

## Probing Spin Polarized Electron Dynamics at Photocatalytic Interfaces Using Circularly Polarized XUV Light

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This talk describes the recent ability to directly observe spin-polarized electron transport at semiconductor surfaces using XUV Magnetic Circular Dichroism (XUV-MCD). The ability to produce spin polarized currents at interfaces underlies many applications ranging from information processing to enantioselective photocatalysis; however, designing materials to support these applications requires an improved understanding of spin-dependent electron dynamics at interfaces. Towards this goal, XUV-MCD reflection-absorption spectroscopy provides direct observation of spin dynamics with ultrafast time resolution and surface sensitivity. Using this technique, we perform a detailed spectroscopic investigation of the spin dependent electron dynamics in yttrium iron garnet ( $\text{Y}_3\text{Fe}_5\text{O}_{12}$ , YIG) that give rise to efficient, spin selective photocatalysis.

YIG is a ferrimagnetic semiconductor, consisting of two sub-lattices based on octahedrally and tetrahedrally coordinated Fe(III) centers. Despite the similar electronic structures of YIG and hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), YIG significantly outperforms hematite as a water oxidation catalyst, displaying nearly an order of magnitude increase in photocurrent density and a factor of two increase in Faradaic efficiency for  $\text{H}_2\text{O}$  over  $\text{H}_2\text{O}_2$ . Probing the charge and spin dynamics by surface sensitive XUV spectroscopy reveals that the enhanced performance arises from 1) reduced polaron formation in YIG compared to hematite and 2) intrinsic spin polarization of catalytic photocurrents in YIG.

Ultrafast measurements using linearly polarized XUV light show a 70% reduction in the formation of surface electron polarons in YIG compared to hematite due to site-dependent electron-phonon coupling. Circularly polarized XUV-MCD measurements show that spin-aligned holes accumulate in the hybridized O 2p / Fe 3d valence band giving rise to spin-polarized Fe(IV) redox-active states in the octahedral sublattice of YIG. These long-lived, spin aligned holes improve the selectivity of water oxidation to  $\text{O}_2$  by favoring the triplet reaction pathway over the single pathway to produce  $\text{H}_2\text{O}_2$ . Together, these results provide a detailed understanding of enhanced water splitting efficiency using a spin-selective photocatalyst and open the door for probing the effects of spin-polarized currents in systems ranging from magnetic oxides to chiral matter.

D. Kwabena Bediako  
*University of California, Berkeley*

### **Magnetic and charge order in transition metal dichalcogenide heterostructures**

Next-generation electronic devices will exploit correlated electronic phenomena in quantum materials to encode information for ultra-fast, ultralow-power, and non-volatile storage and retrieval. Spin–spin correlations in exotic magnetic materials are one basis for this new paradigm of compact, energy-efficient electronic systems, but these will require a nanoscale control over long-range magnetic ordering. Conceptually, this may be realized by designing materials that are inherently two-dimensional in their atomic connectivity, or by harnessing nanoscale, non-collinear spin textures in three-dimensional crystals. Likewise, electronic correlations that produce complex charge order can be manipulated to exhibit multi-state resistance phenomena, analogous to phase change materials, but without fatigue.

This talk will describe how transition metal dichalcogenides (TMDs) intercalated with open-shell transition metals represent a family of materials allowing fine control over the chemical and electronic structure of a magnetic material to tailor the interplay between (anti)ferromagnetic exchange, magnetocrystalline anisotropy, and anisotropic exchange (Dzyaloshinskii–Moriya interactions) to bring about exotic magnetic orders in two-dimensional (2D) materials or bulk crystals. The talk will show how soft-chemical methods can be used to prepare the highly coercive 2D ferromagnetic intercalation compound,  $\text{Fe}_x\text{TaS}_2$ , and the use of angle-resolved photoemission spectroscopy to understand differences in chiral helimagnetic order in related 3D compounds,  $\text{Cr}_{1/3}\text{NbS}_2$  and  $\text{Cr}_{1/3}\text{TaS}_2$ . The role of intercalant disorder on magnetic order will be explored in these chiral helimagnets as well as the intrinsically disordered  $\text{Fe}_{0.17}\text{ZrSe}_2$ . Finally, the talk will show how endotaxial polytype heterostructures of  $\text{TaS}_2$  enable multistate resistivity and chirality switching of charge density wave phases.

# Direct Observation of Infrared Energy Transfer Using Focused Electron Beams

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<sup>2</sup>Department of Chemistry, University of Washington

## ABSTRACT

In this talk, we will discuss collaborative work leveraging recent advances in energy-monochromated electron energy loss spectroscopy (EELS) operated in aberration-corrected scanning transmission electron microscope (STEM) to characterize the low energy mid-IR excitations of individual carrier-doped semiconductor nanocrystal assemblies [1] and Fabry-Perot excitations of metallic triangular nanocavities [2]. Time permitting, we present a new approach for mapping [3] and focusing [4] thermal energy within localized photonic cavities at the nanoscale using in-situ electron microscopy, as shown in Figure 1. Specifically, we combine experimental measurements and theoretical modeling of the correlated spectral- and spatial-dependent electron energy loss (EEL) and gain (EEG) signals to elucidate the mechanisms for energy transfer within precision engineered nanoparticle assemblies in the strong coupling regime as well as between thermalized substrate surroundings and weakly coupled individual IR-active nanoparticle components. Taken together this collaborative work highlights the ability of state-of-the-art STEM-EELS/EEGS to fundamentally understand energy transfer to develop new strategies to harvest waste heat and deriving chemical processes at the nanoscale in the IR region.

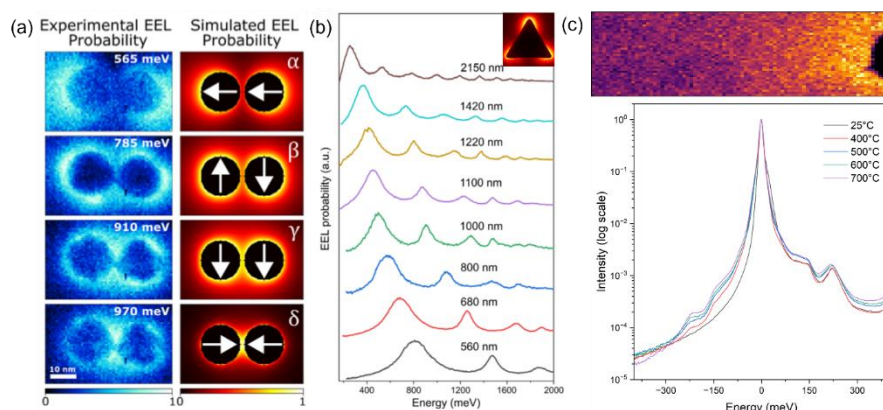


Figure 1: (a) Mapping infrared plasmon hybridization in doped semiconductor assemblies, (b) EELS profiles of gold triangular nanocavities exhibiting wide near- and mid-IR plasmons with tuning edge-length, and (c) EEG spectrum image (700°C) and corresponding point spectrum showing thermal gain with increasing temperature at plasmon energy (-210 meV).

1. Olafsson, A., et al., *Imaging Infrared Plasmon Hybridization in Doped Semiconductor Nanocrystal Dimers*. The Journal of Physical Chemistry Letters, 2021. **12**(42): p. 10270-10276.
2. Kumar, V., et al., *Infrared Near-Field Spectroscopy of Gold Nanotriangle Fabry-Pérot Resonances*. The Journal of Physical Chemistry C, 2023.
3. Bourgeois, M.R., et al., *Polarization-Resolved Electron Energy Gain Nanospectroscopy With Phase-Structured Electron Beams*. Nano Letters, 2022. **22**(17): p. 7158-7165.
4. Kumar V. et al., *Heat Scavenging using Mid-Infrared Plasmonic Nanostructures*. In preparation

# **From Ionic Liquids to Deep Eutectics: New Frontiers in Green Propellants**

Steven D. Chambreau<sup>1</sup>

<sup>1</sup>Jacobs Technology, Inc., Air Force Research Laboratory  
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In the quest to replace toxic legacy hydrazine-based propulsion systems, ionic liquids and deep eutectic propellants (DeEP) show great promise in that they have low vapor toxicity, high energy content and potentially can be used in a multi-mode propulsion system. In this work, a machine learning approach is used to predict surface tensions and electrical conductivities of ionic liquids and deep eutectic propellant candidates. Density functional theory (DFT) coupled with a quantitative structure property relationship (QSPR) method are employed to identify structural trends that can lead to the design of ionic liquid and deep eutectic-based propellants with optimized performance in electrospray thrusters.

## Recent Advances in Correlated Quantum Chemistry in the Condensed Phase

Garnet Kin-Lic Chan  
California Institute of Technology

I will report on some advances in the description of correlated quantum materials using the techniques of quantum chemistry, including the ab initio description of the Kondo temperatures of magnetic impurities, and the first principles prediction of high-temperature superconductor transition temperatures. This work is funded in part by an AFOSR MURI. If time permits, I will talk about other work, including the development of techniques for the description of excited states and reactive molecular dynamics in liquid condensed phases at the correlated quantum chemistry level.

An Integrated Experimental and Theoretical Approach Toward Understanding Novel Reactivity, Structure  
and Chemical Gradients in Aqueous Microdroplets

Robert E. Continetti, Vicki H. Grassian, Rommie E. Amaro, Kimberly A. Prather, and Wei Xiong  
University of California, San Diego

Cari S. Dutcher  
University of Minnesota

The goal of this MURI project is to better understand enhanced reactivity within microdroplets and the physicochemical characteristics leading to these enhancements. A dual approach under two research themes is being pursued. The first is to investigate reactions in single droplets using different measurement approaches and different droplet generation methods to determine factors (e.g. size, charge, pH) that lead to enhanced reactivity. The second is to integrate experiment and theory to provide fundamental insights into the physicochemical characteristics of the droplets that lead to enhanced droplet activity. These characteristics include surface properties (charge, coverage, molecular orientation), chemical gradients and bulk-to-surface diffusion. In this talk, examples will be highlighted including reactions of pyruvic acid within microdroplets of varying size and charge, measurements of microdroplet pH, diffusion models for microdroplet chemistry, and chemistry in the impact of pyruvic acid entrained in ice grains.

This work is supported by the Air Force Office of Scientific Research FA9550-22-1-0199 (MURI-22).

## **Ballistic excitons in 2D superatomic materials**

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Achieving long-range ballistic (coherent) electron flow in materials at room temperature is a long-standing goal that could unlock lossless energy harvesting and wave-based information technologies. The key challenge is to overcome short-range scattering between electrons and lattice vibrations (phonons). I will describe two avenues to achieve ballistic transport by harnessing strong interactions between coherent and incoherent excitations in extended lattices of atomic and molecular semiconductors. The first is to leverage polaritons, part-light part-matter quasiparticles resulting from hybridization between microcavity photons and semiconductor excitons. The second is to leverage strong interactions between electrons and delocalized phonons, yielding acoustic polarons that are intrinsically shielded from phonon scattering. The formation of acoustic polarons is uniquely enabled by the interplay of flat electronic bands and strong exciton-phonon interactions in a special class of two-dimensional superatomic materials pioneered in this program. To track polaritons and acoustic polarons, we develop ultrafast optical technologies capable of directly imaging quasiparticle propagation with 50-femtosecond resolution and few-nanometer spatial precision, providing a precise measurement of quasiparticle velocity, scattering pathways, and transition from coherent to incoherent transport. Ongoing instrument development will enable reaching sub-10 femtosecond resolution with single-electron sensitivity to directly image and control the formation of quasiparticles.

## 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 hopping 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 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; (iv) theoretical determination of electronic coupling and reorganization energy for hole-hopping, which agree remarkably well with the experimental measurements.

This 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.

### Recent publications supported by this award:

1. K. E. Shulenberger, M. R. Jilek, S. J. Sherman, B. T. Hohman, G. Dukovic. "Electronic Structure and Excited State Dynamics of Cadmium Chalcogenide Nanorods." *Chemical Reviews*, **2023**, 123 (7), 3852-3903.
2. 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.
3. 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.
4. 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**)
5. 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.
6. 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.



## Photonic Electrochemistry

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**ABSTRACT.** Voltage ranks among the most foundational properties in science and engineering. Without voltage, biological cells are dead, batteries don't work, and the lights are out. Today's voltage measurements are either invasive (requiring electrical leads stuck into the sample) or time-limited (requiring slow electrokinetic or scanning methods, or dyes that quickly bleach), thus restricting our understanding of spatiotemporal voltage evolution and limiting fundamental progress and technological innovations in charged systems. What is needed is quantitative, non-invasive, label-free voltage imaging in time and space. Our proof-of-concept pilot in a non-imaging geometry shows measurements of a sample's nonlinear optical amplitude and phase directly yield the total potential of an oxide:water interface in just a few seconds (JACS, 144, 16338, '22; JPCL, 12, 5649, '21; JPCL, 10, 2328, '19; Nat. Comm. 8, 1032, '17). The method fully recapitulates X-ray and electrical impedance measurements, which are much slower. Employing interferometry that exploits the optical dispersion in fused silica as opposed to air, we now present a new, compact, and phase stable nonlinear optical spectrometer as a first step towards realizing photonic electrochemical microscopy. The new instrument reveals pronounced hysteresis of up to several 100 mV in the flipping of Stern layer water molecules when a 10 nm thin nickel electrode is subjected to anodic and cathodic scans between -0.4 and +0.8 V at pH 13 (oxygen evolution). The underlying mechanistic understanding and prospects towards developing photonic electrochemical microscopy are discussed.

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## **Plasmonic Photocatalysis with Antenna-Reactor Nanoparticle Complexes**

**Naomi J. Halas, Rice University**

Traditionally, most chemical reactions have been driven by heat. But a chemical reaction on a plasmonic nanoparticle can be driven by multiple mechanisms that also include nonthermal effects, which may even dominate. In particular, energetically hot carriers that are generated when plasmons decay can substantially reduce reaction barriers, change reaction pathways, and greatly alter reaction specificity. The energy of the generated carriers is controlled by the plasmon resonance energy of the nanoparticle, a property that can be geometrically tuned for specific chemical reactions. By introducing specific binding sites of catalytic metals onto plasmonic nanoparticles, one adds “reactors” to the “antenna”, which can greatly increase reaction rates and efficiencies in comparison to the analogous thermally-driven chemical reaction. In my talk, we will examine several examples of how light-driven plasmonic photocatalysis controls reactions in a fundamentally different manner than thermally excited processes. This includes reaction temperatures hundreds of degrees below the same reaction driven thermally. We will also show how plasmon-induced desorption, a mechanism unique to plasmonic photocatalysis, can make active sites on the photocatalyst surface more readily available for reactant binding than in thermal processes, and can even be designed to eliminate coking. Because of this additional desorption mechanism, reactors in plasmonic photocatalytic complexes are not limited to metals in the platinum group, but more earth-abundant elements can now be used as reactor candidates with similar reactivities. Finally, we will examine how the technological breakthrough of solid-state lighting in the form of light-emitting diodes can provide remarkably inexpensive light sources for practical applications of light-driven reactions capable of being transferred into industrial contexts.

# Unraveling the Initial Steps of the Ignition Chemistry of the Hypergolic Ionic Liquid 1-Ethyl-3-Methylimidazolium Cyanoborohydride ([EMIM][CBH]) with Nitric Acid (HNO<sub>3</sub>) Exploiting Chirped Pulse Triggered Droplet Merging

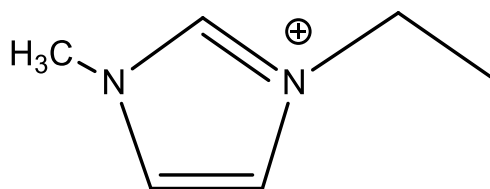
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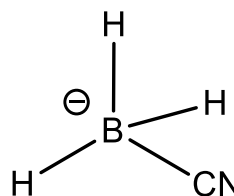
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The reactions of hypergolic ionic liquid (HIL) 1-ethyl-3-methylimidazolium cyanoborohydride ([EMIM][CBH]) and nitric acid (HNO<sub>3</sub>) at various concentrations from 10 % to 70 % were explored using single droplet merging within an ultrasonic levitation setup in an inert atmosphere of argon to reveal the initial steps that cause hypergolicity. The reactions were initiated through controlled droplet-merging manipulation triggered by a frequency chirp pulse amplitude modulation. Utilizing the high-speed optical and infrared cameras surrounding the levitation process chamber intriguing visual images unveiled: (i) extensive gas release and (ii) temperature rises of up to 435 K in the merged droplets. The gas development was validated qualitatively and quantitatively with Fourier Transform Infrared Spectroscopy (FTIR) indicating the major gas-phase products to be hydrogen cyanide (HCN) and nitrous oxide (N<sub>2</sub>O). The merged droplet was also probed by pulsed Raman spectroscopy which deciphered features for key functional groups of the reaction products and intermediates (BH, BH<sub>2</sub>, BH<sub>3</sub>, -NCO); reaction kinetics revealed that the reaction was initiated by the interaction of the [CBH]<sup>-</sup> anion of the HIL with the oxidizer (HNO<sub>3</sub>) through proton transfer, whereas the [EMIM]<sup>+</sup> cation was noted to be less reactive quantified by decay rates of the anion exceeding those of the cation by up to one order of magnitude. The experimental results were merged with data from a recent computational investigation. Overall, the reaction was found to be initiated by the formation of a van-der-Waals complex between the [CBH]<sup>-</sup> anion and HNO<sub>3</sub>, followed by proton transfer from the acid to the anion and subsequent extensive isomerization; these rearrangements were found to be essential for the formation of hydrogen cyanide (HCN) and nitrous oxide (N<sub>2</sub>O). The exoergicity observed during the merging process provides a molar enthalpy change up to 10 kJ mol<sup>-1</sup> to the system, which could be sufficient for a significant fraction of the reactants of about 12 % to overcome the reaction barriers in the individual steps of the computationally determined minimum energy pathways.



EMIM  
[1]



CBH  
[2]

Structure of 1-ethyl-3-methylimidazolium [1] [EMIM]<sup>+</sup> - cyanoborohydride [2] [CBH]<sup>-</sup>

S. Biswas, I. Antonov, K. Fujioka, G. L. Rizzo, S. D. Chambreau, S. Schneider, R. Sun, R. I. Kaiser, Unraveling the initial steps of the ignition chemistry of the hypergolic ionic liquid 1-ethyl-3-methylimidazolium cyanoborohydride ([EMIM][CBH]) with nitric acid (HNO<sub>3</sub>) exploiting chirped pulse triggered droplet merging, Phys. Chem. Chem. Phys., 25, 6602-6625 (2023).

## **Understanding and controlling chemistry at interfaces using ion soft landing**

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Controlled deposition of complex ions onto surfaces enables the exploration of fundamental processes underlying the design of functional 2D and 3D interfaces of interest to materials science, energy production, and other research fields. Ion soft landing, in which intact polyatomic ions are deposited onto surfaces with or without charge retention, is a powerful tool for fundamental studies of phenomena underlying ion deposition. Precise control of the ion composition and kinetic energy make soft landing an attractive approach for surface modification. High-purity uniform thin films generated using this technique facilitate understanding of interfacial phenomena relevant to a broad range of applications. Experimental studies of mass-selected deposition of complex ions on surfaces have shown efficient charge retention by anions and facile charge loss by cations soft-landed onto self-assembled monolayer surfaces. Charge retention by soft landed ions results in formation of charge-imbalanced interfaces stabilized by the image charge. Recent advances in the soft-landing instrumentation have enabled high-coverage deposition of both stable molecular ions and reactive fragments generated in the gas phase, revealing new physical phenomena related to multilayer deposition of well-defined ions and the reactivity of novel ionic species on surfaces. In this presentation, I will discuss the fundamental aspects of ion-surface interactions revealed by ion soft landing experiments and present examples of the unusual surface reactivity of fragment ions.

## **Safe, energy-dense ionic liquid fuels for electrochemical devices**

Karthish Manthiram, Caltech

Energy-dense condensable fuels are essential for driving decarbonization of the transportation sector, especially in applications where energy needs far-surpass what can be reasonably provided by lithium-ion batteries. Ammonia has recently gained attention for its favorable characteristics, as a fuel that can be generated from just air and water, at relatively low cost. While this may be an attractive fuel for many use cases, its volatility and high vapor pressure make it undesirable for use in military contexts. It is here that our group has focused on developing electrochemical fuel ionic liquids, a class of fuels that have reduced volatility due to their ionic nature, formed by combining just ammonia and formic acid to produce ammonium formate. We will share foundational results that prove the viability of electrochemical fuel ionic liquids, including highlighting opportunities for future development.

# Electrical Double Layer Modulation of Organic Reactions at Electrode Interfaces

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Georgia Tech

**Abstract:** Chemical and physical transformations at electrochemical interfaces are fundamental to electrocatalysis, electrosynthesis, and electrochemical energy storage technologies. Complexity results from these chemical and physical processes often being coupled, with redox and chemical reactions modulated by the electrical double layer at the heterogeneous electrode/electrolyte interface. We will discuss our recent efforts at developing and applying computational electrochemistry techniques to understand how chemical reactions are modulated by electrical double layers at large applied voltages. We will present an electrosynthesis case study of an anodic olefin coupling reaction for which we predict significant reaction selectivity/yield modulation from the electrical double layer, and demonstrate how choice of electrolyte alters product selectivity. Our simulations elucidate general double layer effects for this class of reactions, including solvophobic attraction of the organic substrate to the carbon electrode surface as modulated by electrolyte composition, and stabilization of the oxidized intermediate(s) at the anode due to electrostatic interactions with surrounding counterions. We will discuss our method/software development for Fixed-Voltage QM/MM computational approach, which enables molecular dynamics prediction of reaction free energies at electrochemical interfaces under applied voltage.

# The Chiral Induced Spin Selectivity (CISS) effect- From Electron Transfer in Biology to Spintronics.

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Spin based properties, applications, and devices are commonly related to magnetic effects and to magnetic materials. However, we established that chiral organic molecules can act as spin filters for photoelectrons transmission, in electron transfer, and in electron transport. The effect, termed Chiral Induced Spin Selectivity (CISS),<sup>1</sup> has interesting implications for the production of new types of spintronics devices<sup>2</sup> and on the importance of chiral molecules in biological systems.<sup>3</sup> The basic effect, and its applications and implications, will be presented.

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<sup>1</sup> T. K. Das, F. Tassinari, R. Naaman, J. Fransson, The Temperature-Dependent Chiral-Induced Spin Selectivity Effect: Experiments and Theory. *J. Phys. Chem. C*, **126**, 3257–3264 (2022).

<sup>2</sup> S.-H. Yang, R. Naaman, Y. Paltiel, S. Parkin, Chiral spintronics, *Nat. Rev. Phys.* **3**, 328–343 (2021).

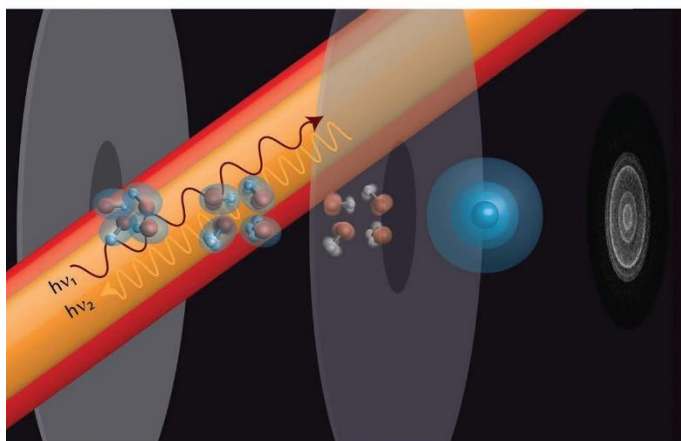
<sup>3</sup> R. Naaman, Y. Paltiel, D. H. Waldeck, Chiral Induced Spin Selectivity and Its Implications for Biological Functions, *Annu. Rev. Biophys.* **51**, 99-114 (2022).

## High Resolution Photoelectron Spectra of Vibrationally Excited Anions

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The method of slow-electron velocity-map imaging of cryogenically-cooled anions (cryo-SEVI) has been developed over the last several years in our laboratory.<sup>1</sup> This experiment is a high resolution variant of anion photoelectron spectroscopy and yields well-resolved photoelectron spectra for polyatomic molecular and cluster anions for which more conventional methods show little or no resolved vibrational structure. Cryo-SEVI has been shown to be a powerful spectroscopic probe of bare and complexed metal oxide clusters that serve as model systems for a range of catalytic reactions. In addition, it has been applied to the transition state spectroscopy of benchmark bimolecular and unimolecular chemical reactions.

We have recently incorporated a tunable infrared laser into this experiment that can vibrationally excite anions prior to photodetachment. This new implementation, IR cryo-SEVI, enables one to access neutral vibrational levels that cannot be reached from the anion ground state. It also provides a novel probe of anharmonic coupling in both the anion and neutral. Moreover, IR cryo-SEVI provides a means of obtaining anion vibrational frequencies in the gas phase without rare-gas tagging. Hence, both anion and neutral vibrational frequencies can be obtained from a single experimental protocol. Examples will be presented for  $\text{OH}^-$ ,  $\text{CH}_2\text{CHO}^-$  (vinoxide), and  $\text{H}_2\text{CC}^-$  (vinylidene).<sup>2-3</sup> The extension of this method to more complex species including metal oxide clusters will be discussed.



1. Weichman, M. L.; Neumark, D. M., Slow Photoelectron Velocity-Map Imaging of Cryogenically Cooled Anions. In *Annual Review of Physical Chemistry, Vol 69*, Johnson, M. A.; Martinez, T. J., Eds. 2018; Vol. 69, pp 101-124.
2. DeWitt, M.; Babin, M. C.; Neumark, D. M., High-Resolution Photoelectron Spectroscopy of Vibrationally Excited  $\text{OH}^-$ . *J. Phys. Chem. A* **2021**, 125, 7260-7265.
3. Lau, J. A.; DeWitt, M.; Boyer, M. A.; Babin, M. C.; Solomis, T.; Grellmann, M.; Asmis, K. R.; McCoy, A. B.; Neumark, D. M., High-Resolution Photoelectron Spectroscopy of Vibrationally Excited Vinoxide Anions. *J. Phys. Chem. A* **2023**, 127, 3133-3147.



# Chemistry in merged molecular beams and in merged microjets

Andreas Osterwalder

*Institute for Chemistry and Chemical Engineering (ISIC), Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland*

I will be giving a status report on our experiments on stereodynamics in merged molecular beams where two reactant beams are superposed using curved electric and magnetic guides. We have studied sub-Kelvin stereodynamics in prototypical energy transfer reactions, namely between metastable  $\text{Ne}(^3\text{P}_2)$  and rare gas atoms or diatomic molecules.

Such reactions can lead to Penning ionization (producing  $\text{X}^+$ ) or associative ionization (producing  $\text{NeX}^+$ ), respectively, and the branching ratio is highly dependent on the reactant orientation and the collision energy.

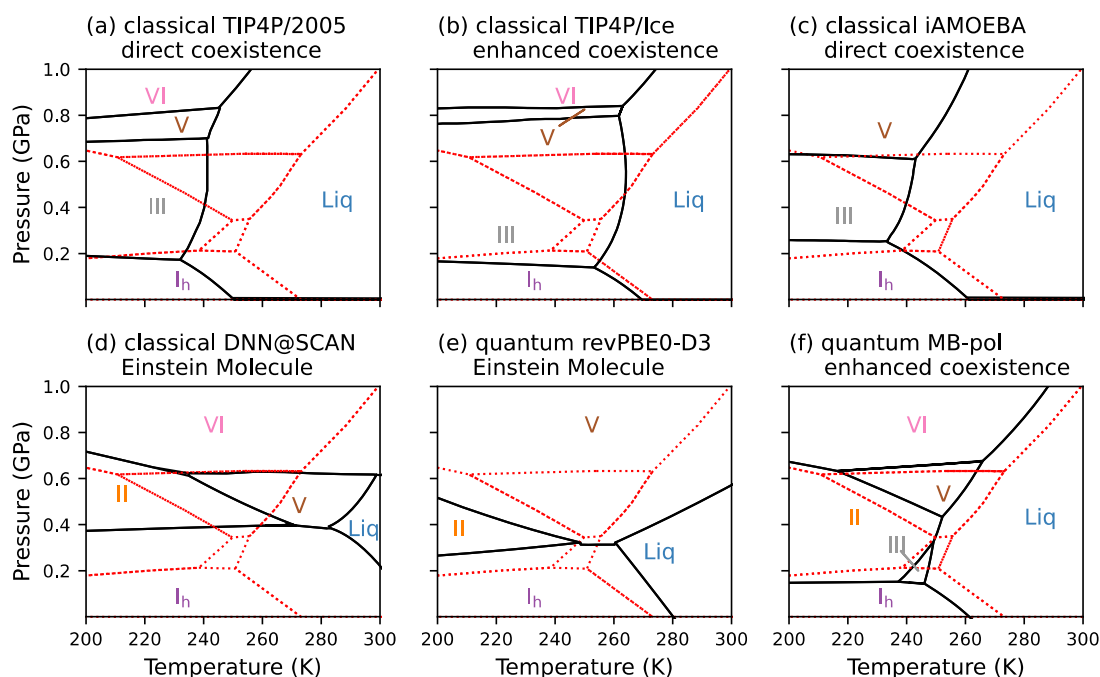
In the second part of the presentation I will review our work in liquid microjets where we have recently demonstrated a new approach to measure chemical kinetics at liquid-liquid interfaces.

# Molecular Interactions, Machine Learning, and the Quest of Realistic Molecular Simulations

Francesco Paesani

*Department of Chemistry and Biochemistry, Materials Science and Engineering,  
Halicioğlu Data Science Institute, and San Diego Supercomputer Center  
University of California, San Diego*

Two of the most challenging problems at the intersection of electronic structure theory and molecular dynamics simulations are the accurate representation of intermolecular interactions and the development of efficient algorithms applicable to large systems. To some extent, these two problems are antithetical, since accurate calculations of molecular interactions typically require correlated electronic structure methods that are computationally too expensive for applications to large systems. I will describe our data-driven many-body energy (MB-nrg) formalism that overcomes these limitations and enables computer simulations of from the gas to the condensed phase, with chemical and spectroscopic accuracy. MB-nrg is a unified theoretical/computational framework that integrates data-driven many-body representations for the low-order terms of the many-body expansion of the energy with mean-field-like representations of classical many-body interactions. I will specifically illustrate the accuracy, transferability, and predictive power of our MB-pol potential for water, demonstrating that MB-pol is the first and, currently, only model that correctly reproduces the phase diagram of water, which makes it particularly well suited to explore the phase behavior of water and ice in different environments. When possible, I will make connections with models based on density functional theory as well as neural network potentials.



**Title:****Extending the Promise of Stochastic Methods to Catalysis via Machine Learning**

**Authors:** Brenda Rubenstein, Gopal Iyer, Cancan Huang, Edgar Landinez-Borda, and Noah Whelpley

**Abstract:**

Quantum Monte Carlo (QMC) methods are a promising suite of stochastic electronic structure methods that enable the high-accuracy modeling of strongly correlated molecules and materials at comparatively modest costs through the sampling of random numbers. Historically, these methods have excelled at computing energies, but have struggled to efficiently compute forces and scale to large system sizes that approach the thermodynamic limit, curtailing their applicability to catalysis. In this work, we illustrate how a potent combination of stochastic methods and machine learning can address these and other critical shortcomings to provide useful insights into catalysis. We will first describe our recent endeavors employing active learning with AMP Torch to predict QMC-quality forces for the relaxation of molecular geometries and molecular dynamics simulations. We will illustrate how active learning is particularly crucial in the QMC context because of the lack of forces that can be leveraged for training. We will then describe how surrogate methods, including Density Functional Theory and machine learning, can be combined with QMC to identify transition states at QMC-level accuracy. Altogether, this work demonstrates how machine learning can be used to extend the capabilities of stochastic methods, increasing their overall applicability and accelerating their performance.

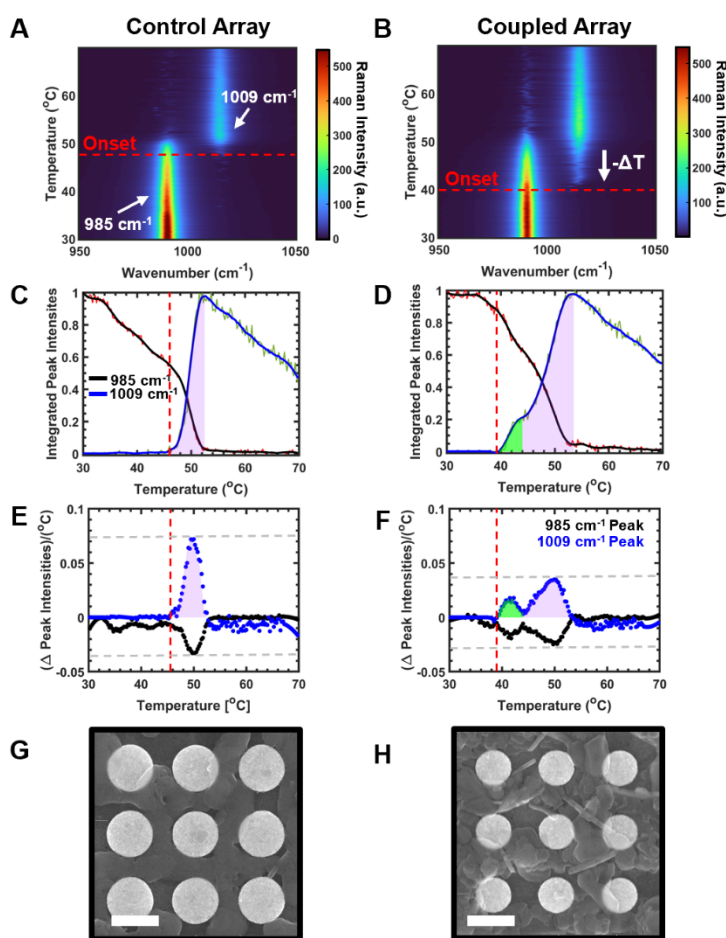
**Title:** Plasmonic substrates modify dehydration reactions via vibrational strong coupling

**Author:** Matthew Sheldon, Texas A&M University

Vibrational strong coupling (VSC) has been explored recently as a means to alter chemical reactions. However, a full mechanistic description remains controversial. Usually, Fabry–Pérot (F.P.) cavities are used for coupling due to their high Q-factors; however, the chemical effects that can be expected are intrinsically limited by dipole misorientation with molecules, relatively small coupling per molecule, and a large number of dark modes. To better understand how this impacts chemical behavior, we have developed plasmonic substrates as alternative optical platforms that can systematically probe and overcome these different limitations.

In this study, we quantified how plasmonic substrates modify the dehydration temperature of copper sulfate pentahydrate. This analyte is advantageous because it undergoes four dehydration states that can be monitored as a function of temperature using confocal Raman spectroscopy. We measured up to a 15-degree decrease for the onset for dehydration when there is VSC, quantifying the ratio of molecules with modified dehydration temperatures, and spatially mapped where the modified reaction occurred with sub-wavelength imaging resolution.

We determined that the dehydration reaction occurs at significantly lower temperatures only at locations with the largest local density of optical states (LDOS) at the same frequency as the coupled vibrational mode. This work has the potential to be generalized to a broad range of molecular and plasmonic systems, opening new pathways in plasmon-mediated chemical reactions and how they can be impacted by strong coupling.



**FIGURE: Thermal dehydration study.** Molecular Raman spectra of  $\text{CuSO}_4(\text{H}_2\text{O})_5$  deposited on a nanocavity array (A) without or (B) with strong coupling during stage heating ramps (0.5 °C/min). (C) – (D) Integrated counts as well as the differential signal (E) – (F). Unperturbed chemical species (purple shading) and species with decreased onset temperature (green shading) are apparent during strong coupling. SEM images of the differences in morphology of  $\text{CuSO}_4(\text{H}_2\text{O})_5$  deposited on arrays (G) without or (H) with strong coupling.

## Common early barriers in surface and cluster ion reaction with O<sub>2</sub>

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Gas phase metal cluster ion reactivity is often used as a model system for valence interactions of surface processes, but in the particular case of reaction with O<sub>2</sub> the longer-range forces are also similar. The kinetics O<sub>2</sub> incident on an Al(111) surface have been shown to be affected by a long-range barrier at which electron transfer to the O<sub>2</sub> occurs. Here, we show that gas phase Al<sub>n</sub><sup>-</sup> clusters reacting with O<sub>2</sub> are controlled by an analogous early barrier formed by the avoided crossing of the Al<sub>n</sub><sup>-</sup> + O<sub>2</sub> and Al<sub>n</sub> + O<sub>2</sub><sup>-</sup> surfaces, without spin restrictions as previously proposed. Kinetics of various transition metal cluster anions show evidence of the same barrier being prominent, suggesting the mechanism is quite common. Most interestingly, the kinetics of lanthanide atoms and atomic cations with O<sub>2</sub> show a similar early barrier, although in these cases it may be due not to charge transfer, but to an excited state promoting covalent bonding. We suggest that the general scheme may offer additional control of oxygen activation processes.

Separately, the kinetics of O<sub>3</sub> with meteoric metal ions and their higher oxides are reported. Ablated meteoric material consolidates in the upper mesosphere and lower thermosphere and causes Sporadic E events; the conversion of atomic cations to polyatomic cations by reaction with O<sub>3</sub> leads to termination of the Sporadic E. The literature is plagued by underestimation of these reaction rates due to analyses not properly accounting for sequential chemistry with O<sub>3</sub>. Here, corrected rate constants are reported and the general mechanism of O<sub>3</sub> leading to both oxidized and reduced cation products is deduced. The data for Ca<sup>+</sup> is used to update an atmospheric model resulting in improved agreement with field measurements.

# Suppressed reactivity via cavity-induced selective vibrational cooling

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Molecular vibrations can couple to optical cavities to create new hybrid states called polaritons. The magnitude of this coupling, measured as the vacuum Rabi splitting ( $\Omega$ ), correlates with modified materials processes such as photon emission, molecular energy transfer, and chemical reaction rates. In this talk, I will first discuss modeling and active control of cavity coupling to molecular vibrations. Next, I will discuss results indicating modified chemical reaction rates for an alcoholysis addition reaction forming urethane monomers. Cavity tuning was used to selectively couple to reactant, solvent, and product vibrational modes resulting in a chemical response that is cavity tuning dependent. An open quantum system model attempting to rationalize such reaction suppression is presented which identifies bond-selective cooling via cavity-induced stationary population redistribution as the culprit.

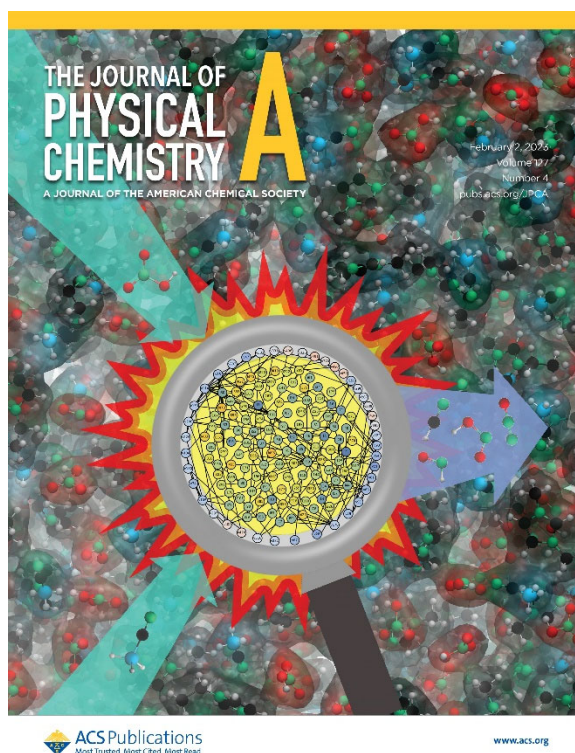
# Unsupervised Reaction Pathways Search for the Oxidation of Hypergolic Ionic Liquids

Rui Sun

University of Hawaii, Manoa

## Abstract:

Ionic liquid, 1-ethyl-3-methylimidazolium/cyanoborohydride ( $\text{EMIM}^+/\text{CBH}^-$ ), and oxidant, nitric acid ( $\text{HNO}_3$ ), have been previously reported to be hypergolic on contact. However, recent experiments and *ab initio* molecular dynamics simulations indicate that the reaction took place in a non-hypergolic manner [Phys. Chem. Chem. Phys. **2023**, 25, 6602 and J. Phys. Chem. A **2023** 127, 913]. In this computational study, the potential energy surface of the reaction system is studied with an in-depth, unsupervised reaction pathway search over all possible isomerizations. For a system of such complexity, chemical intuition could fall short of identifying the true minimal potential energy path. A reaction network consisting of over 3,000 intermediates is constructed, from which the reaction mechanism is derived and agrees well with the experiments. This network, initiating at the reactant and ending at the first gaseous product, offers a comprehensive understanding of the progress of the reaction and lays the foundation for 1) developing collective variables for condensed phase simulations as well as 2) the study of consecutive reactions. This presentation will report the preliminary result of those efforts as well.



## **The Critical Role of Electrical Polarization in Thermochemical Surface Catalysis**

**Jaeyune Ryu, Thejas S. Wesley, Will Howland, Kunal M. Lodaya, Bryan Tang, Max J. Hülsey, Karl S. Westendorff, Noah B. Lewis, Ethan Crumlin, Yuriy Román-Leshkov, Yogesh Surendranath**

**Department of Chemistry, Massachusetts Institute of Technology**

The sustainable upgrading of renewable and waste resources requires precision control of catalysis occurring at solid-liquid interfaces. Unlike for gas-solid interfaces, at all solid-liquid interfaces, the exchange of ions and/or electrons with the solution can lead to electrostatic charging or polarization of the interface and a corresponding oriented electric field. Although intrinsic electric fields are known to play an important role in molecular and biological catalysis, interfacial charge transfer reactions and electrostatic polarization has been largely ignored as a controlling factor in heterogeneous thermochemical catalysis. We have developed general methods for tracking and controlling the degree of interfacial polarization during catalytic turnover and have used this approach to understand and tune thermochemical oxidation and hydrogenation catalysis. We have found that many net thermochemical reactions proceed as coupled electrochemical half-reactions and that the degree of interfacial polarization tunes the energy landscape of catalysis. These findings providing new opportunities to tune and design thermochemical catalysis by applying the principles of electrochemistry.



# Probing charge-transfer neutralization reactions of atmospheric relevance using the ion storage facility DESIREE

**R. D. Thomas**

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Double ElectroStatic Ion Ring ExpERiment (DESIREE) facility located at Stockholm University, Sweden, uniquely allows for studies of mutual neutralization interactions between cations and anions at low and well-defined internal temperatures and centre-of-mass collision energies down to about 20 K and  $\sim 50$  meV, respectively [1-3], and a schematic is shown in Figure 1.

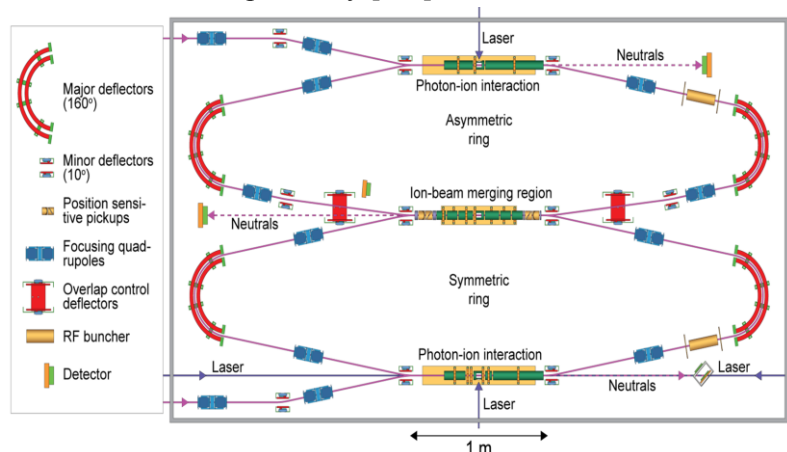


Figure 1: Schematic of the heart of the DESIREE facility: the two cryogenically cooled storage rings

Using this facility, we aim for a better understanding of how small and large molecules are formed and processed in astrophysical, atmospheric, and combustion plasmas, where we combine several novel experimental methods to build a fundamental picture of the transfer of charge-, energy- and mass in collisional reactions. Control over the reaction environment [1-6] means that desired information, e.g., reaction products, can be obtained over many of the conditions needed to accurately model plasmas where these processes are important.

Here, I highlight how this facility can play a crucial role in studying in mutual neutralization reactions relevant to cool atmospheric plasmas: providing insights into ion balance processes, and, e.g., in the production of F-layer UV airglows. I focus on reactions involving the primary atomic and molecular oxygen and nitrogen ions [4,6], i.e:  $O^- + O^+$ ,  $O^- + N^+$ ,  $O^- + NO^+$ ,  $O^- + O_2^+$ , and  $O^- + N_2^+$  where, in the processes with molecular cations, I can further determine the fractionation into two- and three-body product channels and study the effects of the rovibrational energy of the molecular ion on the reaction process.

## References

- [1] R. D. Thomas et al., Rev. Sci. Instrum. 82, 065112 (2011)
- [2] H. T. Schmidt et al., Rev. Sci. Instrum. 84, 055115 (2013)
- [3] H. T. Schmidt et al., Phys. Rev. Lett. 119, 073001 (2017)
- [4] M. Poline et al. Phys. Chem. Chem. Phys. 23, 24607 (2021)
- [5] M. Poline et al. Phys. Rev. A, 105, 062825 (2022)
- [6] M. Poline et al. Phys. Rev. A, 106, 012812 (2022)

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# Ongoing Advances in the Simulation of Room Temperature Ionic Liquid Interfaces

Gregory A. Voth

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Advances in molecular dynamics simulations of room temperature ionic liquids (RTILs) interfaces will be presented that aim to accurately predict their interfacial properties. The interfacial properties of RTILs play an important role in many applications, such as propulsion, electrolytes in batteries, and capture media for greenhouse gases, which highlights the need to understand the nature of their interfaces. While computational studies have used nonpolarizable force fields (FFs) with scaled-charge to study the structure of the air-liquid interface of RTILs, the accuracy of these models remains an issue. On the other hand, polarizable FFs are believed to be more accurate compared to nonpolarizable models, but they come at a higher computational cost. Here we present a comprehensive benchmark of different FFs and systematically examine the behavior of different models on interfacial properties. We also determine whether the *ad hoc* scaled-charge method can provide an acceptable alternative for polarizable FFs. We examine several critical structural and dynamical properties of the air-liquid interface of the RTIL [C<sub>4</sub>mim][NTf<sub>2</sub>], including density profile, surface tension, radial distribution function, survival time of interfacial ions, and the reorientation correlation function of ions, using three different kinds of FFs developed by Canongia, Lopes, and Pádua (CL&P): the fixed-charge model, the scaled-charge model, and the polarizable model. Our analysis is characterized by interface layers, which accounts for the thermal fluctuations of the fluid interface, to elucidate how properties change in different layers. In general, the fixed-charge model predicts too-ordered structures and too-sluggish dynamics, while the scaled-charge model can serve as a simple cure for some bulk properties. However, the scaled-charge model fails to reproduce the results of the polarizable model at the interface, due to an inappropriate scaled-down charge near the interface. It should be noted that the polarizable model is not perfect as well, as it predicts a lower surface tension and higher self-diffusion coefficient than seen in experiment.

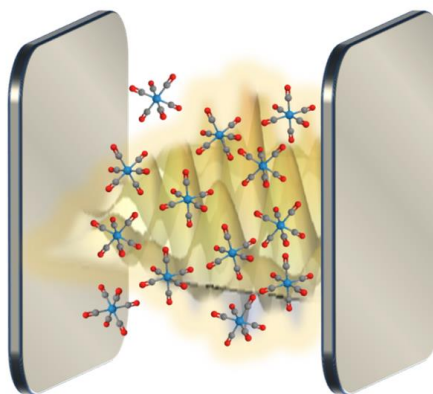
The parameterization of the FF can clearly have a large impact on its behavior. We have also tested another kind of FF developed by McDaniel co-workers, which is primarily based on first principals electronic structure data. While the general trend from the nonpolarizable to polarizable model remains the same in this FF, the structural and dynamical properties can be different from those in the nonpolarizable/polarizable CL&P model. For example, the anion undergoes a much longer survival time at the interface using the polarizable McDaniel FF than the polarizable CL&P FF. At the same time, the polarizable McDaniel FF predicts a lower surface tension along with a lower self-diffusion coefficient than seen in experiment.

Therefore, none of these FFs are perfect in predicting key interfacial properties, thus leading us to pursue further improvements of (especially polarizable) FFs to render them more accurate in predicting the interfacial properties of RTILs.

# Polariton chemistry: challenges and prospects

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**Fig. 1.** Molecules in an optical microcavity (adapted from Ref. 1).

The strong coupling of molecular transitions to photonic modes in optical microcavities gives rise to hybrid light-matter modes known as polaritons. In recent years, there has been much interest in polariton chemistry, namely, the use of polaritons to control chemical and material properties and processes. However, some of the mechanisms whereby polaritons can control chemistry remain rather opaque. For instance, theoretical efforts to explain vibropolaritonic chemistry, namely, the use of vibrational strong coupling (VSC) to modify the chemical kinetics of electronic ground state reactions in the absence of optical pumping, have failed to account for all the important observations reported for the corresponding experiments [1].

On the other hand, phenomena associated with optical pumping of polaritons seem to have a much easier path forward in terms of theory/experiment agreement. In this talk, I will briefly discuss our AFOSR sponsored efforts (FA9550-18-1-0289 & MURI: Polariton chemistry) to uncover new nonlinear optical phenomena as well as other photoinitiated molecular processes [2-5]. Central to these efforts is a new theoretical development of our group, which we call Collective dynamics Using Truncated Equations (CUT-E) which dramatically simplifies the computational problem of  $N \approx 10^6 - 10^{10}$  molecules coupled to a cavity mode, by mapping it into the problem of an *effective* single molecule coupled to a cavity mode [6].

[1] Campos-Gonzalez-Angulo, J. A., Poh, Y. R., Du, M. & Yuen-Zhou, J. Swinging between shine and shadow: Theoretical advances on thermally-activated vibropolaritonic chemistry (a perspective), in press, J. Chem. Phys. (2023) doi:10.48550/arxiv.2212.04017.

[2] B. Xiang, R.F. Ribeiro, M. Du, L. Chen, Z. Yang, J. Wang, J. Yuen-Zhou, and W. Xiong, Intermolecular vibrational energy transfer enabled by microcavity strong light-matter coupling, *Science* 368, 6491 (2020). (\*)

[3] R. F. Ribeiro, J. A. Campos-González-Angulo, N. C. Giebink, W. Xiong, and J. Yuen-Zhou, Enhanced optical nonlinearities under strong light-matter coupling, *Phys. Rev. A* 103, 063111 (2021).

[4] J. A. Campos-González-Angulo, R. F. Ribeiro, and J. Yuen-Zhou, Generalization of the Tavis–Cummings model for multi-level anharmonic systems, *New J. Phys.* 23, 063081 (2021).

[5] J. A. Campos-Gonzalez-Angulo and J. Yuen-Zhou, Generalization of the Tavis-Cummings model for multi-level anharmonic systems: insights on the second excitation manifold, *J. Chem. Phys.* 156, 194308 (2022).

[6] Pérez-Sánchez, J. B., Koner, A., Stern, N. P. & Yuen-Zhou, J. Simulating the collective strong coupling regime with few-molecule models, *Proc. Nat. Acad. Sci.* 120.15 (2023): e2219223120.

## Review of the AFOSR MURI: Mechanistic Studies of Microdroplet Chemistry

Richard N. Zare, Stanford University

A team of us (Prof. R. Graham Cooks, Purdue; Prof. Jahan Dawlaty, USC; Prof. Teresa Head-Gordon, UC Berkeley; Prof. Mark Johnson, Yale; Prof. Wei Min, Columbia; and Prof. Richard N. Zare, Stanford) are investigating why water droplets differ so sharply from bulk water in accelerating many chemical reactions and even creating new products not found when the same reagents at the same concentrations are present in bulk water. We are finding that a number of interrelated factors account for these dramatic differences. They point to the special properties of hydrophilic-hydrophobic interfaces. These include the partial solvation of reagents at and near the interface, evaporative concentration at the interface, the strong electric field at the interface caused by the formation of an electric double layer, the alignment of reagents at and near the interface, the change in thermodynamic properties, and the increased ionic strength of water at the interface. A brief summary will be presented of some of the highlights of recent results this team has reported in this area.

## **On the Fundamentals of Interfacial Solvation: Molecular Imaging, Atomistic Simulations, and Statistical Mechanics Models**

Yingjie Zhang, University of Illinois Urbana-Champaign

The spatial distribution of liquid species near solid (or macromolecular) surfaces is of fundamental importance for electrochemistry, catalysis, biology, and more. Such interfacial regions of liquid, called solvation layers or electrical double layers (EDLs), have puzzled theorists and experimentalists for decades. Currently there are mainly two types of models to explain the EDL structures. One is Gouy-Chapman-Stern (GCS) model that is widely introduced in electrochemistry textbooks. This model is based on classical electrostatics and predicts smooth potential distributions that roughly explains double layer capacitance effects of dilute aqueous solutions. However, it contains no atomic or molecular details that are oftentimes critical for the chemical, electrochemical, and biological functions derived from such interfaces. The other type of model is atomistic simulations, mainly including density functional theory (DFT) and molecular dynamics (MD). Such models include atomistic details, and oftentimes predict oscillatory atomic/molecular density profiles in the EDL. While these simulations are in general powerful, they tend to be computationally costly, and the results may vary, depending on the choice of detailed force field or density functional parameters. Experimental validations of the atomic-scale density profiles are oftentimes desired, yet challenging to achieve due to limitations in existing imaging methods.

In this talk, I will discuss our recent efforts on developing and using electrochemical 3D atomic force microscopy (EC-3D-AFM) to image the electrode and EDL structures in operando conditions, with atomic-scale resolution. We observe discrete, (nearly) periodic layers of EDL for a large range of electrolytes on crystalline graphite electrodes. Under different electrode potentials, we observe pronounced reconfigurations of the innermost EDL, while the upper layers mostly remain the same. At heterogeneous electrodes, we find the EDL to be strongly modulated by the local atomic configurations of the electrode surface. Overall, our EC-3D-AFM images are consistent with MD simulation results for the series of electrolytes we measure, revealing that the molecular distribution and orientation in the innermost EDL is highly dependent on the electrolyte composition, while the overall multilayer packing of the EDL contains surprisingly similar patterns among different electrolytes. To explain such similarities, we propose a statistical mechanics model, which successfully reproduces and predicts the overall EDL configuration near both the flat, crystalline electrodes and various electrode heterogeneities.