

Novel NMR quantum sensors for chemical applications

Ashok Ajoy, UC Berkeley

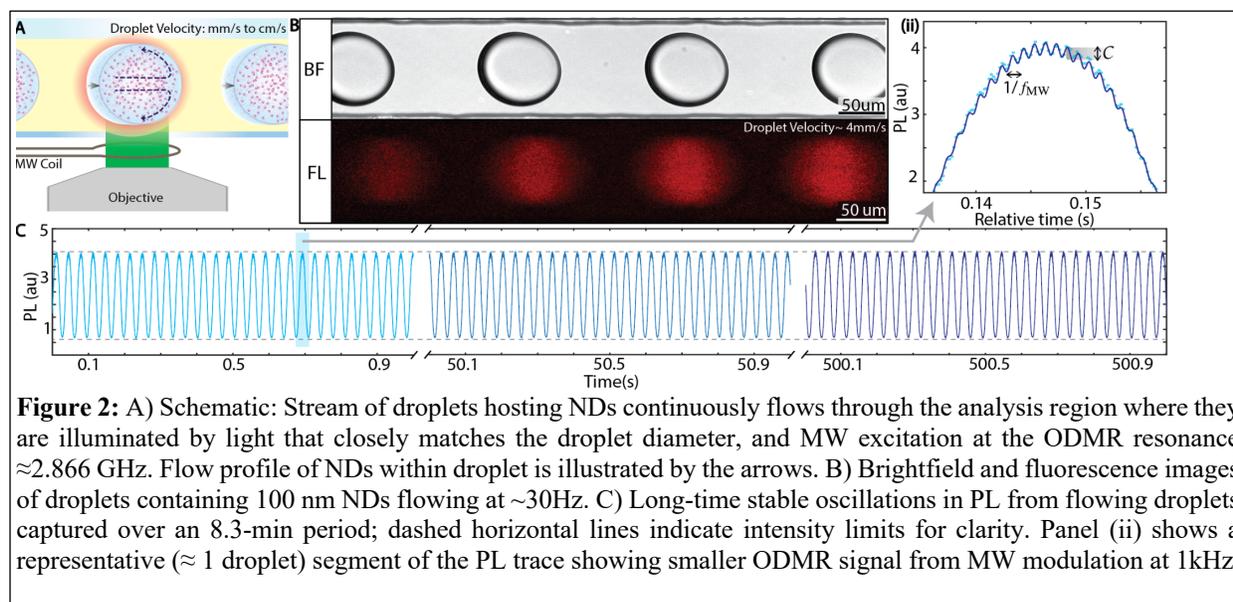
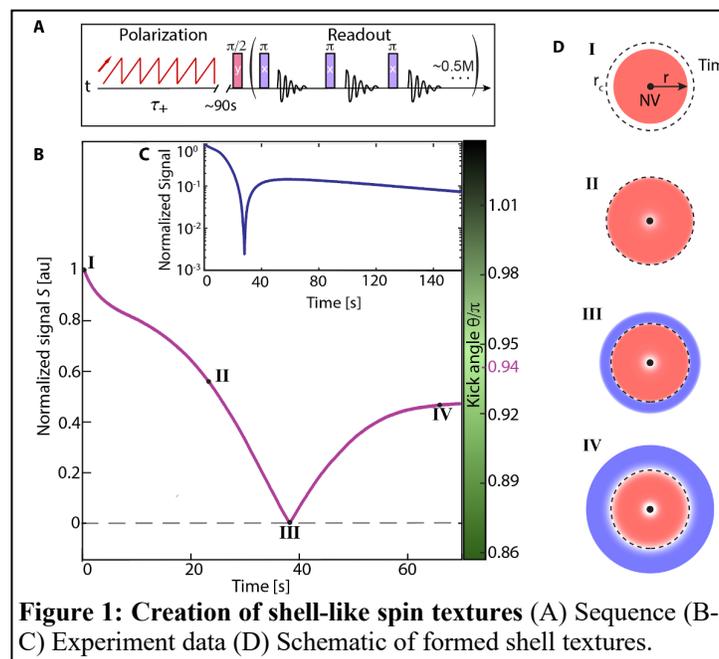
I will describe our efforts in developing hyperpolarized NMR sensors for various applications in analyte detection

and nanoscale chemical imaging. Broadly, I will describe our work in three complementary directions:

(1) We exploit hyperpolarization and long nuclear spin coherences to engineer *stable* mesoscale spin textures that extend over several nanometers [1]. Specifically, we showcase the capacity to generate, control, stabilize, and read out “shell-like” spin texture with interacting ^{13}C nuclear spins in diamond, wherein spins are polarized oppositely on either side of a critical radius. The texture spans several nanometers and encompasses many hundred spins. This presents a new approach to robust nanoscale spin state engineering and paves the way for new applications in nanoscale chemical imaging.

(2) We report on a method for high-precision chemical sensing, merging quantum sensing within microdroplets [2]. We exploit nanodiamond (ND) particles hosting nitrogen-vacancy (NV) defect centers as quantum sensors within rapidly flowing,

monodisperse, picoliter-volume microdroplets containing analyte molecules. Rapid ND movement within these microcompartments facilitates close sensor-analyte interaction and eliminates ND heterogeneity. Simultaneously, droplet flow is rapid ($>200\text{Hz}$) and controlled (drift $<0.1\text{Hz}$ over 3hr). Pairing this controlled flow with microwave control of NV electronic spin, we develop a new noise-suppressed mode of Optically Detected Magnetic Resonance (ODMR) method, sensitive to chemical analytes and resilient against experimental variations.



References: [1] K.Harkins *et al*, arxiv: 2310.05635, Sci. Adv. (in revision); [2] A. Sarkar *et al*, arxiv: 2404.19313, Sci. Adv. (in review)

Kinetic Energy Dependence and Potential Energy Surface of the Spin-forbidden Reaction Sm^+
(^8F) + N_2O ($^1\Sigma^+$) \rightarrow SmO^+ ($^6\Delta$) + N_2 ($^1\Sigma_g^+$)

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ABSTRACT

The kinetic energy dependence of the title reaction is examined using guided ion beam tandem mass spectrometry. Because this reaction is spin-forbidden, crossings between octet and sextet hypersurfaces presumably must occur. Further, Sm^+ must transition from a $4f^66s^1$ configuration in the reactant to $4f^55d^2$ in order to have the orbital occupancy required to form the triple bond in SmO^+ ($^6\Delta$). Despite being strongly exothermic (~ 4 eV), the reaction proceeds with low efficiency ($18 \pm 4\%$) via a barrierless process at low energies. Below ~ 0.3 eV, the cross section follows a kinetic energy dependence that roughly parallels that of the collision rate for ion-dipole reactions. At higher collision energies, the reaction cross section increases until it follows the trajectory cross section closely from 3 - 5 eV, indicating that another pathway opens on the reaction hypersurface. Modeling this increase yields a threshold energy for this new pathway at 0.54 ± 0.05 eV. Theoretical potential energy surfaces that do not include spin-orbit interactions for the reaction show that there is a barrier of height 1.19 eV (MP2) or 0.49 eV (CCSD(T)) to insertion of Sm^+ into the $\text{N}_2\text{-O}$ bond and that there are several places where octet and sextet surfaces can intersect and interact. By considering the distribution of spin-orbit states generated in the ion source, the internal energy of the N_2O reactant, and the influence of coupling between electronic, orbital, and rotational angular momentum, the low-efficiency, exothermic behavior as well as the increase in efficiency at higher energies can plausibly be explained.

Spin Polarized Electron Dynamics in Yttrium Iron Garnet Probed with Circularly Polarized XUV Light: A New Platform for Spin Selective Photocatalysis

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The goal of this project is to use circularly polarized XUV light as an ultrafast probe of spin selective electron dynamics at photocatalytic surfaces. Yttrium iron garnet ($\text{Y}_3\text{Fe}_5\text{O}_{12}$, YIG) is a ferrimagnetic semiconductor consisting of two sublattices based on octahedrally (O_h) and tetrahedrally (T_d) coordinated Fe^{3+} metal centers. Within each sublattice, high spin Fe^{3+} centers are ferromagnetically aligned, while the O_h and T_d sublattice are anti-aligned with respect to each other. Using ultrafast XUV reflection-absorption spectroscopy we measure the rate and efficiency of small polaron formation in photoexcited YIG and compare results to widely studied hematite ($\alpha\text{-Fe}_2\text{O}_3$).

Ultrafast measurements at the Fe M-edge show that YIG is characterized by a significantly lower polaron formation efficiency compared to hematite suggesting a much higher electron mobility and weaker electron phonon coupling in YIG. Quantitative analysis indicates that polaron formation efficiency in YIG is site dependent, where the O_h lattice efficiently traps photoexcited electrons by strong coupling to optical phonons, while electrons in T_d lattice sites remain delocalized. Due to the anti-ferromagnetic coupling between O_h and T_d sublattices, this difference in electron mobility gives rise to spin-dependent electron transport, where photoexcited O_h electrons trap at the surface as small polarons, while T_d electrons drift to bulk under the influence of the negative interface potential.

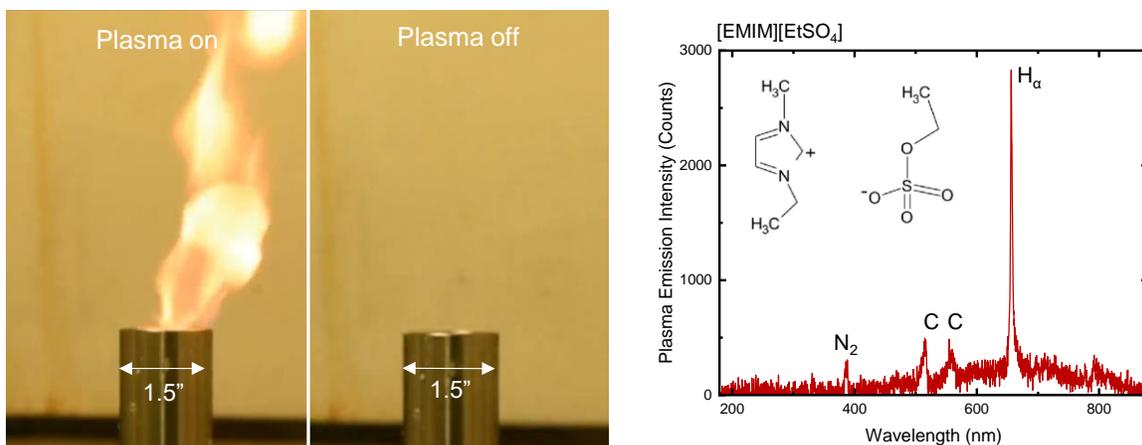
To understand the effects of spin dependent electron transport, we also measure the surface spin polarization in YIG using XUV magnetic circular dichroism (XUV-MCD). XUV-MCD measurements show that spin-aligned holes resulting from the fast drift of T_d electrons accumulate at the YIG surface. These holes occupy the hybridized O $2p$ / Fe $3d$ valence band giving rise to spin-polarized Fe^{4+} redox-active surface states that are long-lived. In collaboration with David Waldeck (University of Pittsburgh) we evaluate the performance of YIG as a photocatalyst for water splitting. Photo-electrochemical measurements confirm that the combination of enhanced electron mobility and spin polarized redox carriers in YIG result in significantly improved performance for photocatalytic water oxidation as demonstrated by a 15-fold enhancement in the photocurrent density for YIG compared to hematite. Together these findings demonstrate the ability of magnetic semiconductors to serve as an efficient platform for spin selective photocatalysis. These results also highlight the ability of ultrafast XUV-MCD to elucidate the spin dependent electron dynamics that control the formation spin polarized redox active surface states, and these measurements will soon be extended to study spin selective electron dynamics in chiral metal oxides.

In Situ Spectroscopy of Plasma-driven Combustion of Ionic Liquid-based Rocket Propellants

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Abstract: We report the use of nanosecond pulse transient plasma to initiate the catalyst-free combustion of ionic liquid-based rocket propellants and demonstrate on/off throttling. Here, we fabricate a cylindrical end-burning propellant sample with a co-axial center wire electrode filled with hydroxylammonium nitrate (HAN)-based monopropellants, including ethyl sulfate (Et SO₄)-HAN mixtures and, polyvinyl alcohol (PVA)-HAN mixtures. High voltage (20 kV) nanosecond pulses (20 nsec) produce a plasma discharge in the liquid that initiates combustion and provides electronic throttling of the propellant without the use of a catalyst. Realtime imaging is used to characterize the electrically-driven bubble formation, plasma initiation, and evolution of the ignition/extinguishing processes. Ignition and extinguishing of the propellant take place in less than 33 msec. The plasma-driven mechanism of combustion proceeds as follows: 1.) Bubble formation occurs as a result of the high applied electric fields (i.e., electrostriction). 2.) Plasma initiation occurs in these bubble regions where dielectric breakdown occurs. 3.) The plasma provides highly energetic electrons and highly reactive atomic species such as H, O, and C. 4.) These radical species serve as short-lived reaction intermediates that drive new chemical reaction pathways at an accelerated rate. *In situ* plasma emission spectroscopy exhibits sharp peaks corresponding to these monatomic and diatomic species enabling us to identify important plasma-driven reaction pathways, which deviate from those of conventional thermal catalysis and thermal decomposition chemical pathways.



Caption: (a) Photographs of the test cell during combustion with and without plasma discharge. The propellant mixture contains HAN and EMIM EtSO₄. This is an end burner (combustion vessel) open to atmosphere system. The center wire carries the high voltage while the outer shell acts as the ground. (Right) Plasma emission spectra obtained in EtSO₄. The peaks were identified and labeled using the known wavelengths.

Understanding Electron-Initiated Reactions Through Femtosecond Time-Resolved Studies

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In contrast to photon-initiated reactions, there is a notable scarcity of reports on femtosecond time-resolved electron-initiated reactions. Electron-initiated chemistry finds applications across various scientific fields, both fundamental and applied. In Earth's ionosphere, electron ionization surpasses photoionization, significantly contributing to the production of NO_x species in the upper atmosphere. Presently, the understanding of electron interactions with gas phase molecules commonly used in plasma etching, deposition, reactor cleaning, and additives, remains predominantly at a thermodynamic level. In the medical field, secondary electrons generated by x-rays cause direct and indirect DNA damage. Electron-initiated chemistry is integral to techniques such as electron beam induced deposition, extreme ultraviolet photolithography, nanofabrication and mass spectrometry. The widespread impact of electron-initiated chemistry underscores the importance of a detailed time-resolved molecular-level understanding, which can enhance its applications across diverse fields. Our group uses electron recollision following tunnel ionization to enable the femtosecond time-resolved study of electron-initiated reactions. Through this method, we have sought to study the complex chemistry, involving ionization, isomerization, roaming, and multiple pathways, all initiated by 10-100 eV electrons.

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J. Stamm, S. Kwon, S. Sandhu, M. Shaik, R. Das, J. Sandhu, B. Curençon, C. Wicka, B. G. Levine, L. Sun, M. Dantus, "The Surprising Dynamics of the McLafferty Rearrangement," *J. Phys. Chem. Lett.* 14,44, 10088-10093 (2023).

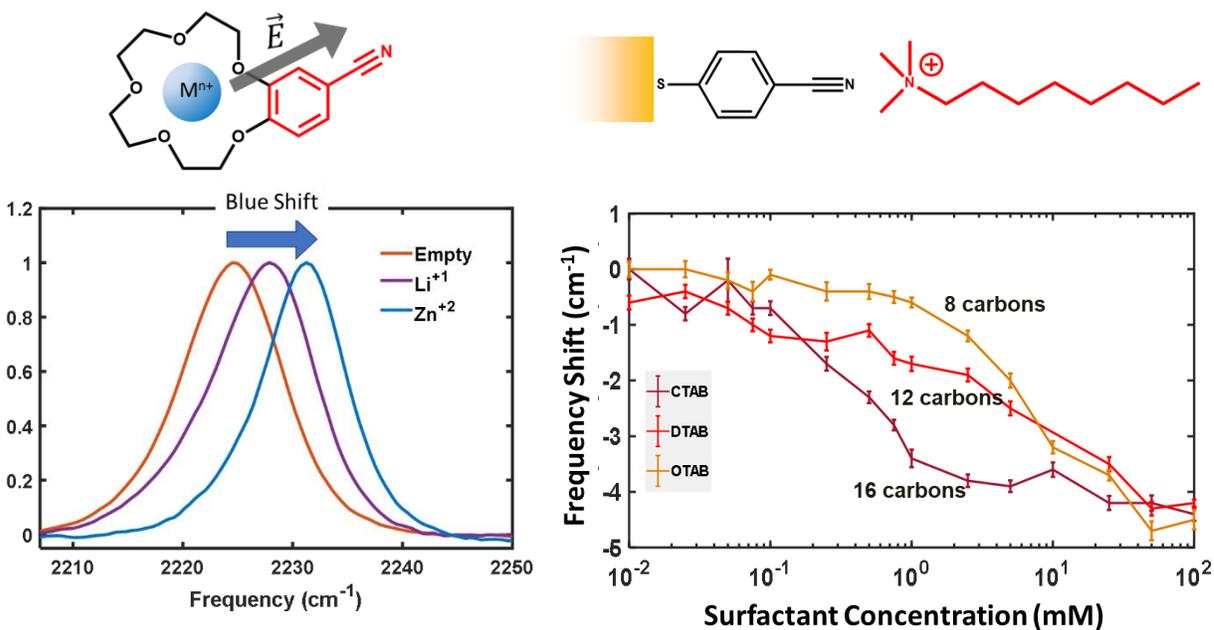
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Taking Charge of Local Electric Fields and Hydration: Crowns, Soaps, Interfaces

A. Maitra, P. Das, A. Mohammed, S. Edington, W. Lake, B. Thompson, M. Johnson, S. Hammes-Schiffer, S. Parsons, D. Eremin, V. Fokin, **J. Dawlaty**

University of Southern California

Controlling electric fields on the molecular scale to drive reactions is a challenge in modern chemistry. The challenge is to engineer the geometry of ions and solvent dipoles around a reactive site. Two approaches for creating such fields are using crowns ethers for capturing and placing ions near a reactive site in the bulk, and surfactants for accumulating excess charge near an electrochemical or air-water interface. Here we use benzonitrile and azide vibrational probes that are sensitive to the local electrostatics to estimate the polarizing influence of the ions in these scenarios. These studies help with creating design rules for tailoring local electric fields with ions.



Online Chemical Analysis of Flowing Hydrocarbon Fuel Surrogates in a Pyrolysis Reactor by Molecular Beam Mass Spectrometry

Authors: Andrew F. DeBlase, Matthew C. Rohan, Elizabeth S. Kurian, Alexander D. Tucker, Christopher R. Bruening, and William K. Lewis

Fuel is the primary thermal management fluid on board an aircraft. For Air Force applications, it is well known that kerosene fuels can experience temperatures in excess of 200 °C and pressures beyond 300 psia, at which the fuel is often a supercritical fluid. At such conditions, decomposition chemistry is possible, which leads to destructive coke deposits. Therefore, to mitigate coking chemistry, it is necessary to identify key intermediates of decomposition and relate the abundances of such species to the rates of aromatic synthesis and, ultimately, coke deposition. In the present work, we describe a new apparatus to probe the pyrolysis of neat, flowing fuels *in situ*. Our strategy combines molecular beam mass spectrometry with optical absorption spectroscopy. Because our method is the first to measure coking rates and product distributions simultaneously, it should be possible to develop a model that relates the deposition rate to the abundance of key chemical species. Such an approach will have great utility for predicting the performances of hydrocarbon fuels in thermal management applications.

Relationships between excited state dynamics and light-driven chemistry of semiconductor nanocrystals

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Semiconductor nanocrystals exhibit remarkable tunability in electronic structure and chemical properties that have led to transformative developments in fundamental science and a variety of applications, including, recently, light-driven multi-electron chemistry. The dynamics of photoexcited electrons and holes are inextricably linked to their ability to drive chemical catalysis. In this project, we examine these relationships through a combination of synthesis, ultrafast spectroscopy, and theory.

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 critically important. We discovered 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 will describe the status of our efforts to understand the mechanisms underlying this motion and its impact on light-driven oxidation by nanocrystals. Theoretical determination of key parameters that determine hole-hopping rates will be presented in a poster by Joel Eaves.

This poster presentation will also feature our nascent efforts to characterize the relaxation of hot electrons in nanocrystals. The nanocrystal field has long been captivated by the quest for long-lived hot carriers that would increase the efficiencies of photon energy conversion and drive catalysis of demanding chemical transformations. We recently reported a photo-charging process intrinsic to CdS nanocrystals that generates long-lived electrons at the conduction band edge. In current work, we found that light absorption in these reduced particles generates remarkably long-lived hot electrons. Such slow electron cooling opens up new possibilities for light-driven catalysis.

Theory of trapped hole diffusion in Cd-Chalcogenide Nanocrystals
Joel Eaves, University of Colorado Boulder

A photon absorbed in Cd-chalcogenide nanoparticles creates an electron-hole pair, and these carriers can fuel redox chemistry. In some Cd-chalcogenide nanoparticles, however, the hole traps to the surface and undergoes slow diffusion, which can severely limit photochemical reactivity. In this poster, I will present our work using theory and computation to uncover the mechanism for hole trapping and diffusion, showing calculations to compute the hole-hopping rate as a function of temperature using large electronic structure theory calculations and molecular dynamics simulations. A key innovation in our work is the application of linear response theory to describe real-time polaron dynamics in molecular dynamics potentials parameterized for electronic ground states. Our theoretical results explain experimental measurements from collaborators in the Dukovic group and provide a computational framework for designing surfaces that increase hole mobility.

Title: Analytic Gradient of the QM-EFP Exchange-Repulsion Energy

Authors: George Elliott, Peng Xu & Mark S. Gordon

Affiliation: Iowa State University

Abstract:

The interfacing of ab initio methods with the Effective Fragment Potential (EFP) method, commonly referred to as QM-EFP, presents a rigorous approach to modeling explicit solvent effects. Formulae for the analytic gradient of the QM-EFP exchange repulsion energy are presented, and current efforts towards implementing the formulae in the software suite GAMESS are briefly discussed.

Tracking Ultrafast Charge Motion In Multiple Dimensions: Deciphering Correlations among Electrons and Nuclei in Photochemistry

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A molecular-level understanding of coherences and correlations involving electron-electron interactions and electronic-vibrational interactions during photochemical dynamics is a most fundamental challenge in chemistry and physics. The couplings and correlations of these degrees of freedom often govern important photochemical and photophysical processes. Obtaining a complete mechanistic picture of nonequilibrium photoexcited dynamics is crucial to enable new catalysts and for predicting and controlling energy transfer processes in molecules and materials. However, a global mechanistic understanding can be particularly difficult to achieve when the nonequilibrium processes of interest involve multiple degrees of freedom that may span temporal ranges from attoseconds to picoseconds and broad spectral ranges from the mid-IR into the extreme ultraviolet and beyond. Coherent multidimensional spectroscopy offers a direct route to measuring couplings, coherences, and correlations between multiple degrees of freedom throughout a photochemical process. Our research group develops, builds, and uses new coherent multidimensional spectroscopic methods that target important correlated phenomena in condensed phase molecules and materials, using a spectroscopic toolbox that spans the mid-IR to the extreme ultraviolet. In particular, we combine attosecond and femtosecond pulses of drastically different spectral ranges in new ways to directly characterize interactions such as electron-electron correlations and electronic-vibrational correlations. This poster will describe current work in the development of a Two-Quantum Two-Dimensional Electronic-Vibrational Spectroscopy for directly capturing non-adiabatic curve crossings and conical intersection dynamics in excited states, as well as very initial experimental data for understanding charge migration and charge transfer in condensed phase molecules.

**Tracking Water Oxidation over Nickel Anodes
with Amplitude- and Phase-Resolved Nonlinear Optics**

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ABSTRACT. While water's oxygen is the electron source in the industrially important oxygen evolution reaction, the strong absorber problem clouds our view of how the Stern layer water molecules orient themselves in response to applied potentials. We report nonlinear optical amplitude and phase measurements on nickel electrodes held at pH 13 that indicating a disorder-to-order transition in the Stern layer water molecules prior to the onset of Faradaic current. A full water monolayer ($1.1 \times 10^{15} \text{ cm}^{-2}$) aligns with oxygen atoms pointing towards the electrode at +0.8 V and the associated work is 80 kJ mol^{-1} . Our experiments identify water flipping energetics as a target for understanding overpotentials, advance molecular electrochemistry, provide benchmarks for electrical double layer models, and serve as a diagnostic tool for understanding electrocatalysis.

Please see [10.26434/chemrxiv-2023-m9d1z-v2](https://doi.org/10.26434/chemrxiv-2023-m9d1z-v2)

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Decoding the Dance of Proteins: From Interactions to Dynamics

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Abstract

The Anfinsen dogma states that “protein sequence determines structure determines function.” In 2020, the deep learning algorithm, AlphaFold2 (AF2), achieved prediction levels of single chain protein structures at atomic precision. With this breakthrough and follow-up developments, molecular biology has reached the stage at which the first half of the Anfinsen dogma has been solved (from protein sequence to structure). In addition, every single sequenced protein now has its atomic structure available. Here, we discuss the second half of the Anfinsen dogma (from structure to function) and demonstrate that protein functions can be deduced from protein interactions and dynamics, starting from the AF2 models. By summarizing the workflows we implemented utilizing the DoD High Performance Computing systems, we illustrate that the AF2 models represent the native states of proteins, and that the protein-ligand and protein-protein interactions can be identified at residual to atomic resolutions. We show that our workflow is applicable to both well-folded and intrinsically disordered proteins. Our results indicate that, from the AF2 models combined with other tools and algorithms, we are now approaching the stage at which the protein functions can be fully decoded from the interactions and dynamics.

Aluminum nanocrystals: from synthesis to photocatalysis to new reactive properties

Naomi Halas, Rice University

Over the past years, under AFOSR support, we have developed the ability to synthesize Aluminum nanocrystals of controlled size and shape. This work has served as a foundation for multiple studies that shed light on the properties and chemistries of Al NCs and their constituent nanomaterials. Aluminum has a 2-4 nm thick surface oxide with unique properties. We have found that one can manipulate the surface oxide properties through various annealing processes, which include manipulating its crystallinity and phase, its density, and its defect density and type. The alumina surface oxide can be replaced by other metal oxides, such as TiO₂, forming a visible-light photocatalyst when surrounding the plasmonic Al NC core. In addition to its photocatalytic properties in antenna-reactor geometries, we have also begun to examine the oxidation of Al NCs of controlled size, shape, and surface oxide properties. By slowly heating optical-quality Al nanocrystals in an O₂-containing atmosphere, we show how oxidation depends quite sensitively on size, morphology, oxide porosity and crystallinity. Comparing the oxidation of cuboctahedra to that of branched nanowire clusters reveals that Al nanoparticle oxidation also depends sensitively on nanoparticle morphology.

Nuclear-Electronic Orbital Theory for Polaritons and Plasmons

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Molecular polaritons are hybrid light-matter states arising from strong coupling between cavity modes and electronic or vibrational transitions in molecules. Surface plasmon resonances are coherent oscillations of electrons within a metal nanoparticle that can transfer electrons or energy to adsorbate molecules. We are developing theoretical methods to enable the investigation of nuclear-electronic quantum dynamics for polaritonic and plasmonic systems. These methods are based on the real-time nuclear-electronic orbital time-dependent density functional theory (RT-NEO-TDDFT) approach, in which all electrons and specified protons are treated quantum mechanically on the same level. The cavity modes for polaritonic systems are coupled to electronic or vibrational transitions in the molecular system described by RT-NEO-TDDFT. The surface plasmon resonances are described using explicit metal atoms within the RT-NEO-TDDFT framework to enable the description of plasmonic electron and energy transfer. These approaches will be illustrated by applications to excited state intramolecular proton transfer under electronic strong coupling in a cavity, as well as plasmon-driven H₂ photodissociation and infrared plasmonic resonance energy transfer from gold nanoparticles or nanowires.

Predicting the Intersystem Branching of $\text{Fe}(\text{phen})_3^{2+}$ using Relativistic Electronic Structure Methods (FA9550-21-1-0344)

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The excitation of low-spin Fe(II) octahedral complexes by visible light populates metal-ligand charge transfer (MLCT) states that decay unanimously to the lowest-lying quintet state $^5\text{T}_{2g}$. Recent work has shown that the decay pathway of $\text{Fe}(\text{phen})_3^{2+}$ involves a metal-centered ^3T intermediate. It is unknown whether the intermediate is $^3\text{T}_{1g}$, $^3\text{T}_{2g}$, or both. However, it has been shown that the intersystem branching ratio from $^3\text{T}_{1g}$ to $^1\text{A}_{1g}:\text{}^5\text{T}_{2g}$ in $\text{Fe}(\text{ptz})_6^{2+}$ is 20:80. Using spin-orbit coupling constants obtained through the exact two-component relativistic complete active space self-consistent-field (X2C-CASSCF) method, we were able to predict the intersystem branching ratio for the $\text{Fe}(\text{phen})_3^{2+}$ $^3\text{T}_{1g}$ state, which was similar to the experimentally observed ratio for $\text{Fe}(\text{ptz})_6^{2+}$. Moreover, our calculations showed near-unity conversion from $^3\text{T}_{2g}$ to $^5\text{T}_{1g}$. This study indicates that the dynamics of branching between systems can be modulated by the intermediate triplet state, establishing a theoretical foundation for manipulating photochemical reactions through the design of ligands.

Machine learning potentials for thermodynamic and transport properties of energetic materials

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Abstract

Classical molecular dynamics (MD) and Monte Carlo (MC) methods rely on force fields to describe the potential energy landscape that governs molecular interactions. A recurrent strategy to parametrize force fields for molecular systems relies on the availability of thermodynamic and transport experimental measurements, such as density or viscosity, which might not be available for the system under study at the conditions of interest. An alternative route to obtain such properties is to conduct ab-initio molecular dynamics (AIMD) simulations, which do not require pre-existing experimental measurements. Despite this clear advantage, AIMD is prohibitively expensive, severely limiting the accessible length and time scales required to compute the physical properties of interest.

Recently, neural networks have raised a significant amount of interest due to their ability to reproduce multi-dimensional potential energy surfaces with high accuracy. They have been proposed as surrogates to costly AIMD simulations, as they faithfully reproduce the underlying quantum mechanical energies and forces with less computational demands. We utilize neural network force fields (NNFFs) that use local descriptors to compute transport and thermodynamic properties of several energetic materials. The NNFFs were trained from energies and forces obtained from AIMD simulations. Taking advantage of the computational efficiency of NNFFs, we are able to reach the nanosecond and nanometer time and length scales required to compute transport and thermodynamic properties such as density, viscosity or diffusion coefficients of the underlying quantum mechanical simulations.

Localizing Low-Grade Heat Using Hybrid Photonic-Phononic Materials

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ABSTRACT

Harnessing and directing the transfer of thermal energy at subdiffraction length scales is critically important for the realization of next-generation nanofabricated materials, engineered to transduce and harvest heat for the purpose of performing useful work. However, detailed characterization of thermally induced energy transfer at the nanoscale is a formidable task due to the simultaneous demand of both high spatial and spectral resolution at infrared (IR) energies. Leveraging recent advancements in scanning transmission electron microscopy electron energy-loss spectroscopy (STEM-EELS), our collaborative research investigates the modes of thermal energy transfer between individual IR active nanostructures and their local environment as well as the spectral responses of such materials with simultaneously high spatial (< 1 nm) and spectral (< 5 meV) resolutions. Our work reveals that individual nanostructures can concentrate energy by the resonant thermal excitation of their photonic Fabry-Perot modes. Specifically, we show that the spatially localized electron energy gain signal (the anti-Stokes partner of the EEL signal) increases upon in situ heating. Theoretical modeling elucidates the mechanism for these observations by showing that a Purcell enhancement in the local photonic density of states drives the increased rate of infrared energy transfer from the delocalized ambient environment to the immediate vicinity of each nanostructure. Taken together, this work provides a guide to the design of devices capable of efficiently harvesting and directing ambient thermal energy at the nanoscale such as the transduction of delocalized mechanical energy in the form of phonons into useful work.

Understanding the reactive site in catalysis through spectroscopy of clusters, reactive intermediates and transition states

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The field of catalysis is an outstanding example of how fundamental science positively impacts society. One of the most important goals of physical chemistry is to gain a molecular level understanding of how catalysts work and, more specifically, how they provide alternate reaction pathways to lower transition state energies in a catalytic cycle. To this end, we investigate the spectroscopy of model catalytic systems in the gas phase, specifically bare and complexed transition metal oxide clusters, using slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI). Cryo-SEVI is a high resolution variant of negative ion photoelectron spectroscopy, in which photoelectron spectra of anions cooled to 10 K are measured with a resolution as high as 1-2 cm^{-1} . At this resolution one observes detailed vibrational features that can be used to elucidate the structures and energetics of the anion cluster and the neutral species created by photodetachment. In complementary work, we use cryo-SEVI to characterize the transition states of benchmark unimolecular and bimolecular reactions. The capabilities of both experiments have recently been enhanced by the incorporation of a tunable infrared laser into the experiment. In this new configuration (IR cryo-SEVI), anions are vibrationally excited prior to photodetachment, enabling one to simultaneously determine anion vibrational frequencies and map out otherwise inaccessible regions of the neutral potential energy surface.

Results will be presented on the complexes of TiO_2^- with CH_3OH and VO_2^- with H_2O . In both cases, the metal oxide splits the neutral reactant to have either a methoxy-hydroxy species ($\text{CH}_3\text{OTi}(\text{O})\text{OH}^-$) or a dihydroxy species ($\text{VO}(\text{OH})_2^-$). Interestingly, the same vanadium dihydroxy species is also formed by the reaction of VO_3^- with H_2 . Hence, by means of cryo-SEVI, we confirm not only the VO_2^- splits water but also the VO_3^- splits H_2 . In addition, we have carried out IR cryo-SEVI experiments on NO_3^- and the vinylidene anion H_2CC^- . The work on NO_3^- addresses a long-standing controversy on the vibrational spectroscopy of NO_3 , while the H_2CC^- experiments enable one to explore how anion pre-excitation can be used to probe potential energy surface that governs the isomerization of neutral H_2CC to HCCH .

Spin Dynamics and Nonlinear Optics in Solids using Ab initio Density-Matrix Dynamics

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Ab-initio spin dynamics and transport simulations are critical for realizing the potential of spintronics and spin-selective photo-chemistry. In particular, simulations would be invaluable to predict key physical parameters including spin lifetime, spin diffusion and coherence length, magneto-optical spectra, and (spin)-photocurrent.

We develop a computational framework and an open-source implementation for simulating spatio-temporal quantum dynamics and transport accounting for a range of quantum degrees of freedom (e.g., charge, spin, orbital, lattice). This framework accounts for scattering processes using an *ab initio* density matrix formalism for electron-phonon, electron-electron, and electron-impurity interactions with self-consistent spin-orbit coupling, and accounting for optical illumination, electric and magnetic fields.

We will enable the simulation of spin and charge dynamics and transport, from DC to terahertz, in disparate materials up to micrometer length scales, which is essential to study complex chemical systems. We will first show first-principles simulations of spin relaxation and dephasing in external magnetic fields due to spin-orbit and electron-phonon coupling, as well as fluctuation of g factors in general solids. We then present initial results on novel spin dephasing that manifests in spatially-resolved transport. We will finally present the generation and steady-state of charge/spin photocurrents including excitation, relaxation, and stimulated and spontaneous recombination processes. After Fourier transform, we show we get DC current (photogalvanic effect), second and high harmonic generations simultaneously in one real-time simulation, including quantum many-body interactions and scatterings, which are ideal for simulations of nonlinear optics in general solids or complex materials.

Collisional Radiative Model for Argon-based Electric Propulsion Systems: Experimental Measurements and Initial Model Formulation

Authors: M. L. Hause, C. M. Kucifer and B. D. Prince

High efficiency electric propulsion (EP) systems, such as Hall effect and ion thrusters, commonly use noble gas propellants owing to the propellants stability, ease of ionization and availability in Earth's atmosphere. These high efficiency systems typically generate charged ions with kinetic energies in the 200-450 eV range. When these energetic ions collide with un-ionized propellant, optical signatures in the ultraviolet through infrared can be generated that differ significantly from those generated solely by energetic electron impact. The combination of energetic ion-neutral and electron-neutral collisions results in collisional radiative models (CRM) suitable for EP systems. These CRMs can be used for an indirect, passive determinant of thruster health and for space domain awareness purposes. While traditional propellants such as xenon and krypton have typically been used, SpaceX has recently announced a switch to argon-based propulsion systems in future Starlink spacecraft. This poster describes the results of ground measurements of argon ion and neutral collisions at EP relevant collision energies, the expansion of electron-based CRMs to now include the relevant additional ion-neutral processes, and an initial assessment of the expanded CRM performance against published laboratory thruster data for argon EP systems. Specific experimental results include quantifying the emission excitation cross sections (optical emissions) resulting from the $\text{Ar}^+ + \text{Ar}$ and $\text{Ar}^{2+} + \text{Ar}$ collision systems over the 30 to 600 eV/charge kinetic energy range for the UV through the near-infrared electromagnetic spectrum. An assessment of the role of fast neutrals colliding with Ar will also be presented and discussed. Finally, the constructed CRM is focused on the most intense transitions from electronically excited neutral argon.

Coherent Transport of Energy and Information in 2D Superatomic Crystals

Milan Delor, Colin Nuckolls, Xavier Roy and Xiaoyang Zhu
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Over the past 20 years, two-dimensional (2D) materials have garnered significant attention due to their exceptional physical, mechanical, and chemical properties, as well as our ability to seamlessly incorporate them into various devices. This poster presents our recent advancements in the development of the next generation of 2D materials. We discuss our efforts to assemble atomically defined clusters of atoms, which we refer to as "superatoms", into hierarchical 2D structures. These superatoms mimic the role of atoms in conventional 2D "atomic" solids, resulting in remarkable material properties. In particular, we introduce the new carbon allotrope graphullerene and the superatomic semiconductor $\text{Re}_6\text{Se}_8\text{Cl}_2$. We highlight recent synthetic breakthroughs and explore the distinctive coherent transport behaviors that emerge due to the atomic precision of the 2D lattice and the specific interactions between these superatomic building blocks.

Reactive Hypergolic Fuels with Hydrogen Peroxide

Developing Metal-Free Promoters

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There are three types of hypergolic fuels with hydrogen peroxide. The first type are room temperature ionic liquids which have the promotor for hypergolic ignition built into the fuel itself. To the best of our knowledge there are only two classes of such ionic liquids known in the literature. One from our own group based on the tetrakis(tetrahydroborato)aluminate anion¹ and the other based on the thiocyanate anion, published first by a group in Germany in 2021.¹ While these findings were groundbreaking, ionic liquids are an exclusive and still rather expensive class of materials probably too valuable to be simply burned. The propellant chemist needs to look for more cheaply available materials like alcohols, kerosenes, and simple amines for the propellant to be viable. In this case one must either rely on a precombustor technology or on two different types of additives which make the fuel hypergolic with the oxidizer. The first class of additives does not directly participate in the combustion process, but only decomposes H₂O₂ (much the same idea like in a precombustor scenario). This is a catalytic hypergolic fuel. Heat is evolved and the fuel ignites when the temperature exceeds its autoignition temperature. If the additive actively reacts with H₂O₂, the second class of additives, it can be classified as a promoter. These fuels are called reactive hypergolic fuels. The fuel ignites because of the highly exothermic reaction between the promoter and the oxidant. Most additives are alkaline, or transition-metal based, elements which cause solid particles in the exhaust, are responsible for combustion instabilities, and reduced overall performance. Therefore, there is a need for metal-free catalysts or promoters and some new approaches and results will be discussed.

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Studies of Dynamic Materials in Extreme Environments – On-Surface Chemical Dynamics
Steven J. Sibener, The James Franck Institute & Dept. of Chemistry, University of Chicago

The scattering of atomic and molecular beams from well-characterized surfaces is an incisive method for studying the dynamics of gas-surface interactions, providing precise information on energy and momentum transfer as well as complex reaction mechanisms. Scanning probe measurements provide a powerful complement to scattering data as SPM measurements give a direct route to the visualization and spectroscopic characterization of interfacial atomic and nanosystems. This AFOSR program is examining critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme terrestrial and space environments. Extreme conditions encompass high and low temperature regimes, high velocity gas flows, optical and charged particle illumination, and severe oxidative environments where interfacial aerodynamic performance (energy and momentum transfer characteristics), morphological change, and chemical stability need to be assessed and quantified. This effort is also focussed on the formation, collisional energy transfer, and reactivity of interfacial molecular ices in support of AFOSR fundamental science needs for materials and flight operations in arctic environments. Six recent publications are listed below illustrative of current efforts.

This year's poster presentation will focus on activities in our newest endeavor, *the study of on-surface chemical dynamics*, which provides a new and information-rich complement to more traditional scattering or STM only experiments. We have developed the capability to elucidate interfacial reaction dynamics using an arguably unique combination of supersonic molecular beams combined with *in situ* STM visualization. These capabilities have been implemented to reveal the complex spatio-temporal correlations that govern heterogeneous reactions spanning atomic, nano, and meso length-scales. For example, time-lapse visualization of reacting interfaces is allowing us to probe the reactivity of specific sites at interfaces and how the presence of a reacted site or local region influences the subsequent reaction probability at proximal sites. Such correlations are important in chemisorption, catalysis, materials oxidation and erosion, and film processing. This approach also opens a new view for interfacial reaction dynamics where incident beam kinetic energy and angle of incidence can be used for reaction control parameters with outcomes such as site-specific reactivity, changes for overall time-evolving mechanisms, and where the on-surface fate of chemisorbed species can be ascertained. In this work the time-evolving interface can be probed either in real-time or, for reactions occurring under extreme thermal conditions, using time-lapse sequential imagery. This presentation will examine illustrative examples from our recent work on the atomic and multiscale oxidative reactivity of carbon, O interactions with single and multilayer graphene including moiré superlattices, and N₂ chemisorption on Ru. Other projects not featured this year include isotope dependencies in gaseous condensation

¹STM Visualization of N₂ Dissociative Chemisorption on Ru(0001) at High Impinging Kinetic Energies, Joshua Wagner, Tim Grabnic, and S. J. Sibener, *J. Phys. Chem. C*, **126**, 18333-18342 (2022).

²Isotopic Enrichment Resulting from Differential Condensation of Methane Isotopologues Involving Non-equilibrium Gas-Surface Collisions Modeled with Molecular Dynamics Simulations, Michelle R. Brann, Xinyou Ma, and S. J. Sibener, *J. Phys. Chem. C* **127**, 13286-13294 (2023).

³On-Surface Chemical Dynamics of Monolayer, Bilayer, and Many-Layered Graphene Surfaces Probed with Supersonic Beam Scattering and STM Imaging, Joshua Wagner, Ross Edel, Tim Grabnic, Bryan Wiggins, and Steven J. Sibener, *Faraday Discussion on New Directions in Molecular Scattering*, doi.org/10.1039/D3FD00178D (Web Published 2024).

⁴Coverage Dependent Site-Specific Placement and Correlated Diffusion of Atomic Oxygen on Moiré Patterned Graphene on Ru(0001), Joshua Wagner and S. J. Sibener, *J. Phys. Chem. Lett.*, **15**, 2936-2943 (2024).

⁵Correlating Electron-Phonon Coupling and *in situ* High Temperature Atomic-Scale Surface Structure at the Metallic Nb(100) Surface by Helium Atom Scattering and Density-Functional Theory, Caleb J. Thompson, Michael F. Van Duinen, Michelle M. Kelley, Tomás A. Arias, and S. J. Sibener, *J. Phys. Chem. C*, **128**, 6149-6157 (2024).

⁶The Initial Sticking of High Velocity Water onto Graphite Under Non-equilibrium Supersonic Flow Conditions, Kevin D. Gibson, Yuheng Luo, Christopher Kang, Rui Sun, S. J. Sibener, submitted *J. Chem. Phys.* (2024).

Crossed Beam Imaging of Associative Ionization and State-to-State Scattering Dynamics at High Collision Energy: Fundamental Studies for Hypersonics

FA9550-22-1-0445

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We will present a progress report on our studies relevant to plasma formation in hypersonic flows. These are pursued along two distinct directions: In the first, we have combined velocity map imaging with stimulated emission pumping to prepare NO in highly excited vibrational levels for collision with rare gases. This allows us to study state-to-state scattering dynamics from arbitrary initial states to selected final states. This approach is employed in a near-counterpropagating crossed-beam geometry that allows us to access collision energies up to 1.4 eV with rotational excitations up to $\sim \Delta j = 60$ recorded for the first time for single inelastic collisions. These take the NO molecule from low rotational levels well-characterized as Hund's case (a) to product states described by Hund's case (b) and these are reported for the first time. We will examine the implications of this and highlight unexpected effects on the parity-dependent differential cross sections.

The second project thrust involves development of a new instrument using electron-ion coincidence detection to reveal the electronic states of atoms involved in associative ionization. We have adapted a new experimental approach that involves intrabeam scattering of fast (3 kV) atomic beams formed by charge transfer of atomic ions formed in the same discharge. In the N + O reaction, for example, we have demonstrated selective acceleration of the slower O⁺ beam allowing for matching velocities of the neutral O and N beams in the interaction region to give controllable relative energies. A complete description of the instrument and the latest progress will be presented.

Structure and function of engineered MXene surfaces

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Two-dimensional (2D) transition-metal carbides and nitrides (MXenes) show impressive performance in supercapacitors, batteries, electromagnetic interference shielding, and electrocatalysts. These materials combine the electronic and mechanical properties of 2D inorganic crystals with chemically modifiable surfaces, and surface-engineered MXenes represent an ideal platform for fundamental and applied studies of interfaces in 2D functional materials.

The comprehensive understanding of MXene surfaces is required for prescriptive engineering of their physical and chemical properties. We discuss general strategies to install and remove surface groups by performing topotactic substitution and reductive elimination reactions. Successful synthesis of MXenes with halido-, oxo-, imido-, thio-, seleno-, or telluro- terminations, as well as bare MXenes (no surface termination) can be synthesized both by traditionally (from MAX phases) and directly synthesized MXenes. We also successfully synthesized a series of hybrid organic-inorganic MXenes by covalently attaching dense carpets of organic surface groups. Since organic and inorganic materials are, in many aspects, complimentary to each other, organic-inorganic MXenes open a pathway to merge the benefits of both worlds into a hybrid matter that combines engineerability of molecules with the electronic, thermal, and mechanical properties of inorganic 2D materials. The description of MXene surface structure and reactivity requires a mix of concepts from the fields of coordination chemistry, self-assembled monolayers, and surface science. MXene surface groups control biaxial lattice strain, phonon frequencies, electrochemical performance, and strength of the electron-phonon coupling, making MXene surfaces not spectators but active contributors to conductivity, superconductivity, and catalytic activity.

Asymmetric chiral plasmonic nanomaterials via circularly polarized light

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Chiral plasmonic nanostructures have great potential for photonics and sensing applications, especially at visible wavelengths where natural products and meta-materials resonate less effectively. Chemical sources of chirality, e.g. optically active small molecules, have enabled the colloidal production of homogeneous chiral plasmonic nanoparticles. However, the use of circularly polarized light (CPL) as a chirality source to fabricate chiral hybrid semiconductor-metal heterostructures offers another handle to introduce optical dissymmetry without the need for complicated purification downstream. Unfortunately, the mechanism by which these chiral structures develop with CPL has remained largely unexplored. Our latest study has revealed that the wavelength and polarization of light are critical factors in determining the symmetry of Au/PbO₂ heterostructures and their resulting chiroptical properties. Here, we further demonstrate that the asymmetry of the initial plasmonic nanocrystals plays a crucial role in generating chiral nanostructures. Specifically, we compare gold bipyramids to silver nanorods and gold nanoprisms as the precursors. These noble metal nanostructures have varying aspect ratios. Circularly polarized excitation can create chiral structures by generating chiral electric fields, inducing photooxidation by hot holes in a site-selective manner. We show that the optical activity increases with aspect ratio of the nanoparticle precursors, and that tuning the excitation wavelength can yield larger dissymmetry in the morphology due to the larger number of higher-order modes accessible in longer nanorods. Our study underscores the importance of carefully selecting the starting material and excitation wavelength to maximize the chirality in these plasmonic nanostructures.

Mixed quantum–classical modeling of topological phenomena

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Topological effects are at the heart of a variety of phenomena of fundamental and technological interest, including spintronics, conical intersections, and chiral-induced spin selectivity (CISS). Computational modeling is critical in building an understanding of such effects. While trajectory-based mixed quantum–classical (MQC) methods are exceptionally well-suited for such modeling, their standard formulations are incompatible with nontrivial topologies. Here, I present our efforts in developing an MQC approach wherein topology is faithfully incorporated. Promising results are obtained for various problems involving a nuclear wavepacket traversing a series of topological avoided crossings, as well as a Jahn–Teller model involving a conical intersection at its high-symmetry point. For the latter, we find our MQC approach to produce nuclear interference effects in qualitative agreement with exact modeling (Figure) and in accordance with recent measurements based on a trapped ion quantum simulator. Altogether, these developments offer promising prospects for the modeling of topological phenomena.

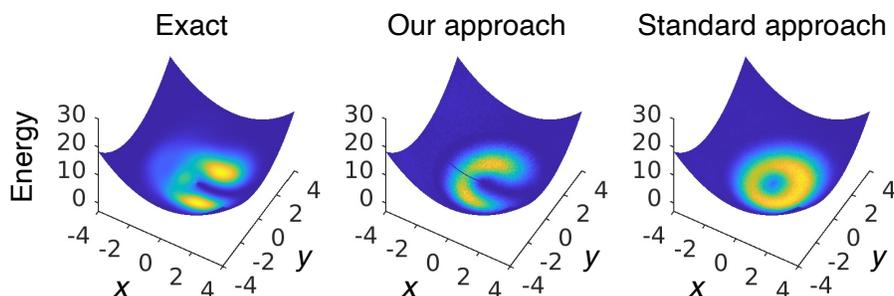


Figure: Computational results for a nuclear wavepacket governed by a Jahn–Teller Hamiltonian. Shown are a snapshot of the wavepacket (depicted as a heatmap) on top of the lowest adiabatic energy surface resulting from exact modeling, our MQC approach incorporating topology, and the standard MQC approach (in all cases, we are considering adiabatic propagation). Note that lack of wavepacket interference for the standard approach.

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

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The 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 ~ 50 meV, respectively [1-3], and a schematic is shown in Figure 1.

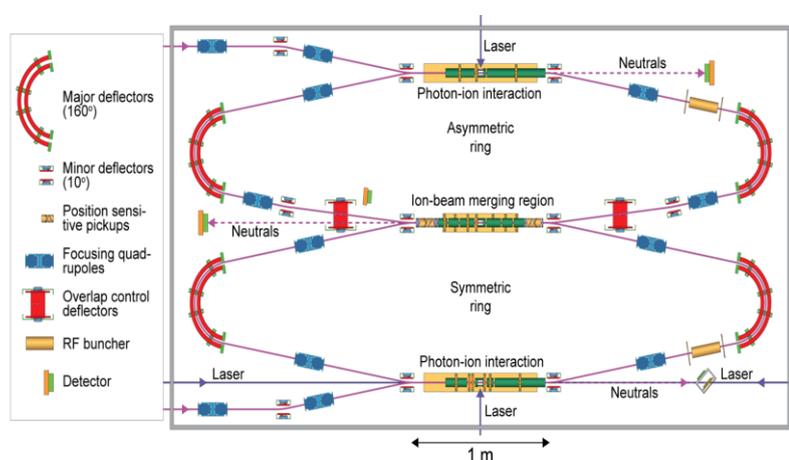


Figure 1: Schematic of the heart of the DESIREE facility: the two cryogenically cooled storage rings

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 transient phenomena such as sprites. I focus on reactions involving the primary atomic and molecular oxygen and nitrogen ions [4-6], i.e., $O^- + NO^+$, $O^- + O_2^+$, 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.

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Spin and charge dynamics in transition metal complexes measured with ultrafast X-rays

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As part of an AFOSR MURI, we are studying chirality-induced spin selectivity in electron transfer through well-defined molecular donor-bridge-acceptor complexes. Previous studies of this spin-filtering effect have predominantly focused on electron transport through self-assembled monolayers either via photoelectron spectroscopy or bulk conductance measurements. We take inspiration from the field of electron transfer chemistry, in which rules such as Marcus Theory were solidified using photoinduced electron transfer through well-defined donor-acceptor molecules. We have synthesized ferrocene-cobaltocenium dimers and used transient absorption spectroscopy in the infrared, UV/Vis, and X-ray energy ranges to measure their photophysics. Photoexcitation forms a metal-to-metal charge transfer state ($\text{Fe}^{\text{II}}\text{Co}^{\text{III}} \rightarrow \text{Fe}^{\text{III}}\text{Co}^{\text{II}}$) that undergoes back-electron-transfer (BET) to a local triplet excited state on the Fe^{II} in less than 200 fs. This triplet relaxes to a local Fe^{II} quintet in 30 ps, then to the singlet ground state in 500 ps. This behavior sharply contrasts with other MMCT systems, which generally undergo ultrafast BET to vibrationally hot ground states, and with other Fe^{II} chromophores, whose triplet excited states generally relax to the quintet in ps or less. This work also identifies the quintet state of ferrocene as an overlooked intermediary in the photochemistry of this common electron donor. Updates will be shown on the synthesis of a chiral version of this complex and on the implementation of transient X-ray circular dichroism experiments in the Vura-Weis lab and at the Linac Coherent Light Source. Finally, we will show preliminary spectra from a new soft X-ray transient absorption instrument that spans 100-300 eV. This energy range covers the core-to-valence transitions of elements such as B, C, P, S, and most lanthanides/actinides. This instrument will be used to measure the influence of non-innocent ligands on photochemical transformations.

Nonlinear response formalism for molecular polaritons

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Abstract

The standard nonlinear response formalism together with the double-sided Feynman diagram machinery due to Mukamel provides an unambiguous framework to predict and model such spectroscopies where multiple ultrafast pulses perturb a molecular ensemble generating dipole-allowed transitions. This formalism, however, must be modified to correctly describe the NLOS of microcavity polaritons, where pulses tunnel through an optical cavity and can be modified in real time by the polarization of the ensemble before they act again on the latter. This feedback between light and matter gives rise to a proliferation of additional Feynman diagrams that explain some interesting behavior recently observed in the context of vibrational and electronic molecular polaritons. I will show the generalized formalism and some of its intuitive consequences.

This work was funded through MURI: Polariton Chemistry.

Synthesis of Silver Nanoparticles Capped with Alginate or Glycerate by Spraying Aqueous Mixtures of Silver Nitrate with Sodium Alginate or Glycerol

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Over the past decades, many advances have been made in the development of cost-effective and greener methodologies for the synthesis of silver nanoparticles (Ag Nps). This has been motivated by their broad utilization as anti-bacterial agents for surgery applications as well as wound and burn treatments. Traditionally, silver nanoparticles have been synthesized using reducing agents such as sodium borohydride (NaBH_4) to reduce silver ions into silver nanoparticles. Bare Ag NPs quickly undergo self-aggregation. To overcome this self-aggregation issue, organic molecules have been utilized as capping agents, but this approach has the drawback of requiring organic solvents and taking long times at elevated temperatures.

We present an eco-friendly approach that allows in situ, on-demand generation of Ag Nps. A room-temperature solution is prepared by dissolving a 1:1 mixture of silver nitrate (AgNO_3) and glycerol ($\text{C}_3\text{H}_8\text{O}_3$) or sodium alginate in water. No reaction occurs in bulk solution without a reducing agent, but when the solution is sprayed with N_2 or air as a nebulizing gas (120 psi), we achieve the synthesis of silver nanoparticles (Ag Nps) capped with silver glycerate or silver alginate having a minimum diameter of 5 nm in less than one millisecond. The synthesis and small-size validation of Ag Nps were confirmed by using field emission scanning electron microscopy (FE-SEM), high resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction analysis (XRD).

Support from the Air Force Office of Scientific Research through the Multidisciplinary University Research Initiative (MURI) program (AFOSR FA9550-21-1-0170) is gratefully acknowledged.

Bulk and Interfacial Structure of Highly Ionic Electrolytes

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The high demand in renewable energy and fuels has driven the innovative design of liquid electrolytes. Moving beyond the traditional dilute solutions, electrolytes with high ionic strength, including ionic liquids and highly concentrated electrolytes, emerge as promising alternatives for surprisingly efficient ionic conduction and tailored interfacial reactions. In particular, these highly ionic electrolytes (HIEs) have been utilized for safer batteries and for selective CO₂ reduction. However, in contrast to dilute solutions where the bulk and interfacial configurations have been known to a certain extent, the structure of HIEs remains an open puzzle, even in the bulk state. A handful of theories have been proposed, yet none has been conclusively verified.

In this poster, I will show our recent efforts on both experimental characterization and theoretical understanding of HIE structures, in the bulk and at the interface with solid electrodes. Experimentally, we use 3D atomic force microscopy (3D-AFM) to obtain the force maps of solid-liquid interfaces, from which the pair correlation functions and other key structural factors of both bulk and interfacial liquid are extracted. In addition, vibrational spectroscopy studies provide insights into the molecular configurations of the HIEs. Combining the microscopy and spectroscopy results, we find that the HIE structure exhibits striking similarity to dilute solutions in their course-grained correlation functions, revealing strong local pairing and clustering effects. Under weak electrical polarization, the interfacial HIE exhibits ion pair/cluster dissociation effects; stronger polarization, in contrast, tends to induce long range clustering and possible gelation behaviors. Such rich structural reconfigurations provide fascinating opportunities both for the fundamental liquid theories and for practical applications in energy storage, electrocatalysis, and photochemistry. We have developed a statistical mechanics-based model to describe the course-grained bulk and interfacial structures of HIEs, which offers a promising starting point for adding more molecular details.

Many-Body Quantum Chemical Insights into Electrocatalytic CO₂ Reduction on Single Atom Catalysts

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Although much progress has been made in the first-principles simulation of heterogeneous electrocatalysis, a quantitative *ab initio* description remains challenging. A principal reason is that current electrocatalysis calculations almost exclusively rely on density functional theory (DFT), often in the semilocal approximation, but their predictions are very sensitive to the choice of DFT parameters due to inherent errors in treating charge delocalization and electron correlation. This ultimately impairs their predictive power and may result in qualitatively diverging conclusions in catalytic mechanisms.

In this poster, we present a quantum embedding strategy to enable gold-standard coupled-cluster CCSD(T) simulation of heterogeneous single-atom catalysis for the first time, where we investigate electrochemical CO₂ reduction reaction (CO₂RR) catalyzed by single iron atoms supported on nitrogen-doped graphene (Fe–N–C). We demonstrate that the potential-dependent CCSD(T) simulation agrees with major experimental findings, including CO binding energy, CO₂RR onset potential, pH dependence, and potential of maximal Faradaic efficiency, while other tested DFT methods fall short. More importantly, this high accuracy allows us to quantitatively determine the impact of applied potential, surface charge, and active-site environment on activity and selectivity of Fe–N–C electrocatalysts, as well as to examine the reliability of popular density functionals in the simulation of single-atom catalysis.

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