

2022 AFOSR Molecular Dynamics and Theoretical Chemistry Program Review

Plasmonic Photocatalysis with Antenna-Reactor Nanoparticle Complexes

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The dual effects induced by illuminating a plasmonic nanoparticle of photothermal heating and hot carrier generation can both play important roles in chemical catalysis. For processes where hot carrier generation is dominant, catalytic rates can depend upon the specific plasmonic nanoparticle geometry, when the plasmonic response of the various geometries is equivalent. By introducing binding sites onto plasmonic nanoparticles one adds “reactors” to the “antenna”, which can greatly increase reaction rates and efficiencies in comparison to the analogous thermocatalytic processes. We will discuss several different types of antenna-reactor complexes and their characteristics for promoting various gas phase reactions. While some antenna-reactors can be chemically synthesized, an alternative approach of planar fabrication allows one to study chemical reactions under illumination in new ways that allow one to examine proximity effects of adjacent reactors in complex chemical reactions in a systematic manner. In addition, we have observed that reactors in photocatalytic complexes are not limited to metals in the platinum group, as is frequently seen in thermally driven catalyzed reactions, due to photoinduced desorption of intermediates on the reactive sites of the photocatalyst. We also have observed that “cheap” photons from LED light sources can effectively drive photocatalytic reactions, opening the door to industrial applications.

Energy Transfer in Strained Metal Nanostructures

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Abstract. Electron dynamics and optical properties of metals confined to the Ångstrom-length scale will be described. This presentation will focus on two types of metals: 1) 2-D crystalline films and 2) sub-nm 3-D nanoclusters. 2-D crystalline films are formed at high-energy silicon carbide surfaces and are passivated by bi-layer graphene. Templated by the silicon carbide lattice, the metals adopt highly strained and otherwise inaccessible lattices. This templating method results in the formation of highly strained, few-atomic layer films that exhibit structural ordering persistent on macroscopic length scales. As a result, the microscopic (i.e. Ångstrom-level) structure determines many of the macroscopic material properties. These include optical polarizabilities and electron-phonon scattering rates. In particular, lateral rotation of metal atoms at step edges results in accelerated electron-phonon scattering and interfacial energy transfer rates for group III metals.¹ Similar structural control over energy dissipation rates are not observed for bulk metals. Hence, 2-D metals may provide opportunities for achieving microscopic control over macroscopic energy flow. 3-D sub-nanometer metals exhibit electronic, magnetic, and optical properties that are determined by atomic-level structure. Electronically excited metal clusters relax through a series of competitive internal conversion and intersystem crossing pathways, resulting in varying degrees of transient spin polarization. In particular, spin polarized emission for these systems can be modulated by metal-atom substitution and ligand exchange.^{2,3} The ability to control electron dynamics in both metal 2-D films and nanoclusters are expected to have impacts for metal-mediated catalysis, quantum information technologies, and many other applications. Future directions toward controlling macroscopic properties through microscopic structure will be presented.

References:

1. M. A. Steves, K.L.K. et al. Atomic-Level Structure Determines Electron-Phonon Scattering Rates in 2-D Polar Metal Heterostructures. *ACS Nano*, **15**, 17780 (2021).
2. P. J. Herbert, K.L.K. et al. The Influence of Pd-atom Substitution on Au₂₅(SC₈H₉)₁₈ Cluster Photoluminescence. *J. Phys. Chem. C*. **125**, 7267-7275 (2021).
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Dynamics of Layered (2D) Pseudo-Halide Perovskites

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Initially discovered in 1839, perovskites, a broad family of crystalline materials, have seen a great reemergence recently. In particular, halide-perovskite semiconductors show promise in a wide variety of fields, most notably as photovoltaics and as illumination sources. Recently, layered perovskites have emerged as a versatile class of two-dimensional (2D) materials for optoelectronics. They are promising candidates as components in photovoltaics, light-emitting diodes and other photonic applications due to a multitude of properties, e.g., strong light absorption and emission, shallow defect formation, and facile solution-state deposition methods. The larger bandgap and higher exciton binding energy of 2D perovskites in comparison to their 3D counterparts are a result of their reduced dimensionality. In 2D perovskites, optical excitation generates excitons that are thought to self-trap through transient lattice distortions, leading to a very broad and Stokes-shifted emission. Although self-trapping can occur in static or flexible lattices, dynamic lattice fluctuations can allow the exciton to sample a more extensive landscape of energy minima and promote exciton localization and stabilization through lattice distortions.

The mechanism of white-light emission from 2D perovskites following UV excitation has generated considerable interest. Prior time-dependent studies indicated that the broadband photoluminescence (PL) arises from a distribution of self-trapped excitonic sites emitting in different regions of the visible spectrum with different decay dynamics. Using time-correlated single photon counting, we showed that the white-light emission decay from the perovskite 2,2'-(ethylenedioxy)-bis-(ethylammonium)) behaves as a single ensemble. The broad emission line shape is constant to 100 ns. We proposed that rapid local structural fluctuations cause the self-trapped excitons to experience a wide range of energies, resulting in the very broad PL. Therefore, it is important to investigate fast structural evolution of 2D perovskites

We have employed Two Dimensional Infrared Spectroscopy (2D IR) and Polarization Selective Pump-Probe (PSP) experiments to investigate the structural dynamics (spectral diffusion), lifetimes, and anisotropy in several 2D pseudo-halide perovskites. In the pseudo-halide perovskites, SCN^- as well as halides are anions in the unit cell. The CN stretch of the SCN^- anions served as the vibrational probes. We investigated $(\text{CH}_3\text{NH}_3)_2[\text{PbI}_2(\text{SCN})_2]$, $\text{Cs}_2\text{Pb}(\text{SCN})_2\text{Br}_2$, and $\text{Cs}_2\text{Pb}(\text{SCN})_2\text{I}_2$. A major difference among these perovskites is the lack of an organic cation (methylammonium – MA) in the two Cs^+ perovskites. The perovskites were spin-coated on a SiO_2 surface as a thin film, with a thickness of a few tens of nm.

Spectral diffusion arises from structural fluctuations that result in sampling of frequencies within the distribution of frequencies that comprise the inhomogeneously broadened absorption spectrum. The MA perovskite has a spectral diffusion time constant of 4.1 ± 0.1 ps, while the two Cs^+ perovskites have time constants of 24.6 ± 3.3 ps (Br^-) and 20.4 ± 1.8 ps (I^-), which are the same within error. The CN stretch vibrational lifetimes are 11.6 ± 0.1 ps for the MA perovskite, and 55.7 ± 0.2 ps (Br^-) and 55.4 ± 0.3 ps (I^-) for the Cs^+ perovskites. Full deuteration of the MA reduces the MA perovskite CN lifetime to 7.4 ± 0.1 ps. The MA and Cs^+ perovskites have similar crystal structures. The faster spectral diffusion and shorter lifetime of the MA perovskites compared to the Cs^+ perovskites are attributed to the structural degrees of freedom and the high frequency vibrational modes of the methylammonium moiety of the MA perovskites.

The sample contain 99% ^{13}CN and 1% ^{12}CN . The experiments are conducted on the low concentration ^{12}CN species to eliminate resonant couplings among nearby CNs which complicate the spectra and cause vibrational excitation transfer. In the Cs^+ perovskites, the 1% ^{12}CN IR absorption displays a small side peak. Its lifetime demonstrates that it is a CN species. The amplitude of the side peak increases with temperature with 160 cm^{-1} activation energy. These observations indicate the SCN^- resides in two slightly different configurations in the lattice, with the side peak arising from a 160 cm^{-1} higher energy structure. PSP measurements of the orientational anisotropy make it possible to determine the angular range (θ_c – half angle) sampled by the ultrafast librational motions of the SCN^- in the Cs^+ perovskites. The tilted cone anisotropy theory is used to obtain θ_c . The θ_c are $13 \pm 2^\circ$ and $16 \pm 2^\circ$ for the Br^- and I^- perovskites respectively.

“Dynamics and Vibrational Coupling in a Pb-I-SCN Layered Perovskite,” J. Nishida, J. P. Breen, D. Umeyama, H. I. Karunadasa, M. D. Fayer J. Am. Chem. Soc. **140**, 9882-9890 (2018).

“Single Ensemble Nonexponential Photoluminescent Population Decays from a Broadband White-Light-Emitting Perovskite,” J. E. Thomaz, K. P. Lindquist, H. I. Karunadasa, and M. D. Fayer J. Am. Chem. Soc. **142**, 16622–16631 (2020).

“Probing Lattice Dynamics in Two-Dimensional Inorganic Pseudohalide Perovskites with Ultrafast Infrared Spectroscopy,” X. Xing, J. Li, J. P. Breen, J. Nishida, H. I. Karunadasa, and M. D. Fayer submitted J. Phys. Chem. C (2022).

Molecular Vibrational Polaritons Dynamics

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Molecular vibrational polaritons are hybrid half-light, half-matter quasiparticle under vibrational strong coupling. These hybrid quasiparticles not only inherit properties of both photons and matter, but also processes unique new photonic and molecular phenomena, including tilting chemical potential landscapes of reactions¹, adding new energy transfer pathways and strong photonic interactions. Many of these developments hinge on the fundamental understanding of the physical properties of molecular vibrational polaritons. Pump-probe and 2D IR spectroscopy provide unique insights to this emerging research area by resolving the dynamics of various states.²⁻⁴ In this talk, I will discuss how polariton could influence inter and intramolecular interactions, including energy transfer between molecules⁵ and barrier crossing events. Lastly, I will show some exciting opportunities of using vibrational polaritons as quantum bits for quantum information technology, including coherent transfer among polaritons^{6,7} and confinement effects in polaritons, visualized by 2D IR imaging technique.

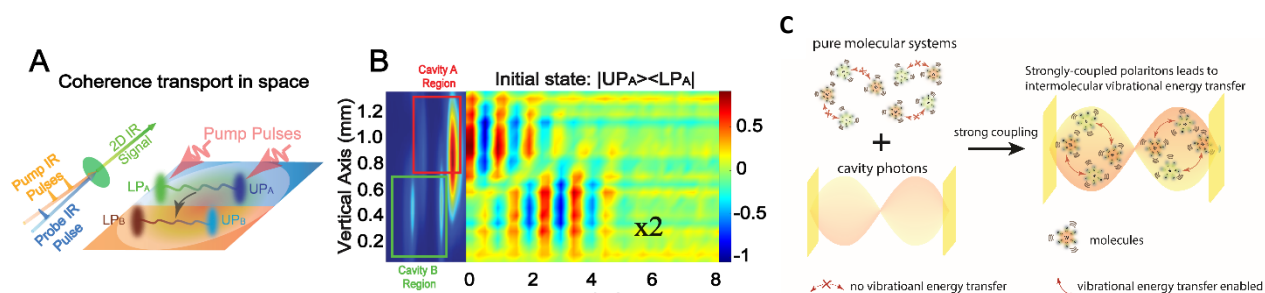


Figure 1. Polariton enabled coherence transfer (A and B) and intermolecular energy transfer (C)

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- (3) Xiang, B.; Ribeiro, R. F.; Li, Y.; Dunkelberger, A. D.; Simpkins, B. B.; Yuen-Zhou, J.; Xiong, W. *Sci. Adv.* **2019**, *5* (September), eaax5196.
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- (5) Xiang, B.; Ribeiro, R. F.; Du, M.; Chen, L.; Yang, Z.; Wang, J.; Yuen-Zhou, J.; Xiong, W. *Science* (80-.). **2020**, *368* (6491), 665–667.
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Understanding the Interplay of Complex Molecules with Complex Cavities

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The strong coupling of molecular electrons to photons confined in planar micro-resonators leads to the formation of hybrid light-matter states known as cavity polaritons. While treating molecules like simple two-level systems leads to the prediction of some cavity polariton properties, the effects of complex interactions between electronic and nuclear molecular degrees of freedom on polariton formation remains unclear. Furthermore, the effect of simultaneous coupling of multiple molecular electronic resonances to distinct, well-defined cavity modes is unexplored. In this talk, I will present predictions of a class of energy dispersive states in coupled copper (II) tetraphenylporphyrin (CuTPP)-photon systems that stem from the presence of simultaneous strong light-matter and intramolecular vibronic couplings. Following an assessment of the properties of these states relative to dark states formed from an energetically disordered ensemble of CuTPP molecules, I will present experimental evidence for the appearance of Herzberg-Teller (HT) polaritons in photoluminescence spectra of CuTPP cavity polariton samples. This evidence includes an order of magnitude enhancement of inefficient light emission from a short-lived excited state of CuTPP in the presence of a spectrally proximate cavity mode, which does not participate in polariton formation. Through quantum optics modeling, I explain the observed light emission enhancement stems from a vibrational sideband of the cavity photon energy due to the presence of both strong light-matter and vibronic couplings. These results demonstrate the large phase space of molecular processes and photonic structures available to the physical chemistry and chemical physics research community to control the non-radiative and radiative decay of polaritonic systems towards enhancements in light harvesting, energy transduction, and light-driven fuel production.

Energy cascade in carbon nanotube polaritons

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Exciton-polaritons are hybrid states formed when molecular excitons are strongly coupled to photons trapped in an optical cavity. These systems have many attractive properties, including large delocalization lengths, but many questions regarding how energy flows and relaxes in polariton cavities are still up for debate. This talk will present ultrafast 2D White-Light spectra and Redfield simulations of energy transfer phenomena and dynamics in semiconducting carbon nanotube polariton microcavities. Carbon nanotubes are appealing materials for polaritonics because of their strong, narrow excitonic light absorption and highly tunable bandgaps. We leverage them to create a series of planar microcavities designed to explore how energetic disorder impacts energy transfer in polaritons. We discover that energy cascades down a manifold of hybrid states when the energetic disorder is tailored to match the exciton-photon coupling strength. This cascade is analogous in many ways to the flow of energy in light harvesting complexes in plants. The cascade is specifically evidenced by a delayed growth and slow decay of a cross peak between upper- and lower- polariton states that is resolved in the 2D White-Light spectra (Fig. 1) and that is absent in samples with less, mismatched disorder. Long-range > 150 nm energy transfer through an insulating barrier is also evidenced in this system. Future experiments will be outlined that we anticipate will provide a detailed probe into how to explore and control the spatial and energetic phenomena governing energy transfer in polariton microcavities.

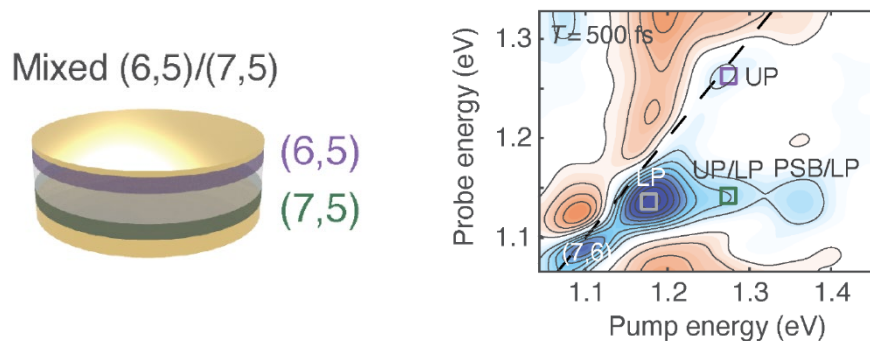


Fig. 1. Energy cascade in carbon nanotube polaritons. (Left) Schematic diagram of nanotube microcavity fabricated from two bandgaps of nanotubes [(6,5) and (7,5)] with an engineered bandgap difference that therefore incorporates 50 meV of disorder. (Right) Representative 2D White-Light spectrum of a microcavity at waiting time (T) of 500 fs evidencing a cross-peak between upper (UP) and lower (LP) states. The kinetics of this cross-peak reveal an energy cascade.

Vibrational SFG probe of the electrode/catalyst/electrolyte interface: electrode induction effect and mapping field profile by Stark shift ruler

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Abstract:

Attachment of molecular catalysts onto semiconductor or metal electrodes is a promising approach for rational design of efficient photoelectrochemical cells for solar water splitting and CO₂ reduction. The understanding and improvement of such devices requires fundamental understanding of the structure and dynamics of catalysts as well as the interfacial electrolyte environment at electrode-liquid interfaces. Vibrational sum frequency generation (VSFG) spectroscopy is an *in situ* interface specific technique for probing interfacial properties at the electrode/catalyst/electrolyte interface at the molecular level. In this talk, we discuss our recent efforts in developing and applying *in situ* VSFG for studying structure, electrode induction effect and interfacial microenvironment of transition metal catalysts on metal electrodes. For rhenium tricarbonyl bipyridine CO₂ reduction catalysts on Au electrodes, we show that by combining VSFG experiment with advanced computational modeling, the catalyst adsorption geometry can be determined; and the electrode polarization leads to large shift of the CO stretching mode frequency of attached catalysts, indicate a strong electrode induction effect on the charge density of the metal center that is significantly larger than that can be achieved by substituent effect. We introduce a spectroscopic method based on a Stark shift electric field ruler that enables mapping the electric field strength across the electric double-layer of electrode/catalyst/electrolyte interfaces. Using the tungsten-pentacarbonyl(1,4-phenylene)diisocyanide complex as an interfacial electric field ruler, measurements of Stark shifts under *operando* electrochemical conditions and direct comparisons to DFT simulations reveals how the interfacial electric field and the electrode induction effect decay with distance from the electrode surface. Comparison with Gouy-Chapman-Stern reveals a microscopic picture of the electric double layer at the electrode/catalysts/electrolyte interface.

Electrochemistry, Electron Transfer and Chiral Induced Spin Selectivity

In this talk, I will introduce three vignettes of our research in the areas of electrochemistry, electron transfer and chiral induced spin selectivity.

First, I will highlight our program to develop an open source code through which one can model I-V cyclic voltammetry curves. For such problems, one must overcome a series of stiff differential equations (arising from the drastically different times scales of diffusion and electron transfer [especially if there is nonlinear absorption]). Whereas most such programs today are proprietary, we are preparing an open source platform that can be easily modified by interested students.

Second, I will address a series of advances in electronic structure and dynamical which are necessary for modeling electron transfer. Electron transfer represents the fundamental coupling of electronic to nuclear motion, and modeling electron transfer dynamics requires accurate multireference electronic structure theory and advances in nonadiabatic dynamics algorithms that can treat many electronic states. I will give several updates about both of these areas.

Third, for molecular dynamics at a metal surface, I will highlight how our recent work in electronic friction can be extended to include the presence of spin-orbit coupling. In such a case, I will show that a novel Berry pseudo-magnetic force appears which can move nuclear wavepackets in different ways depending on the electronic spin. I will argue that such an effect likely contributes to the chiral induced spin-selectivity effect.

Oral Abstract, 2022 AFOSR Contractors Meeting, May 2022

Hydrogen and Gold: Isotope Effects and Nanoparticles, Shaken not Stirred

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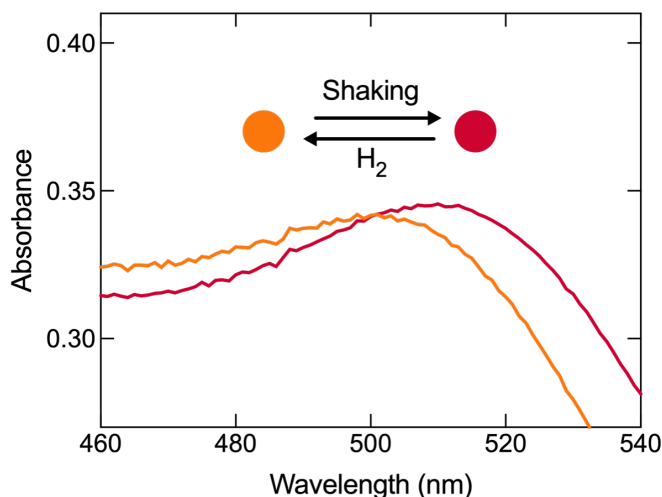
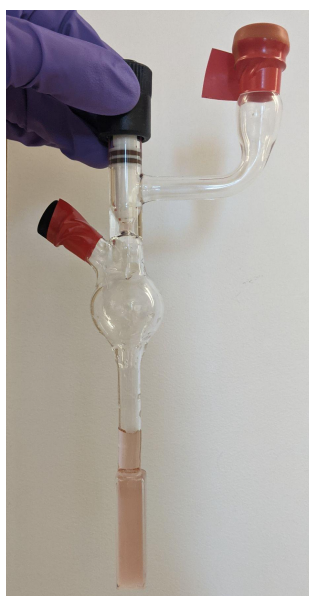
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A key challenge of heterogeneous catalysis and electrocatalysis is understanding the surface-bound intermediates. Many of these reactions involve transfers of hydrogen, yet there are many uncertainties about the coverage and chemical reactivity of surface H, even on relatively simple metal surfaces. Electrocatalysis at single-crystal Pt(111) surfaces is a valuable case study. Gold has also long been a preferred electrode material because of its chemical inertness, for instance binding hydrogen only weakly under most conditions. Yet gold at the nanoscale has been found to bind hydrogen and have much more catalytic activity.

Two aspects of hydrogen on gold will be presented. First, the product isotope effect for hydrogen evolution on polycrystalline gold — H_2 vs. HD vs. D_2 from mixed $\text{H}_2\text{O}/\text{D}_2\text{O}$ solutions — has been examined using differential electrochemical mass spectrometry (DEMS). A substantial and potential-independent H/D isotope effect was observed, which has some mechanistic implications. In parallel, the chemical oxidation and reduction of aqueous colloidal gold nanocrystals is being examined, as monitored principally by the gold surface plasmon resonance (SPR; see images below). For example, the Au nanocrystals are reduced with borohydrides and then re-oxidized by the nitroxyl radical 4-MeO-TEMPO. The gold colloids change color when exposed to H_2 gas, a process that is reversible in a number of ways. The chemical nature of these reactions, and their likelihood of being proton coupled electron transfer (PCET), will be discussed.



Applications of hybrid high resolution mass spectrometry/cryogenic ion spectroscopy to thermochemistry and kinetics

An ongoing focus of our AFOSR program is the development of a powerful new platform for chemical analysis. This involves integration of ambient mass spectrometry with optical spectroscopy to extract complex molecular architectures from solution, isolate specific species of interest, and characterize their structures using optical spectroscopy. By controlling the temperature of the composition-selected species, we can follow changes in structure and molecular speciation as systems begin to explore large amplitude motions on reactive potential energy surfaces. In this presentation, we focus on two applications that are most relevant to our AFOSR program. First, we will discuss the thermochemistry associated with the production of artificial plasma. In an extensive collaboration with ARFL (Kirtland) and university laboratories (Emory, Berkeley, Utah, Washington), we carried out a spectroscopic determination of the key SmO^+ bond dissociation energy by threshold photodissociation of the cryogenically cooled cation. This was accomplished using the extensive ion processing capabilities of the Thermo Fisher LTQ Orbitrap in conjunction with uv photoexcitation of the temperature-controlled ions using buffer gas cooling in a radiofrequency ion trap. In a second example, we follow large amplitude electrical charge migration in an aromatic organic scaffold. Migration is calculated to occur over very large barriers, and preliminary calculations indicate this process is catalyzed by molecular hydrogen through a transient hydride motif. We also find chemical consequences of charge migration including C-C bond formation in benzophenone derivatives. Analogous experiments to follow migration of excess positive charge by water-mediated proton translocation across similar aromatic scaffolds will also be discussed.

Femtosecond Time-Resolved Electron Ionization Mass Spectrometry

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Mass spectrometry (MS), one of the most useful analytical tools in chemistry, remains a ‘black box,’ with molecules entering one end and fragment ions coming out the other end. The goal of this work is to determine the molecule-specific reaction mechanisms that lead to the fragmentation patterns used for molecular identification. We achieve ultrafast electron ionization by taking advantage of femtosecond strong-field ionization and electron rescattering. When such an event is followed by a weak probe pulse, one is able to track simultaneously the time-dependent yield of tens of different product ions. Femtosecond time-resolved electron ionization MS (TREIMS) yields time-resolved data that can help uncover the fundamental steps between reactant and product ions. This information is valuable for understanding and predicting the fragmentation patterns occurring in mass spectrometry. The research involves molecules, radicals, and multi-charged species far from equilibrium and can determine intramolecular vibrational energy relaxation rates, uncover vibrational coherence, identify cases where a reaction occurs prior to a statistical distribution of energy, and discover interesting new reaction mechanisms such as those involving roaming radicals and neutral species. Following a description of the experimental approach, I will present initial results on a project aimed at understanding why nonpolar perfluorinated n-alkane substances (PFAS), which are of interest because of their great global warming potential, have very similar mass spectra. In particular, we find that femtosecond ionization MS can allow identification and quantification of mixtures of C_5F_{12} and C_6F_{14} . Time-resolved data reveals the sub-picosecond (α)-cleavage processes that give rise to the final fragmentation patterns, and the associated intramolecular vibrational energy redistribution (IVR). Surprisingly, the ions used for identification have identical reaction dynamics. We find evidence of coherent vibrational dynamics in only the $C_3F_7^+$ ion, a result we consider to be consistent with fast IVR following ionization of these compounds.

Metal Catalyzed Combustion Chemistry Studied with Cluster Ion Spectroscopy

FA9550-20-1-0327

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Metal-catalyzed combustion is a key aspect of propulsion planned for Air Force hypersonic vehicles and weapons. Optimizing the chemistry of such systems requires a knowledge of the structures of hydrocarbon molecules interacting with metal catalytic sites, the possible reaction intermediates involved in hydrocarbon cracking or metathesis reactions, and the likely structures of soot nucleation centers. The fundamental interactions involved in such metal-molecular systems are investigated in our lab with infrared and UV-visible spectroscopy and computational chemistry on gas phase metal ion complexes. Additional experiments employ mass-selected ion photofragment imaging to investigate cation-molecular bonding energetics. Infrared spectroscopy measurements focus on the prototypical interactions in $M^+(C_2H_2)_n$ and $M^+(C_2H_4)_n$ complexes ($M = Fe, Pt, V, Ti, Zn$, etc.) in the C–H stretching region. Infrared band patterns and dissociation behavior determine the nature of the interactions (covalent versus electrostatic), the structures formed, the coordination numbers, and the occurrence of intracuster ligand coupling reactions. Computational studies complement the spectroscopy and provide the energetics of the potential energy surfaces involved in the chemistry, including the role of specific electronic and spin states on the metal. Ion photofragment imaging experiments on $Zn^+(CH_3OH)$ and $Zn^+(C_2H_4)$ provide metal-ligand bonding energetics.

Progress towards automated force field generation useful for ionic liquid-based propulsion systems

Dr. Benjamin Prince, Air Force Research Laboratory

Ionic liquids serve as the propellants in state-of-the-art electrospray thrusters. Experimental measurements of laboratory electrospray thrusters have identified a significant correlation between the values of the physical properties of ionic liquids and attributes of their thruster performance. Additionally, experimental and modelling reports have highlighted the impacts of contamination of the thruster by the plume on the longevity of operation among other impacts. We have recently performed a series of modelling efforts using classical molecular dynamics in order to predict and understand the dynamics occurring in the electrospray thruster plume. The focus of today's talk will be on the use of classical molecular dynamics and various force fields towards the accurate reproduction of experimental measurements. An emphasis will be on the relevance of typical force fields used for property prediction that have been optimized for the condensed phase and their applicability to fundamentally gas-phase processes.

Studies of Dynamic Materials in Extreme Environments

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 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 characteristics, and reactivity of interfacial molecular ices in support of AFOSR fundamental science needs for materials and flight operations in arctic environments.

We will report at this year's meeting on several achievements: (i) Our newest scattering instrument that combines supersonic beam surface interactions with *in situ* STM visualization is now fully operational, is examining N₂ dissociation on Ru to probe energy dissipation and non-adiabatic effects in reactive chemisorption. We are also examining energy transfer involving N₂/SiC and Ne/SiC to help elicit information about how internal degrees of freedom affect energy exchange with high-T surfaces. We have also extended our studies of energetic interactions with different structural ices [1] to include embedding and capture of neutral species into ice [2]. This is an important new mechanism for understanding gas-surface energy & momentum exchange in high velocity gas flows with ice and thin molecular films. Moreover, we have demonstrated three new methods for the separation of isotopologues and isotopes and have filed patent applications which acknowledge AFOSR support. In these methods we use (i) atomic diffraction, (ii) the threshold for molecular or atomic embedding into ice as a gateway filter for the preferential absorption of heavier species, and (iii) the preferential condensation of competing isotopologues under carefully chosen non-equilibrium gas-surface collision conditions [3]. Such isotope selectivity during deposition and scattering may open new routes for *in-situ* isotopic materials engineering. In many of these experiments we continue to innovate precision elastic and inelastic neutral helium atom scattering as an insightful tool for probing, *in situ*, the structure and dynamics of complex interfaces. Finally, in ongoing experiments, we are examining the sticking and bonding of water and other molecules [4] as a function of gas velocity and surface temperature on hydrophilic vs. hydrophobic surfaces, studies that are revealing new details of ice formation in cold environments.

Selected Recent Publications

1. Sticking Probability of High-Energy Methane on Crystalline, Amorphous, and Porous Amorphous Ice Films, Rebecca S. Thompson, M. R. Brann, and S. J. Sibener, *J. Phys. Chem. C* **123**, 17855-17863 (2019)
2. A New Method of Isotope Enrichment and Separation: Preferential Embedding of Heavier Isotopes of Xe into Amorphous Solid Water, K. D. Gibson and S. J. Sibener, *PCCP* **23**, 7902-7907 (2021).
3. Differential Condensation of Methane Isotopologues Leading to Isotopic Enrichment Under Non-equilibrium Gas-Surface Collision Conditions, Michelle R. Brann, Stephen P. Hansknecht, Xinyou Ma, and S. J. Sibener, Invited Submission to the Special Issue "Celebrating 125 Years of The Journal of Physical Chemistry", *J. Phys. Chem. A*, **125**, 9405-9413 (2021).
4. Acetone-Water Interactions in Crystalline and Amorphous Ice Environments, Michelle R. Brann, Stephen P. Hansknecht, Mark Muir, and S. J. Sibener, *J. Phys. Chem A*, Invited submission to the Virtual Issue: 10 Years ACS PHYS Astrochemistry Subdivision, <https://doi.org/10.1021/acs.jpca.2c01437> (2022).

Fluxional cluster catalysts for endothermic cooling

Patricia Poths, Harry Morgan, Anastassia Alexandrova

Chemistry and Biochemistry, UCLA

Guangjing Li, Autumn Fuchs, Marc Malek, Scott Anderson

Chemistry Department, University of Utah

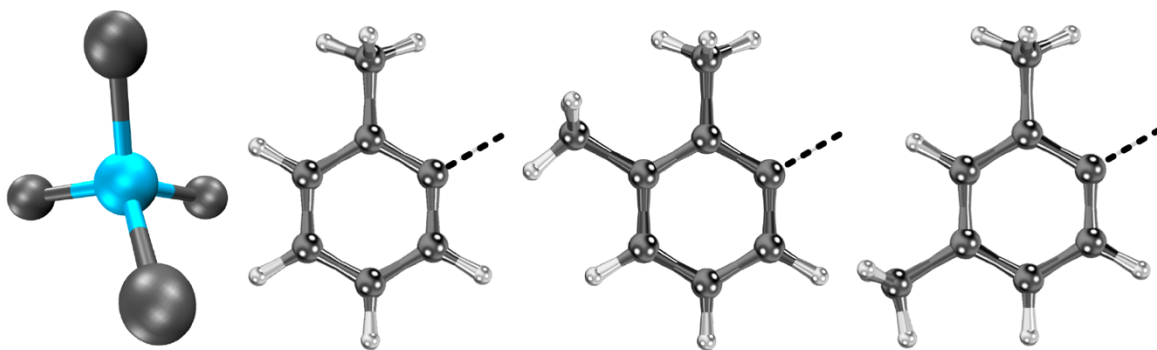
The talk will focus on the catalysis for endothermic cooling applications, on fluxional supported nanocluster catalysts. This type of highly dynamic interfaces both represent a big challenge for theory and *operando* characterization, and open a wealth of new fundamental phenomena, as well as opportunities for catalyst optimization. A fluxional interface exposed to harsh conditions, whether catalytic (thermal, electro-, photo-), or otherwise chemically or physically aggressive, will undergo relentless dynamics that would couple in non-trivial ways to the chemistry occurring at it. In endothermic catalysis, supported clusters populate a large ensemble of states, distinct in their structures, stoichiometries, sites on the support, and properties, such as activity, selectivity, spectral signatures, and degradation propensities. Cluster dynamics can couple to the catalytic reaction, becoming part of it. Central theories operating in this field, such as Ostwald theory of ripening and scaling relations, require revisions in view of the fluxionality. This paradigm will be illustrated by several systems, but mostly focusing on a newly developed highly selective and stable catalyst for endothermic partial dehydrogenation of alkanes: a PtGe cluster alloy supported on alumina. Through a combination of theory and experiment, we found this catalyst to undergo a self-limiting coking that *creates* the actual stable catalyst. The initial PtGe clusters slowly convert to the key slightly coked structure via a metastable and non-selective isomer that's populated at a level of only a few per-cent in the as prepared catalyst. Ge and C engage in an electronic relationship the net result of which is the preservation of the electronic state of close to pure Pt in the PtGeC alloy, which is highly catalytic for alkane dehydrogenation, but suppresses deeper dehydrogenation. The mechanism of cluster catalyst stabilization through self-limiting poisoning is new, and indeed opens a possibility of other cluster catalysts to become practicable through similar mechanisms. This discovery also points toward an important frontier in cluster catalysis: the goal is to collapse the massive catalytic ensemble of states to a few or even just one super-stable and catalytically selective and active state, to avoid selectivity issues brought forth by the many populated states with different chemistries.

Multiconfiguration Pair-Density Functional Theory for Molecular Qubits

Arturo Sauza-de la Vega, Riddhish Pandharkar, Gautam D. Strosio, Arup Sarkar, Donald G. Truhlar, and Laura Gagliardi

A computational protocol based on multiconfiguration pair-density functional theory (MC-PDFT) for computing singlet-triplet gaps and zero-field splitting (ZFS) parameters in promising molecular qubit candidates will be presented.

Results on pseudo-tetrahedral organometallic complexes containing chromium(IV) and aryl ligands will be discussed. We investigated changes in these computed physical parameters with respect to: (i) molecular geometry, (ii) choice of active space, and (iii) choice of multireference method. We also studied the origin of the small ZFS values in the examined complexes. Overall, the analysis reported herein demonstrates the remarkable performance of multiconfiguration pair-density functional theory for the computation of triplet-singlet gaps and zero-field splitting parameters with accuracy comparable to the more expensive multiconfigurational complete active space second-order perturbation theory.

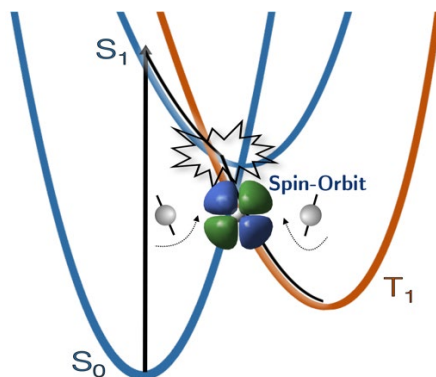


Pseudo tetrahedral Cr(IV) systems with different ligands: 2-methylphenyl; 2,3-dimethylphenyl; 2,4-dimethylphenyl

Intersystem Crossing from Light to Heavy Element

Xiaosong Li

Department of Chemistry, University of Washington



Intersystem crossing (ISC), a vital component of the electronic and nuclear transitions that compose photophysics, has been successfully simulated in light elements and transition metal complexes. Derived from the Z -dependent spin-orbit coupling (SOC), ISC is expected to be of greater importance as the atomic number increases. Different theoretical approaches to compute ISC and their limitations will be discussed. We will place a special emphasis on several of the challenges that will need to be overcome in order to treat ISC in late-row elements, including: the loss of spin as a good quantum number, the need to include SOC variationally via two- or four-component electronic structure, and the high density of states present in late-row complexes. Particularly, variational relativistic methods will be necessary in order to capture the electronic structure of molecules with very strong spin-orbit coupling. This therefore will also require explicit nonadiabatic simulations of the photoexcited molecule in the fully spin-adiabatic basis. Further challenges are presented by the large number of electrons and high density of states in these molecules. Overcoming these challenges will require further development of low-scaling electronic structure and dynamics methods in order to treat ISC in late-row transition metal complexes accurately.

Ultrafast Ion Hopping and Correlations in Solid State Electrolytes

Scott Cushing, Caltech

Li ions can transport through certain solids, named superionic conductors, at speeds that surpass water or polymer electrolytes. The Li ion transport occurs on picosecond timescales via vibrationally activated hopping along symmetric channels in the lattice. The passage of the Li ion through the lattice leads to correlations with the electron cloud, other ions, and the phonon modes themselves. Intriguingly, these many-body correlations are theoretically predicted to increase the ionic conductivity of the solid-state material rather than hinder transport. However, a measurement technique does not yet exist that can directly measure ion transport in solids on ultrafast timescales.

In this talk, we will discuss our progress towards creating new techniques that can measure ultrafast ion transport and the associated many-body interactions. This involves the creation of a new laser-driven, ultrafast impedance methodology that can measure the relative strength of possible ion hopping Hamiltonian contributions. Based on these results, appropriate driving frequencies are selected for transient extreme ultraviolet (XUV) spectroscopy measurements to gain more atomistic insight. The element specific X-ray technique measures the role of the different lattice cage atoms relative to the Li ion to determine how material composition controls the many-body effects that lead to superionic conduction.

The Surface Science of MXenes

Dmitri V. Talapin

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MXenes are a large family of two-dimensional (2D) transition-metal carbides and nitrides. This class of materials currently includes about 30 distinct phases demonstrated experimentally, with at least 100 more compositions predicted computationally. The research on MXenes is experiencing exponential growth, with numerous reports pointing to the potential for electromagnetic interference (EMI) shielding, electrochemical energy storage, optoelectronics, sensors and catalysts. In contrast to other 2D materials, MXenes combine excellent electronic properties with nearly endless possibilities for covalent surface functionalization. In this regard, MXenes represent an ideal platform for fundamental and applied studies of interfaces in 2D functional materials.

The comprehensive understanding of MXene surfaces introduces novel approaches for prescriptive engineering of physical and chemical properties of low-dimensional materials. Chemical transformations of MXene surface functional groups open a previously unexplored design space for this broad class of functional materials. We discuss general strategies to install and remove inorganic or organic surface groups by performing substitution and elimination reactions. Successful synthesis of MXenes with oxygen, imido, sulfur, chlorine, selenium, bromine, and tellurium surface terminations, bare MXenes (no surface termination), and hybrid organic-inorganic MXenes (*h*-MXenes) are demonstrated. The description of MXene surfaces requires an intricate mix of concepts from the fields of coordination chemistry, self-assembled monolayers (SAMs) and surface science. MXene surface groups control biaxial lattice strain, phonon frequencies, electrochemical performance, the strength of electron-phonon coupling, making MXene surfaces not spectators but active contributors to conductivity, superconductivity and catalytic activity. The optical properties of hybrid organic-inorganic MXenes reveal coherent coupling between the organic and inorganic components.

Title:

Molecular access to the high density of states in inorganic nanocrystals enabled by covalent conjugation

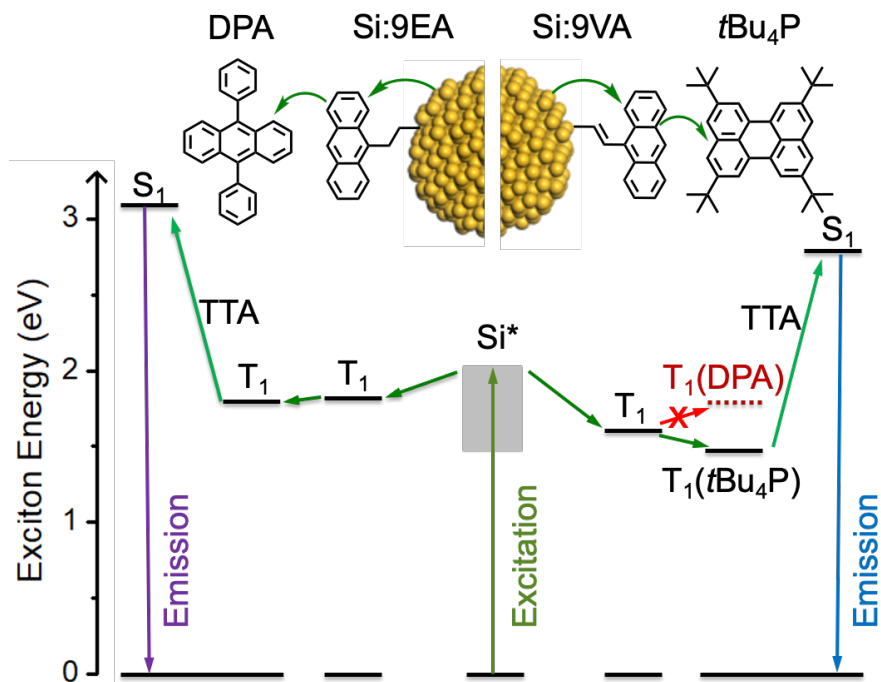
Authors:

Kefu Wang, R. Peyton Cline, Joel D. Eaves, Ming Lee Tang

Institution:

The University of Colorado, Boulder; The University of Utah.

Abstract:



We demonstrate in this work that triplet energy transfer in a silicon quantum dot-molecular hybrid system can be enhanced with a conjugated linker that promotes electronic coupling. New is a hybrid excitonic state delocalized over the organic and inorganic semiconductor components that is distinct from the individual constituents. Here, we compare two identical systems comprising of a Si QD donor and anthracene acceptor that differ only by an ethyl or ethene bridge, i.e. **Si:9EA** and **Si:9VA** respectively. Photon upconversion measurements, a proxy for triplet energy transfer, show that **Si:9VA** enables an efficient upconversion of 532nm green light into 480nm blue light with the efficiency as high as 17.21% and the corresponding threshold intensity as low as 500 mW/cm². Using transient absorption spectra, we find that a strong electronic coupling indeed exists between Si QD and bound **9VA** molecules. This coupling becomes more pronounced as more **9VA** molecules are attached to Si QD surface, while negligible coupling was found in **Si:9EA** system. Analysis of triplet kinetics shows that the triplet transfer time constant from Si QD to surface bound anthracene decreases from 15 ns to 3 ns comparing **Si:9EA** with **Si:9VA**, revealing that the *sp*² bridge can increase the triplet transfer rate. This explains the high upconversion efficiency for **Si:9VA** system and the low excitation threshold compared to **Si:9EA**. The strongly coupled spin-active state experimentally shown here offers an avenue to control electronic and spin states degrees of freedom important for quantum information systems. It provides a new strategy for controlling energy or charge transfer at nanoscale interfaces.

Project Abstract

“Artificial Atoms, Molecules, and Solids: Multiple Functions and Emergent Properties”

Program Officer: Dr. Michael R. Berman, AFSOR/RTB2

PI: Colin Nuckolls

Co-PIs: Milan Delor, Xavier Roy, Xiaoyang Zhu, and Michael Steigerwald,
Department of Chemistry, Columbia University, New York, NY, 10027, USA

This presentation will describe our research in creating electronic materials from molecular and superatomic building blocks. We are designing crystalline and self-assembled systems from these building blocks. Our recent efforts have been using superatoms as the building blocks for two-dimensional materials. We are now able to create 2D superatom sheets that span from insulators, to semiconductors, to metals and to superconductors. The power of this approach is in being able to tune the coupling between the building blocks. In addition to controlling the coupling between the superatoms, we have also been able to write information into the superatom core that imbues the material with a desired property.

Within this context we have had a big breakthrough in being able to synthesize *a new allotrope of carbon*. It is single crystalline, pristine, and can be exfoliated down to a single layer. It is intellectual fusion of the most exotic carbon allotrope, fullerene, with the 2D allotrope of carbon, graphene. We have named this material graphullerene. We are currently testing this new carbon allotrope at the ultimate, 2D limit in devices.

Graphullerene highlights one of the important aspects of these superatomic materials: their electronic coupling often exists in the intermediate regime between molecules and delocalized two-dimensional materials. This allows unusual physics to result. One such material is the extended two-dimensional material $\text{Re}_6\text{Se}_8\text{Cl}_2$. Through a series of key experiments, we have developed a method for site-selective surface functionalization of $\text{Re}_6\text{Se}_8\text{Cl}_2$ monolayers. We demonstrated this by creating four previously unknown surface-functionalized 2D superatomic materials: $\text{Re}_6\text{Se}_8\text{I}_2$, $\text{Re}_6\text{Se}_8(\text{SPh})_2$, $\text{Re}_6\text{Se}_8(\text{SPhNH}_2)_2$, and $\text{Re}_6\text{Se}_8(\text{SC}_{16}\text{H}_{33})_2$. We made an important discovery that, for the first time, allows coherent (directional, scatter-free) transport of excitons in 2D semiconductors at room temperature. In all previously known semiconductors, the transport of energy and information is limited by rapid scattering between energy carriers and lattice phonons, leading to non-directional, lossy transport that curtails the efficiency and functional diversity of all semiconductor technologies.

The Electric Field from a Single Ion and Ionic Layers Measured by Vibrational Spectroscopy

Jahan Dawlaty, University of Southern California

Influencing reactions with directed electric field is a continuing challenge in chemistry. The topic of electric fields appears at least in two contexts – first interfacial electric field at electrode-electrolyte junction, and second local fields in enzymes or near organometallic catalysts. To gain a unifying view of the influence of electric field in such diverse environments, it is necessary to measure them with similar techniques. Towards that goal, we will present results on using vibrational Stark shift spectroscopy to estimate the electric field emanating from a single cation captured in crown ethers, and from layers of surfactants near an electrode. Our crown ethers bear a vibrational Stark probe and can capture a variety of +1, +2 and +3 metal cations. We find that the ions induce a blue shift on the Stark probes as expected. This shift, in general, increases for ions with larger charge. However, the magnitude of this shift has some variation even for cations of the same charge. We propose that such variations arise from the geometry of the coordination of the ion in the crown. Similarly, we show that layers of quaternary ammonium surfactants can exert an electric field at metal-water junctions, where the metal is decorated with our Stark probes. To correlate this effect with a potential that is directly applied on the metal, we compare these results to the observed frequency shift of the Stark probe in response to potential. The results imply that a few tens of mM of surfactants can generate the same magnitude of interfacial fields produced by potentials as large as -0.5 V. This work will help guide molecular designs for engineering tailored electric fields at the microscopic scales.

How do bacteria respond to environmental challenges?

Perspectives from membrane transport studied by nonlinear light scattering

Hai-Lung Dai

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Abstract

Bacteria are known to survive, or even proliferate, in environments hostile to living organisms. These environments may subject bacteria to extreme temperatures, high acidity, or toxic molecules. How do bacteria respond to these challenges? In particular, how do these environmental conditions affect the bacteria membranes which regulate bacterial interactions with the environment.

In this study, we examine specifically molecular transport through the bacterial membranes in response to the presence of hostile molecules or undesirable temperatures. Transport through the ion channels of the outer membrane and diffusive transport through the inner membrane were individually examined using Second Harmonic Light Scattering. We will discuss 1) how the messenger molecule indole, always present in a flora of bacteria, influence the bacterial resistance toward antimicrobials; 2) how E-Flux pumps regulate molecular transport for bacteria in environments saturated with hydrocarbons; and 3) how does temperature induced phase-transitions in a bacterial membrane affect diffusive molecular transport through the bacterial cell.

MURI-ice: From Understanding Molecular Interactions to Controlling Ice Formation

Francesco Paesani

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

The overarching goal of our MURI is to elucidate the molecular mechanisms of ice nucleation, antifreeze, anti-icing, and de-icing, and then use this information to characterize, design and discover molecules, molecular assemblies, and materials that can control ice formation and adhesion. I will provide an update on our current efforts that revolve around four main interconnected thrusts focusing on: 1) characterizing the structure and dynamics of hydration water at the surface of ice binding molecules, 2) developing a multiscale approach that allows for modeling the reaction network responsible for antifreeze and ice recrystallization inhibition activities, 3) elucidating how biological and organic molecules and crystals nucleate ice, and 4) developing new experimental and simulation techniques to probe buried ice interfaces. Particular focus will be on our progress in describing the properties of supercooled water, identifying ice-binding surfaces, and characterizing the thermodynamics and kinetics of ice-binding processes.