

Stabilizing sub-nano catalysts for high temperature reactions of interest for fuel cooling

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Sub-nano supported clusters have potential as active and selective catalysts, with properties that are tunable by varying size and composition, however, they also are highly unstable with respect to deactivation by both thermal sintering and poisoning under reaction conditions. We have been combining experiments with size-selected clusters deposited on surfaces, and detailed density functional theory, to understand the mechanisms for cluster catalytic activity, and the processes leading to deactivation. We have found that selectively doping the clusters with germanium stabilizes the clusters against both thermal and poisoning (coking) effects under hydrocarbon-rich, high temperature conditions, and explored the mechanisms for deactivation and stabilization. Stabilization is found to result largely from Ge-induced changes in the electronic/bonding properties in the clusters. The result is that poisoning becomes self-limiting, i.e., Ge does not completely stop coking, but limits coking to an extent that the cluster remains active, with stable strong hydrocarbon bonding sites. Interestingly, the coking limit,  $\sim 2$  C atoms/cluster, is essentially independent of cluster size, at least in the size range studied.

The initial work was done using C<sub>2</sub> hydrocarbons as the test system, with experiments only under UHV surface-science conditions. In the past year we have been examining butane, iso-butane, butene, and iso-butene on Pt<sub>n</sub>Ge<sub>m</sub>/alumina model catalysts, allowing fuel structure effects to be probed. The results are largely similar to what was observed for C<sub>2</sub> reactions. In addition, experiments are now being done both in UHV and with an AFOSR-funded high pressure microreactor system, with photo-ionization mass spectral product detection.

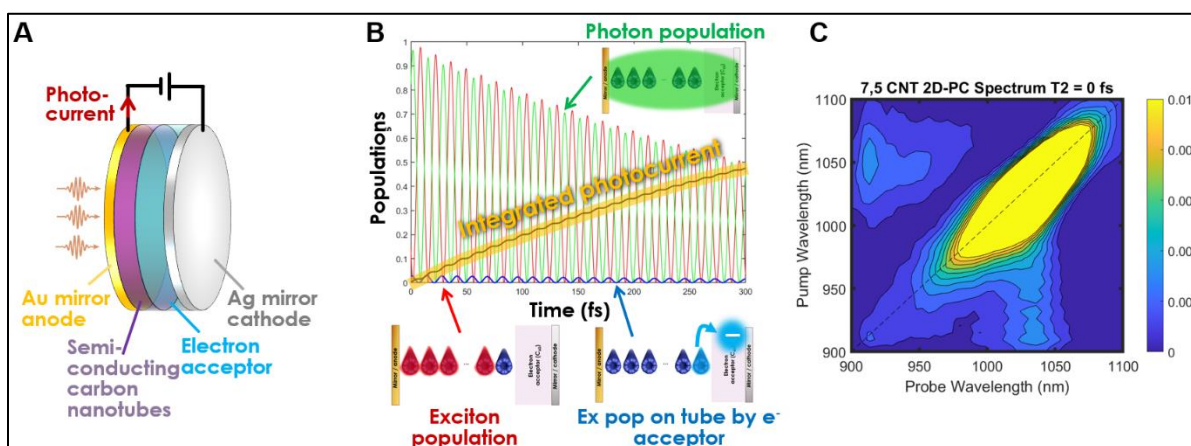
# Photocurrent readout of polaritons: Physical evidence for long range exciton transfer

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Exciton polaritons are thought to be spatially delocalized across the molecules that are coupled by the light field of the microcavity. If so, then it might be possible to collapse the wavefunction into desirable locations, such as the interface responsible for dissociating excitons into charges in photovoltaic devices. To test this idea, we have built a photovoltaic device into a microcavity, using the microcavity mirrors as the electrodes. Carbon nanotubes are the light absorbing materials and  $C_{60}$  is the electron acceptor that dissociates the excitons into charges that are collected and externally measured as photocurrent (Fig. 1A). When these microcavities are illuminated with monochromatic light to create polaritons, photocurrent is generated even without an applied voltage – indicating that polariton-to-photocurrent conversion occurs spontaneously. This powerful photocurrent readout approach is allowing us to study the fundamentals of polariton photophysics in new ways, explore disorder and dark states in these systems, and understand how to leverage long-range polariton energy transfer phenomena to improve photovoltaic-type devices.

This talk will specifically present on (1) the use of photocurrent readout spectroscopy to evidence long-range energy transfer in polariton microcavities, (2) the theory underpinning this energy transfer in which the polariton modes oscillate (with a period of a few fs) between having photon character, exciton character on nanotubes far from the electron acceptor, and exciton character on charge generating nanotubes next to the electron acceptor (Fig. 1B), and (3) 2D white light spectra using photocurrent detection rather than absorption detection to discriminate between productive energy transfer pathways that lead to charges and unproductive pathways that end in trap states (Fig. 1C). These experiments are important because they assess the plausibility of harnessing new exciton and energy transfer physics for more efficiently leveraging excitonic semiconductors as the light harvesting components of photodetectors and possibly solar cells, while answering fundamental questions for how energy flows and relaxes in polariton cavities.



**Figure 1. Photocurrent readout of polaritons.** (A) Schematic of nanotube/acceptor heterojunction embedded in microcavity. (B) Simulation of time-evolution of photon and exciton components of polariton wavefunction. Electron transfer is incorporated for nanotubes near the electron acceptor. (C) 2D white light photocurrent spectrum generated by our new spectrometer.

## **Ab initio surface chemistry with chemical accuracy**

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First-principles calculations are a cornerstone of modern surface science and heterogeneous catalysis. However, accurate reaction energies and barrier heights are frequently inaccessible due to the approximations demanded by the large number of atoms. I'll describe our recent developments, especially the use of local natural orbitals in periodic coupled-cluster theory, which enable electronic structure calculations of molecules on surfaces with chemical accuracy of about 1 kcal/mol. Two applications will be presented concerning metal oxide surfaces, including the dissociative adsorption of water and the vibrational spectroscopy of adsorbed carbon monoxide.

## Dynamics, Structure, and Interactions in Thin Films and Bulk RTILs

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Room temperature ionic liquids (RTILs) are salts that are liquids at ambient temperatures. They often consist of bulky and asymmetric ions with delocalized charges. RTILs have many applications, such as electrolytes in batteries and capacitors, media in CO<sub>2</sub> capture, solvents in chemical synthesis, lubricants, and propellants. In addition to the importance of the properties of RTILs in bulk liquids, the changes in their behavior near interfaces are relevant in various applications.

We have examined very thin films of 1-butyl-3-methylimidazolium cation - tetrafluoroborate anion (BmimBF<sub>4</sub>) and anion bis(trifluoromethylsulfonyl) imide, (BmimTFSI or BminNTf<sub>2</sub>). The thicknesses range from a few tens to a few hundreds of nanometers. The films can be formed reproducibly with controlled thicknesses on 100 nm SiO<sub>2</sub> layers deposited on CaF<sub>2</sub> substrates. To obtain uniform high-quality films, it is necessary to functionalize the SiO<sub>2</sub> surfaces to make them chemically similar to the RTILs. The functionalization produces a layer ~1 nm thick. We use ultrafast nonlinear IR experiments conducted on a vibration probe, e.g., the CN stretch of SCN<sup>-</sup> to measure different types of film dynamics. We have studied the IL dynamics with 2D IR and, more recently, with IR pump-probe experiments. 2D IR measures the structural fluctuations of the films, and the pump-probe experiments measure vibrational lifetimes. We are just now obtaining the first data to determine the orientational relaxation of the probe molecules in the thin films. All of the experiments are conducted as a function of film thickness.

To understand the significant differences in dynamics observed in the thin films, we are initially collaborating with Professor Jesse McDaniel, Georgia Tech, on three bulk liquids. We are measuring the probe orientational dynamics in BmimBF<sub>4</sub>, BminTFSI, and BmimPF<sub>6</sub>. The orientational dynamics observable is very useful for comparisons with simulations. The first results compare the experimental and simulated orientational relaxation for the three liquids.

The vibrational lifetime measurements as a function of film thickness were conducted on BminBF<sub>4</sub> and BminTFSI. A model was used to determine how rapidly the influence of the interface falls off with distance. The fall-off is modeled as exponential. The decay constant is the correlation length,  $l$ . We found the correlation  $l = 44$  nm for BminBF<sub>4</sub> and 48 nm for BminTFSI. These values are consistent with prior measurements using 2D IR, but they are more robust. The results of measurements of thin film orientation relaxation of SCN<sup>-</sup> in BminBF<sub>4</sub> will also be presented.

Comparisons will be made between our three bulk IL liquid orientational relaxation measurements and Jesse McDaniel's simulations. Jesse's calculations of the charge-correlation structure factors and their possible relation to the orientation relaxation experiments will be discussed. It will be speculated that the relationship between the charge-correlation structure factor and the bulk orientational relaxation measurements might be connected to the long correlation lengths found in the distance dependence of the dynamic observables in thin films.

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“Long-Range Interface Effects in Room Temperature Ionic Liquids: Vibrational Lifetime Studies of Thin Films,” John P. Breen, Laura C. Leibfried, Xiangyu Xing, and Michael D. Fayer J. Phys. Chem. B 127, 6217-6226 (2023). [doi.org/10.1021/acs.jpcc.3c02948](https://doi.org/10.1021/acs.jpcc.3c02948)

## Exploring Multimetallic Molecules with Localized Multireference Methods

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Transition metal systems present a significant challenge in quantum chemistry owing to the near-degeneracy of d-shell electrons. I will describe advancements in electronic structure theory, focusing on the exploration of multimetallic molecular systems characterized by strong electron correlation. A specific case study will delve into the exploration of antiferromagnetic and ligand field effects on spin crossover in a dimeric Cr(II) complex [1] using multiconfigurational methods. I will also discuss the development of the localized active space self-consistent field (LASSCF) method. This approach factorizes a complete active space wave function into localized active space wave function fragments, facilitating the reintroduction of correlation between fragments through LAS state interaction (LASSI). I will outline our latest efforts to automate the LASSI method and its application to tri- and tetra-iron complexes.[2]

[1] A. Sarkar, M. R. Hermes, C. J. Cramer, J. S. Anderson, and L. Gagliardi *Understanding Antiferromagnetic and Ligand Field Effects on Spin Crossover in a Triple-Decker Dimeric Cr(II) Complex* J. Am. Chem. Soc. 2023, 145, 41, 22394–22402 DOI: 10.1021/jacs.3c05277

[2] V. Agarawal, D. King, M. R. Hermes, L. Gagliardi *Automatic State Interaction with Large Localized Active Spaces for Multimetallic Systems* 2024 <https://arxiv.org/abs/2403.15495>

## Size-Dependent Condensation and Oxidation Reactions in Aqueous Microdroplets

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The UCSD-based MURI entitled “An integrated experimental and theoretical approach toward understanding novel reactivity, structure and chemical gradients in aqueous microdroplets.” is focused on utilizing spectroscopy, theory and kinetic modeling to probe reactions within aqueous microdroplets. In particular, condensation and oxidation reactions have been shown to be enhanced in aqueous microdroplets relative to the bulk aqueous phase. Although the surface of the microdroplet has been proposed to play a role in this enhanced reactivity, there are few studies that probe the size-dependent aqueous microdroplet chemistry under relative humidity and temperature control. In this talk, two examples of size dependent microdroplet chemistry will be given. The first is the acid-catalyzed condensation of pyruvic acid at 298 K. Utilizing confocal and cavity enhanced Raman spectroscopy as a probe of the condensation reaction, the Grassian and Continetti groups have shown that the reaction readily occurs within microdroplets but not in the bulk aqueous phase. Furthermore, the unusual sigmoidal kinetics for this reaction, involving an induction period, a reaction period, and a completion period, show size-dependent behavior. In particular, there is a surface area dependence of the induction time and a surface-to-volume ratio dependence of the rate during the reaction period. These size-dependent measurements are combined with theory (Amaro group), SFG measurements (Xiong group) and kinetic modeling (Dutcher group) to explain surface energetics, surface speciation and the sigmoidal reaction kinetics, respectively. Based on the experimental, theoretical and kinetic modeling results, we propose an autocatalytic reaction at the air/water interface where the condensation product, pyruvic acid, catalyzes its own formation. The second reaction that will be briefly discussed is the oxidation reaction of soluble S(IV) to S(VI), i.e. sulfite to sulfate. This reaction is also shown to be size dependent. The surface-to-volume ratio dependence of sulfate formation indicates that the surface plays an important role in the oxidation chemistry. Additionally, by measuring the rates of sulfate oxidation as a function of gas-phase oxygen pressure, molecular oxygen is shown to be the oxidant in the reaction. Overall, these two examples show size-dependent reactivity of microdroplets and provide insights into aqueous microdroplet interfacial chemistry.

# **Role of Interfaces and Electrostatics for Chemical Transformations**

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Chemical transformations rarely occur in a single homogeneous aqueous phase, but instead occur in niches, crevices, and impurity sites at confining interfaces between two or more phases of gases, liquids or solids. The effects of interfaces on molecular properties are ubiquitously present across diverse fields spanning nanochemistry and chemical (bio)catalysis, environmental and energy sciences, geosciences, and functional materials. Fundamentally, interfaces can alter solvent and solution compositions and phases to reformulate the transition states and pathways of chemical reactions and underlying transport mechanisms. I will introduce new theoretical models and methods, and applications to examine interfacial problems for reactive chemistry, to investigate and formulate recent hypotheses around microdroplet chemistry.

# Quantum Chemistry for Quantum Logic

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Chemists are largely absent from the world-wide effort to realize *useful* quantum technology, relegating chemistry to merely an afterthought when qubits and their associated quantum machinery are built. This talk will be a call-to-arms for the chemical community. I will argue that elevating chemical considerations in the design process would lead to improved performance for current quantum processors [1,2] and wholly new routes to quantum technology [3,4,5]. Chemists, we need you!

**Acknowledgments:** US ARO, US AFOSR, and US NSF.

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- [3] G.Z. Zhu et al., “Functionalizing aromatic compounds with optical cycling centres”, *Nature Chemistry* **14**, 995 (2022).
- [4] S.J. Jain et al., “AE Codes,” arXiv:2311.12324 (2023).



# Molecular Cavity Quantum Electrodynamics and Polariton Chemistry

Frank Huo, University of Rochester

Coupling molecules to a quantized radiation field inside an optical cavity has shown great promise in modifying chemical reactivity. In this talk, I will report on our recent progress in theoretical investigations of Molecular Cavity Quantum Electrodynamics (QED) funded by AFOSR.

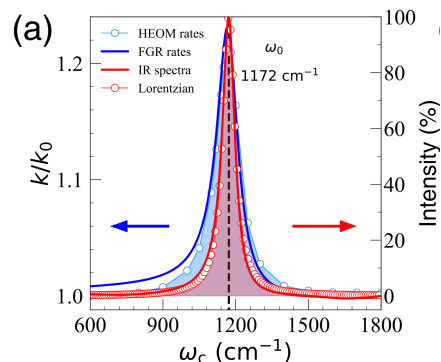
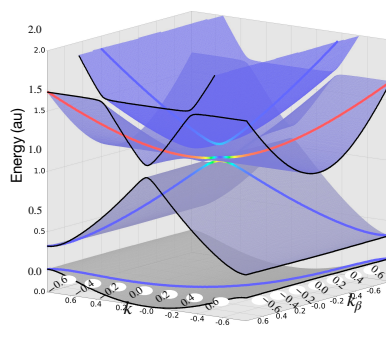
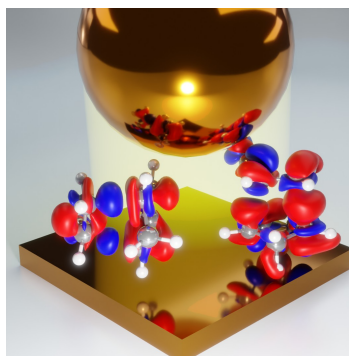
First, I will briefly discuss our effort to use ab initio theory to investigate molecular polaritons [1]. Using our recently developed parameterized QED approach along with time-dependent density functional theory, we theoretically investigated that the ground state selectivity of a Diels-Alder reaction can be fundamentally changed by strongly coupling to the cavity, generating preferential endo or exo isomers which are formed with equal probability for the same reaction outside the cavity. Our results are within a quantitative agreement with the coupled cluster level of theory for QED with significantly reduced computational costs. If time allows, I will also present a new theoretical formalism [2] that describes light-matter interactions going beyond the typical long-wavelength approximation and converging much faster in the ultra-strong and deep-strong coupling regimes.

Second, I will discuss our recent efforts in developing an analytic rate theory to understand vibrational strong coupling (VSC) modified rate constants in polariton chemistry when coupling a single molecule to an optical cavity [3]. The analytic expression exhibits a sharp resonance behavior, where the maximum rate constant is reached when the cavity frequency matches the vibration frequency. The theory also explains why VSC rate constant modification closely resembles the optical spectra of the vibration outside the cavity. Our analytic theory suggests that there will be a turnover of the rate constant as one changes the cavity lifetime, and the rate constant will first scale quadratically with respect to the light-matter coupling strength and then saturate. The analytic rate constants agree well with the numerically exact hierarchical equations of motion (HEOM) simulations for all explored regimes.

[1] Investigating Cavity Quantum Electrodynamics-Enabled Endo/Exo-Selectivities in a Diels-Alder Reaction, Wang, Weight, and Huo, ChemRxiv, DOI: 10.26434/chemrxiv-2024-6xsr6

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## Molecular-level aspects of the electrostatic “reaction field” around solvated ionic structures through cryogenic spectroscopy

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Chemical processes at the air-water interface that involve ions occur in a unique regime due to the asymmetric solvation environment. This is particularly important in the case of reactions in microdroplets which feature large surface-to-volume ratios. One example of this is the behavior of acids close to the interface. This talk will first focus on the speciation of formic acid at the surface of methanol microdroplets that contain trace (1%) water. Our MURI co-PI Cooks suggested that the accelerated condensation reaction between diaminobenzene and formic acid to form benzimidazole is driven by protonated formic acid ( $\text{HCO}_2\text{H}_2^+$ ). Although unusual in typical aqueous chemistry, this ion could be created due to the low pH at the interface and the presence of a few water molecules. To address the behavior of protonated formic acid in the presence of trace water, we isolated cluster ions with composition  $\text{HCO}_2\text{H}_2^+(\text{H}_2\text{O})_{n=1-10}$  and investigated their structures by analyzing their vibrational spectra at low temperature. Anharmonic calculations by MURI co-PI Head-Gordon established that the sequential addition of water molecules incrementally pulls the excess proton into the water network to yield a neutral formic acid moiety complexed to a nearby hydronium ion. Isomer-selective vibrational spectroscopy then reveals how the extent of the partial proton transfer depends on the local network topologies.

We also explored the related acid-base process in which carboxylate anions are re-protonated when complexed with size- and -shape-selected water networks. This is the cluster analogue of the base hydrolysis reaction familiar from base titration by strong acid in general chemistry laboratories. The vibrational bands of the carboxylate group are observed to undergo very large solvatochromic shifts upon addition of water molecules. This effect is traced to the changing electric fields at the anionic charge center due to the reaction electric field of the solvent network. An interesting aspect of this symbiotic interaction between solute ion and finite solvent shell is that specific water network sites are identified that drive the re-protonation event. The solvatochromic behavior was further explored by following the spectral responses of carboxylates complexed with divalent metal ions. This effectively inverts the direction of the reaction field as the water network shape is dominated by electrostatic interaction with the cation.

Ongoing work will also be discussed in which we follow chemical reactions at elevated temperatures in size-selected and temperature-controlled cluster ensembles. As a demonstration system, we are monitoring the slow kinetics of water network-mediated, long-range proton translocation across the organic scaffold 4-aminobenzoic acid. The goal for this approach is to determine the behavior of microscopic systems under conditions closer to those at play in microdroplet chemistry.

## Surface Plasmon Polaritons of MXenes

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Layered transition metal carbides and nitrides, colloquially referred to as MXenes, are a new class of two-dimensional materials with tunable properties for catalysis, photonics, and sensing. The mixed-termination titanium carbide MXene,  $\text{Ti}_3\text{C}_2\text{T}_x$ , synthesized from the parent  $\text{Ti}_3\text{AlC}_2$  (MAX) phase through in-situ generated HF etching is widely reported as a 2D metal. While localized plasmon resonances of MXenes have been observed with monochromated EELS microscopy, these resonances have been confined to the infrared portion of the electromagnetic spectrum.<sup>1</sup> In this talk, I will discuss experiments where we directly observe surface plasmon polaritons of  $\text{Ti}_3\text{C}_2\text{T}_x$  that span the entire visible portion of the spectrum and how to describe these 2D plasmons theoretically.<sup>2,3</sup>

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2. Rieger, J., Raab, C., Ghosh, A., King, S. B., Surface Plasmon Polaritons of  $\text{Ti}_3\text{C}_2\text{T}_x$  MXenes, *In Preparation*.
3. Raab, C., Rieger, J. Ghosh, A., King, S. B., Theoretical models for surface plasmons of 2D metals, *In Preparation*.

## Chiroptical Excitation and Ultrafast Dynamics in Atomically Ordered Metals

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We have made significant progress in understanding the relationship between lattice structure and the nonlinear optical properties and ultrafast electron dynamics of Ag 2D-polar metal heterostructures (PMets). Silver PMets are formed as crystalline monolayers, intercalated at the confines between SiC and graphene. Silver adopts one of two phases, depending on intercalation conditions. One phase is a Ag monolayer with 3:3 registry to the hexagonal SiC lattice – termed Ag<sub>1</sub>. This Ag phase exhibits visible electronic resonances. A second, denser phase is formed in a slightly rotated 4:3 lattice with a Ag atom occupying an interstitial site. This so-called Ag<sub>2</sub> phase supports resonances in the high-energy visible spectrum. SHG from Ag<sub>2</sub> is very efficient, exhibiting an effective  $\chi^{(2)}$  of 11.4 nm/V, approximately 3x larger than our previous values for Ga and In PMets. In contrast, Ag<sub>1</sub> exhibits saturable SHG intensities. Using ultrafast Fourier transform SHG, we have resolved the importance of resonance excitation and sub-cycle population transfer for enabling the saturable effect. Following multi-photon excitation, energy transfer between  $3\omega$  and  $2\omega$  resonances occurs on a sub-cycle ( $< 2\text{fs}$ ) timescale, creating a population inversion and saturable optical effects. The two different SHG responses result from atomic-scale differences in lattice structure that impact carrier dynamics. The ability to synthetically control structure in select spatial domains could translate to developing ultra-high resolution spatial light modulators and optical-limiting materials, which would have impacts in many technology areas. We have also made significant advances in understanding metal-to-graphene energy transfer using high harmonic generation (HHG). Interfacial carrier transfer was quantified using both HHG intensities and polarization dependences. The HHG signals were correlated to the heterostructure work function, as determined by angle-resolved photoelectron spectroscopy. The studies demonstrate the effectiveness of high-order harmonic generation for studying interfacial energy transfer in 2D material heterostructures.

In a related project, we have examined the influence of atomic- and molecular-level structure on chiroptical excitation, spin, and electron dynamics at metal-ligand interfaces. Gold nanoclusters spanning from sub-to-two nanometer –diameters show a diverse range of magneto-chiral excitation behaviors. The visible magnetic circular dichroism (MCD) spectrum of Au<sub>144</sub>(SC<sub>8</sub>H<sub>9</sub>)<sub>60</sub> includes nineteen distinct peaks. Among these, signatures of paramagnetic, diamagnetic, and mixed charge transfer excitations are all resolved. The results indicate that structurally well-defined gold clusters near the onset of metallicity present many opportunities for understanding and tailoring spin properties at metal-ligand interfaces.

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# Quantum Wigner molecules in semi-conductor quantum dots, TMD moiré materials & their superlattices, and polymeric electron zig-zag chains in inter quantum-dot couplers

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Understanding the electronic spectral and configurational organization beyond that of natural atoms is rapidly becoming a major research direction focusing on the exploration of the nature of charged carriers trapped in artificially fabricated, isolated or superlattice-assembled, quantum dots (QDs). Such research is motivated by the potential for utilizing these systems, with high tunability and control, in future quantum information and computational platforms. Earlier studies have unveiled a novel fundamental-physics aspect in such nano-systems, namely, formation of quantum Wigner molecules (WMs) [1,2], originally predicted theoretically [1, 2] in two-dimensional (2D) semiconductor QDs, as well as trapped in ultracold atoms, and subsequently observed experimentally in GaAs QDs [2], Si/SiGe QDs, and carbon nanotubes. Remarkably, recent work [3, 4] extended the WM portfolio to the newly arising and highly pursued field of transition-metal dichalcogenide (TMD) moiré materials, owing mainly to the promise for fundamental-physics discoveries and the potential for advancing quantum-device applications.

Adopting a bottom-up methodology, and building on the demonstrated emergence [3] of WMs (with  $N=2-6$  trapped electrons or holes) in the quasi-isolated moiré pockets [most often referred to as moiré quantum dots (MQDs)], we addressed the inevitable incorporation of such single MQDs in a superlattice structure. Specifically, we focused on the effects on WM formation resulting from the interaction between neighboring MQDs. Two different methodologies are used in this endeavor, namely: (i) the spin-and-space unrestricted Hartree-Fock (sS-UHF) [1,2], and (ii) the full configuration interaction (FCI) [1]. We uncovered that going beyond the (single-determinant) UHF mean-field treatment via symmetry-restorations of the broken-symmetry UHF solutions (resulting in a multi-determinant entangled wavefunctions, allows a much improved, efficient and feasible, descriptions of confined Wigner-molecular structures in moiré coupled quantum-dots [4]. Recently, we discovered with this approach, formation of polymeric multi-stranded Wigner electron molecules in a modeled patterned (quasi-one-dimensional, wire-like) elongated silicone quantum dot investigated as an inter-dot, on-chip, coupler.

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## Attosecond XUV Probing of Spin Dynamics

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As a quantum mechanical parameter, the properties pertaining to spin are often the most challenging to develop intuition about, yet they are some of the most fundamental and important to physical and chemical phenomena. The spins of electrons and holes are important parameters that govern many chemical and energy transfer processes, magnetic materials, material phase transformations, topological spin protection, and key methodologies for quantum information and quantum computing. An excellent method to quantify spin transport is ultrafast extreme ultraviolet (XUV) or X-ray magnetic circular dichroism (XMCD). It is a unique ultrafast spectroscopic tool due to its attosecond and few-femtosecond time resolution, element specificity, spin sensitivity, and large magnetic contrast. It offers unique capabilities to address spin tunneling and injection mechanisms from one material to another in solids. Ultrafast XUV and X-ray circular dichroism spectroscopy represents a new frontier in the realm of materials measurement techniques. Circular dichroism retains the excellent element specificity and time resolution recognized in other short pulse XUV techniques and adds spin sensitivity to its range of capabilities. These unique abilities not only allow for detection of macroscopic properties such as ultrafast magnetism, but also band-resolved spin-dynamics of electrons and holes and element-resolved spin transfer dynamics across interfaces.

Using attosecond XUV transient absorption spectroscopy with a four-mirror polarizer to provide circular polarization, a measurement of induced circular dichroism in excited states of atomic helium was performed for the first time. The experiment shows a clear dependence of the accessed magnetic sublevel transition probabilities, demonstrating the spin-selectivity of the method. Considering solids, early work investigated experimentally and theoretically the relaxation of spin polarization in bulk semiconductors. Due to the strong spin-orbit interaction and momentum-coupling of holes, their spin relaxation is often approximated as instantaneous. As there have been very few actual measurements of the relaxation timescales, researchers do not know what rates and mechanisms should be expected. In germanium and gallium arsenide, typical timescales for hole spin relaxation of 100 fs were described, while the pulses themselves were also 100 fs. Applying the same XUV circular dichroism methodology to holes in the valence band of germanium, formed by visible light absorption of circularly polarized pulses, but in this case with pulses of 4 fs duration, new observations of spin relaxation of the holes in germanium are found to be remarkably rapid:  $3.6 \pm 0.6$  fs. The result puts new scrutiny on theories of hole spin-relaxation and will illuminate the relevance of possible relaxation pathways.

A focus of this program over the years has been to use XUV transient absorption to measure ultrafast photoinduced processes of charge localization at the surface of photocatalytic materials and the transport of charge across junctions. This work is now being extended to include spin transfer systems, the results of which are potentially important for chiral chemistry and quantum information systems. A layered system consisting of 20 stacked replicas of 6   Co / 8   Pt layers was investigated. In this experiment a 4 fs, broadband linearly polarized infrared laser pulse was used to drive injection of magnetically prepared spin-polarized electrons of the cobalt layers into the Pt layers (the sample is placed in a static magnetic field of 350 mT to align the spins in the cobalt). Changes in the XUV absorption of the system in both the Pt and Co were monitored by circularly polarized XUV probe pulses upon excitation by the optical pump pulse, spanning a broadband XUV energy of 45-70 eV. On long timescales there is an overall decrease in the dichroism at all energies, consistent with the expected process of femtosecond optical demagnetization of the sample overall. With 333 attosecond time resolution steps, the initial electronic response is also similar in both Co and Pt, following expectations of rapid carrier thermalization in metals. However, in the XMCD measurements, a sub-5 fs spike of new magnetization is observed in the Pt that follows the shape of the optical pulse, indicating a rapid transfer of the spin polarization from Co into the Pt. Theory indicates that injection of majority carrier electrons from the spin-polarized cobalt to the platinum results in the abrupt few-femtosecond spike of magnetism experienced by the platinum.

## Hot Carrier Driven Processes on Electrode Surfaces

Tianquan Lian

Affiliations:

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There have been recent reports photo-enhanced electrocatalytic process on metal electrodes. This process is related to the much more extensively studied plasmonic photocatalysis, but the electrode offers a way to tune the strength of interaction between the metal and adsorbates, thus controlling the photocatalytic process. The mechanisms of plasmonic photocatalysis are conventionally divided into two categories: thermal and nonthermal pathways. In this talk, we will discuss our recent progress in advancing the understanding of two main problems in plasmonic photocatalysis: 1) differentiating the contributions of thermal and nonthermal pathways to the reaction by direct measurement of adsorbate and electrode temperatures, and 2) identifying the mechanism of nonthermal pathways by direct time-resolved studies.

Although differentiating the contribution of thermal and nonthermal pathway has been widely recognized as the key to optimizing plasmon-mediated chemistry, measuring temperature down to the nanoscale at the reaction sites has been challenging. To address this challenge, we develop an in-situ spectroscopic approach that to simultaneously measure the temperature of the electrode and the adsorbate. The former is measured by the broad background of surface-enhanced Raman signal of the metal (plasmonic thermometry) and the latter is obtained through the ratio of Stokes and AntiStokes intensities of molecular vibrational modes (molecular thermometry). Using gold NP/4-nitrothiophenol as a prototype model, we demonstrate the agreement between two thermometries and prove that the dimerization of 4-nitrothiophenol occur through the nonthermal pathway.

The nonthermal pathways is often attributed to direct interaction of the plasmonic hot electrons or holes with adsorbate, although the detail mechanism remains unclear. One possible mechanism is selective excitation of adsorbate vibrational modes by rapid hot electron transfer and back transfer between the metal and the adsorbate. Using time-resolved vibrational sum frequency generation (VSFG) spectroscopy, we directly measure hot electron induced vibrational dynamics of adsorbates on metal electrodes. For CO adsorbed on Au electrodes, we show that excitation of the metal leads to the generation of vibrationally excited CO molecules. Detailed analysis reveals that the formation and decay of the excited adsorbates follows the electronic temperature of the electron, and the processes appears to be vibrational mode specific and dependent on the applied bias. This result suggests the possibility of plasmon (or light)-enhanced electrochemistry on metal electrodes.

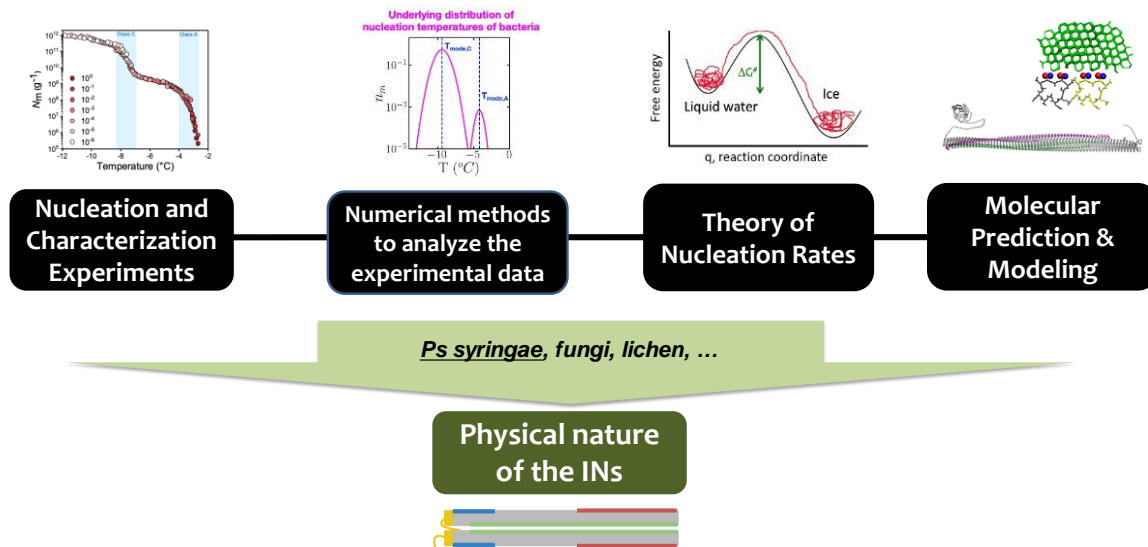
# The Most Potent Snow Makers

Valeria Molinero  
The University of Utah

Several species of bacteria, fungi, lichen, and insects have evolved proteins that are potent ice nucleants. Bacteria and fungi are aerosolized and uplifted to the clouds, where they contribute to cloud glaciation and precipitation. Indeed, bacteria are so powerful ice nucleants that are routinely used for the synthetic production of snow. Despite the importance of biological ice nucleation for the survival and thriving of organisms and atmospheric processes, little is known about sequence and/or structure of the ice nucleating proteins, the mechanisms by which they promote water crystallization, and what makes them so outstanding. This presentation will discuss our approach to bridge the results of laboratory experiments, theory, numerical and molecular simulations, and artificial intelligence to elucidate the mode of action of biological ice nucleants. Our studies reveal that nature uses a common strategy among organisms in several kingdoms, “E pluribus unum” (out of many, one), to nucleate ice at temperatures close to the 0°C by assembly of ice-nucleating proteins into large functional aggregates.

This work is supported by the MURI project “Unraveling the Mechanisms of Ice Nucleation and Anti-Icing Through an Integrated Multiscale Approach” in collaboration with the groups of Prof. Konrad Meister at Boise State University and Dr. Rajiv Berry at the Air Force Research Laboratory.

## Abstract figure:





## Ultrafast Hot Electron Cooling Dynamics in Plasmonic Nanostructures and Single Molecule Biophysics of Riboswitch Folding

David J. Nesbitt

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This talk will present recent results on two different topics. 1) Efficient excitation and harvesting of hot carriers from nanoscale metals is central to many emerging photochemical, photovoltaic, and ultrafast optoelectronic applications. Yet direct experimental evidence of the energy-dependent femtosecond dynamics in nanometer-scale gold structures remains elusive, despite the rich interplay between interfacial and internal plasmonic fields, electron-hole pair excitation distributions, and scattering processes. To explore the effects of nanoscale structure on these dynamics, we exploit a novel approach for simultaneous time-, angle-, and energy-resolved electron photoemission from single plasmonic nanoparticles *in vacuo*. Near the plasmon resonance, the measured photoelectron velocity and theoretical electric field distributions highlight the predominance of bulk-like ballistic hot electron transport dynamics, lacking strong signatures of surface effects. Specifically, ultrafast energy-resolved hot electron decays are measured in the 1–2 eV range and extrapolated to lower energies via Boltzmann theory, providing a detailed view of hot electron lifetimes within nanoscale gold. We find that particles with relevant dimensions as small as 10 nm serve as exemplary platforms for studying intrinsic metal dynamics and excellent comparison with Fermi liquid theory. 2) The ability to look at single biomolecules with lasers has led to a revolution in chemical biophysics and offers novel opportunities for highly specific biosensing. This talk will present recent results based on confocal microscopy, fluorescence resonance energy transfer (FRET), and single photon counting methods for exploring single molecule kinetics and thermodynamics relevant to conformational folding of RNA “riboswitches”. Exquisite temperature control in single molecule “nanobathbaths” is used to permit systematic deconstruction of free energy landscapes ( $\Delta G^0$ ) into enthalpic ( $\Delta H^0$ ) and entropic ( $-T\Delta S^0$ ) components, as well as help elucidate the nature of transition state barriers (e.g.,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ) for nucleic acid folding/unfolding. Recent extensions of these methods toward single molecule microscopy under high hydrostatic pressure conditions ( $P_{\text{ext}} = 1\text{--}4000$  bar) allow one to interrogate the thermodynamic stabilities and associated free volumes ( $\Delta V^0$ ,  $\Delta V^\ddagger$ ) for nucleic acid folding, as well as the impact of oligo sequence, mono/divalent cations, osmolytes, etc. on the ligand binding and folding event.

# **Plasmon-enhanced photocatalysis for green and sustainable hydrogen production**

**Peter Nordlander**

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Houston, TX 77005, USA*

Nanoparticle plasmons can serve as highly efficient generators of hot electrons and holes that can be exploited in chemical applications. The physical mechanism for plasmon-induced hot carrier generation is non-radiative plasmon decay.[1] This is a quantum mechanical process in which one plasmon quantum is transferred to the conduction electrons of the nanostructure by creating an electron-hole pair, i.e., excitation of an electron below the Fermi level of the metal into a state above the Fermi level. These hot carriers can activate molecules adsorbed on the nanoparticle surface and significantly lower the activation energies for bond breaking processes. I will present recent applications of plasmon-enhanced photocatalysis for hydrogen production, specifically from Ammonia decomposition,[2,3] Hydrogen sulfide decomposition, [4] and from dry[5] and steam[6] reforming of methane.

[1] J.G. Liu *et al.*, ACS Photonics 5(2018)2584

[2] L. Zhou *et al.*, Science 362(2018)69

[3] Y. Yuan *et al.*, Science 378(2022)889

[4] M. Lou *et al.*, ACS Energy Lett. 7(2022)3666

[5] L. Zhou *et al.*, Nature Energy 5 (2020)61

[6] Y. Yuan *et al.*, to be published 2023

## **Chiroptics and spin selectivity in helicenes and twistacenes**

Jeffrey McNeill, Milan Delor, Xavier Roy, Xiaoyang Zhu, David Reichman, and Colin Nuckolls  
Columbia University  
Department of Chemistry

This presentation will detail our efforts to create materials from contorted aromatic molecules. In particular, I will discuss how to create helicenes and twistacenes from perylene diimide building blocks. These materials have extraordinary properties as materials. The helicenes have the largest chiroptic response of any molecular species. The twistacenes helicity is dynamic and can be controlled by light and chemical/electrochemical reductions. These molecules can be attached to surfaces and measurements with magnetized substrates, and these monolayers excel in CISS measurements. Spectroscopy reveals that thin films of these materials support spin transport over long distances.

## A General Method for Single Molecule Spectroscopy

David Patterson, UCSB

Single molecular ions present a highly attractive platform for high resolution and highly sensitive spectroscopy. These molecules can be held for many hours in a pristine environment, and can be motionally laser cooled into the millikelvin regime and below. Prior to this work, methods to study "generic" single molecules have not been demonstrated. Here, we demonstrate a novel single molecule action-spectroscopy technique that is compatible with high precision measurement, and present the first spectra ever recorded of single polyatomic gas-phase molecules. The method is generally applicable to a wide range of polyatomic molecular ions, and promises spectral resolution comparable to state of the art quantum logic methods, with significantly less stringent experimental overhead. Progress towards extending this technique to include chiral recognition of single molecules will be discussed. Adaptations of this technique will prove useful in a wide range of precision spectroscopy arenas including the search for parity violating effects in chiral molecules and searches for biological signatures in samples from beyond Earth.

**Non-Equilibrium Flow Experiments in the GALCIT T5 Reflected Shock Tunnel:  
Aerothermochemistry Measurements and Modeling**

*Christopher Strand, Peter Finch, Julian Girard, Tal Schwartz, & Ronald Hanson - Stanford University*

*Wesley Yu, Ying Luo, Joanna Austin, & Hans Hornung - California Institute of Technology*

*Thomas Gross, Tom Schwartzentruber, Graham Candler, & Don Truhlar - University of Minnesota*

New flight vehicle concepts are being developed that involve flight at high speeds in the atmosphere where nonequilibrium effects become important. To support this endeavor, new nonequilibrium chemistry models for high-temperature air are under development using results from computational chemistry. However, the validation of kinetic models for flight applications is hampered by the lack of experimental data that directly probe molecular interactions in hypersonic flows. To address this deficiency, a research collaboration between Caltech, Stanford, and the University of Minnesota has applied spectroscopic measurement techniques to probe molecular and atomic states in hypervelocity, nonequilibrium air flows directly. Closely coordinated experiment design, involving modelling & simulation, laser spectroscopy, and wind tunnel researchers, has employed predictive aerothermochemistry CFD models to optimize test conditions, model geometries, and diagnostic designs to emphasize relevant physics (thermal/chemical nonequilibrium, dissociation, and recombination) and ensure maximum measurement accuracy. The resulting datasets aim to differentiate historic and state-of-the-art aerothermochemistry models, validate predictive air chemistry CFD, and create high-fidelity archival experimental datasets for the hypersonics community.

Joseph Subotnik

University of Pennsylvania

Towards a Fundamental Theory of the Chiral Induced Spin Selectivity Effect

There is still no consensus as to the fundamental mechanism underlying the Chiral Spin Selectivity effect, but it has been suggested that nuclear motion (and in particular, chiral phonons) may play a role, with an exchange of angular momentum between nuclear and spin degrees of freedom leading to nonequilibrium spin populations. Unfortunately, modern approaches based on Born-Oppenheimer theory are likely not trustworthy because they do conserve the total linear or angular momentum, and the electronic spin is by definition a small amount of angular momentum. To that end, in this talk, I will discuss our recent proposal to use phase-space electronic Hamiltonians so as to incorporate electronic momentum correctly and semiclassically simulate nuclear and electronic and spin motion all together, and I will highlight how we will investigate the possibility of spin-dependence in electron transfer.

# Inverse Chirality-Induced Spin Selectivity Effect in Chiral Assemblies of $\pi$ -Conjugated Polymers

Dali Sun

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## Abstract

Coupling of spin and charge currents to structural chirality in non-magnetic materials, known as chirality-induced spin selectivity (CISS), is promising for application in spintronic devices at room temperature. Although the CISS effect has been identified in various chiral materials, its Onsager reciprocal process, the inverse CISS (ICISS) effect remains unexplored. Here we report the observation of the ICISS effect in chiral assemblies of  $\pi$ -conjugated polymers [1]. Using spin-pumping techniques, the ICISS effect enables quantification of the magnitude of the CISS-driven longitudinal spin-to-charge conversion in different chiral polymers. The sign of the ICISS effect depends on the chirality of the polymers and occurs solely when the injected spin polarization aligns with the chiral axis. It's attributed to an unconventional spin orbit coupling related to the structural-chirality-induced Berry curvature leading to a linear spin-to-charge conversion. By widely tuning conductivities and supramolecular chiral structures via a printing method, we found a very long spin relaxation time of up to several nanoseconds parallel to the chiral axis. Our demonstration of the ICISS effect opens possibilities for elucidating the puzzling interplay between spin and chirality, and opens a route for spintronic applications using printable chiral assemblies.

## References

[1] Sun, R. *et al.* Inverse chirality-induced spin selectivity effect in chiral assemblies of  $\pi$ -conjugated polymers. *Nat. Mater.* (2024) doi:10.1038/s41563-024-01838-8.

## **Tailoring Metal-Oxide Interactions for Enhanced Catalytic Activity and Stability**

**Aleksandra Vojvodic**

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[alevoj@seas.upenn.edu](mailto:alevoj@seas.upenn.edu)

This talk will describe recent computational and experimental efforts at Penn (Raymond Gorte, John Vohs, and Aleksandra Vojvodic) of mechanisms underlying formation of metal species and particles from metal-doped perovskite oxide films and their unique catalytic properties (high activity and anti-coking). This will be exemplified through studies of (i) how the metal particles are formed on and interact with the thin oxide film, (ii) how the properties of the thin oxide film can be changed through its interactions with a support to influence the formation of the metal particles, and (iii) how the metal-perovskite interactions influence the catalytic properties of the metal particle. The results of our studies suggest that viable options are available for removing large amounts of heat by endothermic reactions which can play a significant role for engine thermal management in hypersonic aircraft.



## Chiral Induced Spin Selectivity and Its Application for Spin Control in Redox Chemistry

David Waldeck, University of Pittsburgh

The chiral induced spin selectivity (CISS) effect embodies the connection between the chiral symmetry of matter and the electron spin. After introducing some of the seminal works on the CISS effect as background, I will describe recent studies which illustrate its implications in electrocatalysis and redox chemistry.

## **Recent Progress of Polariton Chemistry Research (MURI)**

Wei Xiong

University of California, San Diego

Molecular polaritons, the hybrid half-matter, half-photon quasiparticles, offering exciting prospects for altering chemical reactions, mediating energy transfer and unlocking novel physical phenomena. In this talk, I will give an overview of the MURI team efforts towards elucidating the mechanisms of polariton chemistry and advancing its frontiers. Specifically, I will focus on a few advancements within my group, including (1) efforts to minimize the photonic cavity volume, achieving polariton at the small  $N$  limit; (2) a theoretical effort to understand the influence of disorder to the delocalization of polariton wavefunction and its dynamics; (3) examining how photonic environments influence energy dissipation and chemical dynamics. Together, these efforts together create the groundwork for harnessing light-matter strong coupling and novel photonic environments to steer chemistry.