, such as LiNbO_3 . These outstanding optical properties originate from multiple sources, including persistent plasmon coherence times, suppressed inter-band scattering by group III metals (w.r.t. gold), and intrinsic symmetry breaking at the metal-substrate interface. Many of these advances were made possible by the combined use of spatially resolved coherent nonlinear optical spectroscopy and correlative structural probes. Strategies for leveraging the unique properties of these inter-dimensional metals for controlled energy transfer will be described. Progress toward understanding energy transfer from these metals to molecular and semiconducting substrates will also be presented.

Acknowledgements. This work was supported by the Air Force Office of Scientific Research (FA-9550-18-1-0347)

Computational Modeling of Solid Propellant Aging

Garrett Tow and Edward Maginn
Department of Chemical and Biomolecular Engineering
University of Notre Dame
Notre Dame, IN 46556 USA

Solid propellants are essential to the Air Force because of their low risk, high performance, competitive cost, storability, and "instant" readiness. The most commonly used composite propellants typically contain ammonium perchlorate, aluminum powder, and a polymeric binder, such as hydroxy-terminated polybutadiene (HTPB)-based polyurethanes. The HTPB is susceptible to oxidative degradation, and therefore loss of mechanical properties and subsequent failure of the propellant. Because the degradation process occurs over several years, most experimental studies rely on accelerated aging techniques utilizing an elevated temperature. These studies are often in the diffusion-limited oxidation regime and only provide empirical data. In conjunction with the Gordon group at Iowa State, we are carrying out a combined quantum and classical simulation study to investigate the mechanisms of aging of HTPB-based binders. Quantum methods will probe potential routes of degradation and provide activation energies and pre-exponential factors for bond dissociations. These quantities will be coupled with classical simulations using reactive Monte Carlo (RxMC) to determine how the surrounding environment affects the decomposition rates.

We have evaluated a classical model for ammonium perchlorate and have shown that the model sufficiently reproduces experimental trends in the bulk modulus, vibrational behavior, hydrogen bonding, and rotational dynamics of the ions. Current efforts are focused on equilibrating the HTPB prepolymer melt using hybrid MD/MC methods. Once equilibrated, crosslinked structures will be generated using isophorone diisocyanate (IPDI) to produce the elastomer found in conventional solid propellant formulations. The ammonium perchlorate model will be placed in contact with the HTPB-based binder to allow for the work of adhesion to be calculated. The polymeric binder will be progressively aged by introducing defects via a kinetic Monte Carlo scheme. Material properties will be assessed as a function of the quantity and type of defects introduced, effectively studying the effect of aging on the material properties at the molecular level.

Asymmetric Response of Interfacial Water to Positive vs. Negative Electric Fields

Prof. Steve Cronin and Alex Benderskii
University of Southern California
Los Angeles, CA 90089

The importance and ubiquity of aqueous interfaces can hardly be overstated. They play crucial role in areas ranging from biology and life sciences, environmental and atmospheric chemistry, and oceanography, to heterogeneous catalysis, electrochemistry, and energy conversion applications. In particular, the solvation properties of interfacial water dictate the chemical equilibria and rates of heterogeneous processes such as catalytic and electrochemical reactions. Our understanding of water as a dielectric medium is based on the linear response theory, which explicitly implies that any response to a weak perturbation, such as electric field near a charged surface, is of the same magnitude and opposite sign for positive vs. negative applied field of a given strength.

In our study, vibrational sum frequency generation (VSFG) spectroscopy was used to study interfacial water at a monolayer graphene electrode, which allows us to continuously tune the applied voltage from positive to negative through the potential of zero charge. The frequency shift of the G-band Raman mode of graphene was used as an internal calibration of the doping concentration as a function of applied potential, in addition to electrochemical measurements using a 3-terminal setup. The VSFG spectra of the water OD-stretch mode show pronounced asymmetry with respect to positive vs. negative electrode potential. The non-hydrogen-bonded “free” OD groups, manifested by a narrow peak at 2695 cm^{-1} , were detected only at negative applied potential below -1.5 V vs Ag/AgCl. On the other hand, the spectra are dominated by the H-bonded species ($2300\text{--}2600\text{ cm}^{-1}$) at zero or positive potentials. The results imply that the interfacial water does not follow linear response for the external DC fields of the order of 0.1 V/\AA .

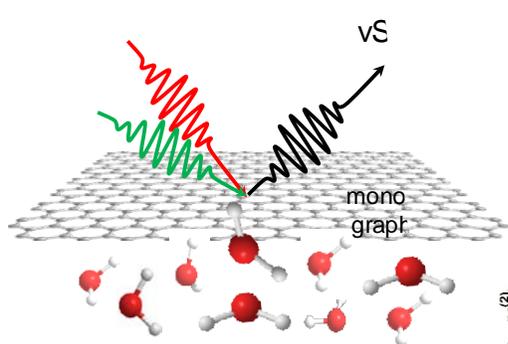
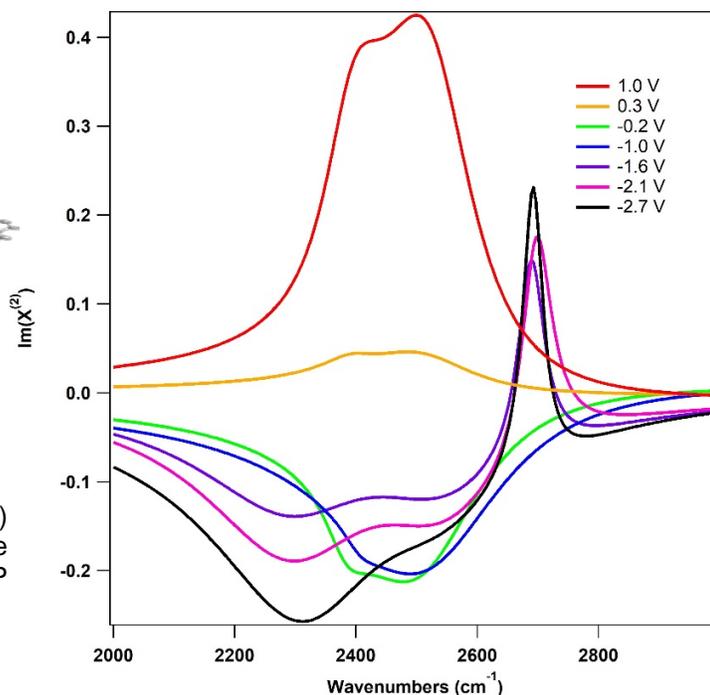


Figure 1: Voltage (vs. Ag/AgCl) dependence of the VSFG spectra of the graphene-D₂O interface (SSP polarization combination).



Low energy states of NdO⁺ probed by photoelectron spectroscopy

Robert A. VanGundy, Thomas D. Persinger and Michael C. Heaven[†]

Department of Chemistry, Emory University, Atlanta, GA 30322

Abstract

The ionization energy (IE) of NdO and the low-energy electronic states of NdO⁺ have been examined by means of two-color photoionization spectroscopy. The value obtained for the IE, 5.5083(2) eV is 0.54 eV higher than previous estimates. This leads to the conclusion that the auto-ionization reaction $\text{Nd} + \text{O} \rightarrow \text{NdO}^+ + e^-$ is exothermic by 1.76(10) eV, a result of significance for controlled modulation of the electron density in the thermosphere.

Thirty vibronic levels of NdO⁺ arising from eight electronic states were observed with partial rotational resolution. The energy level pattern and supporting electronic structure calculations indicated that all of the observed states correlated with the Nd³⁺(4f³, ⁴I)O²⁻ configuration. The structure was consistent with a ligand field theory model where the electronic states of the Nd³⁺(4f³, ⁴I) atomic ion define a repeated motif in the electronic state energy intervals of the molecular ion. Comparisons with UO⁺ show close similarity in the electronic structures of these isoelectronic species.

Quantifying the Membrane-Specific Antimicrobial Mode-of-Action with Time-Resolved Second Harmonic Light Scattering

Michael J. Wilhelm and Hai-Lung Dai

Department of Chemistry, Temple University, 1901 N. 13th Street, Philadelphia, PA 19122, USA.

ABSTRACT

Time-resolved second harmonic light scattering (SHS) is a sensitive experimental technique capable of monitoring interface-specific molecular interactions at the membrane surfaces of living cells. In particular, SHS is remarkably well-suited for studying the propensity for passive molecular diffusion across a plasma membrane, as well as for quantifying the associated transport rates. We have recently demonstrated that this capability can be applied as the foundation of a novel experimental approach for monitoring the membrane-specific response following initiation of an antimicrobial insult.^{1,2} Antimicrobial agents are known to disrupt plasma membranes in order to kill cells, or simply as a means of gaining entrance into the cytosol to compromise normal cellular activity. Consequently, with respect to the design and optimization of new antimicrobial targets, it is of utility to be able to experimentally monitor chemically-induced variations in membrane permeability as a function of dose duration and concentration. By monitoring the uptake response of an SHS-active probe molecule before and after administration of an antimicrobial agent, perturbations in the measured molecular transport rates can reveal chemically-induced changes in the permeability of the bacterial membranes. As proof-of-principle, we now apply time-resolved SHS for deducing the membrane-specific mode-of-action (MoA) of the recently developed antimicrobial compound, Bricilidin (Bn). Bn is a synthetic arylamide foldamer that exhibits an amphiphilic topology similar to that of the so-called cell-penetrating or antimicrobial peptides.³ Using the amphiphilic cation, malachite green (MG), as an SHS-active probe molecule, we characterize the MoA of Bn in a continuously flowing liquid colloidal suspension of living bacteria. In particular, we focus on non-pathogenic lab strains of *Escherichia (E.) coli*. *E. coli* is a gram-negative bacteria and therefore possess a pair of phospholipid membranes: an outer membrane (OM) and an inner cytoplasmic membrane (CM), which are separated by a thin peptidoglycan mesh. Of importance, using time-resolved SHS, we can simultaneously monitor antimicrobial-induced changes to both the OM and the CM. Briefly, for sub-minimum inhibitory concentrations (MIC) and short interaction periods, Bn is observed to primarily affect the bacterial OM, resulting in enhanced permeability (i.e., an increased MG transport rate). However, for above MIC conditions and longer interaction periods, Bn begins to likewise affect the bacterial CM. However, dissimilar from the OM response, application of Bn results in an apparent decrease in CM permeability (i.e., a decreased MG transport rate). At longer times, and for sufficiently high concentrations, exposure to Bn results in complete membrane disruption. In addition to the physical origins of the various induced effects, direct comparison to more traditional fluorescence-based assays will be discussed.

REFERENCES

- (1) Wilhelm, M. J.; Sharifian Gh., M.; Dai, H.-L. Chemically Induced Changes to Membrane Permeability in Living Cells Probed by Nonlinear Light Scattering. *Biochemistry* **2015**, *54*, 4427–4430.
- (2) Sharifian Gh., M.; Wilhelm, M. J.; Dai, H.-L. Azithromycin-Induced Changes to Bacterial Membrane Properties Monitored in Vitro by Second-Harmonic Light Scattering. *ACS Med. Chem. Lett.* **2018**, *9*, 569–574.
- (3) Mensa, B.; Kim, Y. H.; Choi, S.; Scott, R.; Caputo, G. a.; DeGrado, W. F. Antibacterial Mechanism of Action of Arylamide Foldamers. *Antimicrob. Agents Chemother.* **2011**, *55*, 5043–5053.

Can Photolysis of Larger Parent Cyanides Account for the Anomalous Overabundance of Astrophysical Hydrogen Isocyanide?

Michael J. Wilhelm and Hai-Lung Dai

Department of Chemistry, Temple University, 1901 N. 13th Street, Philadelphia, PA 19122, USA.

ABSTRACT

The simple geometric isomers, hydrogen cyanide (HCN) and hydrogen isocyanide (HNC), are fascinating astrophysical oddities, known to persist well outside predicted thermodynamic equilibrium in numerous regions of the interstellar medium (ISM). Specifically, HNC exists as a local minimum on the HCN potential energy surface, roughly 5000 cm⁻¹ above the global zero point energy. For typical ISM temperatures on the order of 100 K, this suggests a predicted HNC:HCN equilibrium abundance ratio on the order of 10⁻³³. In reality, however, HNC is known to be significantly more prevalent in the ISM with measured abundance ratios that are often significantly closer to unity. In an effort to reconcile this long standing puzzle, we have begun investigating the photolysis reactions of representative parent cyanides as possible sources of astrophysical HNC. Specifically, we examine the UV-induced photodissociation dynamics of precursor cyanides using time- and frequency-resolved Fourier transform infrared emission spectroscopy. Emission spectroscopy is a sensitive probe of vibrationally excited molecules and permits simultaneous characterization of all ro-vibrationally excited molecular fragments produced in a photolysis reaction. In particular, spectral fit analysis of the anharmonic ν_1 C-H stretch of HCN and the ν_1 N-H stretch of HNC permits a quantitative characterization of the internal energies and population distributions of these two photofragments, from which a relative nascent branching ratio can be deduced. We have now demonstrated that the precursor cyanides: vinyl cyanide (CH₂CHCN), methyl cyanoformate (CH₃O(O)CCN), and pyrazine (C₄H₂N) are all viable photolytic sources of both HCN and HNC.¹⁻³ Moreover, our experimental results reveal nascent relative abundance ratios well above the thermodynamically predicted equilibrium ratio (ca. HNC:HCN ~ 0.1), consistent with astrophysical observations. The propensity for cyano-containing hydrocarbons to act as photolytic sources for ro-vibrationally excited HCN and HNC, as well as their significance to astrophysical environments, will be discussed.

REFERENCES

- (1) Wilhelm, M. J.; Nikow, M.; Letendre, L.; Dai, H. L. Photodissociation of Vinyl Cyanide at 193 Nm: Nascent Product Distributions of the Molecular Elimination Channels. *J. Chem. Phys.* **2009**, *130*, 044307.
- (2) Wilhelm, M. J.; Martínez-Núñez, E.; González-Vázquez, J.; Vázquez, S. A.; Smith, J. M.; Dai, H.-L. Is Photolytic Production a Viable Source of HCN and HNC in Astrophysical Environments? A Laboratory-Based Feasibility Study of Methyl Cyanoformate. *Astrophys. J.* **2017**, *849*, 15.
- (3) Wilhelm, M. J.; Petersson, G. A.; Smith, J. M.; Behrendt, D.; Ma, J.; Letendre, L.; Dai, H. L. UV Photolysis of Pyrazine and the Production of Hydrogen Isocyanide. *J. Phys. Chem. A* **2018**, *122*, 9001–9013.

Experimental and Theoretical Investigation of the Catalytic Reactivity of Hydroxylamine with Size-Selected Iridium Anion Clusters

Gaoxiang Liu,¹ Sandra M. Ciborowski¹ and Kit H. Bowen¹

Jerry A. Boatz² and Steven D. Chambreau³

¹Department of Chemistry, Johns Hopkins University, 3400 N. Charles Street, Baltimore, MD 21218, USA

²Aerospace Systems Directorate and ³ERC Incorporated, Air Force Research Laboratory, Edwards Air Force Base, California 93524, United States

Abstract

In aerospace propulsion systems, pre-ignition chemistry describes the condensed phase heterogeneous processes involved in the formation and evolution of reactive gaseous species leading to the formation of a gaseous mixture within the proper flammability limits, followed by ignition and sustained combustion. For hypergolic ignition, exothermic reactions of the oxidizer – both solvated within the fuel and at the liquid-liquid interface of the fuel/oxidizer – generate heat and reactive gasses. In contrast, for catalytic ignition, the monopropellant fuel is catalytically decomposed in an exothermic, heterogeneous process on the metal catalyst surface on a suitable support matrix. This study describes the preliminary experimental and theoretical efforts to understand the catalytic reactivity of hydroxylamine (H_2NOH , HA) with iridium experimentally by reacting size-selected Ir_n^- clusters with HA by photoelectron spectroscopy of the $\text{Ir}_n^- + \text{HA}$ product and theoretically by high-level *ab initio* methods. HA is the primary decomposition product of hydroxylammonium nitrate (HAN), a major component of the AF-M315E ionic liquid formulation set to be tested in NASA's upcoming Green Propellant Infusion Mission.

An Analysis of Ethylammonium Nitrate, 1-Amino-1,2,3-Triazole, and their Deep Eutectic Mixture using Quantum Based Fragmentation Methods.

Justin Conrad and Mark Gordon

Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011, United States

As an energetic deep eutectic solvent, the 1:2 molar mixture of ethylammonium nitrate and 1-amino-1,2,3-triazole is a potential candidate to replace current, highly volatile propellants. Replacing traditional propellants with deep eutectic solvents with lower evaporation pressures would reduce potential risks to personnel and the environment in both handling and storage. Little is known of the cause of the eutectic properties of the mixture of ethylammonium nitrate and 1-amino-1,2,3-triazole. This investigation considers the structural and intermolecular interactions, with respect to increasing system size, of pure ethylammonium nitrate, pure 1-amino-1,2,3-triazole, and their eutectic 1:2 molar mixture to gain insight into the structural and intermolecular interactions responsible for the eutectic properties of the mixture using quantum based fragmentation methods.

The roles of plasmon-pumped adsorbate excitation and charge transfer in plasmon-driven photochemical transformation

Tefera E. Tesema, Hamed Kookhaee and Terefe G. Habteyes

University of New Mexico

Plasmon-driven surface photochemical reaction is attracting increasing research interest from both the perspective of fundamental understanding of surface-molecule interaction and applications to drive selective photochemistry at photon flux comparable to that of solar radiation. In most literatures, the mechanism of the reaction is explained in terms of hot electron transfer to the adsorbed analyte molecules. Our group has recently published a Feature Article [*J. Phys. Chem. C*, 2019, 123 (14), pp 8469–8483] that highlights the importance of both hot electron transfer and plasmon-pumped HOMO-LUMO electron transition of adsorbate in plasmon-driven reaction mechanisms. In this poster, very recent results that appear to indicate the competition between charge transfer and plasmon pumped adsorbate excitation depending on the proximity of the molecule to the plasmonic surface will be discussed. Broad band plasmon resonance modes and the strong dipole-surface coupling properties are used to map the excitation energy of molecules in the proximity of plasmonic surfaces.

Preparation of Coke-Tolerant Endothermic Reforming Catalysts by ALD

R. J. Gorte, J. M. Vohs, and A. Vojvodic
Chemical & Biomolecular Engineering
University of Pennsylvania
Philadelphia, PA 19104

Abstract:

Catalysts based on exsolution of Ni from Ni-doped perovskites have demonstrated a high resistance to coking and are promising as catalysts for endothermic reforming of fuels in hypersonic aircraft. However, low surface areas and the fact that some exsolved metal remains in the bulk of the perovskites prevent the practical application of these materials. To get around these problems, we are developing thin-film perovskite supports prepared by Atomic Layer Deposition on both high-surface-area substrates and model, flat surfaces. Since the films may be similar in thickness to the metal-particle size, we are investigating the effect of film thickness on the properties of the metal particles. In addition to reaction studies, thermodynamic coulometric-titration measurements are being performed to determine how exsolution affects metal reducibility. The model, flat samples are being examined by AFM and surface spectroscopies to achieve insights into the reasons behind the nature of the exsolved particles and the reasons for their high coking tolerance. First-principle, theoretical studies are guiding the choices of metals and perovskites in the experimental studies. Here, we will present preliminary results on the preparation and characterization of these materials.

Molecular Beam Studies of Carbon and Silicon Carbide Ablation by Atomic Oxygen

Timothy K. Minton

Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT, 59717 USA; E-mail: tminton@montana.edu

Abstract

Understanding the oxidation mechanisms of heat shields is key to reliable design with low uncertainties. We have been using molecular beam-surface scattering experiments to gain an understanding of the high temperature oxidation of model materials. We have conducted extensive investigations of three types of carbon, (1) highly oriented pyrolytic graphite (HOPG), (2) vitreous carbon, and (3) carbon fiber preform (FiberForm), and new work is underway to understand the detailed oxidation mechanisms of silicon carbide (SiC).

The experiments are performed with a laser-detonation molecular beam source that produces ground-state O and O₂ with a mole ratio of approximately 90:10 and a nominal velocity of 8 km s⁻¹. The vitreous carbon and FiberForm samples are heated resistively, and the HOPG and SiC samples are heated radiatively by placing the sample in close proximity to a resistively heated vitreous carbon sample. The products that scatter either reactively or non-reactively from the surface are detected with a rotatable mass spectrometer detector. The primary data are number density distributions as a function of arrival time at the detector, with a particular incident angle (θ_i) and final angle (θ_f). These number density distributions are referred to as time-of-flight (TOF) distributions. These distributions allow the simultaneous characterization of the products and the timescale of the reactions. The data are able to distinguish between products that scatter on a timescale too short for thermal equilibrium to be attained (impulsive scattering in the case of non-reactive scattering, and Eley-Rideal in the case of a reaction) and products that desorb in thermal equilibrium with the surface (trapping desorption in the case of non-reactive scattering, and Langmuir-Hinshelwood in the case of reaction).

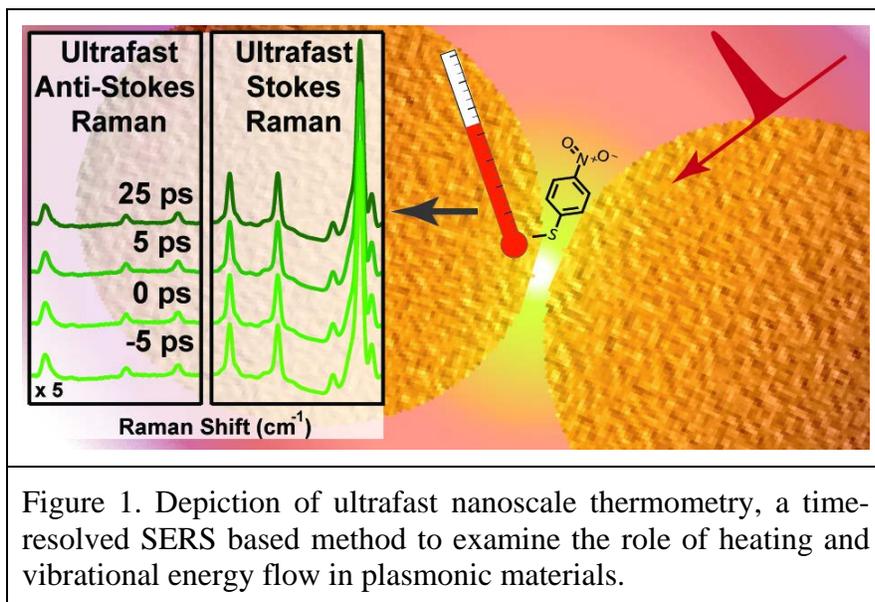
The reactive scattering dynamics on all three carbon surfaces are similar yet the details of the dynamics differ, suggesting that the oxidation mechanisms on all *sp*² types of carbon are similar but that surface morphology influences the relative importance of the individual mechanisms. Furthermore, the data indicate that the reaction mechanisms occur in thermal equilibrium with the surface and that the surface oxygen coverage is high except at the highest temperatures; therefore, the beam-surface scattering data are relevant to hypersonic gas-surface interactions. In general, we have learned that incoming O atoms increase surface coverage and lower the barriers to CO and CO₂ formation. Increasing surface temperature promotes reactions as long as sufficient O is present. At high temperatures, desorption of O and CO lowers the surface coverage of O, which increases reaction barriers and reduces the number of surface O atoms that are available for reaction, thus lowering the reactivity of carbon with O atoms. A higher flux of O atoms on the surface can maintain the surface coverage of oxygen and allow high reactivity even at higher temperatures. There are both prompt and slow processes that lead to the production of CO reaction products, and the rates of all these processes must be considered in a finite rate model for CFD.

In the new experiments on SiC, we have used 6H single crystal surfaces and have started by oxidizing these surfaces in the atomic oxygen beam to produce an SiO₂ layer that is approximately 5 nm thick. Upon heating in vacuum, the oxide layer decomposes quickly at a temperature of ~1400 °C and produces volatile SiO. As the sample is heated further, no more SiO is produced and a graphitic carbon layer remains with a thickness indicative of more than 10 layers of graphene (determined by Raman analysis of a sample that has been heated and then cooled to room temperature). When the atomic oxygen beam is directed at the oxidized SiC surface, no reaction products are observed until the surface temperature increases above 1400 °C where the oxide layer is removed. This is thus the transition temperature from passive to active oxidation. Above this transition temperature, the scattering dynamics are indicative of scattering from graphitic carbon (similar to what we observed on HOPG). Apparently, the O-atom flux of our beam is not sufficient to remove the graphitic layer on the time scale of our experiments. Further experiments are underway to investigate the detailed reaction mechanisms in the active oxidation regime with a higher O-atom flux. In addition, additional experiments are planned to study the reaction mechanisms that occur at the transition temperature, during the decomposition of the oxide layer.

Ultrafast Surface-Enhanced Raman Spectroscopy for Quantification of Directed Energy Flow in Plasmon-Molecule systems

Emily L. Keller, James L. Brooks, Chris L. Warkentin, and Renee R. Frontiera
Department of Chemistry, University of Minnesota, Minneapolis, MN 55104

Plasmonic nanomaterials are promising candidates for solar-driven energy conversion systems, as they interact strongly with light and are known to be capable of driving energetically unfavorable chemical reactions. Their ability to concentrate light to subwavelength volumes leads to the formation of hot spots and hot electrons, which can drive energy flow, modify potential energy surfaces, and enable new photochemical and photophysical processes. However, significant questions remain as to the mechanism of action of a plasmonic photocatalytic system, in part because of difficulties in characterizing the rapid photo-induced dynamics and interactions between the nanoparticle surfaces and proximal molecular species. In particular, the contribution of thermal effects on increases in the rate and yield of plasmonic photocatalysis is unclear, as measurements designed to look at transfer of energy from plasmonic materials to molecules on the ultrafast timescale of chemical reactivity are lacking.



Here we use ultrafast surface-enhanced Raman spectroscopy, a new pump-probe technique designed to follow the molecular response of molecules adsorbed on plasmonic nanomaterials (Figure 1). We quantify carrier transfer by monitoring generation of cationic and anionic molecular species on the ultrafast time scale, proving that a significant number of molecules in

plasmonic hot spots undergo charge transfer. By tracking the transient Raman frequency evolution on the Stokes and anti-Stokes sides, we can determine the role of heating in plasmonic catalysis. We probe the effective temperature, equivalent to the mode-specific increase of vibrational kinetic energy on the picosecond timescale of molecular motion. We find that plasmon excitation increases the effective temperature of the system by less than 100 K, even at peak fluences 10^8 stronger than focused sunlight. This modest energy transfer of the most active plasmonic regions proves that thermal contributions to plasmonic catalysis are surprisingly small. Additionally, we probe phonon-mediated mode-specific energy transfer to adsorbates on the 100s of ps timescale, a promising new route for long-lived coherent control of molecular reactivity. This material is based on work supported by the Air Force Office of Scientific Research under AFOSR Award No. FA9550-15-1-0022.

Hot carriers in plasmonic nanostructures

*Department of Chemistry, Department of Electrical and Computer Engineering
Rice University, Houston, TX, U.S.A.
email: slink@rice.edu*

Metallic nanoparticles have found applications for thousands of years, starting with their use in stained glasses. We now know that the intense colors are due surface plasmons, the coherent oscillations of the conduction band electrons leading to intense absorption and scattering. Since then, surface plasmons have been exploited in many different ways, including recent efforts to generate hot carriers from plasmon decay and drive chemical reactions. Unlike in semiconductor photocatalysts, hot electrons and holes are, however, short-lived, leading to low overall quantum yields. Low efficiencies can be offset by large absorption cross sections and tunable resonances to match molecular orbital energies. However, to further enhance plasmonic photocatalysts an improved understanding of the generation and relaxation of hot carriers in different plasmonic nanostructures as a function of their surface chemistry is still necessary. In our recent work on plasmon generated hot carriers in gold and aluminum nanostructures, we have employed single-particle spectroscopy to eliminate signal averaging over a heterogeneous distribution of nanoparticles and were able to quantify a variety of fundamental processes: interfacial energy and charge transfer^{1,2}, radiative emission³, and electron-phonon coupling.^{4,5}

1. B. Foerster, A. Joplin, K. Kaefer, S. Celiksoy, S. Link, C. Sönnichsen *Chemical Interface Damping Depends on Electrons Reaching the Surface*. ACS Nano, 11, 2886 (2017).
2. B. Foerster, V. A. Spata, E. A. Carter, C. Sönnichsen, S. Link *Plasmon Damping Depends on the Chemical Nature of the Nanoparticle Interface*. Sci. Adv., accepted.
3. Y.-Y. Cai, E. Sung, R. Zhang, L. J. Tauzin, J. G. Liu, B. Ostovar, Y. Zhang, W.-S. Chang, P. Nordlander, S. Link *Anti-Stokes Emission from Hot Carriers in Gold Nanorods*. Nano Lett. 19, 1067 (2019).
4. M.-N. Su, P. D. Dongare, D. Chakraborty, Y. Zhang, C. Yi, F. Wen, W.-S. Chang, P. Nordlander, J. E. Sader, N. J. Halas, S. Link *Opto-mechanics of single aluminum nanodisks*. Nano Lett. 17, 2575 (2017).
5. M.-N. Su, C. J. Ciccarino, S. Kumar, P. D. Dongare, S. A. H. Jebeli, D. Renard, Y. Zhang, B. Ostovar, W.-S. Chang, P. Nordlander, N. J. Halas, R. Sundararaman, P. Narang, S. Link *Ultrafast Electron Dynamics in Single Aluminum Nanostructures*. Submitted.

Yogesh Surendranath, MIT

Molecular Probes of Electric Field Driven Interfacial Reactions

The rational design and improvement of interfacial electrocatalysts for energy conversion reactions requires a quantitative understanding of (1) the interfacial electric field strength under reaction conditions and (2) the influence of the interfacial electric field on the thermodynamics and kinetics of bond-breaking and bond-forming reactions on electrode surfaces. In this context, we first establish a rigorous framework for measuring electric field strength at Pt surface while it catalyzes the interconversion of H^+ and H_2 . We use the H_2/H^+ couple to pin the Pt electrode at the reversible potential for this reaction across a wide pH range and then introduce a non-faradaic reaction probe to sense the local pH at the Pt surface. We show that the electromigration of protons to the surfaces lowers the local pH relative to the bulk value at low ionic strengths, causing a change in the selectivity of the probe reaction. By quantifying the selectivity as a function of ionic strength and pH, we extract the electrostatic potential inside the double layer. Second, we use the interfacial field strength to drive the electrosorption of anions to and from graphite conjugated organometallic rhodium complexes. Using a conjunction of thermodynamic and kinetic analyses allows us to probe the role of the interfacial field strength on the rate of anion binding to well-defined molecular active sites confined within the double layer. We find that these anion-coupled electron transfer reactions obey a non-linear activation barrier-driving force relationship with a small intrinsic barrier, despite breaking a strong Rh(III)-Cl bond on the electrode surface. Collectively, these studies advance a quantitative and molecular-level understanding of how interfacial electric fields drive bond-breaking and bond-forming reactions on electrode surfaces.

Abstract

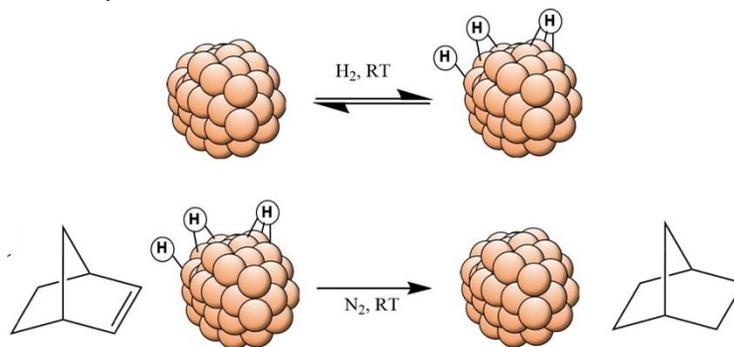
Proton-Coupled Electron Transfer Reactions of Colloidal Metal Nanocrystals

Nico Dwarica, Noreen Gentry, James M. Mayer

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

Department of Chemistry, Yale University
james.mayer@yale.edu

Hydrogen transfer reactions are central to most energy-related electrocatalytic reactions, from fuel cells to electrolytic fuel production. Developing improved processes and new catalysts will require understanding of the behavior of hydrogen on reactive surfaces. We are approaching this challenge by examining the chemistry of hydrogen on colloidal metal nanocrystals (NCs). These materials are intermediate between bulk metals and molecular compounds, and they are models for supported nanoscale electrocatalysts. The colloidal nature of the NCs and their high surface area make them amenable to traditional methods to probe molecular composition and reactivity in solution. For example, the equations below illustrate some reactions of ca. 3 nm iron nanocrystals Fe_x (the oleate capping ligands are not shown). These NCs add H_2 to form Fe_xH_y , both as colloids and as a solid (upper reaction). After removal of the residual H_2 , the Fe_xH_y hydrogenate alkenes to alkanes. The amount of alkane formed measures the number of reactive H that were on the NCs. This presentation will describe initial studies with iron, iron-carbide and gold NCs, with the goal of understanding the stoichiometry, spectroscopy and reactivity of these hydrogen-containing materials under a variety of conditions.



Nanochemical Strategies for Propulsion Enhancement

Timothy Gorey,^a Borna Zandkarimi,^b Guangjing Li,^a Eric Baxter,^a Mai-Anh Ha,^b Huancehn Zhai,^b Scott L. Anderson,^{a,*} Anastassia N. Alexandrova^{b,*}

^aChemistry Department, University of Utah, Salt Lake City, UT 84112

^bChemistry and Biochemistry, UCLA, 607 Charles E Young Dr E, Los Angeles, CA 90095

E-mails: anderson@chem.utah.edu, ana@chem.ucla.edu

We report on our joint theory and experiment efforts toward the development of sub-nano supported cluster catalysts for endothermic cooling. Size-selected deposition is used to prepare highly uniform and well characterized catalysts, and detailed theory is done on the same systems, allowing direct comparisons that are seldom possible in catalysis. Selective dehydrogenation of alkanes catalyzed by Pt-based bimetallic clusters is the target endothermic reaction. Pure Pt clusters and cluster alloys are prepared by laser vaporization and mass-selected deposition, followed by selectively atomic layer modification to add alloying elements. Catalytic activity, selectivity, and stability are assessed via temperature programmed desorption/reaction (TPD/R), CO TPD, ISS, and DFT calculations. The theoretical insight into the properties of cluster catalysis required a paradigm shift in modelling, toward statistical mechanical description involving many distinct catalyst states thermally populated in reaction conditions and dynamically evolving and interconverting in response to the environment. The number of such relevant catalyst states can be large, up to 30 for our systems. Through our joint approach, we developed an understanding of cluster size-activity dependence as arising from the accessibility of higher energy reactive isomers of the catalyst. We developed several dopants that enhance the selectivity of dehydrogenation and stability of cluster catalysts. Of these, B and Sn have been characterized both theoretically and experimentally, and Si and Ge were identified only theoretically so far. The electronic structure reasons for the effect of the dopants were explicated, and found to be different for B, versus Sn, Si, and Ge.

Griffin Mead, Kyle Virgil, & Geoffrey A. Blake

Division of Chemistry and Chemical Engineering,

California Institute of Technology

Pasadena, CA 91125

The section of the electromagnetic spectrum extending roughly from wavelengths of 3 millimeters to 30 microns is commonly known as the far-infrared or TeraHertz (THz) region. It contains the great majority of the photons emitted by the universe, and THz pulses can be used to probe processes as diverse as the fundamental nature of charge separation in semiconductors, the interrogation of spintronic and topological materials, and the molecular dynamics of liquids and polymers. Here we report on the design and performance of an echelon-based single shot visible/near-infrared spectrometer with adequate sensitivity to measure the linear and nonlinear optical and terahertz response of liquids and solids. Particular examples presented include the THz emission from layered, 2D hybrid perovskite films and the nonlinear Optical and THz Kerr Effect (OKE/TKE) signatures of neat molecular liquids at room temperature. Useful information spanning tens of picoseconds can be measured in just a few milliseconds, and the signal-to-noise performance is dramatically superior to delay line techniques. These results demonstrate the viability of stage-free nonlinear Kerr effect measurements and provide a route for improvements to the speed of future multidimensional THz studies, including the coherent control of molecular dynamics and new approaches to quantum information science.

Matthew Sheldon, Texas A&M University

Plasmonic Strategies for Control of Hot Electron Dynamics and Photo-Thermal Emission

This poster provides a summary of major findings of our YIP supported research studying mechanisms for electron transfer that can be enhanced by photothermal energy concentration and optical excitation in plasmonic nanostructures. In particular, we have explored thermionic power conversion using nanostructured plasmonic metal absorbers that promote resonant photo-thermalization and direct photo-emission of electrons, in order to enhance the rate of electron emission. In addition, we have developed new fundamental mechanisms of unidirectional charge transfer in nanostructured metal geometries that have an asymmetric spatial distribution of optical absorption and photothermal heating across tunneling gaps. Our computational analysis and experiments have outlined new strategies that maximize the cooperative interactions of low energy, thermalized electrons in addition to optically excited hot carriers for photochemistry and power generation. Concurrently, we have also developed new in situ anti-stokes Raman spectroscopy techniques for quantifying both thermal and non-thermal carriers in fabricated resonant metal geometries during optical excitation, while simultaneously monitoring lattice temperature. In combination with measurements of these structures integrated into thermionic test devices in vacuum, our studies have laid the foundation for how to modify fundamental aspects of the nonequilibrium electron gas that are important for photocatalysis, such as extending carrier lifetime by orders of magnitude, decreasing electron-phonon coupling, and controlling chemical dampening, based on nanoscale structuring. In addition to the remarkable optical response, we have shown how plasmonic resonances can also be used to optimize electron dynamics.

Energetics and Reactivity of Surface-localized States on Semiconductor Nanocrystals

Jillian L. Dempsey, Carolyn Hartley, Melody Kessler

University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290

Charge carriers in semiconductor nanocrystals can be trapped in localized states—typically in lattice defects or surface-based states. These trap states impact charge carrier dynamics and their presence deleteriously impacts the performance of nanocrystal-based optoelectronic devices. Yet while the impact of various trap states is well-known, their structural origins and relative energetics are poorly understood. Using outer sphere chemical reductants, the reduction of CdSe and PbS semiconductor nanocrystals can be carefully controlled. Monitoring the nanocrystals upon reduction using a combination of optical, FT-IR, and ^1H NMR spectroscopies reveals that changes to the charge carrier population of a nanocrystal is coupled strongly to structural and composition changes at the surface of the nanocrystal surface that result upon electron trapping in localized states. Because the identity of the localized state determines the structural changes that accompany charging, we have been able to correlate the identity, availability, and energetics of specific trap states from their redox reactivity. Insight to the changes in electronic structure and surface chemistry induced by the addition of charge carriers broadly impact our understanding of energy and electron flow through arrays of nanocrystals. Our ability to probe — and interpret — the molecular changes that occur at nanocrystal surfaces upon carrier trapping will enable us to evaluate the role of these states in electron transfer pathways at nanocrystal interfaces.

Imaging Charge Carrier Collection Efficiency and Transport in Ultrathin Semiconductors

Li Wang, R. Colby Evans and Justin B. Sambur

Department of Chemistry
Colorado State University
Fort Collins, CO 80523

Ultrathin photovoltaics made of 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. However, 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 demonstrate proof-of-concept monolayer and bilayer TMD|I⁻,I₃⁻|Pt photoelectrochemical solar cells that use a conformal liquid electrolyte junction for efficient perpendicular charge transport over significantly larger active areas than solid state systems. 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. Interestingly, correlated Raman and scanning photoelectrochemical microscopy measurements revealed a non-linear scaling relation between IQE and layer thickness for MoS₂, WSe₂, and MoS₂/MoS₂/WSe₂ domains within the heterojunction film. Specifically, the monochromatic energy conversion efficiency of bilayer MoS₂ is an order of magnitude greater than monolayer MoS₂ and MoS₂/MoS₂/WSe₂ exceeds MoS₂/WSe₂ by a factor of four. The structure/function relationships are hidden in ensemble-level photoelectrochemical measurements. While nanostructured or plasmonic electrode architectures are still needed to enhance overall light absorption, our study shows that the liquid junction approach represents a simple and rapid strategy to screen ultrathin TMD materials combinations, tune interfacial energetics, and make conformal electrical contacts in photoelectrochemical energy conversion systems for electricity or solar fuels production.

Resolving Links between Gold Nanocluster Surface Chemistry and Electronic Structure

Christopher J. Johnson
Department of Chemistry
Stony Brook University

Gold nanoclusters are an emerging class of atomically-precise materials whose electronic properties are readily tunable with discrete changes in composition, ligand architecture, local environment, and stereochemistry. Establishing synthetic design rules for chemically controlling electronic properties has remained elusive due to the lack of a sensitive and selective probe for electronic structure. Common approaches to measuring UV-Vis absorption spectra often obfuscate spectral features via thermal broadening and heterogeneity effects. To overcome such experimental limitations, we have turned to variable-temperature mass-selective photodissociation spectroscopy. Using triphenylphosphine-protected gold nanoclusters as a model system, our technique enables us to determine the effect of cluster composition, ligand para-substituent, and solvation environment over the energies of intracore metal-metal and metal-to-ligand charge transfer (MLCT) bands with unprecedented detail. We have determined that ligand chemistry establishes the foundational electronic structure of the nanocluster, with ligand-based correlations suggesting that electronic coupling between the metal core and ligand shell can be rationally tuned by $\sim 100\text{--}300\text{meV}$. Composition is equally as effective in modulating metal-metal transitions ($\sim 100\text{--}300\text{meV}$) as the geometric core structure reorganizes upon changes in ligand or metal-atom count. Further, the combination of ligand and core chemistry allow us to experimentally differentiate between intracore and MLCT transitions. Surprisingly, we also observe that even weakly-interacting solvents (e.g., He vs. N₂) are capable of inducing $\sim 10\text{--}50\text{ meV}$ solvatochromic peak shifts.

Amending Non-Condon Molecular Photophysics using Cavity Polariton Formation

**Aaron S. Rury, Department of Chemistry, Wayne State University
5101 Cass Ave. Detroit, MI 48202**

Controlling excited state molecular dynamics remains a crucial goal towards designing photochemistry from a fundamental quantum perspective. While synthetic chemists have made significant progress toward molecular structures capable of tuning excited dynamics, a gap exists in our ability to carefully manipulate structure necessary to control photochemistry at a quantum level. In this study, we explore a possible mechanism to control excited state molecular dynamics using cavity polaritons, hybrid states of cavity-confined photons and molecules. Several theoretical studies have proposed molecular cavity polariton formation causes significant structural reorganization of the excited molecular state strongly coupled to cavity photons. By analyzing simple models of non-Condon coupling in metalloporphyrins, we extend these models to propose polariton formation using the intense Soret transition of these molecules will result in changes to the properties of low lying excited electronic states. Calculations indicate spontaneous Raman spectroscopy in resonance with different transitions can establish the validity of these proposals. We also present initial experimental results demonstrating cavity polariton formation using the Soret transition of Zn- and Cu-centered tetraphenyl porphyrin molecules and comparisons of light emission spectra from polaritonic and free space samples. These results indicate molecular cavity polariton formation could provide a mechanism to control excited state dynamics central to energy transduction, photo-catalysis, and chemical sensing technologies critical for Air Force missions.

Nicholas Shuman, AFRL

Mutual Neutralization Reactions in Two Atom Systems

Until recently, thermal rate constants for an atomic cation neutralizing with an atomic anion were limited to the rare gas cations $\text{He}^+ - \text{Xe}^+$ and the halide anions $\text{Cl}^- - \text{I}^-$. In an effort to better understand this fundamental reaction, we have extended the chemical diversity of measured thermal rate constants for mutual neutralization reactions by studying the reaction of the atomic cations H^+ , C^+ , N^+ , and O^+ with the atomic halide anions $\text{Cl}^- - \text{I}^-$. The thermal rate constants measured range from below our detection limit of $\sim 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ to close to an upper limit of $\sim 5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$. Overlap in theoretical and experimental studies for $\text{H}^+ + \text{Cl}^-$ and $\text{C}^+ + \text{Cl}^-$ reactions provide a unique perspective into the quantum chemical mechanisms that control mutual neutralization reactions.

Advances in Green Propellants: Chemistry and Engineering Challenges

Steven D. Chambreau,¹ Stefan Schneider² and Ghanshyam L. Vaghjiani³

¹ERC Incorporated, Air Force Research Laboratory
Edwards Air Force Base, California 93524, United States

²Aerospace Systems Directorate, Propellants Branch, RQRC, Air Force Research Laboratory
Edwards Air Force Base, California 93524, United States

³Aerospace Systems Directorate, Spacecraft Branch, RQRS, Air Force Research Laboratory
Edwards Air Force Base, California 93524, United States

Abstract

Recent interest in replacing hydrazine-based propellants with low-volatility ionic-liquid-based alternatives has inspired a substantial amount of research in these potential “greener” fuels. From both chemistry and engineering perspectives, there are significant challenges in implementing these potential fuels in order to match or increase performance over heritage hydrazine-based fuels. Descriptions of the most recent research and results in this field will be presented here.

Synthesis and Characterization of Energetic Aluminum Core/Shell Nanoparticles

M.B. Bogle,^a B.K. Little,^a C.J. Ridge,^{a,b} K.R. Overdeep,^{a,b} D.K. Smith,^a C. M. Lindsay^a

- a) Energetic Materials Branch, Air Force Research Laboratory, Eglin Air Force Base, FL 32542, USA
- b) Department of Nanochemistry & Nanoengineering, University of Dayton Research Institute, Dayton, Ohio 45469, USA

Aluminum-based core/shell nanoparticles have been created by various means in an effort to develop high-energy content materials that will react on time-scales relevant to a detonation. Clusters produced by Superfluid Helium Droplet Assembly (SHeDA) have been used to investigate the oxidation behavior of aluminum particles at the lower size limit (<10 nm), as well as the reactive and morphological properties of aluminum-gold composite clusters and nano-strings. Two approaches to making core/shell nanothermites have also been developed in which oxidizer-containing shells are chemically synthesized around nano-aluminum particles. The first method uses a siloxane linker to form a copper-oxide shell around the nano-aluminum particles. The second method uses an oxide acid substitution reaction to replace the inert shell of aluminum oxide on the particle with highly reactive aluminum iodate hexahydrate (AIH). This approach has been shown to be effective, leading to a significant increase in laser-induced shock velocity when mixed with TNT.

Metal-ligated clusters: a theoretical study

Jerry A. Boatz

Air Force Research Laboratory
Aerospace Systems Directorate
AFRL/RQRP, 10 E. Saturn Blvd.
Edwards AFB, CA 93524-7680

Abstract

Metal-ligated clusters, with potential applications such as nanocatalysts, are of fundamental interest with respect to their reactivity, structure, and binding energies. Some examples of these systems include metal-benzene clusters $[M_nbz_m]^+$, ($n, m=1, 2, 3, \dots$) where $M = V, Ni, Nb,$ or Ta , and bz =benzene. One of the most fascinating aspects of these systems is the experimentally observed formation of linear sandwich complexes consisting of alternating metal atoms and benzene ligands. In the case of $M =$ vanadium, linear sandwich complexes are formed in the gas-phase complexation reactions of small, covalently bound vanadium clusters V_n^+ ($n=2, 3, 4$) with benzene.[1]

The present study utilizes theoretical calculations using density functional theory to explore possible isomers, electronic spin states, and the corresponding relative energies of a series of $[M_nbz_m]^+$ ($n=1-4$; $m=1-5$), focusing initially on $M=V$ and Ni . The main initial objective is to identify the most stable species, taking into consideration multiple structural isomers and spin states. Preliminary testing of multiple density functional/basis set combinations revealed that in several instances, the computed ground electronic state of a neutral metal atom and/or its cation is in disagreement with experiment,[2] thus illustrating the need for systematic DFT benchmarking for these types of metal-ligated cluster species.[3]

1. Patrick Weis, Paul R. Kemper, and Michael T. Bowers, "Structures and Energetics of $V_n(C_6H_6)_m^+$ Clusters: Evidence for a Quintuple-Decker Sandwich", *J. Phys. Chem. A* 101, 8207-8213 (1997).
2. Xueyuan Wu and A. K. Ray, "A density functional study of small neutral and cationic vanadium clusters V_n and V_n^+ ($n=2-9$)", *J. Chem. Phys.* 110, 2437-2445 (1999).
3. Sijie Luo, Boris Averkiev, Ke R. Yang, Xuefei Xu, and Donald G. Truhlar, "Density Functional Theory of Open-Shell Systems: The 3d-Series Transition-Metal Atoms and Their Cations", *J. Chem. Theory Comput.* 10, 102-121 (2014).

DFT Studies on the Synthesis of Al Core-Shell Nanoclusters

Robert J. Buszek¹ and Jerry A. Boatz²

¹ERC, Inc., Edwards Air Force Base, California 93524

² Propellants Branch, Aerospace Systems Directorate,
Air Force Research Laboratory, AFRL/RQRP, Edwards Air Force Base, CA 93524

Abstract

The identification and development of novel, high performance energetic materials for munitions, chemical propulsion, and other advanced applications is an essential need of the United States Air Force. Nanoparticles, in particular nano-thermites, offer higher surface-to-volume ratios and reduced reaction domains compared to the diffusion-limited mass and thermal transport bottlenecks encountered using bulk materials, offering considerable potential as high-performance energetic materials for applications in explosives and propellant formulations. These types of novel materials are currently being synthesized via Superfluid Helium Droplet Assembly (SHeDA) experiments at AFRL/RWME which occurs via clustering of atoms or molecules within the interior of helium droplets. Presented here are modelling efforts to further understand the potential for synthesis of intermetallic Al core-shell nanocluster in looking at the energetics involved with the Al/Au and Al/Si systems as both Au and Si are well studied nanoparticle systems. DFT methods are employed using an effective core potential and valence-only basis set to investigate the structures and energetics of an Al₃₀ cluster with a multiple Si and Au atoms as well as the inverse systems. Also, to determine whether an inversion process is possible during the cluster formation process, as has been seen in other intermetallic core-shell species, is possible potential energy surface (PES) scans of two surface atoms being forced to the center of the cluster are also presented.

Distribution A: Approved for public release: Distribution Unlimited PA Case #: 15143

Guest Posters

QUANTITATIVE SURFACE POTENTIALS FROM HETERODYNED 3rd-ORDER SPECTROSCOPY

Franz M. Geiger

Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

We report ionic strength-dependent optical phase shifts in second harmonic generation (SHG) signals from charged interfaces that verify a recent model in which dispersion between the fundamental and second harmonic beams modulates observed signal intensities. We show how phase information can be used to unambiguously separate the $\chi(2)$ and interfacial potential-dependent $\chi(3)$ terms that contribute to the total signal and provide a path to test primitive ion models and mean field theories for the electrical double layer with experiments to which theory must conform. Over- and undercharging is observed without *a priori* knowledge of the surface and solute ionization state. Finally, we demonstrate the new method on supported lipid bilayers and comment on the ability of our new instrument to identify hyper-Rayleigh scattering contributions to common homodyne SHG measurements in reflection geometries.

"Beyond Gouy-Chapman Theory with Heterodyne-Detected Second Harmonic Generation"

Paul. E. Ohno, HanByul Chang, Austin Spencer, Yangdongling Liu, Mavis D. Boamah, Hong-fei Wang, and Franz M. Geiger

J. Phys. Chem. Lett., *in press* (2019) and available online at <https://arxiv.org/abs/1903.05707>

"Relative Permittivity in the Electrical Double Layer from Nonlinear Optics"

Mavis Boamah, Paul E. Ohno, Franz M. Geiger, and Kenneth B. Eisenthal, *Chem. Phys. Lett.* 148, 222808 (2018), Special Topic Issue on Ions in Water

"Bulk Contributions Modulate the Sum-Frequency Generation Spectra of Interfacial Water on Model Sea-Spray Aerosols"

Sandeep K Reddy, Raphael Thiriaux, Bethany A Wellen Rudd, Lu Lin, Tehseen Adel, Tatsuya Joutsuka, Franz M. Geiger, Heather C. Allen, Akihiro Morita, and Francesco Paesani *Chem*, 4, 318-33 (2018)

"Second-Order Vibrational Lineshapes from the Air/Water Interface"

Paul E. Ohno, Hong-fei Wang, James Skinner, Francesco Paesani, and Franz M. Geiger, *J. Phys. Chem. A*, 122, 4457-64 (2018)

Second-Order Spectral Lineshapes from Charged Interfaces"

Paul E. Ohno, Hong-fei Wang, and Franz M. Geiger

Nature Communications, 8, 1032 (2017)

"Phase-referenced Nonlinear Spectroscopy of the alpha-Quartz/Water Interface"

Paul. E. Ohno, Sarah A. Saslow, Hong-fei Wang, Franz M. Geiger, and Kenneth B. Eisenthal *Nature Communications*, 7, 13587 (2016)

Visualizing Chemical Dynamics in Ionic Liquids with 2D IR Microscopy

Clara A. Tibbetts, Bradley M. Luther, and Amber T. Krummel

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

2D IR spectroscopy is a nonlinear optical spectroscopy with the ability to characterize condensed phase chemical systems. It offers information regarding chemical structure and dynamics. 2D IR spectra are rich in observables, thus recent efforts have been made to demonstrate the feasibility of ultrafast 2D IR microscopy. In this work, we demonstrate 2D IR microscopy with a 100 kHz repetition rate source. Taking advantage of the 100 kHz repetition rate, our system provides a path to 2D IR microscopy experiments that explore chemical dynamics in heterogenous chemical systems. A recent imaging experiment will be discussed to demonstrate the power of 2D IR microscopy for investigating chemical dynamics. 2D IR microscopy reveals chemical dynamics in a room temperature ionic liquid microdroplet that are otherwise hidden. Spatially resolved time-dependent 2D IR signals reveal three regions with different chemical dynamics—the bulk, the interface, and a region between the bulk and interface. Quantifying the chemical dynamics within the RTIL microdroplet provides insights as to the utility of RTIL microdroplets as reaction vessels and as fuel cell electrolytes.

Symmetry breaking, local correlation and Monte Carlo for strong electron correlation

Sandeep Sharma (sanshar@gmail.com)¹

¹*Department of Chemistry, University of Colorado Boulder, Boulder, CO 80302, USA*

In this poster I will demonstrate that the confluence on three powerful techniques: symmetry breaking, local correlation and Monte Carlo, allows us to improve the efficiency of several well-established methods by many orders of magnitude.

As a first example, I will show that by using ideas from local correlation, a four decade old technique of selected configuration interaction can be made several orders of magnitude faster. The resulting method is called the semistochastic heat bath configuration interactions (SHCI), which allowed us to obtain the correct spin state ordering of the Fe-porphyrin cluster^[1]. To obtain this result we had to perform a SHCI calculation with an active space consisting of 44 electrons in 44 orbitals (a feat that was previously either not possible or too expensive).

As a second example, I will show that by using local correlation and symmetry breaking, we can reduce the scaling of orbital space VMC from $O(N^4)$ down to $O(N^2)$, where N is the system size. This reduced scaling allowed us to lower the cost of calculating the ground state energy of a modestly sized system (containing 50 electrons) by about 3 orders of magnitude. Using the improved low-scaling algorithm, we were able to perform some of the most accurate calculations to date on 2-D Hubbard model which is one of the most challenging unsolved problems in electronic structure theory^[2].

Finally, I will also show that by using techniques from local correlation and quantum Monte Carlo, we are able to perform multireference configuration interaction (MRCI) calculations with large active spaces^[3]. The ability to perform such calculations has been one of the most significant challenges in multireference quantum chemistry. Our proof of principle calculations show that we might be at the precipice of being able to solve this problem.

1. Smith, Mussard, Holmes, Sharma, *Journal of Chemical Theory and Computations* (2017), **13**, 5468. Sharma, Holmes, Jeanmairet, Alavi, Umrigar, *Journal of Chemical Theory and Computations* (2017), **13**, 1595.

2. Mahajan, Sharma, *Journal of physical chemistry* (submitted). Sabzevari, Sandeep Sharma, *Journal of Chemical Theory and Computations* (2018), **14**, 6276.

2. Mahajan, Sharma, *Journal of chemical physics* (in preparation).

Title: Semiconductor nanocrystals as triplet photosensitizers for photon upconversion

MingLee Tang, UC Riverside.

This poster will describe energy transfer between semiconductor quantum dots (QDs) and π -conjugated molecules, focusing on the transmitter ligand at the organic– inorganic interface. Efficient transfer of triplet excitons across this interface allows photons to be directed for effective use of the solar spectrum. For example, a photon upconversion system composed of semiconductor QDs as sensitizers, surface bound organic ligands as transmitters, and molecular annihilators has the advantage of large, tunable absorption cross sections across the visible and near-infrared wavelengths. This may allow the near-infrared photons to be harnessed for photovoltaics and photocatalysis. This poster summarizes the progress in this recently reported hybrid upconversion platform from my group, including strategies to overcome the bottlenecks with molecular design in terms of tuning molecular energetics, photophysics, binding affinity, stability, and energy offsets with respect to the QD donor. Efficient triplet energy transfer in this hybrid platform will find utility in both up- and down-conversion, with potential for exceeding the Shockley– Queisser limit

Micro-Lasers with Ultra-Narrow Linewidth for Atom-Based Devices

Andrey Matsko, Anatoliy Savchenkov, Danny Eliyahu, David Seidel and Skip Williams

OEwaves Inc.

465 North Halstead Street, Suite 140
Pasadena, California 91107, U.S.A.

E-mail: skip.williams@oewaves.com

Abstract: Atom-based high-performance devices call for spectrally pure and stable optical sources operating in a broad range of optical and infrared wavelengths. We report on the development of spectrally pure lasers operating from 370-4500 nm with ultra-narrow linewidths suitable for application in compact optical clocks, quantum computers, quantum communication sources, and inertial sensors. The laser linewidth reduction is achieved by locking a laser chip to a crystalline whispering gallery mode resonator characterized with quality factor exceeding a billion. Self-injection locking ensures single longitudinal mode operation of the laser. Currently available photonic integrated circuits (PICs) operate in 850 nm–1,650 nm wavelength range and usually do not provide the coherent light characterized with desirable spectral purity and stability. Usage of high-Q stable monolithic micro-resonators flip-chipped into both existing and advanced PIC systems will result in a novel class of optical devices enabling inexpensive and robust optical modules suitable for fieldable atom-based devices.

Nanopore sensing reveals ligand-based kinetics of individual metallic nanoclusters

Joseph E Reiner and Massimo F Bertino: VCU Physics Department, Richmond, VA.

We recently demonstrated the ability to study kinetics of ligand-induced fluctuations on individual metallic nanoclusters (*J. Am. Chem. Soc.*, **2019**, *141*, 3792). Our approach utilizes resistive-pulse nanopore sensing where individual gold clusters partition into a nanoscale pore and disrupt the flow of ionic current through the pore for extended periods of time (~10s). Clusters trapped in the pore exhibit structural changes, which induce sizable current fluctuations. The main result of our aforementioned work was to show that different ligands (*p*-MBA, tiopronin, S-PEG) give rise to distinct current fluctuations and these fluctuations inform about the size and flexibility of the ligands on the cluster. The nanopore provides a unique perspective to observe ligand-induced fluctuations in real-time at the single cluster limit. The ability to observe these reactions at the single cluster limit represents a new development in the study of metallic nanoclusters, and we will discuss these results and frame them in the context of future efforts that look to explore ligand fluctuations and their role in a variety of applications.