Ni ingress and egress on (100) and (110) surface of $SrTiO_3$

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Ni catalysts prepared by exsolution from $SrTiO_3$ exhibit a high tolerance against coke formation and are under consideration for application to endothermic reforming. Here, we investigated the ingress and egress of Ni on $SrTiO_3$ (STO) (100) and (110) single crystals by studying NiO films using Atomic Force Microscopy, Scanning Transmission Electron Microscopy, and theoretical tools such as density functional theory (DFT) and molecular dynamics (MD) techniques. The migration of Ni in and out of the surfaces was studied as a function of temperature under oxidizing and reducing conditions. Experimentally, Ni was found to migrate in and out of the (110) facet but not the (001) facet. DFT also showed a higher propensity for Ni to migrate in and out of the (110) orientation, and lower in the (001) orientation with either SrO (AO) or TiO_2 (BO_2) terminations, while MD showed distinct ingress/egress pathways in the NVT ensemble. These results reveal the anisotropic nature of Ni ingress and egress from the perovskite phase.

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Size- and Composition-selected Pt_nGe_x/alumina Catalysts for Endothermic Dehydrogenation: Size Effects and Selective Carbon Addition to Form the Stable Catalyst

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To enhance endothermic cooling by hydrocarbon fuels, it is important to minimize thermal coking that occurs at high temperatures, and active and highly selective catalysts are needed, able to catalyze the desired endothermic reactions at temperature below the onset of thermal coking, with selectivity against production of coke precursors. We have been using tightly coupled experiments and theory to investigate sub-nano Pt-based cluster catalysts for endothermic alkane-to-alkene dehydrogenation reactions. The recent focus has been on Pt_nGe_x/alumina catalysts, using size-selected Pt_n/alumina prepared by mass-selected Pt_n^+ deposition in UHV, modified by selective, self-limiting addition of Ge atoms, then characterized by surface science methods. It is found that all size Pt_n/alumina bind ethylene (a model, theory-friendly alkene) strongly enough that a substantial fraction decomposes to carbon + H_2(g), rapidly deactivating the Pt clusters as ~2 carbon atoms deposit *per* Pt atom, blocking sites and modifying the cluster properties. Annealing studies show that sintering, which further decreases the accessible Pt surface sites, is another a factor contributing to deactivation.

When Ge atoms are added to Pt_n/alumina to form clusters such as Pt_4Ge/alumina or Pt_7Ge_2/alumina, the ethylene decomposition to deposit carbon is almost, but not completely blocked, such that the catalyst cokes slowly, eventually reaching a limit of ~0.5 C atoms *per* Pt atom in the clusters. The result, however, is a catalyst which is quite stable, retains strong ethylene binding sites, and keeps essentially all the Pt atoms accessible in the surface layer where they can bind reactants.

DFT on Pt_4Ge/alumina reveals the mechanism. The slow coking is explained by a minor, but thermally accessible isomer of Pt_4Ge/alumina that drives deposition of a pair of carbon atoms when ethylene decomposes on it at high temperatures. Because the clusters are fluxional, they all eventually pass through this "gateway" isomer and become coked, forming Pt_4GeC_2/alumina. The Pt_4GeC_2/alumina is, however, predicted to be highly stable, to bind ethylene strongly, but not to dehydrogenate it, i.e., there is no further coking. The Pt_4GeC_2/alumina is predicted to be active for ethane-to-ethylene conversion, thus selective coking is what produces the final, stable catalyst. The C atoms are bound such that they are not on top of Pt, thus explaining why this limited coking does not reduce accessibility of Pt to reactants.

To allow the catalysis to be examined under high pressure conditions, we have developed a microreactor experiment, in which the clusters can be deposited on micromachined chips in UHV, which are then assembled to create a microreactor allowing reactions to be studied at temperatures to 1000 K and pressures to two atmospheres. The reaction mixture exiting the microreactor is sampled by a molecular beam mass spectrometer, equipped for both variable energy electron impact and photo-ionization, in order allow complex mixtures to be analyzed. Initial experiments on ethane-to-ethylene conversion in the high pressure reactor will be discussed.

Lanthanide cation chemistry: Chemi-ionization reactions of holmium and periodic trends

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The reactivity of several lanthanide cations (Ln^+) have been evaluated using guided ion beam tandem mass spectrometry (GIBMS). This technique permits the measurement of the kinetic energy dependence of the reaction of interest, which can then be interpreted to yield thermodynamic and dynamic information. One focus has been the determination of the LnO^+ bond energies, which are useful in evaluating the chemi-ionization process, reaction 1.

$$Ln + O \rightarrow LnO^+ + e^- \qquad (1)$$

This reaction is of interest to the Air Force as a means to mitigate scintillation effects that disrupt radio wave communication. To date, this thermochemistry has been evaluated for five lanthanides with preliminary data available for another. The present poster features results for holmium (Ho). In addition the poster will show the periodic trends in the LnO^+ bond energies evaluated to date and exhibit a predictive correlation found with the $Ln^{2+} + O^-$ asymptote.

Transient Absorption and Photocurrent Spectroscopy of Bright and Dark Polaritons in Carbon Nanotube Microcavities

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Strong light-matter coupling results in eigenstates called polaritons which share properties of both light and matter and provide a useful way to engineer electronic energies and behaviors. In this poster, we present on two types of studies of nearly monochiral (6,5) semiconducting carbon nanotubes (CNTs) in Fabry-Pérot microcavities. In these microcavities, light-matter coupling leads to the formation of three bands of bright polariton states [upper, middle, lower (Fig. 1a) – resulting from coupling to the bright S_{11} CNT exciton and the X_1 phonon-sideband of the K-momentum dark exciton state (KDE)]. These microcavities also support many exciton-like subradiant states at the bright S_{11} and X_1 energies. In the first part of this poster, ultrafast transient reflection spectroscopy is used to study the dynamics and spectral signatures of excited subradiant state polariton populations and the pathways by which they are populated, in the ultrastrong coupling regime. After a pump pulse, the excited subradiant state population is revealed by (i) spectral signatures with relaxation times (~ 5 ps) similar to those of CNT S_{11} bandgap excitons outside of the cavity and (ii) a Rabi contraction of the lower polariton energy, the magnitude of which quantifies the excited subradiant state population. Data show that, following the excitation of the upper polariton (UP), the excited subradiant state population is maximized in microcavities with detuning of 118 meV, light-matter coupling of 336 meV, and a UP transition energy of 1.52 eV. The X_1 Hopfield coefficient of the UP also peaks at the same energy, revealing UP to X_1 scattering as a potentially efficient relaxation pathway. In the second part of this poster, donor-acceptor CNT-C_{60} heterojunctions are incorporated into planar microcavities. Both exciton to photocurrent and sub-bandgap polariton to photocurrent conversion are achieved in weak and strong coupling regimes, respectively. In the strong coupling regime, photocurrent generation is realized from each of the lower (LP), middle (MP), and upper polariton (UP) modes (Fig. 1b), varying in efficiency with the degree of detuning and light-matter coupling strength. These results will be important for understanding and controlling energy relaxation and transport in future CNT polariton devices.

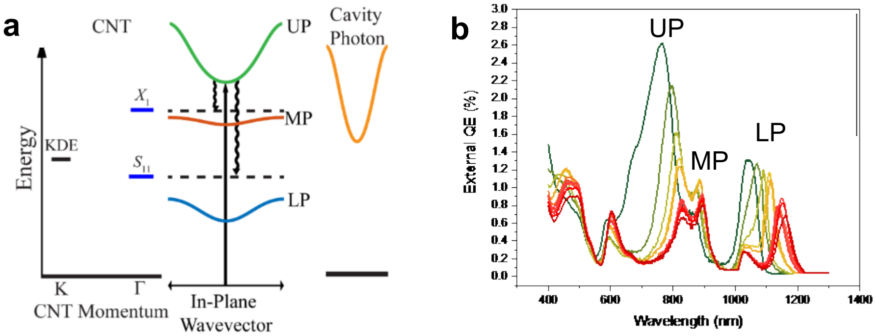

Fig. 1. (a) Diagram of CNT states and transitions contributing to light-matter coupling (left), the cavity mode involved in coupling (right), and resulting bright polariton and subradiant states (middle). **(b)** Example of photocurrent generation driven by optical excitation of LP, MP, and UP modes, for microcavities with varying detuning and light-matter coupling strength, in the strong coupling regime.

Probing Spin Polarized Electron Dynamics at Interfaces Using XUV Reflection-Absorption Circular Dichroism Spectroscopy

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Extreme Ultraviolet Reflection-Absorption (XUV-RA) spectroscopy enables direct observation of electron dynamics at surfaces by combining the benefits of traditional X-ray absorption, such as element, oxidation, and spin state resolution, with surface sensitivity and ultrafast time resolution. While absorption of linearly polarized XUV light can probe the local oxidation state and spin configuration of individual elements (e.g. high spin vs. low spin), it cannot differentiate between M_J states. In other words, linearly polarized light is insensitive to the net alignment between spin centers required to generate a non-zero magnetic moment. In contrast, circularly polarized XUV light can resolve the M_J states providing a platform for studying spin-dependent electron transport and magnetization dynamics at interfaces with ultrafast time resolution.

The ability to produce spin polarized currents underlies many promising applications ranging from spintronics to enantioselective photocatalysis, but designing materials capable of these applications requires an improved understanding of spin-dependent electron dynamics at interfaces. With support from this project, we have developed the ability to measure spin polarized electron transport using XUV Magnetic Circular Dichroism (XUV-MCD). Employing XUV-MCD in a reflection geometry, we are now studying the ultrafast surface electron dynamics that give rise to spin polarized photocurrents in magnetic and chiral semiconductors.

As an example, yttrium iron garnet ($Y_3Fe_5O_{12}$, YIG) is a ferrimagnetic oxide with a visible band gap, consisting of two sub-lattices based on octahedrally and tetrahedrally coordinated Fe(III) centers. A combination of linearly and circularly polarized XUV measurements at the Fe $M_{2,3}$-edge provides a detailed picture of these lattice-dependent electron dynamics. Linear measurements show that electron-phonon coupling and polaron formation rates differ significantly between octahedral and tetrahedral centers leading to very different charge carrier recombination rates between the two sub-lattices. Circular measurements show that this difference in recombination rate gives rise to long-lived, spin-aligned charge accumulation at the YIG surface. These findings have important applications towards the development of spin selective photocatalysts as well as new platforms for light-induced control of ultrafast spin polarization at material interfaces.

Imaging Plasmonic Energy Transfer in Individual Nanoparticles and their Assemblies

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Waste heat generation is an unavoidable consequence of work performed across all areas of human activity, including industrial processes, electricity generation, transportation, and information processing. It is estimated that 20 − 50% of commercial energy input is lost to the environment as waste heat; therefore, the ability to reclaim even a fraction of this lost heat represents a major opportunity to improve energy efficiency.

Towards this end, rationally designed infrared (IR) plasmonic and phononic materials offer the potential to harness and direct the flow of energy from thermal sources, but controlling the energetic location of their responses is challenging yet necessary to align with those thermal sources. In this research, we investigate a promising new class of semiconductor materials that offer robust, wavelength-tunable mid-IR plasmonic excitations through introduction or removal of free charge carriers. This spectral tunability lies above and beyond the tunability achieved through the hybridization of multiple material units. Specifically, using energy-monochromated scanning transmission electron microscopy (STEM) electron energy-loss spectroscopy (EELS), we spatially and spectrally map the mid-IR plasmonic excitations of individual indium tin oxide (ITO) nanocrystals as a function of Sn^{4+} composition. Both nanocrystal monomers[1] and dimers are studied,[2] with the latter showing enhanced local fields that are surprisingly comparable to those of the more familiar noble metals in the visible part of the spectrum. With the tunability of their carrier density and enhanced local fields of their hybrid modes, ITO nanocrystals offer a promising new class of materials that we are now coupling to other infrared active materials and thermal heat sources and imaging their interactions via STEM-EELS.

1. Olafsson, A.; Busche, J. A.; Araujo, J. J.; Maitit, A.; Idrobo, J. C.; Gamelin, D. R.; Masiello, D. J.; Camden, J. P., Electron Beam Infrared Nano-Ellipsometry of Individual Indium Tin Oxide Nanocrystals. *Nano Letters*, (2020), 20, 11, 7987-7994. DOI: 10.1021/acs.nanolett.0c02772

2. Olafsson, A.; Khorasani, S.; Busche, J. A.; Araujo, J. J.; Idrobo, J. C.; Gamelin, D. R.; Masiello, D. J.; Camden, J. P., Imaging Infrared Plasmon Hybridization in Doped Semiconductor Nanocrystal Dimers. *J. Phys. Chem. Lett.*, (2021), 12(42), 10270-10276. DOI: 10.1021/acs/jpclett.1c02741

Liquid-Organic hydrogen carrier: A potential family of endothermic fuels

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Liquid-organic hydrogen carriers (LOHC) are a family of cyclic molecules that can undergo dehydrogenation reversibly. LOHCs consisting of nitrogen-containing heterocycles have been reported to show special stability. Here, we examined a member of this family, 1,2,3,4-tetrahydroquinoline (THQ), as a potential endothermic fuel. The conversion and endothermic heats of reaction were measured over a Pd-Al_2O_3 catalyst at 60 bar and temperatures between 500 and 600 °C. Heats of reaction as large as 950 kJ kg^{-1} were obtained; more importantly, the reaction was stable over a period of at least several hours, with no coking, even at 600 °C. For comparison, the reaction of methylcyclohexane formed tars that quickly blocked the reactor, even at 500 °C on this catalyst. These results suggest that LOHCs could serve as alternative fuels for endothermic cooling.

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Dynamics of Protic Ionic Liquid Catalysis

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Abstract

Interest in low-volatility ionic liquids as replacements for hydrazine-based propellants has gained significant traction in recent years. Protic, nitrate anion-based ionic liquids demonstrated improved performance and significantly reduced hazards over legacy hydrazine/iridium monopropulsion systems. In order to apply these ionic liquids to developing propulsion systems, the chemical dynamics of these systems must be better understood. The heterogeneous catalytic dynamics of nitrate ionic liquids is largely overlooked and not well understood, especially with regards to nitrogen mechanisms on catalytic surfaces. Recent developments in probing and understanding the chemical dynamics involved in the heterogeneous catalysis of ionic liquid propellants will be discussed.

Distinguishing Condensed-Phase Cracking Products with the Same Mass-To-Charge Ratio Using a Triple Quadrupole Mass Spectrometer in Product Scan Mode

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High-speed flight applications require the use of aviation fuel as the primary thermal management fluid. One strategy has been the use of heterogeneous catalysis to promote endothermic chemistry at temperatures below the threshold for coke deposition. Given the relationship between reaction enthalpy and fluid density, *in situ* probes of the chemical speciation for fuels at extreme conditions (200-1000 °C and 400-1000 psi) are critical to evaluate the efficacy of these catalysis reactions. In our present work, we use a triple quadrupole mass spectrometer to distinguish between isomeric cracking products formed when alkanes are reacted over a zeolite cracking catalyst. We showcase our technique by identifying different predominant classes of products when the fuel is cracked with *vs.* without the catalyst. These include alkyl chain-substituted aromatics, which are formed at lower temperatures (≈ 500 ºC) associated with catalytic cracking and methyl-substituted aromatics that arise at extreme temperatures (>650 ºC) in the absence of a catalyst. We expect that the structures of these condensed phase products influence reaction enthalpy (*i.e.*, Hess' law), which further motivates the use of online mass spectrometry as an *in situ* diagnostic.

Trapped hole diffusion in semiconductor nanocrystals and related photochemical and photophysical processes

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Semiconductor nanocrystals exhibit remarkable tunability in electronic structure and chemical properties that have led to transformative developments in fundamental science as well as a variety of applications, including, recently, light-driven multi-electron chemistry. One of the persistent and ubiquitous features of excited state dynamics in nanocrystalline materials is the fast and efficient trapping of photoexcited holes to the particle surface. These trapped holes play a pivotal role in electron-hole recombination and light-driven chemistry, so the understanding and control of their dynamics is of critical importance. We recently reported that the trapped photoexcited holes are mobile on surfaces of CdS and CdSe nanocrystals, undergoing random-walk diffusion by hoping between chalcogen sites on the particle surface. We have since endeavored to understand the mechanisms underlying this motion and its impact on light-driven oxidation by nanocrystals.

The poster presentation will focus on our recently published and in-progress work supported by this AFOSR award. Some highlights include: (i) temperature-dependent transient absorption measurements that provide estimates of electronic coupling and reorganization energy for the hole hopping as well as the diffusion constant; (ii) determination of hole-hopping rate constant through a combination of experiments and simulations; (iii) quantification of the competition between hole hopping and photochemical oxidation to elucidate the role of trapped-hole diffusion in light-driven chemistry. Theoretical insights into trapped-hole dynamics will be described in a separate poster presentation by Prof. Joel Eaves.

This poster presentation will also describe our efforts to understand excited state processes in nanocrystals that relate to trapped-hole dynamics and electron-hole dynamics more broadly. We recently discovered a photo-charging process intrinsic to a variety of CdS nanocrystals that generates long-lived electrons and enables efficient photo-reduction reactions. We have also developed analysis methods that simultaneously extract the transient absorption spectra and the kinetics that accompany relaxation of multiexciton states in nanocrystals, which revealed that some commonly-used assumptions about multiexciton relaxation are incorrect. In particular, our work enables accurate quantification of multi-exciton generation, which is an important mechanism for solar-energy conversion in nanocrystals.

Publications from the last 3 years supported by this award:

1. K. E. Shulenberger, H. R. Keller, L. M. Pellows, N. L. Brown, G. Dukovic. "Photocharging of Colloidal CdS Nanocrystals." *Journal of Physical Chemistry C*, **2021**, *125,* 22650-22659.
2. J. K. Utterback, R. P. Cline, K. E. Shulenberger, J. D. Eaves, G. Dukovic. "The Motion of Trapped Holes on Nanocrystal Surfaces." *J. Phys. Chem. Lett.*, **2020**, *11* (22), 9876-9885.
3. Cline, R. P. and Eaves, J. D. “Surface-Trapped Hole Diffusion in CdS and CdSe: The Superexchange Mechanism*”* *J. Phys. Chem. C*, *124*(51), 28244-28251. (**2020**)
4. T. Labrador, G. Dukovic. "Simultaneous Determination of Spectral Signatures and Decay Kinetics of Excited State Species in Semiconductor Nanocrystals Probed by Transient Absorption Spectroscopy." *Journal of Physical Chemistry C*, **2020**, *124*, 8439-8447.
5. J. K. Utterback, J. L. Ruzicka, H. Hamby, J. D. Eaves, G. Dukovic. "Temperature-Dependent Transient Absorption Spectroscopy Elucidates Trapped-Hole Dynamics in CdS and CdSe Nanorods." *J. Phys. Chem. Lett.*, **2019**, *10*, 2782−2787.

The superexchange mechanism and large reorganization energy for hole hopping in nanocrystals

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Through a combination of theory and experiment, we discovered that, in Cd-chalcogenide nanoparticles, photogenerated holes readily trap to the surfaces, where they form small polarons and hop from site to site via phonon-assisted tunneling.[1–4] The small hole-hopping can be a limiting factor in redox chemical reactions that take place in these nanocrystals. With AFOSR support, we have recently shown that by calculating the superexchange mechanism from microscopic electronic structure calculations, using localization and Green's function methods, tunneling amplitudes compare with those measured in temperature-dependent transient absorption spectra quantitatively.[5,6] But the hopping rate depends on both the tunneling matrix element and the nuclear dynamics, which, judging by the large reorganization energy at high temperatures, bottleneck the hole mobility. I will show recent results from nonequilibrium molecular dynamics simulations that are consistent with the large reorganization energy measured experimentally by our collaborator, Gordana Dukovic. These calculations shed light on why the reorganization energy is so large, but also intimate that the phonon dynamics contain both fast and slow components; complications that the conventional high-temperature approximation of the Marcus theory is unable to capture.

References

1. Utterback, J. K. *et al.* Observation of trapped-hole diffusion on the surfaces of CdS nanorods. *Nature Chemistry* 8, 1061–1066 (2016).

2. Cline, R. P., Utterback, J. K., Strong, S. E., Dukovic, G. & Eaves, J. D. On the Nature of Trapped-Hole States in CdS Nanocrystals and the Mechanism of Their Diffusion. *Journal of Physical Chemistry Letters* 9, 3532–3537 (2018).

3. Utterback, J. K., Cline, R. P., Shulenberger, K. E., Eaves, J. D. & Dukovic, G. The Motion of Trapped Holes on Nanocrystal Surfaces. *J Phys Chem Lett* 11, 9876–9885 (2020).

4. Utterback, J. K., Hamby, H., Pearce, O. M., Eaves, J. D. & Dukovic, G. Trapped-Hole Diffusion in Photoexcited CdSe Nanorods. *Journal of Physical Chemistry C* 122, 16974–16982 (2018).

5. Cline, R. P. & Eaves, J. D. Surface-Trapped Hole Diffusion in CdS and CdSe: The Superexchange Mechanism. *J Phys Chem C* 124, 28244–28251 (2020).

6. Utterback, J. K., Ruzicka, J. L., Hamby, H., Eaves, J. D. & Dukovic, G. Temperature-Dependent Transient Absorption Spectroscopy Elucidates Trapped-Hole Dynamics in CdS and CdSe Nanorods. *The Journal of Physical Chemistry Letters* 10, 2782–2787 (2019).

To correctly model propellant degradation over long periods of time, chemical insight is required. Quantum chemical methods are a great tool to accurately model the chemical behavior of systems. In the current work, quantum chemical methods are applied to model the chemical degradation of hydroxyl terminated poly butadiene (HTPBD), a common solid propellant. The study uses a combination of bonding analysis methodologies to predict the weakest, most prone to break bonds with composite method to obtain accurate thermodynamical quantities, such as the heat of formation. Sample degradation pathways are presented and heats of formation for all the quantities are obtained with near experimental accuracy.

Spectroscopy of Metal Oxide Space Clouds

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Natural variations of the electron density within high-altitude regions of the atmosphere (≥70 km) significantly impact the propagation of radio waves with effects that are frequency dependent. When uncontrolled, these signal modifications are detrimental to communications, targeting and GPS systems. The artificial release of electrons at high altitudes is being investigated as a means to reduce the electron density fluctuations. The chemi-ionization reactions $Sm+O \rightarrow SmO^+ + e^-$ and $Nd+O \rightarrow NdO^+ + e^-$ are being evaluated as sources of free electrons. Sounding rocket experiments, where Sm or Nd are vaporized by means of thermite reactions, have yielded spectra that have been tentatively assigned to the metal oxides and the metal oxide ions. The interpretation of these data has been hampered by the limited spectroscopic data available for the neutral molecules, and the absence of electronic spectra that can be reliably assigned to the molecular ions.

We are currently using laser excitation and dispersed fluorescence measurements to map and assign the prominent band systems of SmO and NdO that have been observed in the sounding rocket experiments. For example, the most prominent emission band of the Sm release experiment is unambiguously assigned as the SmO $[15.35]1\text{-}X0^-$ 0-0 transition with molecular constants determined from measurements made at a resolution of 40 MHz. Pulsed UV excitation is being used to simulate the emission bands generated by solar excitation, and generate molecular ions by means of photoionization. Recent progress will be presented.

Exact Generalization of Einstein's Absorption-Emission Relations

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Einstein's relationships between absorption, stimulated emission, and spontaneous emission conflict with the time-energy uncertainty principle by ascribing a finite radiative lifetime to the upper state of an infinitely narrow spectroscopic line. Since all quantum energy levels are broadened, this raises the question of whether an exact generalization to transitions with a broadened lineshape exists. In this poster, we generalize Einstein's relationships in a way that is compatible with the time-energy uncertainty principle, detailed balance, and causality.

We introduce Einstein coefficient spectra and derive relationships between them for transitions between broadened levels or bands. The frequency integral of an Einstein coefficient spectrum gives the corresponding Einstein coefficient. For each band, a thermodynamic state function, the standard free energy, replaces both the energy and the degeneracy of a quantum level. For transitions between two bands, four Einstein coefficient spectra replace the three Einstein coefficients. For each pair of bands, a single underlying lineshape generates four different Einstein coefficient lineshapes. These new generalized Einstein relations between Einstein coefficient spectra are universally valid at thermodynamic equilibrium. For radiatively broadened transitions in vacuum, the integrated Einstein coefficients approach Einstein's relationships asymptotically in the narrow line limit.

Applications are numerous. These relations can replace the approximate Forster cycle for photoacidity by an exact thermodynamic cycle. The measurement of excited state free energies under different conditions provides access to all the thermodynamic properties of excited states - for example, entropy can be measured by changing temperature. The equilibrium generalized Einstein relations have powerful applications to non-equilibrium emission, including measurement of heterogeneity, non-equilibrium free energies and non-equilibrium entropies.

Ionic Hydrogen bonds and intermolecular interactions in Ethylammonium nitrate and 1-Amino-1,2,3-triazole

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The hydrogen bonds and intermolecular interaction energies of ethylammonium nitrate (EAN) and 1-Amino-1,2,3-triazole (1-AT) based deep eutectic propellant (DeEP) are examined. 1-AT was introduced as a neutral hydrogen bond donor to EAN in order to form a eutectic mixture. The effective fragment potential (EFP) is used to examine the bonding interactions of EAN:1-AT eutectic mixtures. The EFP method predicts that there are significant polarization and charge transfer effects in the complexes, along with Coulombic, dispersion and repulsion interactions.

The quasi-atomic orbital (QUAO) bonding analysis and kinetic bond order (KBO) analyses are used to develop an understanding of the DeEP hydrogen bonding interactions as a function of the size of the system; hydrogen bonding interactions are examined by systematically increasing the number 1-AT molecules to EAN monomer ion pair. The significance of orbital interactions was analyzed based on the QUAOs and the relative strength of hydrogen bonds is numerically analyzed by KBOs. QUAO and KBO analysis suggest that the hydrogen bonds in EAN:1-AT eutectic mixtures follow the characteristic three-center four electron interactions.

In general, the strength of the hydrogen bonds decreased as more 1-AT molecules are introduced into EAN monomer. The strongest hydrogen bond interactions in EAN:$(1\text{-AT})_n$ (n=1-5) are formed between ethylammonium cation and nitrate anion (Average KBO=-3.44kcal/mol) but the weakest hydrogen bond interaction occurs between nitrate anion ($[NO3]^-$) and 1-AT (Average KBO=-1.21kcal/mol). The QUAO bonding analysis also suggests that 1-AT acts as both hydrogen bond donor and hydrogen bond acceptor simultaneously. Although KBO of hydrogen bonding interactions in 1) $[NO3]^-$ and 1-AT, 2) between two 1-AT molecules are weaker than the ionic hydrogen bonds in EAN, the weak hydrogen bonding networks with 1-AT (e.g. $[NO3]^-$:1-AT and 1-AT:1-AT interactions) are important to form a stable DeEP.

Electron Thermalization in Metals

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Transient spectroscopy provides the ability to observe the fundamental processes that bring an out of equilibrium material back to its original, equilibrium state. Attosecond transient extreme ultraviolet light (XUV) absorption spectroscopy has the unique ability to observe element specific changes within a material on the attosecond timescale. Here, attosecond XUV transient absorption spectroscopy is used to provide insight into electron-electron scattering in metals, which is the fastest relaxation dynamics that occur in this material type. The results show a strong correlation between initial carrier thermalization and the structure of the interrogated metal's density of states above the Fermi level.

A few-femtosecond, 480 nm – 920 nm optical laser pulse excites electrons from just below the Fermi level to unoccupied states above the Fermi level. Initially the electrons are in a highly non-equilibrium, nascent, distribution that resembles the intensity profile of the optical pump weighted by the wavelength-dependent absorption cross section of the metal. This nascent distribution transitions to a hot Fermi-Dirac distribution within the first few femtoseconds via electron-electron scattering. Fe and Pt, two metals with significantly different structures in their respective densities of states above the Fermi level, were selected to study the effect of that structure on electron-electron thermalization. With attosecond transient XUV absorption studies, the initial electron thermalization times after deconvolution for the instrument response time were measured to be 15 ± 3 fs and 2.7 ± 2.0 fs for Pt and Fe, respectively.

The dramatic difference in electron thermalization times can be understood by considering the density of states for these two metals. For Pt there is a significant density of both *s*-orbitals and *d*-orbitals available for the excited electrons to occupy. In contrast to this, Fe has predominantly *d*-orbitals available above the Fermi level. When the pump excited electrons occupy orbitals of the same character, which is the case for Fe and not Pt, electron-electron interactions are enhanced, and consequently, electron thermalization occurs much more rapidly.

The enhanced electron-electron interactions arising from the electrons being in the same orbital type is called the local field effect (LFE). Because the LFE arises from the distribution of unoccupied states available for optically excited electrons to access, the strength of the LFE can be predicted by considering these densities of states. Metals that have a variety of orbitals available above the Fermi level, like Pt, will have a relatively weak LFE and therefore a longer electron thermalization time. Conversely, metals with a single orbital type above the Fermi level, like Fe, will have a strong LFE and accordingly a fast electron thermalization time. This link provides a fundamental prediction for electron thermalization rates in metals.

The elemental sensitivity of XUV transient absorption spectroscopy provides a direct insight into the electron thermalization. Along with this, the excellent time resolution enables the measurement of the electron thermalization time within the first few femtoseconds of optical excitation, which is crucial for observing these very fast dynamics. Through the measurement of electron thermalization in metals, the powerful capabilities of attosecond transient XUV absorption spectroscopy are evidenced.

Modeling Molecular Polaritons with Semiclassical Nuclear-Electronic Orbital Dynamics

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Molecular polaritons have become an emerging platform for remotely controlling molecular properties through strong light-matter interactions. During the past several years, many different theoretical approaches have been developed in an effort to model molecular polaritons, including advanced analytic models, multiscale molecular dynamics, and quantum-electrodynamical electronic structure theory. Recently we developed a semiclassical approach [1] for efficiently describing molecular polaritons by self-consistently propagating the real-time dynamics of classical cavity modes and a quantum molecular subsystem described by the nuclear-electronic orbital (NEO) method, where electrons and specified nuclei are treated quantum mechanically on the same level by real-time time-dependent density functional theory (RT-TDDFT). With the computational cost similar to conventional RT-TDDFT, our semiclassical RT-NEO-TDDFT approach provides a unified description of electronic and vibrational strong couplings and describes the impact of the cavity on coupled nuclear-electronic dynamics while including nuclear quantum effects. For example, for a single o-hydroxybenzaldehyde molecule under electronic strong coupling, this approach shows that the cavity suppression of excited state intramolecular proton transfer is influenced not only by the polaritonic potential energy surface but also by the time scale of the chemical reaction. Looking forward, future work is needed for exploring collective strong coupling in nuclear-electronic quantum dynamical systems.

1. Li, T. E., Tao, Z. & Hammes-Schiffer, S. Semiclassical Real-Time Nuclear-Electronic Orbital Dynamics for Molecular Polaritons: Unified Theory of Electronic and Vibrational Strong Couplings. *J. Chem. Theory Comput*. (2022). doi:10.1021/acs.jctc.2c00096

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QM/MM Advancements for Computational Electrochemistry: Predicting Absolute Redox Potentials in Strongly Associating Electrolytes.

A major challenge for electrochemistry of non-aqueous electrolytes is the significant uncertainty associated with extrapolating experimental measurements to a common reference electrode scale (e.g. S.H.E.). These uncertainties arise from uncontrollable liquid-junction potentials, which become increasingly problematic for concentrated electrolytes with highly non-ideal activities. High accuracy, first-principles calculations of absolute redox potentials would importantly allow extrapolation to a common electrode scale with reduced error. Towards this goal, we have developed a novel QM/MM method and software implementation that incorporates exact long-range electrostatics utilizing direct particle mesh Ewald integration. We present an analysis of the importance of long-range electrostatics for accurately predicting redox potentials from first-principles. We then present a case-study in which we compute absolute redox potentials of Ferrocene in highly concentrated ionic liquid based electrolytes. These electrolytes are highly associating, and ion pairing effects contribute substantially to the thermodynamic redox potentials. Overall, our results show that computational electrochemistry methods must go beyond implicit solvent models for predictive accuracy, as well as correct physical insight.

The field of catalysis represents one of the most prominent examples of how fundamental science positively impacts society. Catalysis is generally concerned with the behavior of bulk materials, but the underlying chemistry remains a molecular-scale phenomenon. One of the primary goals of physical chemistry is to gain a molecular-level understanding of the catalytic sites where chemical reactions take place and to ascertain how catalysts lower the energies of transition states in these reactions. As these sites typically consist of small groups of atoms, gas phase molecular and ionic clusters serve as tractable model systems for probing the underlying factors which give rise to catalytic behavior. To this end, we carry out complementary spectroscopic measurements on bare and complexed metal oxide clusters using two techniques: slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI) and infrared photodissociation (IRPD) of cold cations and anions. Recent examples of both types of measurements will be presented. In addition, a tunable infrared laser has been incorporated into the cryo-SEVI experiment, enabling high resolution photoelectron spectroscopy of vibrationally excited anions. Results for OH^- and $C_2H_3O^-$ (vinoxide) will be shown. The vinoxide results show evidence for intramolecular vibrational redistribution (IVR) as the IR excitation energy is increased. This new method holds considerable promise for future studies of metal oxides and next generation transition state spectroscopy experiments.

Calculation of the optical properties of colloidal nanostructures across material scales

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In aiming to develop materials that exhibit large optical nonlinearities, we discuss one- and two-photon absorption (OPA, TPA) spectra of CdS and CdSe 2D nanoplatelets (NPLs), which are grown from atomically precise semiconductor nanoclusters, and have recently demonstrated large TPA cross-sections. To enable improved accuracy in modeling the large material systems, initial structures were obtained using our recently developed deep neural network potential, and low-energy geometries were optimized by density functional theory (DFT). Linear- and nonlinear-response calculations were performed using time-dependent DFT (TDDFT), and to enable handling larger systems the simplified Tamm-Dancoff approximation (sTDA) was benchmarked. We found good agreement between observed and calculated TDDFT and sTDA linear spectra for 2- and 3-layer NPLs, and that the TPA for the CdE (E = S, Se) NPLs is dominated by dark states. Effects of ligands on low-energy OPA bands were found to be small for NPL structures with extended lateral dimensions, while the red-shift for the 3- vs. 2-layer NPLs can be attributed to electron delocalization in the lateral and vertical directions. Furthermore, we assess the utility of phosphine-ligated gold clusters for TPA application, specifically $Au_9(PR_3)_8^{3+}$ and $Au_8(PR_3)_7^{2+}$. OPA of $Au_9(PR_3)_8^{3+}$ and $Au_8(PR_3)_7^{2+}$ were calculated using TDDFT and the many-body GW-BSE (G-Green's function, and W-screened Coulomb interaction)-BSE (Bethe Salpeter Equation) method compared to experimental measurements. Results with the GW-BSE method at the evGW level demonstrated good agreement with the experimental data, comparable to the best TDDFT results, but with less dependence on the reference exchange-correlation functional. The TPA cross-sections were found to be larger for $Au_9(PR_3)_8^{3+}$ than $Au_8(PR_3)_7^{2+}$.

Modeling Correlated Catalysts Using Machine Learning-Accelerated Quantum Monte Carlo

Brenda M. Rubenstein, Edgar Landinez-Borda, Cancan Huang, and Gopal Iyer

The accurate prediction of reaction mechanisms in heterogeneous (surface) catalysis is one of the central challenges in computational chemistry. To date, the majority of such modeling has been performed using Density Functional Theory (DFT). While DFT predicts reasonable binding energies and reaction pathways for many materials and surface reactions, it can be highly unreliable for predicting the properties of correlated materials and the reactions they catalyze. One suite of methods that are increasingly being recognized as higher-accuracy, albeit more computationally expensive, alternatives to DFT for modeling catalytic systems are Quantum Monte Carlo (QMC) methods.

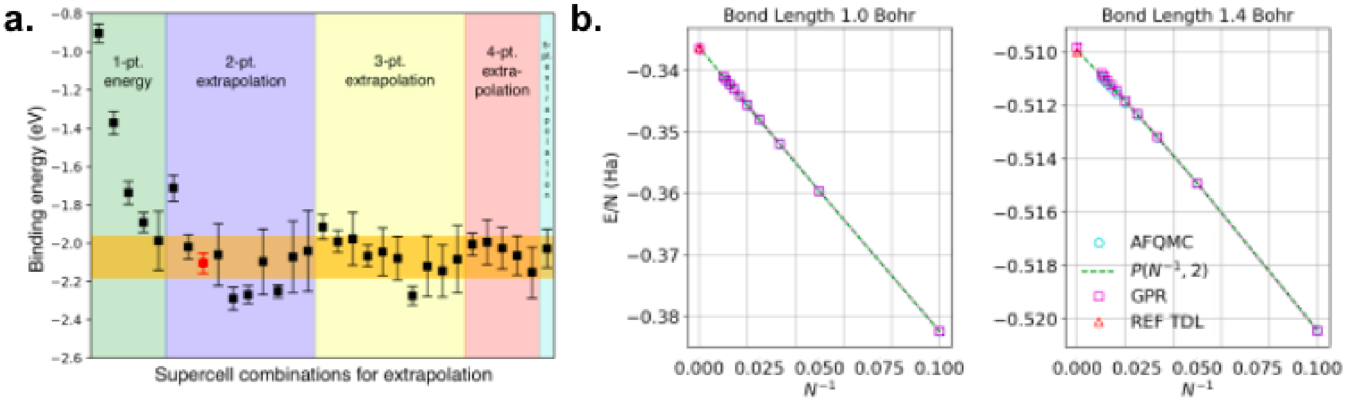

Figure 1: a. DMC binding energies of CO on a Pt(111) surface in the thermodynamic limit predicted using different supercell sizes and combinations for extrapolation. **b.** Finite size extrapolation of the energy per atom of a hydrogen chain using Gaussian Process Regression trained on AFQMC energies.

In this poster, we present our recent advances modeling heterogeneous catalysis using QMC simulations and how we have accelerated these calculations to the point of practicality using machine learning techniques (see Figure 1). In particular, we show that it is possible to significantly reduce the computational cost of QMC for catalysis by leveraging the cancellation of many-body finite-size errors that accompanies the evaluation of energy differences when calculating quantities like adsorption (binding) energies and mapping potential energy surfaces. We analyze the cancellation and convergence of many-body finite-size errors in two well-known adsorbate/slab systems, H_2O/LiH(001) and CO/Pt(111). Based on this analysis, we identify strategies for obtaining binding energies in the thermodynamic limit that optimally utilize error cancellation to balance accuracy and computational efficiency. We also illustrate how machine learning techniques such as Gaussian Process Regression (GPR) can be used to more efficiently extrapolate to the thermodynamic limit and techniques such as Behler-Parinello Neural Networks can be employed to accelerate surface diffusion calculations. Altogether, this collection of advances paves the way for realizing computationally practical correlated simulations of heterogeneous catalysts.

Ultrafast Dynamics of Strongly Correlated Metal Oxide Clusters

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Abstract:

A local rearrangement of 3d-electrons plays a crucial role in many properties of correlated transition metal oxide materials and supplies important information on their reactivity and magnetic interactions. Point defects, such as oxygen vacancies and their associated electrons, can lead to emergent phenomena that influence the lifetime of photoexcited states and therefore influence chemical reactivity. The ultrafast electronic relaxation dynamics of neutral metal oxide clusters were investigated with femtosecond pump-probe spectroscopy and supported by theoretical calculations to show that their excited state lifetimes are strongly dependent on the nature of the electronic transition.[1–4] We employ the atomic precision and tunability of gas phase clusters to stress that changes to the character of the orbital of the photoexcited electron leads to vastly different relaxation dynamics. I will present our recent work on sub-nanometer clusters, where absorption of a UV (400 nm) photon initiates several relaxation processes. The simple picture of sequential oxidation of metal atoms reveals a linear tunability to the contributions of each relaxation component to the total transient signal. In particular, in chromium oxides a ~30 fs transient signal fraction grows linearly with oxidation, matching the amount of O to Cr charge transfer character of the photoexcitation and highlighting a gradual transition between semiconducting and metallic behavior at the molecular level. We reveal that half-metal behavior (uniquely associated with bulk CrO2) is achieved at the molecular level and for all (sub)-nanometer clusters examined, thereby opening possibilities for the design of new molecular spintronic materials. In contrast, the photoexcited lifetimes of nickel oxide exhibit a unique reliance on the nature of the atomic orbital contributions, providing new insights to the analogous band edge excitation dynamics of strongly correlated bulk-scale NiO material. Short lived dynamics in stoichiometric $(NiO)_n$ clusters are attributed to excitation between Ni-3d and Ni-4s orbitals, where their strong exchange coupling produces metallic-like electron-electron scattering. Oxygen vacancies introduce 3d→4p transitions, which increases the lifetimes of the sub-picosecond transient by 20-60% and enables the formation of long-lived (lifetimes > 2.5 ps) states.

(1) Garcia, J. M.; Heald, L. F.; Shaffer, R. E.; Sayres, S. G. Oscillation in Excited State Lifetimes with Size of Sub-Nanometer Neutral $(TiO_2)_N$ Clusters Observed with Ultrafast Pump-Probe Spectroscopy. *J. Phys. Chem. Lett.* **2021**, *12* (16), 4098–4103.
(2) Garcia, J. M.; Sayres, S. G. Increased Excited State Metallicity in Neutral Cr_2O_n Clusters ($N < 5$). *J. Am. Chem. Soc.* **2021**, *143* (38), 15572–15575.
(3) Garcia, J. M.; Sayres, S. G. Orbital-Dependent Photodynamics of Strongly Correlated Nickel Oxide Clusters. *Phys. Chem. Chem. Phys.* **2022**, *24*, 5590–5597.
(4) Garcia, J. M.; Sayres, S. G. Tuning the Photodynamics of Sub-Nanometer Neutral Chromium Oxide Clusters Through Sequential Oxidation. *Nanoscale* **2022**, DOI: 10.1039/D2NR00464J.

From deep eutectic solvents to sustainable propellants

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Abstract

Deep Eutectic solvents (DES) are a versatile concept which can be tailored to more than just the originally indicated application. We are investigating the potential for deep eutectic propellants (DeEP) utilizing the DES concept relevant to space application. DeEP, in contrast to “classical” ILs, could fulfill multiple principles of green chemistry, especially less hazardous chemical syntheses, safer solvents and auxiliaries, prevention of waste, design for energy efficiency, and atom economy. There is a strong interest for low cost systems and sustainability of propellants which entails the cost and availability of starting materials, the total energy consumption making the propellant, as well as minimizing the resulting waste stream. In the past all propellant work was almost exclusively performance driven but some performance can now be traded for lower cost and especially if multimode operations are enabled. Multimode systems allow for maximum mission adaptability and flexibility since they do not require pre-allocation of propellant to a specific mode of operation which poses a major advantage for space operations.

In a first example we present the formation of a DeEP derived from a solvated ionic liquid (SIL) and demonstrate its potential as a hypergolic bipropellant in combination with H_2O_2. All rocket oxidizers are hazardous by their very nature, and so reduction of those hazards, even though the resulting materials might not be completely harmless, is at the heart of green initiatives in propulsion. Apart from cryogens, hydrogen peroxide seems to be especially promising because of its high performance, lower-toxic vapor and corrosivity, and its environmentally benign decomposition products.

A Combined Experimental and Theoretical Investigation on the Fundamental Reaction Mechanisms of Cyanoborohydride Hypergolic Ionic Liquids with Key Oxidizers

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Hypergolic bipropellants (HPs) are combinations of a fuel and an oxidizer that spontaneously ignite upon contact with each other and have been utilized as fuels of space vehicles such as satellites and rockets. Since first synthesis in 2008, hypergolic ionic liquids (HILs) have attracted attention as candidate HPs but there is currently an incomplete understanding of the elementary steps involved in the ignition and oxidation of HILs. In this study, we explore experimentally and computationally the fundamental mechanisms involved in the oxidation of prototype cyanoborohydride HILs, namely $EMIM^+/CBH^-$, with HNO_3 (Figure 1).

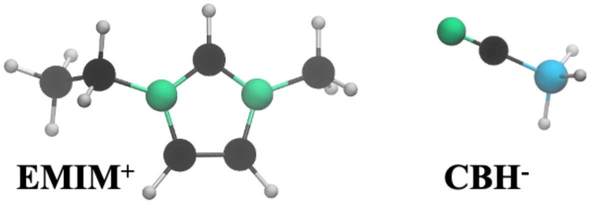

Figure 1. Structures of EMIM cation (1-ethyl-3-methylimidazolium) and CBH anion (cyanoborohydride).

Here we report the results from chirped pulse induced merging of droplets of $EMIM^+/CBH^-$ and droplets of nitric acid (HNO_3) at concentrations of 10, 20, 30, 50, and 70 % under container-less conditions in an argon inert atmosphere at initially 300 K in an ultrasonic levitator. Reaction mechanisms are unraveled in real time via a complementary array of spectroscopic techniques (FTIR, Raman) and optical/IR cameras. FTIR spectroscopy and kinetic traces of the gas-phase products identified two primary decomposition species (hydrogen cyanide, HCN; nitrous oxide, N_2O), whereas nitrogen dioxide (NO_2) and nitrogen monoxide (NO) represent higher order products. The temporal evolution of the Raman spectra exposed an initial degradation of the CBH anion. *Ab initio* molecular dynamics simulations took into account of various species in the reaction systems and bimolecular collision between different species revealed that most of the collisions are non-reactive, except for those involving CBH anion and protonated CBH. Simulations initiated from various intermediates revealed the processes that lead to the formation of gas-phase products identified in the experiments. Both the experiment and computation converge that the CBH anion is largely responsible for hypergolic behavior, and the role of the EMIM cation needs be future explored.

Metal Cation-Ozone Reactions: O_3 as an Oxidizing Agent, a Reducing Agent, and an Ionospherically Relevant Species

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Metal oxide formation is a key step in numerous metal catalyzed reactions and ozone is one of the simplest and strongest oxidants, capable of oxidizing most metals. Reactions between ozone and meteoric metals play a role in ionospheric chemistry, including phenomena such as "Sporadic E", which affects radio wave propagation. Oxidation of lanthanides is of great interest to the Air Force due to the ability of several lanthanides to chemi-ionize (i.e. $Ln + O \rightarrow LnO^+ + e^-$). AFRL's selected-ion flow tube (VISTA-SIFT) was used to measure rate constants and product branching. Sm and Nd are found to react collisionally with O_3, with the oxidation of Sm^+ producing large amounts of excited SmO^{+*} with $E > 1.5$ eV excess energy. More broadly, MO_n^+ produces both MO_{n-1}^+ and MO_{n+1}^+ products when energetically accessible, with the reduction proceeding sequentially by oxidizing MO_n^+ then dissociating to the reduced M^+ and O_2. Future work will explore additional metal systems.

Ligand reorganization and spin-state selectivity in transition metal photochemistry

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Catalyst development and optimization requires detailed understanding of transition states and reactive intermediates. In many transition metal catalysts, electron transfer to/from the metal occurs alongside large geometrical changes. This large molecular reorganization represents a barrier to the reaction, but is difficult to study via traditional steady-state techniques. In particular, we were inspired by a collaboration between the Hammes-Schiffer and Rauchfuss groups which suggested that oxidation of a $Ni^{I}Fe^{I}$ state in [NiFe] hydrogenases occurs through a short-lived $Ni^{I}Fe^{II}$ species. The Ni^{I} is most stable in a tetrahedral geometry, while Ni^{II} is square planar, so brief oxidation of the Fe reduces the barrier to electron transfer onto the catalyst. To test this hypothesis, we synthesized a chromophore-catalyst dyad in which photoinduced electron transfer serves as a “starting pistol” for the catalyst oxidation. Optical transient absorption reveals formation of the oxidized NiFe state in 2 ps, as evidenced by reduction of the chromophore. Part of this population decays in tens of ps, but a significant fraction remains for hundreds of ps. This biphasic decay suggests that rapid back-electron transfer is possible from the Fe-oxidized state but that geometric relaxation to the Ni-oxidized state traps the catalyst in the square planar geometry.

In a separate project, we have begun to investigate the phenomenon of chiral-induced spin selectivity in well-defined molecular complexes. Previous studies of this spin-filtering effect have predominantly focused on electron transport through self-assembled monolayers either via photoelectron spectroscopy or bulk conductance measurements. We take inspiration from the field of electron transfer chemistry, in which rules such as Marcus Theory were solidified using photoinduced electron transfer through well-defined donor-acceptor molecules. We have synthesized ferrocene-cobaltocenium dimers and used transient absorption spectroscopy to measure ultrafast back-electron transfer to a local quintet state after metal-to-metal charge transfer excitation. Planned experiments will use XUV circular dichroism, made possible by a DURIP grant, to measure the spin polarization of the initial MMCT state after optical electron transfer through the chiral bridge.

Explaining plasmon-activated ammonia and hydrogen decomposition on Pd and Fe-decorated Al nanoparticles via first-principles atomic-scale simulations

Xuelan Wen, J. Mark P. Martirez, and Emily A. Carter

Abstract

Ammonia decomposition is an important reaction that could enable liquid ammonia to serve as a hydrogen fuel carrier. However, this reaction must be carried out at an elevated temperature to achieve high conversion rates. Antenna-reactor nanoparticle complexes can convert light energy to chemical energy and potentially serve as efficient plasmonic photocatalysts. In this work, we simulate the ammonia-deuterium exchange reaction ($NH_3+D_2 \rightarrow NH_2D + HD$) recently studied experimentally on Al-Pd-Fe trimer nanoparticles by the Halas group (Rice University), in order to reveal the roles of Pd and Fe "reactors" and Al "antennae" in the plasmon-assisted dissociation of NH_3 and H_2. We examine the synergistic effect of Pd and Fe reactors using density functional theory (DFT), as well as the effect of the forced plasmon on Pd reactors using embedded correlated wavefunction (ECW) theory. We find that deuterium spillover from Pd to clean up the *N/*NH-poisoned Fe surface and plasmon-mediated excited states on Pd are crucial for ammonia decomposition and deuterium/hydrogen exchange to proceed.

Probing the Voltage Dependent Water Structure and Dynamics at an Electrode Interface with Surface Enhanced 2DIR

Electric field plays a vital role in modulating structure and reactivity in electrochemical systems. For example, recent study has found that the water reorientation under applied electric field, which points the OH group at the negatively charged electrode, facilitates the reduction of hydrogen. The voltage dependency of the structure and dynamics of hydrogen bonding network at electrode interfaces can provide insight into how electrochemical reaction is tuned by the applied potential. To probe the interfacial spectrum and dynamics, we developed an IR-transparent, conductive, electrochemically stable, and plasmonically active multi-layer thin film on CaF_2 substrate. Such device allows us to obtain surface enhanced 2DIR spectrum with applied electric field, free of Fano-lineshape distortion. To obtain information about the interfacial electric field as well as the hydrogen bond environment, a monolayer of CN probe molecules (4-mercaptoenzonitrile) was tethered onto the plasmonically active gold surface. And 2DIR spectrum were obtained at various voltages and waiting times in different concentration salt solutions. It was observed that negatively charged interface accelerates the H-bond dynamics near the CN probe in different concentration and various salt solutions. Two timescales were observed for spectral diffusion: the fast timescale is around 500-800 fs which probes the H-bond environment change due to water reorientation in the first second hydration shell of the CN group, these dynamics slow down with applied negative voltage at the interface. In contrary, the slow timescale corresponds to breaking and forming of H-bond with the CN group itself is slower than 10 ps and speeds up with negative voltage. Molecular dynamics simulations are underway to decode the cause for the acceleration in dynamics. We are also working on using this technique to study the effect of electric field on membrane protein such as voltage gated ion channels.

Molecular Imaging, Spectroscopy, and Simulations of Ionic Liquids at Electrified Interfaces

Yingjie Zhang, University of Illinois at Urbana-Champaign

The interconversion between chemical energy and electricity relies critically on electrode-electrolyte interfaces, which consists of the electrode surface regions and the solvation layers, also called the electric double layers (EDLs). While the electrode morphology and composition have been extensively studied using in-situ characterization techniques, to date the structure of EDLs remains largely elusive. I will discuss our recent efforts on multi-modal characterization of electrode-electrolyte interfaces at the molecular level. In particular, we have developed a novel technique, electrochemical three-dimensional atomic force microscopy (EC-3D-AFM), to directly image both the electrode surface and EDLs with atomic-scale resolution. We also use surface-sensitive Raman spectroscopy to probe the chemical bonding states of these interfaces. In addition, through collaborative efforts, we use molecular dynamics simulations to complement the experimental data.

We have studied the EDL structure of ionic liquids on both crystalline and heterogeneous electrode surfaces. On flat surfaces, ionic liquids form multiple discrete layers, as a result of the strong Coulomb interaction among the ionic species. When electric potential is applied, the EDL reconfigures its structure as expected, but with changes occurring mainly in the first layer. In this innermost layer, ions change their location and orientation while remaining paired/associated with counter ions at different potentials. In contrast, at the heterogeneous step edge sites, the EDL becomes mostly diffuse, with more random spatial distribution and orientation. Implications on both the fundamental EDL theory and practical energy conversion/storage applications will be discussed.