



2025 Molecular Dynamics and Theoretical Chemistry Program Review

Dr. Michael Berman | May 20-22, 2025 | Chantilly, VA -hybrid

Oral Presentation Abstracts

Toward predictive chemistry for ionospheric impacts of novel metals

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Meteoric metals (Fe, Na, Mg, Ca) are deposited daily in the mesosphere/lower thermosphere (MLT) region of the atmosphere. Despite being present in very low equilibrium densities ($\sim 1 - 100 \mu\text{g km}^{-3}$) these species initiate chemistry that has large impact on transient electron densities affecting HF and VHF communications. Significant work spanning decades has detailed the chemical networks of the meteoric metals, informing upper atmospheric and ionospheric models. Recently, enhanced concentrations of over two dozen non-meteoric metals have been observed in the stratosphere, presumably resulting from ablation of spacecraft during reentry. Vertical transport will result in undetermined concentrations of these metals in the MLT and at altitudes as high as 300 km. It is of interest to determine the chemical networks each metal will initiate as a function of altitude, allowing for incorporation into atmospheric models to evaluate impacts as well as to identify any reservoir species amenable to quantification by lidar. This requires kinetics and thermochemical information of each species with atmospheric neutral and ionic constituents as well as associated photoexcitation and photoionization rates. While many of these quantities are accessible by experiment, the sheer scope of measurements needed to detail dozens of species is prohibitive. *Ab initio* methods are a promising alternative for exploring these small-molecule gas-phase chemistries. Here we discuss joint experiment and theoretical efforts to validate treatments of transition metal ion chemistries, including contributions of non-adiabatic dynamics and excited electronic states.

Understanding the Reactive Site in Catalysis through Spectroscopy of Clusters, Reactive Intermediates, and Transition States

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Our research uses novel spectroscopic probes based on negative ion photodetachment to investigate bare and complexed transition metal oxide clusters as these are model systems for important catalytic reactions such as water splitting. We also study anions and radicals of interest to atmospheric and ionospheric chemistry. Finally, we use negative ion photodetachment as a probe of transition states in benchmark unimolecular and bimolecular chemical reactions.

The primary experimental method used in our work is slow electron velocity-map imaging of cryogenically cooled anions (cryo-SEVI), a variant of negative ion photoelectron spectroscopy with a spectral resolution as high as $1\text{-}2\text{ cm}^{-1}$. This method yields vibrationally resolved spectra of complexed transition metal oxide clusters that enables their unambiguous structural determination. In recent work, we have shown that TiO_2^- splits MeOH, forming a $\text{CH}_3\text{OTi}(\text{O})\text{OH}^-$ adduct. The complex vibrational structure in the cryo-SEVI spectrum of this anion has been fully assigned by comparison with electronic structure calculation. We have also found that VO_2^- splits water to form the dihydroxide $\text{HOV}(\text{O})\text{OH}^-$, and that the identical species is formed by the reaction of VO_3^- with H_2 .

In a parallel and complementary effort, we carry out experiments in which anions are pre-excited with a tunable infrared laser prior to photodetachment. This new experiment, IR cryo-SEVI, enables one to access neutral vibrational levels that are inaccessible from the anion ground vibrational state and can also operate in an “action spectroscopy” mode to yield anion vibrational frequencies. We have applied IR cryo-SEVI to the NO_3^- anion to determine the ν_3 frequency of the NO_3 radical, thereby settling a two-decade old spectroscopic controversy. We have performed IR cryo-SEVI on the vinylidene anion H_2CC^- in which we selectively excite the close-lying ν_1 and ν_5 modes of the anion, enabling one to access two manifolds of H_2CC vibrational states that couple very differently to the isomerization of H_2CC to HCCH .

Current efforts focus on applying IR cryo-SEVI to bare and complexed transition metal oxide clusters, thereby linking the two parallel thrusts of our research program. Thus far we have preliminary results on TiO_2^- and are working towards more complex anions such as $\text{TiO}_2^-(\text{H}_2\text{O})$ and Zr_2O_4^- .

Ultrafast reaction dynamics initiated by chemically relevant (70 eV) electrons

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High-energy chemistry triggered by ionizing radiation is mediated by secondary electrons with a broad energy distribution, peaking around 70-eV, where the electron cross-section of molecules is highest. This energy range plays a key role in various fields such as EUV photolithography, radiation chemistry, astrochemistry, and electron-impact mass spectrometry, where 70 eV electrons are used to ionize target molecules for fragmentation pattern analysis. The complexity of electron-initiated chemistry highlights the need for a detailed, time-resolved molecular understanding. To address this, we leverage tunnel ionization and electron recollision to enable femtosecond time-resolved studies, uncovering reaction pathways, energy transfer mechanisms, and the timescales of bond formation and breaking.^{1,2} Our findings show that isomerization, bond formation, and bond breaking often precede intramolecular energy redistribution, revealing nonergodic behavior. Using our ability to simultaneously track up to 100 distinct product ions and identify their originating intermediates,³ we have investigated reaction mechanisms involving metastable ions,⁴ proton-transfer-triggered dissociation,⁵ roaming,⁶ and the dissociative ionization of the EUV photoacid generator phenyl triflate, used in amplified photoresists.⁷

1. M. Dantus “Tracking Molecular Fragmentation in Electron-Ionization Mass Spectrometry with Ultrafast Time Resolution,” *Acc. Chem. Res.* **57**, 033003 (2024).
2. M. Dantus, “Ultrafast studies of elusive chemical reactions in the gas phase,” *Science* **385**, eadk1833 (2024).
3. J. Stamm, S. Kwon, S. Sandhu, J. Sandhu, B. Levine, M. Dantus, “Coherence mapping to identify the intermediates of multi-channel dissociative ionization,” *Commun. Chem.* **7**, 103 (2024).
4. J. Stamm, L. DeJesus, A. D. Jones, M. Dantus, “Quantitative Identification of Nonpolar Perfluoralkyl Substances by Mass Spectrometry,” *J. Phys. Chem. A* **126**, 8851 (2022).
5. J. Stamm, S. Kwon, S. Sandhu, M. Shaik, R. Das, J. Sandhu, B. Curenton, C. Wicka, B. G. Levine, L. Sun, M. Dantus, “The Surprising Dynamics of the McLafferty Rearrangement,” *J. Phys. Chem. Lett.* **14**, 44, 10088 (2023).
6. J. Stamm, S. S. Priyadarsini, S. Sandhu, A. Chakraborty, J. Shen, S. Kwon, J. Sandhu, C. Wicka, A. Mehmood, B. G. Levine, P. Piecuch, M. Dantus, “Factors governing H₃⁺ formation from methyl halogens and pseudohalogens,” *Nat. Commun.* **16**, 410 (2025).
7. S. Kwon, J. Stamm, M. Dantus, “Ultrafast Dynamics and Rearrangement of the EUV Photoacid Generator Phenyl Triflate,” *J. Phys. Chem. Lett.* **16**, 3397 (2025).

Reactivity and Energy Dissipation for Energetic Gas-Surface Interactions

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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 effort is examining critical aspects of the chemical and physical behavior of dynamic material interfaces operating in extreme terrestrial and space environments, directly supporting research needs that are of high relevance to both Air Force atmospheric flight and orbital spaceflight systems. 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, morphological change, and chemical stability need to be quantified. This effort is also focussed on the formation, stability, collisional energy transfer, and reactivity of interfacial molecular ices, the quasi-liquid layer, in support of AFOSR science for materials and flight operations in cold environments.

This year's presentation will initially focus on *the study of on-surface chemical dynamics* [1-3], 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 and AFM visualization. These capabilities have been implemented to reveal the complex spatio-temporal correlations that govern heterogeneous reactions spanning atomic, nano, and meso length-scales. 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. 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 to be discussed include isotope and structural dependencies in gaseous condensation [4], the energy dependence of the onset of gaseous condensation under non-equilibrium collision conditions [5,6], electron-phonon energy dissipation in gas-surface collisions with metallic and metallic oxide surfaces [7,8], and, time permitting, the nature of the quasi-liquid layer near ice-material interfaces.

¹STM Visualization of N₂ Dissociative Chemisorption on Ru(0001) at High Impinging Kinetic Energies, Joshua Wagner, Tim Grabnic, and S. J. Sibener, Published as part of The Journal of Physical Chemistry virtual special issue "Honoring Michael R. Berman", *J. Phys. Chem. C*, **126**, 18333-18342 (2022).

²On-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 Discussions* **251**, 435-447 (2024).

³Coverage 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).

⁴Isotopic 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).

⁵The Initial Sticking of High Velocity Water onto Graphite Under Non-equilibrium Supersonic Flow Conditions, Kevin D. Gibson, Yuheng Luo, Chris Kang, Rui Sun, and S. J. Sibener, *J. Chem. Phys.* **160**, 194705/1-13 (2024).

⁶Chemical Dynamics Simulations of Water Collisions with a Graphite Surface, Yuheng Luo, Christopher Kang, Kevin Gibson, and S. J. Sibener, and Rui Sun, *J. Phys. Chem. C*, submitted (2025).

⁷Correlating 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).

⁸Distinguishing the Roles of Atomic-Scale Surface Structure and Chemical Composition in Electron Phonon Coupling of the Nb(100) Surface Oxide Reconstruction, Caleb J. Thompson, Michael F. Van Duinen, Cristobal Mendez, Sarah A. Willson, Van Do, Tomás A. Arias, and S. J. Sibener, *J. Phys. Chem. C* **128**, 10714-10722 (2024).

Toward photochemistry on metal nanoparticle surfaces with atomically precise active sites

Supported metal catalysts, consisting of transition metal nanoparticles on high surface area, insulating oxide supports, are ubiquitously used in the manufacturing of chemicals and fuels. Efforts by industrial and academic researchers focus on improving catalytic process efficiency (higher rates and/or selectivity at lower temperature and pressure) by tuning the composition of the catalytic materials. Alternatively, we (and others) have recently observed that visible photon illumination of metal nanoparticle and single atom catalysts (Pt, Cu, Ag, Rh etc.) on insulating oxide supports (Al_2O_3 , SiO_2) can cause significant changes to catalytic reaction selectivity, rate, and apparent kinetic parameters. Mechanistic studies suggest that photons influence catalytic processes by redistributing charge within adsorbate-metal bonds, thereby changing elementary step energetics. Our group has worked for the past 10 years also on the synthesis of supported metal catalysts where active sites are atomically dispersed (e.g. as single atoms) and are surrounded by controlled reactive environments (metals, oxides, organic ligands) that result in active sites with tailored structures for particular functions. We seek to combine our insights into photochemistry by metal nanostructure and the synthesis of active site with atomic precision to design photochemically responsive catalysts with tailored active site structures. In this talk, I will highlight our initial work toward these goals.

Sub-Nano Cluster Catalysts for Endothermic Cooling:

Design Through Ensemble Representation

AFOSR grant FA9550-22-1-0381

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Abstract

We report on a joint theory and experiment effort to develop supported cluster catalysts for endothermic cooling applications. We theoretically designed and experimentally validated alumina-supported PtGe cluster alloys, which are ultra-stable and selective cluster catalysts, achieving endothermic partial dehydrogenation of alkanes, and resisting both coking and sintering. The electronic mechanism behind the effect is explicated. The PtGe system is shown to work for a range of cluster sizes, as well as structures and sizes of hydrocarbons. The development became possible due to advances both in theory and in experimental capabilities. The talk will highlight theoretical advances, which include the representation of catalysts as statistical ensembles of multiple interconverting states. Additionally, we will share a series of observations, which indicate that optimal catalysts typically function at characteristic phase boundaries (e.g. changes in cluster dimensionality, adsorbate coverage, catalyst phase, etc.) that are reached by the system under the reaction conditions. The catalyst then exploits the associated instability – the desire to exist in multiple states or structures simultaneously - as a driving force for chemical transformations. In other words, phase boundaries are good places to search for new catalysts, and indeed we should focus on at least two phases at once, rather than just one.

Water at the Edge: on-water spectroscopy, electrostatics and chemistry

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Interfacial water exhibits rich and complex behavior, playing a critical role in chemistry, biology, geology, and engineering. Despite its importance, fundamental properties of water at hydrophobic interfaces—such as orientational ordering, hydronium and hydroxide concentrations, improper hydrogen bonding, and the presence of strong electric fields—remain highly debated. These controversies arise from the inherent challenges in probing interfacial systems, even with state-of-the-art experimental techniques. I will present newly developed on-water optical spectroscopy capable of investigating diverse interfacial systems, including oil-water emulsions, protein hydration shell, and even the interior of living mammalian cells. These techniques provide insights into key properties such as interfacial water's tetrahedral structure, free O-H groups, electrostatics, illuminating the remarkable chemical activity observed at hydrophobic-water interfaces such as in microdroplets and contact electro-catalysis. Additionally, I will discuss the broader implications for materials science, environmental studies, and biomedical research.

Chiral Phonon Contributions to Chiral Induced Spin Selectivity

Renee R. Frontiera, Department of Chemistry, University of Minnesota

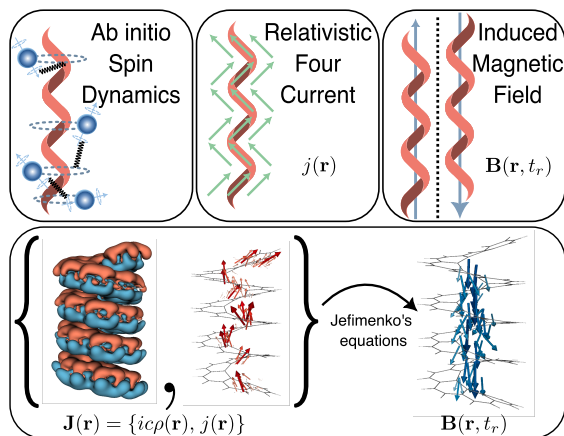
Chiral induced spin selectivity (CISS), a phenomenon in which chiral materials preferentially transmit spin selective electrons, has been observed in a wide range of chiral systems including DNA, proteins, molecular films, metal oxides, and 2D materials. This exciting effect opens new avenues for controlling chemical, biological, and electronic processes by manipulating and controlling spin. However, we currently lack fundamental explanations which can explain and predict the magnitude of the CISS effect. One leading hypothesis is that chiral phonons, or quantized lattice vibrations arising from rotational motion of atoms, could provide the necessary angular momentum for spin selective filtering. However, chiral phonons are challenging to measure, and to date there is no direct evidence linking their existence or magnitude to the magnitude of the CISS effect.

We aim to develop a quantitative correlation between chiral nuclear structure and CISS, which involves connecting experimental observables of chirality and spin selectivity from a wide range of samples with mathematical descriptors of chirality. Our lab's efforts first involve the development and application of Raman spectroscopic approaches to quantifying chiral nuclear motions, including phonon mode Raman optical activity and coherent Raman optical activity. These techniques are compatible with a wide range of samples known to facilitate CISS, while being designed to measure low frequency vibrations in both frequency and time domain measurements. Secondly, we aim to determine the functional role of chiral nuclear motions on CISS, through mode-selective femtosecond stimulated Raman spectroscopy and Raman thermometry measurements. Altogether, our work aims to link spectroscopic observables with chiral nuclear structure and CISS magnitudes, providing fundamental insight into the mechanism of CISS.

Chirality-Driven Magnetization Emerges from Relativistic Four-Current Dynamics

FA9550-21-1-0344 and FA9550-23-10311

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Chirality-induced spin selectivity (CISS) is a striking quantum phenomenon in which electron transport through chiral molecules leads to spin polarization, even in the absence of magnetic fields or magnetic components. Although observed in systems such as DNA, helicenes, proteins, and polymers, the fundamental physical origin of CISS remains unresolved. Here, we introduce a time-dependent relativistic four-current framework, in which charge and current densities evolve according to the time-dependent variational principle. Real-time relativistic four-current simulations enable direct analysis of helical currents and induced magnetization dynamics. Applied to helicenes, axially chiral molecules lacking stereocenters, our simulations reveal curvature-induced helical electron currents that generate spontaneous magnetic fields aligned along the molecular axis. These fields are handedness-dependent and reach magnitudes of 10^{-1} Tesla per single helicene strand. Our results suggest that CISS may arise from intrinsic, relativistic curvature-induced helical currents and the associated magnetic fields within chiral molecules. This four-current mechanism offers a self-contained explanation for spin selectivity, independent of interfacial effects or strong spin-orbit coupling. Furthermore, our results lead to several testable hypotheses that can be explored in experiments.

Ultrafast XUV spectroscopy guides chromophore and photocatalyst design

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The ultrafast dynamics of transition metal chromophores and photocatalysts are defined by their excited-state potential energy surfaces, and the curvature and intersections of these surfaces determine figures of merit such as the excited-state lifetime and photochemical quantum yield. We use extreme ultraviolet (XUV) transient absorption spectroscopy to measure the element-specific electronic structure of coordination complexes on femtosecond timescales, identifying key vibrational modes, electron transfer steps, and spin-state changes. These studies revealed hidden loss mechanisms and guided new molecular design principles for longer-lived chromophores and more efficient catalysts.

In complementary work, we use synchrotron and free-electron based transient hard X-ray absorption spectroscopy to track the femtosecond dynamics of a novel ferrocene-cobaltocenium dimer. Metal-to-metal charge transfer excitation is followed by femtosecond charge recombination and intersystem crossing to a partially delocalized ferrocene triplet, and then to a localized ferrocene quintet. Ferrocene is one of the most common redox-active moieties, and until this work its quintet state had been almost completely neglected in the literature.

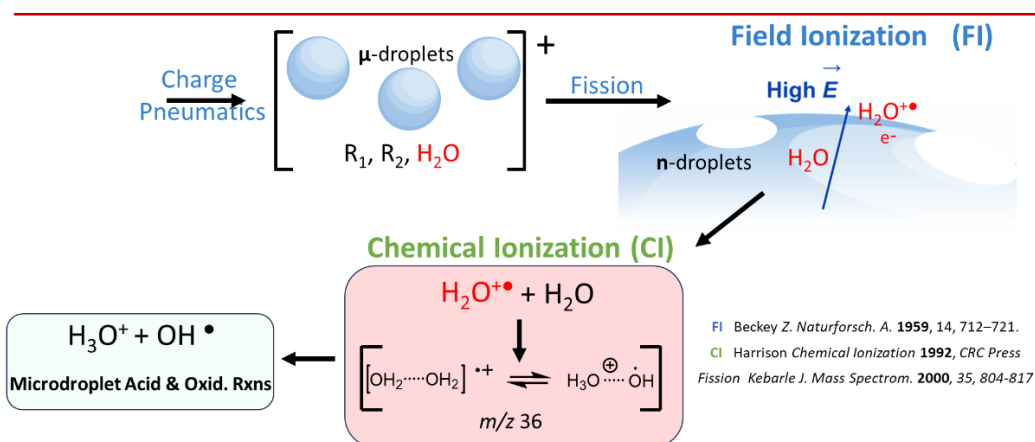
Finally, we present initial results from a DURIP-funded tabletop soft X-ray transient absorption spectrometer. This instrument generates femtosecond pulses of 100-300 eV photons, allowing us to perform core-to-valence spectroscopy of B, C, P, S, Cl, and many actinides and lanthanides.

Reaction Acceleration at the Air/Solution Interface of Microdroplets

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This presentation on accelerated reactions in microdroplets briefly surveys the discovery and scope of the phenomenon, including the two main classes of reactions - redox and acid/base. It then focuses on the underlying physical chemistry which it is argued is partial solvation of molecules at interfaces and the presence of strong interfacial electric fields. These features promote reaction by generating highly reactive entities at the solution/air interface. The reactive intermediate hydronium and hydroxide catalyze acid/base reactions while the water radical cation and anion are responsible for redox reactions. We argue that the strong field at the interface causes ionization of water (or water clusters) by the classical field ionization (FI) mechanism to give $\text{H}_2\text{O}^{+\bullet}$ and $\text{H}_2\text{O}^{\bullet-}$ and that these species evolve into HO^\bullet and $\text{e}^- (\text{aq.})$. "Self-protonation" is a well-known process in chemical ionization (CI) and the water radical cation undergoes self-protonation to give $\text{H}_3\text{O}^+ + \text{HO}^\bullet$. The proposed combination of FI and CI processes that operates at the air interface of water-containing microdroplets is illustrated.



Additional information on the nature of the interface comes from the observed reactivity. The occurrence of multistep reaction sequences (e.g. Hantzsch reaction) indicates that reacting molecules have substantial lifetimes at the interface (compared to droplet flight times) while the widespread occurrence of condensation means that the interface must be relatively dry – perhaps holey, as illustrated. Applications of accelerated reactions in organic synthesis are facilitated by the high speed of reactions and the fact that one reaction channel is often dominant. This allows, for example, green chemical synthesis (mild conditions, no metal catalysts, water as solvent) of many classes of heterocyclic compounds, e.g. imidazoles, pyrazoles, and borazines. It also allows arrays of reaction mixtures to be converted at rates of 1 reaction/second into arrays of products which can then be subjected to bioassays in the context of drug or antibiotic discovery. A high-throughput automated system based on desorption electrospray ionization is used for reaction screening, small scale synthesis with product collection and characterization (by MS and NMR) and then for bioassay. The operation of such a system at rates greater than 1 reaction mixture per second is based on the accelerated reaction phenomenon illustrated above.

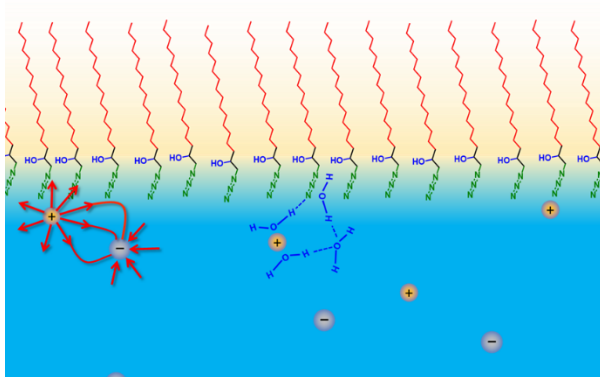
Partial Solvation, Ionic Structure, and Chemical Reactions at the Air-Water Interface

Jahan Dawlaty

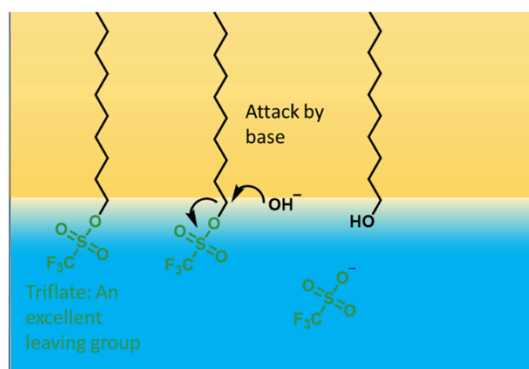
University of Southern California

Understanding chemical reactions at aqueous interfaces is important for many fields, including environmental chemistry, microdroplet reactivity, and electrochemistry. Despite extensive research, many fundamental properties of the interface, such as ionic structure and electrostatics, remain a subject of contentious debate. We use surfactants bearing well-defined azide vibrational probes to understand the solvation, electrostatics, and ionic interactions at the air-water interface. The probes form monolayers with controllable surface density in a Langmuir trough and its spectrum is measured using Infrared Absorption Reflection Spectroscopy, while various parameters of the air-water interface are varied. This approach has enabled two new discoveries. First, comparing the frequency of the azide at the interface to the frequency in the bulk aprotic and aqueous media reveals that the azide feels an intermediate environment that is neither like water nor like an aprotic environment. More importantly, tuning the surface charge density by adding charge surfactants to the interface can induce a change on the azide, but the influence is smaller than that of interfacial partial solvation. Second, we find that many simple inorganic salts do not affect the azide frequency even when they are present in large concentrations. This lends support to the salt-depleted air-water interface hypothesis that has been recently advocated for based on SFG spectroscopy. The latter work inspired us to follow the kinetics of an OH^- driven $\text{S}_\text{N}2$ reaction at the air-water interface. We found that surprisingly the pH of the subphase does not influence the rate of the reaction. Our findings define the range of reasonable parameters for explaining reaction mechanisms at the air-water interface.

Azides for Probing Electrostatics and Hydration at the Air-Water Interface



Following an $\text{S}_\text{N}2$ Hydrolysis Reaction at the Interface



Size-Dependent Condensation and Oxidation Reactions in Aqueous Microdroplets and Ice Grain Impact Phenomena

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The UC San Diego-based MURI is focused on an integrated experimental and theoretical approach toward understanding novel reactivity, structure and chemical gradients in aqueous microdroplets. We use spectroscopic techniques, theory and kinetic modeling to probe reactions and chemical gradients within aqueous microdroplets. Building on reports that condensation and oxidation reaction rates are enhanced in aqueous microdroplets relative to the bulk aqueous phase, we have been pursuing studies of the size-dependent aqueous microdroplet chemistry under conditions of controlled relative humidity and temperature. Recent progress in the Grassian group on understanding the acid-catalyzed condensation of pyruvic and lactic acids using confocal and cavity enhanced Raman spectroscopy as a probe of the condensation reaction, and evidence for a surface area dependence of the induction time and a surface-to-volume ratio dependence of the rate during the reaction period will be reviewed. 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. In the case of pyruvic acid, based on the experimental, theoretical and kinetic modeling results, we propose an autocatalytic reaction at the air/water interface where the condensation product, zymonic acid, catalyzes its own formation. Studies sensitive to chemical gradients are being carried out in the Continetti group using a novel single ice-grain accelerator that permits the size selection, acceleration, and impact-ionization-induced mass spectra of ice grains in the 800 nm – 3 micron diameter size ranges to be measured. Recent progress and challenges in determining the ice grain impact time-of-flight mass spectra accurately will be discussed, along with potential applications of this novel spectrometer.

Deployable NMR sensors based on spins out-of-equilibrium

Ashok Ajoy
UC Berkeley

I will present our experiments leveraging electron and nuclear spins out of equilibrium to build highly sensitive, deployable chemical sensors. These sensors utilize solid-state systems, such as semiconductors, where nuclear spins can be optically "hyperpolarized" to levels thousands of times greater than thermal equilibrium. Remarkably, these nuclei also exhibit extended coherence lifetimes ($T_2' > 800$ seconds), enabling their use in a range of applications. These include serving as highly sensitive quantum sensors for detecting time-varying magnetic fields, enhanced imaging agents, and for creating optically rewritable, nanometer-scale spin textures.

By incorporating them in nanoparticle form, we demonstrate the versatility of these sensors, deploying them in diverse environments such as manufactured materials, single-cells, and living plants, and in flowing microdroplet emulsions. In these dynamic settings, we show the potential for highly sensitive chemical assays, outperforming the current state of the art. Finally, we show the ability to extend this approach to a broad class of materials, including defects in semiconductors and molecules containing rare-earth ions or photoexcited triplet electrons. This opens new avenues for sensor construction harnessing chemical synthesis, and expands possibilities for practical applications.

Water structuring on polyvinyl alcohol surfaces underlies ice recrystallization inhibition

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Water-soluble polyvinyl alcohol (PVA) presents a scalable and modifiable alternative to biological antifreeze agents. I will present our collaborative study investigating the ice recrystallization inhibition (IRI) activity of synthetic PVA enhanced by cosolutes such as trehalose, sucrose, or glycerol. ¹⁷O nuclear magnetic resonance (NMR) chemical shift analysis of water hydrating PVA and electron paramagnetic resonance (EPR) lineshape analysis of spin labeled PVA together showed that PVA's IRI activity is exerted without strongly binding to ice. We provide a new hypothesis that PVA gives rise to a distinct phase of liquid water, with structural property distinct from bulk water, that interfaces between bulk water and ice to exert IRI activity. We offer experimental evidence for the enhanced structural property of the PVA-associated water to have greater tetrahedral ordering, and that PVA rearranges with tetrahedrally ordered water towards the ice to protect its surface from further growing. Together these observations suggest that the state of water that hydrates the surface of PVA plays a crucial role in its antifreeze and IRI function.

Modular Real-Time Path Integral Methods for Quantum Dynamics

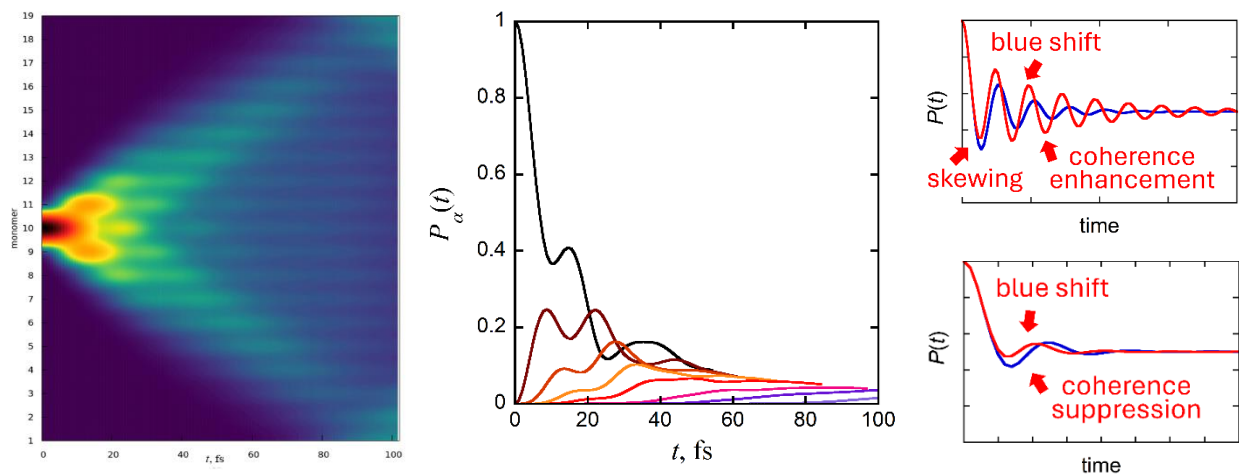
Nancy Makri

*Department of Chemistry, Department of Physics,
and Illinois Quantum Information Science and Technology Center
University of Illinois at Urbana-Champaign*

The unfavorable scaling of wavefunction storage severely impacts the feasibility of quantum dynamical calculations on large molecular and condensed-phase systems. Feynman's path integral formulation offers an attractive alternative, replacing wavefunctions by a sum of quantum mechanical amplitudes along all possible paths. However, the path sum involves astronomical numbers of terms, and stochastic methods are unable to deal with the oscillatory quantum phase.

A series of developments have led to rigorous and efficient real-time path integral methods that allow the accurate simulation of exciton-vibration dynamics. Current efforts focus on the development of modular decompositions of the path integral (MPI), which offer linear scaling with the number of interacting modules. In the case of extended systems with a locally one-dimensional topology, such as linear or ring-shaped molecular aggregates, spin chains, or dendrimers, the MPI decomposition proceeds by sequentially linking the paths of adjacent units within the memory length while simultaneously including the influence functional from intramolecular normal mode vibrations. In order to obtain long-time dynamics, one must propagate beyond the memory length. To this end, one of the modules is treated as the system, while the MPI-linked modules constitute its environment, which is not composed of harmonic degrees of freedom. By parsing the influence functional from a general environment, recent work developed a small matrix decomposition of the path integral for anharmonic environments (anh-SMatPI) and showed that the relevant propagation matrices (which have the minimal size, equal to the size of the desired reduced density matrix) can be computed through a small number of numerical evaluations of the influence functional. In addition, these ideas were extended to allow the inclusion of anharmonic vibrationals through a two-tier, modular treatment.

These numerically exact, fully quantum mechanical methods allow the simulation of dynamical processes in artificial and photosynthetic aggregates, elucidating the interplay among quantum coherence, delocalization, vibrational damping and thermal fluctuations, as well as the role of individual and collective vibrations on exciton transport and spin entanglement. Further, they open up the road for investigating novel effects induced by essential bath anharmonicity from coupled spin and anharmonic vibrational modes, which cannot be captured by effective harmonic bath mappings. These include the emergence of skewed and blue-shifted population oscillations, along with enhanced or suppressed coherence, which arise exclusively from non-removable anharmonicity of vibronic interactions.



Structure and function of engineered surfaces of MXenes and MXenoids

Dmitri V. Talapin

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Two-dimensional transition metal carbides and nitrides, also known as MXenes, combine excellent electronic properties with nearly endless possibilities for surface engineering. These materials represent an ideal platform for experimental and computational studies of complex interfaces. I will discuss different approaches toward engineering MXene surfaces using methods from inorganic, organic and organometallic chemistry, with the ultimate goals to better understand the structure-property relationships for MXenes and develop tools for prescriptive engineering of surfaces and interfaces in these functional 2D materials.

In the parallel effort, we are exploring an opportunity to generalize our surface engineering approaches beyond MXenes. Our recent findings suggest that the methodology and understanding of surface chemistry developed for MXenes can be translated to other 2D materials that we termed “MXenoids.” This generalization aims to expand the scope of MXene-like inorganic and organic-inorganic hybrid functional materials.

Combining *Ab Initio* Molecular Simulation and Machine Learning for Energetic Material Property Prediction

Edward Maginn and Eliseo Marin-Rimoldi
University of Notre Dame

Mark Gordon and George Elliott
Iowa State University and Ames National Laboratory

We describe recent progress on using molecular simulations and *ab initio* quantum chemistry in combination with machine learning to compute the phase behavior and physical properties of energetic materials. In the first part of the talk, we compare the predictive capability of neural network (NN) potentials for hydrazine and unsymmetrical dimethylhydrazine against experimental data and classical force fields. We show that the NN potentials accurately capture the energies and forces of the *ab initio* molecular dynamics (AIMD) simulations used in training. Computed properties such as density and viscosity match experimental data qualitatively but not quantitatively, suggesting that the underlying *ab initio* methods are not accurate enough.

We then test the capabilities of the effective fragment molecular orbital (EFMO) method for training a NN potential for water using EFMO MD simulations. Using small droplet simulations in the training, we again show that the NN potential captures the underlying EFMO energies and forces. Bulk water properties are computed and compared to experiment and results from an optimized classical force field.

In the second part of the talk, we focus on deep eutectic solvents (DESs), low melting liquids made from a combination of higher melting components. DESs are being explored as potential replacements for energetic ionic liquids, due to their low cost and ease of preparation. Similar to ionic liquids, the number of possible DESs is almost limitless, so a purely experimental exploration of compound space is infeasible. We show how Gaussian process models and active learning can be used to minimize the amount of experimental data needed to determine the solid-liquid phase diagram and viscosity of deep eutectic solvents (DESs), thereby speeding up the development of energetic DESs with properties tuned for a given application.

Hypergolic research at AFRL enabling “green”, chemical space propulsion

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Hydrazine propellants are the foundations of the current satellite propulsion systems tying our world together. However, the hazards associated with the hydrazines and ever increasing stringent environmental and safety regulations, together with high production costs and supply chain disruptions, will almost certainly mandate a new generation of rocket propellants. In the past research looking for a suitable hydrazine replacement was mainly focused on maintaining the performance levels near the hydrazines, which proved to be an unattainable task unless the hazards of the propellant are worse. Nowadays, the space propulsion sector seems to be placing a higher priority on lower life cycle costs, hazard reduction, and responsiveness and is willing to sacrifice some performance to enable these new priorities.

We have a long-established expertise in energetic ionic liquids, a class of compounds that have been seen as the solution to the handling difficulties of the hydrazines.

However, many ILs have intrinsic difficulties with purity control (residual solvent, metal contaminants from metatheses, or unreacted amine are laborious to remove) and cost-effective scalability which has limited their transitions as propellants. To address these problems, we started investigating Deep Eutectic Propellants (DeEP) utilizing the concept of Deep Eutectic Solvents (DES) for new energetic liquids.

An overview will be given from the early stages of our work to the current efforts and problems encountered.

Mapping Potential-Dependent Molecular Dances Across an Electrochemical Cell

Amber T. Krummel, Colorado State University

A central objective of this project is to gain a deeper understanding of how room temperature ionic liquids (RTILs) respond to external fields, with a focus on their dynamic behavior near electrode surfaces. RTILs are of significant interest due to their tunability, which enables their use in a wide range of applications—from green solvents to electrolytes in electrochemical systems. However, since RTILs are hygroscopic, it is essential to investigate the role of water in influencing their properties. Previous work in this project focused on determining the effects of limited amounts (under 21.6% χ_{Water}) of water on 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF₄) and 1-butyl-3-methylimidazolium dicyanamide (BmimDCA) room-temperature ionic liquid (RTIL) mixtures. The RTILs were characterized by tracking changes in the vibrational features observed in the linear infrared (IR) and two-dimensional infrared (2D IR) spectra of the dicyanamide anion (DCA). Our results showed clear differences in the dynamic behavior of these different populations of DCA at low (defined here as below 2.5% χ_{Water}), mid (defined here as between 2.5% χ_{Water} and 9.6% χ_{Water}), and high (defined here as between 11.6% χ_{Water} and 21.6% χ_{Water}) range water concentrations. We have used this foundation to interpret our observations of chemical dynamics of this RTIL under external applied biases. We have used linear IR imaging and 2D IR imaging to study the potential-dependent behaviors of the BmimBF₄:BmimDCA mixture in a model electrochemical half-cell. Our experiments reveal spatial dependent chemical dynamics that are also potential dependent. We are now working towards performing similar imaging experiments with a RTIL containing the trifluoroacetate anion to determine how anion choice may influence the dynamic behaviors of the RTIL electrolytes.

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Using Electrical Polarization in Understand and Control Thermochemical Surface Catalysis

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At solid–liquid interfaces, the exchange of ions and/or electrons with the solution can lead to electrostatic charging or polarization of the interface and a corresponding oriented electric field. Although intrinsic electric fields are known to play an important role in molecular and biological catalysis, interfacial charge transfer reactions and electrostatic polarization has been largely ignored as a controlling factor in heterogeneous thermochemical catalysis. We have developed general methods for tracking and controlling the degree of interfacial polarization during catalytic turnover and have used this approach to understand and tune thermochemical oxidation, hydrogenation, and acid catalysis. We have found that many net thermochemical reactions proceed as coupled electrochemical half-reactions and that interfacial polarization can be used to promote catalytic rates by orders of magnitude. These findings expose new opportunities to design and tune thermochemical catalysis by applying the principles of electrochemistry.

Kit Bowen
Johns Hopkins University
Molecular Activation and Single Atom Catalysis: Surface and Gas-Phase Studies

A major theme of our work is molecular activation. Deposition experiments on surfaces have focused on the activation and catalytic decomposition of 2-hydroxyethylhydrazinium nitrate (HEHN) by single iridium atoms, Ir. This work, in collaboration with Steve Chambreau and Jerry Boatz (Edwards AFB), identified the elementary steps in the thermal and heterogeneous catalytic decomposition of HEHN, a promising ionic liquid propellant. Beam-gas experiments confirmed and characterized the theoretically-predicted activation and catalytic conversion of methane to methanol via methane's reaction with specific transition metal, mono-oxide anions, i.e., NiO^- and PtO^- . This and our related gas-phase experimental work on the activation of methane by transition metal, single atomic anions was done in collaboration with the theorist, Evangelos Miliordos (Auburn U.). There, our experiments found and his computational results corroborated that while Cu^- , Co^- , and Ir^- insert into CH_4 , Ag^- and Au^- do not. In other gas-phase experiments, we found water to be activated by Ir^- and also by MoO_3^- . In another part of our work, we explored the little-studied process, Penning Detachment, in which an electronically-excited atom or molecule detaches an excess electron from a negative ion upon their collision. (Steve Berry, whose suggestions motivated our work, had done most of the theory on this process under Air Force support years ago.) In our first study of Penning detachment, we collided excited potassium atoms, K^* , which had been selectively (optically) excited to high Rydberg electronic states, with SF_5^- and observed its depletion as a function of Rydberg state. We then went on to study the Penning detachment H^- by H^* and by metastable He^* , electronically-excited species that are both abundant in the solar atmosphere. [The photodetachment of H^- (ubiquitous in the solar atmosphere) shields us from harmful emissions coming from within the sun.] Our ongoing projects also involve cluster models of single atom catalysis generally and of single atom photocatalysis in particular. There are two main types of single atom, cluster compositions that are of interest to us. These are $\text{M}'(\text{MO})_n$ and $\text{M}'\text{M}_n$, where M' is a single atom, $(\text{MO})_n$ is a metal oxide cluster moiety and M_n is a plasmonic metal cluster moiety. Surface-deposited clusters of $\text{M}'(\text{MO})_n$ (previously mass-selected as anions before grounded surface neutralization) mimic single catalytic atoms on oxide surfaces. When light is also introduced as a reactant, deposited clusters mimicking a single catalytic atom on a semiconductor surface, $\text{M}'(\text{MO})_n$, and a single catalytic atom in a plasmonic environment, $\text{M}'\text{M}_n$, may lead to photocatalytic reaction products. In this work, we are working closely with Ueli Heiz and Martin Tschurl (Tech. U. Munich). These reactions are explored in both gas phase and surface environments. We will report on preliminary results. We have also been involved in two collaborative projects, where we play supporting roles. These involve the study of the role of f-electrons in the bonding of Ce_2 with Knut Asmis (U. Leipzig) and spontaneous reduction processes in water microdroplets Colin/Xinxing Zhang (Nankai U.).

This talk will present our work on selected topics from the above.

Polaritonic metastructures

Andrea Alù

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In this talk, I will discuss our recent progress on the design, modeling, fabrication and characterization of polaritonic heterostructures featuring strong coupling between light and material excitations, including molecules. In particular, I will discuss the role of geometrical rotations, chirality, twisting and broken symmetries in controlling the light coupling and enabling spin-selective responses at the nanoscale and in the far-field, leveraging both the crystal structure of 2D materials and photonic structures engineered at the nanoscale.

MOLECULAR POLARITON CONDENSATES

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Strong light-matter interaction in excitonic materials results in the formation of half-light half-matter quasiparticles called exciton-polaritons (EP) that take on the properties of both its constituents. In this talk I will discuss our recent work on realizing Bose Einstein like condensates using molecular EPs at room temperature using the Small Molecule Ionic Isolation Lattice (SMILES) platform^{1,2}. Realization of lattices of these condensates using lithography and structured illumination will also be presented³. Following this we will discuss the role of polariton condensation on energy transfer dynamics between donor-acceptor systems.

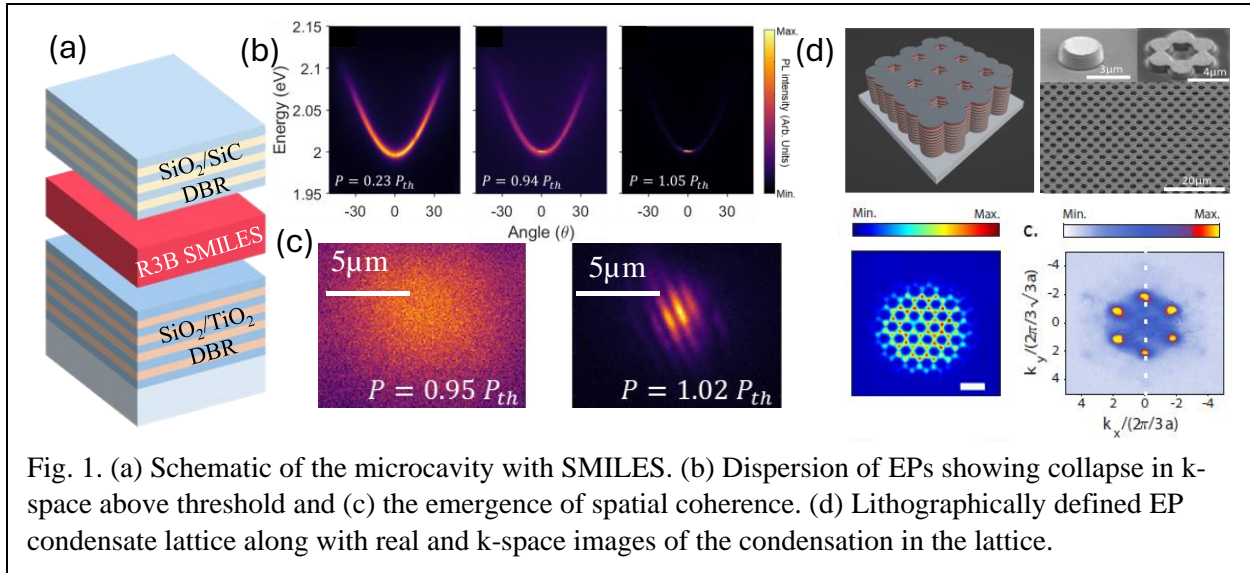


Fig. 1. (a) Schematic of the microcavity with SMILES. (b) Dispersion of EPs showing collapse in k -space above threshold and (c) the emergence of spatial coherence. (d) Lithographically defined EP condensate lattice along with real and k -space images of the condensation in the lattice.

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Real-Time 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 (RT-NEO) approach, in which the time-dependent Schrödinger equation is solved treating all electrons and specified protons quantum mechanically on the same level. In the RT-NEO time-dependent density functional theory (RT-NEO-TDDFT) method, the nonequilibrium electronic and protonic densities are propagated in time, and the other nuclei move classically on the instantaneous vibronic surface. The alternative NEO time-dependent configuration interaction (NEO-TDCI) method is a wavefunction-based approach that captures hydrogen tunneling dynamics and vibronic progressions corresponding to double electron-proton excitations associated with excited electronic states. To describe polaritonic systems, the cavity modes are coupled to electronic or vibrational transitions in the molecular system described by RT-NEO-TDDFT or NEO-TDCI. Coupling to cavity modes is shown to impact the rate of excited state intramolecular proton transfer¹ and hydrogen tunneling dynamics. A comparison of classical and quantum treatments of cavity modes provides insights into quantum entanglement. Simulations of multi-mode electromagnetic environments such as those produced by plasmonic nanocavities show that the nuclear-electronic dynamics can be resolved via cavity emission. Turning to surface plasmon resonances, the RT-NEO-TDDFT approach is used to simulate explicit metal atoms to describe plasmonic electron and energy transfer. Specifically, plasmon-driven H₂ photodissociation² and infrared plasmonic resonance energy transfer from gold nanoparticles or nanowires³ have been examined. These approaches open up the possibility of a wide range of applications to polaritonic and plasmonic chemistry.

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