

A banner image featuring a blue and black background with glowing molecular models. The text is overlaid in white.

**2025 Molecular Dynamics and Theoretical
Chemistry Program Review**

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

Poster Presentation Abstracts

Developing and Validating Sub-Nano Catalysts for Endothermic Cooling:

Experiments and DFT. AFOSR grant FA9550-22-1-0381

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Abstract

A combination of ultra-high vacuum surface science and high pressure microreactor techniques, along with detailed density functional theory (DFT) is being used to study reactions relevant to endothermic cooling by alkane fuels. This poster will focus on use of germanium addition to small Pt clusters supported on alumina to enhance reactivity and selectivity, and reduce deactivation for alkane dehydrogenation to alkenes. The model catalysts are prepared by depositing Pt clusters of controlled size on planar alumina thin film supports. Ge can be added selectively by exposure to GeCl₄ followed by H₂ exposure and heating.

In the UHV experiments, we have examined reactions of n-butane, iso-butane, 2-butene, isobutene, and ethylene on Pt_n and Pt_nGe_m (n = 4, 7, 11, m = 1, 2, 4). It is found that for n-butane on pure Pt_n clusters, carbon deposition (coking) occurs initially, but the partially coked clusters become resistant to further coking yet retain high activity for the desired butane-to-butene reaction. In contrast, iso-butane results in continuous coking, rapidly deactivating the catalysts. Exposure to n- and iso-butenes (without H₂) also results in rapid coking and deactivation. Thus, carbon addition to Pt_n changes the cluster reactivity to suppress coking without suppressing the desired linear alkane-to-alkene reaction, but does not suppress coking for the branched alkane. In contrast, Ge addition to the Pt_n almost completely suppresses coking for both the linear and branched butane, and for the butenes as well. DFT analysis of Pt_nGe_m, Pt_nC_x, and Pt_nGe_mC_x clusters deposited on alumina reveals the cluster structures and the effects of both carbon and Ge addition on the cluster electronic properties, as well as the binding affinities for the C₂ and C₄ alkanes and alkenes.

To complement the UHV studies we constructed a microreactor setup that allows study of these reactions over a wide temperature range, at pressures up to 1 atm. Results will be presented for both alkane dehydrogenation and alkene hydrogenation (the reverse reaction) over Pt/alumina and Ge-treated Pt/alumina catalysts.

Periodic Trends in Kinetic Energy Dependence, Reaction Efficiency, and Potential Energy Surface for Lanthanide Cation Oxidation in the Gas Phase by O₂

David H. Loertscher, Elijah A. Bliss, Talley A. Fenn, Sara Rockow, Brandon C. Stevenson, and P. B. Armentrout

Recently, Ard et al. (“Across Size Regimes: Kinetics of Atomic Lanthanide Cations (La⁺–Lu⁺) with O₂” S. G. Ard, B. C. Sweeny, T. W. R. Lewis, B. A. Long, A. A. Viggiano, and N. S. Shuman, *J. Phys. Chem. A* **2024**, *128*, 5668–5675) reported rate constants for the title reactions forming LnO⁺ + O in a selected-ion flow tube (SIFT) apparatus from 300 to 600 K. When exothermic, the reactions occur efficiently but display positive temperature dependences consistent with small activation energies of 0 – 2 kJ/mol. We have examined these same reactions for Ce⁺, Pr⁺, Nd⁺, Sm⁺, Gd⁺, Tb⁺, Dy⁺, and Ho⁺ as a function of the ion kinetic energy using a guided ion beam tandem mass spectrometer (GIBMS). Rate constants measured at 300 K are in good agreement with the SIFT results with a mean absolute deviation of 5 ± 6%, well within the absolute uncertainties of either method, 20% GIBMS and 25% SIFT. Nevertheless, except for the case of Ce⁺, the GIBMS results do not exhibit an increase in the rate constant with increasing ion energy, belying the presence of an activation barrier to these reactions. Further, we find that the efficiencies of the reactions do not correlate with the activation energy, which might have been expected. Notably, the GIBMS results are always obtained with O₂ at room temperature, in contrast to the higher temperature SIFT results. We are presently exploring why these results are disparate and believe that the insertion barrier needed to form a OLnO⁺ intermediate leading to products may be a key component of the behavior observed.

Photocurrent detection of polariton and exciton transfer: Uncovering energy and charge transport pathways and dynamics in photovoltaic materials

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This poster will present on our work on using photocurrent as a novel means for studying polariton and exciton energy pathways and dynamics in photovoltaic materials comprised of semiconducting carbon nanotubes. The poster will specifically present on three areas: (1) ultrafast 2D spectroscopy detected with photocurrent, (2) photocurrent readout spectroscopy for quantifying long-range energy transfer in polariton microcavities, and (3) the behaviors of charged excitons (called trions).

In (1), we have developed a method for eliminating incoherent background signals in ultrafast 2D spectroscopy detected with photocurrent. Photocurrent detection has been utilized for a decade by the 2D community, but it turns out that most of the spectra reported in those publications are swamped by an artifact. This artifact, which is now called “incoherent background”, was only realized to exist a few years ago and it can be 100-times the signal strength of the coherent signals. Upon learning its existence, we devised a new pulse polarization that eliminates it in samples that have isotropic symmetry, meaning that they are randomly oriented. We present on the use of this polarization technique to generate artifact-free spectra that characterize exciton energy flow and charge generation in thin films and devices made of several different chiralities of carbon nanotubes. In these measurements, we simultaneously acquire 2D white light absorption and photocurrent spectra to differentiate exciton populations that generate current from those that do not. Our measurements have surprisingly revealed that exciton hopping – long assumed to be a key harvesting mechanism – is less impactful than ultrafast charge transfer processes, prompting a reevaluation of standard design paradigms.

In (2), we report on the use of photocurrent readout spectroscopy to study long-range energy transfer in polariton microcavities. Exciton polaritons are thought to be spatially delocalized across the molecules that are coupled by the light field of the microcavity. If this is true, then it should be possible to collapse the wavefunction into desirable locations, such as the interface responsible for dissociating excitons into charges in photovoltaic devices. To test this idea, we have built a photovoltaic device into a microcavity, using the microcavity mirrors as the electrodes. Carbon nanotubes are the light absorbing materials and C_{60} is the electron acceptor that dissociates the excitons into charges that are collected and externally measured as photocurrent. When these microcavities are illuminated with monochromatic light to create polaritons, photocurrent is generated even without an applied voltage – indicating that polariton-to-photocurrent conversion occurs spontaneously. We are using these devices to quantify the efficiency of long-range energy transfer between distant nanotube sites and nanotubes at the charge-generating interfaces, mediated by polaritonic light-matter coupling.

In (3), we reveal how doping levels (exciton-hole trions) control electron transfer rates and affect optimal pathways for photocurrent generation in nanotube thin films.

Together, these studies combine cutting-edge measurement techniques with novel device architectures to assess the plausibility of harnessing new polariton, exciton, and energy transfer physics for more efficiently leveraging excitonic semiconductors as the light harvesting components of photodetectors and possibly solar cells.

Effect of Surface Electron Trapping and Small Polaron Formation on the Photocatalytic Efficiency of Copper(I) and Copper(II) Oxides

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Cu₂O, CuO, and mixed phase Cu₂O/CuO represent promising candidates for photoelectrochemical catalysis due to their strong visible light absorption, earth-abundance, and chemical stability. Unfortunately, the photoelectrochemical efficiency in these materials remains far below the theoretical limit, largely due to poorly understood surface electron dynamics. These dynamics depend on defect states, such as Cu atom vacancies and phase boundaries, which control electron trapping, charge carrier separation, and recombination.

These limitations can be partly mitigated by employing chiral CuO, which has been shown to serve as a spin selective catalyst for the water splitting reaction via the chiral induced spin selectivity (CISS) effect.¹ Despite numerous studies of chiral CuO, the mechanism of spin selectivity in this and related chiral semiconductors remains an open question. To address this question requires first understanding the ultrafast electron dynamics in CuO and its related oxides, which are particularly sensitive to defect chemistry, and second understanding how these dynamics depend on electron spin in chiral structures. Both goals benefit from the ability to directly observe the ultrafast surface electron dynamics with chemical state resolution using extreme ultraviolet reflection–absorption (XUV-RA) spectroscopy.

Employing this tool, we have studied the photoinduced electron and hole dynamics at the surface of various Cu oxides.^{2,3} In Cu₂O we find that photoexcitation occurs as electron promotion from primarily Cu 3d valence band to Cu 4s conduction band states compared to O 2p valence band to Cu 4s conduction band states in CuO. In catalysts with a significant concentration of Cu vacancies, we observe fast electron trapping to the Cu 3d defect band occurring in less than 100 fs. In contrast, photoexcited electrons in phase pure CuO do not trap to midgap states; rather these electrons form small polarons via electron-phonon coupling within approximately 500 fs. Photoelectrochemical measurements of these catalysts show that Cu vacancy-mediated electron trapping correlates with a significant loss of photocurrent. Together, these results provide a detailed picture of the defect states and associated ultrafast carrier dynamics that govern the photocatalytic efficiency in widely studied Cu₂O and CuO photocatalysts. These results also lay the groundwork for ongoing studies of spin selective electron dynamics in chiral Cu oxides using recently developed XUV circular dichroism spectroscopy.⁴

References

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Connected-Triple Electronic Excitations in Quantum-Electrodynamics Coupled-Cluster Theory

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Polaritons are hybrid light-matter states that potentially offer a new way to control chemical reactivity of molecular systems. Recently, there has been a burst of activity in developing *ab initio* quantum-electrodynamics (QED) methods by generalizing the familiar methods of *ab initio* quantum chemistry to describe light, electrons, and their interactions on equal footing. We have recently implemented a variant of QED coupled-cluster (CC) theory that includes the full triples contribution for the electrons (QED-CCSDT). It is well known in standard CC theory that inclusion of some form of the connected-triples contribution for the electrons is essential for quantitative agreement with experiment and, to our knowledge, the QED-CCSDT method is the first to do so for QED-CC. We benchmark the QED-CCSDT method on the H₂ dimer and LiH systems. We also discuss how the derivation of the full triples contribution will enable us to introduce simpler and computationally cheaper approximations to the QED-CCSDT method that still include contributions from connected-triple electronic excitations.

Efficient hot carrier generation and transfer in low carrier concentration plasmonic nanomaterials

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Degenerately doped semiconductor nanocrystals exhibit tunable localized surface plasmon resonances with strong optical absorption cross sections and band gaps. Upon excitation, these materials produce non-equilibrium carrier distributions that rapidly relax, presenting a brief window for utilization. These features mark plasmonic nanocrystals as promising candidates for new applications that require efficient light absorption and highly directed energy and carrier utilization, such as photodetectors, photovoltaics, and photocatalysts, if we can understand and engineer efficient transport mechanisms. To date, studies on hot carrier technologies have focused on coinage metals which have orders of magnitude higher carrier concentrations than semiconductor plasmonic nanomaterials. It's unclear how lower carrier concentrations influence hot carrier generation or transfer in these systems.

Here, we investigate hot carrier and heat transfer from prototypical tin-doped indium oxide (ITO) nanocrystals to adsorbates as a model system for harvesting and utilizing light in plasmonic semiconductor nanocrystals. Using transient absorption spectroscopy, we track carrier and energy transfer from ITO nanocrystals to adsorbates and evaluate the impact of aliovalent dopant concentration, wavelength, and energy level alignment. We find hot thermal carriers, rather than athermal carriers, transfer to adsorbates with external quantum efficiencies $\sim 1\%$. Two-temperature and Marcus Theory modeling show that this is due to the low carrier concentration of ITO. Utilizing local temperature reporters, we simultaneously quantify heat transfer from ITO nanocrystals into their environment. Combining these results, we suggest general design rules to optimize carrier energy transfer from plasmonic semiconductors including scenarios where hot thermal carriers may transfer more efficiently than athermal carriers.

The First Quantitative Measurement of Efflux Rates from Individual Compartments in Living Bacteria Cells – A study by Second Harmonic Light Scattering

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Abstract

Molecular efflux is a mechanism through which bacteria actively expel undesirable substances. This is a crucial line of defense for bacteria against toxic chemicals in harsh environments. Understanding how efflux works is critical for designing antimicrobial strategies. Though much is already known about efflux proteins, important details about the mechanisms of efflux (e.g., importance of specific sub-cellular domains, ejection rates) have yet to be experimentally quantified.

We use the nonlinear optical technique second harmonic light scattering to simultaneously measure efflux rates from the periplasm and cytosol of a Gram-negative bacterium. The influence of efflux on the uptake kinetics of a mild antimicrobial, malachite green (MG), by *P. aeruginosa* was quantified. It is observed that efflux primarily occurs from the periplasm and is two orders of magnitude faster than from the cytosol. Efflux pumps activate to maintain MG concentrations in the periplasm below 1 μM , while efflux from the cytosol maintains MG concentration below 0.1 μM . Efflux pumps are shown to saturate when exogenous MG concentrations are greater than 25 μM , while the cytosol efflux function saturates at >15 μM . Finally, efflux pumps can simultaneously efflux different compounds, as proven by experiments with both MG and hexane, a known effluxable compound.

Revealing the Phonon Bottleneck Limit in Negatively Charged CdS Quantum Dots

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The capture of photoexcited hot electrons in semiconductors before they lose their excess energy to cooling is a long-standing goal in photon energy conversion. Semiconductor nanocrystals have large electron energy spacings that are expected to slow down electron relaxation by phonon emission, but hot electrons in photoexcited nanocrystals nevertheless cool rapidly by energy transfer to holes. This makes the intrinsic phonon-bottleneck limited electron lifetime in nanocrystals elusive. This presentation will focus on our recent determination of this bottleneck-limited lifetime. We used a combination of theory and experiments to probe the hot electron dynamics of negatively charged Cadmium Sulfide (CdS) colloidal quantum dots (QDs) in the absence of holes. Experiments found that these hot electrons cooled on a 100 ps timescale. Theoretical simulations predicted that pure phonon-bottleneck limited electron cooling occurs on a similar timescale. This similarity suggests that the experimental measurements reflect the upper limit on hot electron lifetimes in these CdS QDs and the lower limit on the rates of processes that can harvest those hot electrons. The presentation will also discuss the predicted hot electron lifetimes in CdS and CdSe QDs as a function of QD diameter.

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S. J. Sherman, B. Hou, M. J. Coley-O'Rourke, K. E. Shulenberger, L. M. Pellows, E. Rabani, G. Dukovic. "[Revealing the Phonon Bottleneck Limit in Negatively Charged CdS Quantum Dots](#)." *ACS Nano*, **2025**, *19*, 7055–7063.

M. J. Coley-O'Rourke, B. Hou, S. J. Sherman, G. Dukovic, E. Rabani. "[Intrinsically Slow Cooling of Hot Electrons in CdSe Nanocrystals Compared to CdS](#)." *Nano Letters*, **2025**, *25* (1), 244–250.

K. E. Shulenberger, H. R. Keller, L. M. Pellows, N. L. Brown, G. Dukovic. "[Photocharging of Colloidal CdS Nanocrystals](#)." *Journal of Physical Chemistry C*, **2021**, *125* (41), 22650–22659.

Poster Abstract

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Classical molecular dynamics (MD) simulations rely on force fields (FFs) to efficiently compute the atomic forces and energies. These FFs are often parametrized to reproduce quantum mechanical (QM) calculations or experimental results, offering a computationally efficient framework for modeling large-scale systems. However, classical FFs have intrinsic limitations: they generally neglect critical electronic effects such as polarization, charge transfer, and many-body interactions. This can result in significant inaccuracies when simulating complex systems like bulk liquids or electrolyte systems, ultimately limiting the predictive power of classical simulations for industrial or materials design applications. *Ab-initio* molecular dynamics (AIMD) simulations provide a more accurate, quantum-level description of molecular interactions, but their high computational cost restricts their applicability to small systems and short time scales.

To overcome these limitations, machine learning force fields (MLFFs), particularly neural network force fields (NNFFs), have emerged as a powerful alternative. Trained on energies and forces obtained from AIMD simulations, NNFFs can reproduce quantum mechanical potential energy surfaces with high accuracy while maintaining the computational efficiency needed for large-scale simulations. This enables the simulation of bulk liquids with quantum accuracy over the time and length scales needed to compute thermophysical properties. In this context, the effective fragment molecular orbital (EFMO) method presents a promising strategy for generating accurate training data for NNFFs. This work investigates the potential of using EFMO calculations to train NNFFs through a case study on a water droplet, showcasing its promise as a scalable path forward in force field development.

Theory and Quantum Dynamics of Exciton Polariton transport

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Cavity exciton-polaritons exhibit ballistic transport and can achieve a distance of 100 μm in one picosecond. This ballistic transport significantly enhances mobility compared to that of bare excitons, which often move diffusively and become the bottleneck for energy conversion and transfer devices. Despite being robustly reproduced in experiments and simulations, there is no comprehensive microscopic theory addressing the group velocity of polariton transport and its renormalization due to phonon scattering while still preserving this ballistic behavior. In this work [1,2], we develop a microscopic theory to describe the group velocity renormalization using a finite-temperature Green's function approach. Utilizing the generalized Holstein-Tavis-Cummings Hamiltonian, we analytically derive an expression for the group velocity renormalization and find that it is caused by phonon-mediated transitions from the lower polariton (LP) states to the dark states, then scattering from dark states back to LP. As such, the dark states do not have to be populated and serve as the virtual state for super-exchange (especially true for a large light-matter detuning). The theory predicts that the magnitude of group velocity renormalization scales linearly with the phonon bath reorganization energy under weak coupling conditions and also linearly depends on the temperature in the high-temperature regime. These predictions are numerically verified using quantum dynamics simulations, demonstrating quantitative agreement. Our findings provide theoretical insights and a predictive analytical framework that advance the understanding and design of cavity-modified semiconductors and molecular ensembles, opening new avenues for engineered polaritonic devices.

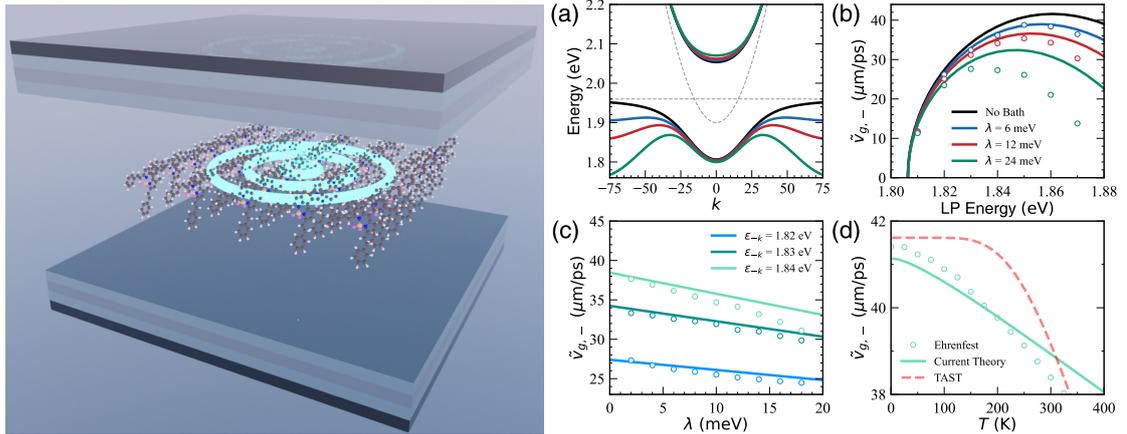


FIG. 1. Polariton band structure modification and group velocity renormalization due to polariton-phonon interaction. (a) Modified polariton band structure under different λ . (b) Group velocity of the LP branch under different λ . (c) Scaling relation of the magnitude of LP group velocity change with λ . (d) Temperature-dependence of the LP group velocity. Theoretical results (solid lines) are compared to quantum dynamics simulations (open circles).

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Measuring electric fields at gas–liquid interfaces

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Electric fields govern chemical reactions in a wide range of contexts, including electrochemistry, biology, and heterogeneous catalysis. Recently, it has been suggested that electric fields at gas–liquid interfaces play a key role in accelerating organic reactions in microdroplets; however, most studies on this topic are computational or focus primarily on the outer-most layer of water molecules. In this study, we use confocal fluorescence microscopy and voltage-sensitive organic dyes to visualize and measure electric fields at gas–liquid interfaces. We use solvatochromic experiments and density functional theory calculations to estimate the strength of the electric field. We then investigate the effects of solvent identity and of the molecular properties of the dye on the strength of the electric field. Our results indicate that the measured electric fields are due to molecular ordering at the air–water interface and that water plays an essential role in enabling the observation of an electric field at gas–liquid interfaces. Finally, we find that these electric fields can be tuned with chemical additives. These results provide direct experimental evidence of local electric fields at gas–liquid interfaces, highlighting their potential role in governing organic reactivity in microdroplets.

Imaging of Surface Plasmon Polaritons in 2D Materials: From MXenes to Hyperbolic Materials

Prof. Sarah King
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Our research bridges molecular chemistry with optical metrology through direct visualization of surface plasmon polaritons (SPPs) in 2D materials. Employing multiphoton photoemission electron microscopy (nP-PEEM), we have documented SPPs in $\text{Ti}_3\text{C}_2\text{T}_x$ MXene flakes with thicknesses exceeding 30 nm at energies up to 1.9 eV, extending plasmonic behaviors into the visible spectrum.^{1,2} Finite-difference time-domain simulations confirm the significance of flake thickness, demonstrating that thinner flakes on silicon substrates cannot support the symmetric SPP mode essential for plasmon propagation because of the influences of asymmetric cladding. Advancing this research to new anisotropic and layered materials, we have now achieved the first direct time-resolved imaging of nanoscale propagation of natural hyperbolic surface plasmon polaritons (HbSPPs) in MoOCl_2 . Our observations reveal distinct in-plane hyperbolicity characterized by hyperbolic lensing and extended propagation lengths. These findings establish a foundation for precise manipulation of electromagnetic phenomena through chemical functionalization and interfacial engineering, potentially enabling enhanced optical metrology with improved sensitivity and spatial resolution in the visible and near-IR spectral regions.

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Superatom magnetism and spin properties of colloidal metal clusters

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Many chemistry applications depend on electronic spin. In spin transport, spin is transferred through a chiral medium with a geometric handedness matching that of the facilitating electronic spin. Molecular switches undergo conformational changes in which the geometric structure is determined by a metal center's spin state. Spin is also a foundational component of in quantum information science (QIS) functions such as quantum computation and quantum sensing. For QIS applications, trapped atomic ions represent the current state-of-the-art for accuracy and error. Unfortunately, these systems are not easily scalable. Colloidal superatomic clusters bridge the desirable electronic properties of gas-phase ions with condensed-phase scalability.

$\text{Au}_{144}(\text{SC}_8\text{H}_9)_{60}$, a colloidal cluster with a 1.7-nm inorganic diameter, exhibits both metallic and molecular-like behavior, along with a distribution of unfilled superatom states. Its 1.7-2.5 eV electronic transitions were probed with variable-temperature, variable-field magnetic circular dichroism (VTV \vec{H} -MCD), revealing two energy regions with distinct responses. Below 2.0 eV, MCD transitions exhibited diverse VTV \vec{H} responses, including both paramagnetic and diamagnetic behavior, implicating multiple non-degenerate initial states originating within the open-shell superatom S, D, and H HOMO manifold. Above 2.0 eV, uniform field-dependent responses suggested spin-vibronic coupling due to metal-ligand mixing. The $\text{Au}_{144}(\text{SC}_8\text{H}_9)_{60}$ magneto-optical response is surprisingly complex given the system's high electronic-state density; discrete cluster structural domains, including the superatomic metal core, likely contribute to this diversity. These results show the potential to investigate and tailor the magneto-optical and spin properties of these clusters through structurally precise synthesis and identify superatomic colloids as candidates for advancing spin-based technologies.

The superatom concept was extended to achieve spin-polarized emission from colloidal metal clusters. Magnetic circular photoluminescence (MCPL) spectra were collected following 3.1 eV excitation of aromatic- and aliphatic-ligand-passivated $\text{Au}_{25}(\text{SR})_{18}$ monolayer-protected clusters (MPCs). Both clusters generated spin-polarized emission; however, the degree of circular polarization noted for the aromatic-ligand-passivated cluster, $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$, was 5x that obtained for the aliphatic-ligand-passivated cluster, $\text{Au}_{25}(\text{SC}_3)_{18}$. Variable-magnetic field data were analyzed to determine Landé g-factors and spectroscopic term symbols for observable transitions contributing to the clusters' MCPL spectra. For $\text{Au}_{25}(\text{SC}_8\text{H}_9)_{18}$, transitions originated from one doublet and two quartet fine-structure superatomic electronic states; by comparison, the $\text{Au}_{25}(\text{SC}_3)_{18}$ spectrum contained only two components, both of which arose from doublet superatomic electronic states. Additionally, greater Faraday B-term contributions, which report on field-induced mixing, were noted for $\text{Au}_{25}(\text{SC}_3)_{18}$ spectral components. Therefore, the decreased spin-polarized emission by $\text{Au}_{25}(\text{SC}_3)_{18}$ was attributed to stronger coupling to nonradiative decay channels. These results suggest the hydrocarbon structure of the $\text{Au}_{25}(\text{SR})_{18}$ cluster's passivating ligand can be used to tune the relative populations of emissive fine-structure states, the extent of mixing between radiative and non-radiative states, and the amplitude of spin-polarized emission in MPCs.

Acknowledgements. This work was supported by a grant from the Air Force Office of Scientific Research (FA9550-22-1-0402).

Understanding and controlling chemistry at interfaces using ion soft landing

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Controlling ion reactivity at interfaces is essential for advancing technologies in electrochemistry, materials synthesis, quantum computing and sensing, spintronics, and molecular electronics. Our research employs ion soft landing to gain fundamental insights into ion–surface interactions that directly affect the performance and stability of materials and devices critical to U.S. Air Force and Space Force missions. Current efforts in our laboratory focus on three main areas. First, we investigate the surface interactions of model photosensitizers to inform the rational design of light-harvesting and photoredox systems. Second, we explore atomically precise nanoclusters as nanoscale building blocks for the development of cluster-based materials and engineered interfaces. Third, we utilize mass-selected ions as precision dopants to enhance the chemical stability and energy storage capacity of technologically important electrode materials. In this presentation, we will discuss how ion–surface interactions influence the structure and reactivity of photosensitizers at interfaces and highlight the use of ion mobility–mass spectrometry (IM-MS) for the structural characterization of heterometallic nanoclusters with mixed ligand shells. These studies provide important insights into the design and optimization of functional surfaces for next-generation technologies.

Structure and Dynamics of Charge Carriers Coupled to Lattice Vibrations

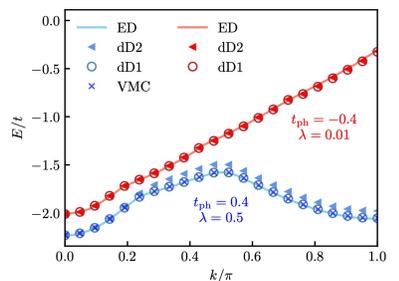
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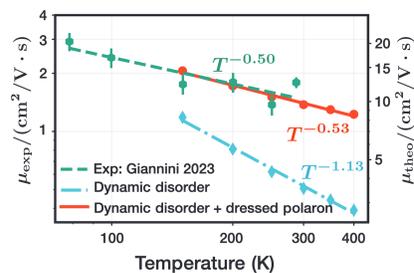
Understanding the structure and dynamics of charge carriers has far-reaching implications for new technology, such as efficient photovoltaics and optoelectronic devices. Computational models have the potential to elucidate the microscopic origin of the structure and dynamics of charge carriers beyond currently available spectroscopic tools. Computational techniques face challenges due to lattice vibrations significantly influencing charge carriers by forming new quasiparticles called polarons. Here, I will present our efforts in developing computationally efficient methods for simulating polarons where carrier and phonon degrees of freedom are treated equally.

I will first demonstrate the power of simple variational ansatz, or Davydov's ansatz, over various simple lattice models. The Davydov wavefunctions are primarily tested on the Holstein model (only on-site carrier-phonon coupling), and their power for more general carrier-phonon models is not fully characterized. We have implemented the most general Davydov wavefunction, dD1, with an optimizer based on an approximate Newton method. Our implementation is efficient and numerically robust, enabling the study of dD1 in challenging regimes that were not studied by the Davydov ansatz in the past. With this method, we have been investigating polaron structure at zero temperature (see figure below).

I will also present our recent results on temperature-dependent mobility and optical conductivity calculations for 2D organic photovoltaics using the lattice models parametrized by ab initio calculations. Remarkably, after careful benchmarks against tensor network and quantum Monte Carlo methods, we found that classical path approximation combined with polaron transformation is exceptionally accurate for simulating the polaron dynamics near room temperature. I will showcase several microscopic insights we gained from this method, including the role of intramolecular phonons (see figure below) and the effect of long-range carrier-phonon coupling.



1D Dispersive Holstein Polaron Band Structure



Temperature-dependent mobility of DNTT

Linear and Circular Dichroism of Core Excitons in LiF

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Core excitons (bound electron-core hole pairs) in ionic insulators provide a unique opportunity to study conditions in the condensed phase that are often typically only observed in atomic systems. A core exciton can form, for example, on a cation, which necessarily has a reduced number of electrons available to screen the core hole, leading to a strong Coulombic attraction between the core hole and the electron and a high degree of localization compared to valence excitons. This is especially true in LiF, in which the 1s2p core exciton is bound by up to 2 eV, compared to the typical tens of meV binding energy of valence excitons. The prospect of leveraging atomic-like selection rules to determine the alignment and orientation of excited states in solid-state materials is particularly important in this ongoing attosecond transient absorption spin dynamics program, given the oftentimes complex density of states in these systems. Here, we investigate the use of linear and circular polarized extreme ultraviolet (XUV) attosecond pump and near-infrared (NIR) probe laser pulses to investigate the orbital composition of bright and dark core exciton states by means of their magnetic sublevels in polycrystalline LiF thin films at the Li K edge [1,2].

A linear (right-handed circular) XUV pump initially prepares an ensemble of Li 1s2p (p-like) core excitons in the $m = 0$ ($m = +1$) sublevel. The polarization of the NIR probe, arriving at variable delay times relative to the pump, is then selected to control the coupling of the prepared 1s2p excitons to resonant higher-lying s-like dark states: Parallel and left-handed circular NIR probe pulses both access absorption transitions into final states with $m = 0$ sublevels, allowed by atomic-like selection rules. Perpendicular (right-handed circular) NIR pulses would require m value of the final state be ± 1 ($+2$), which is not available for an s-like final exciton state. Transient features associated with the coupling between the 1s2p bright and 1s2s dark excitons that are observed when using parallel (counterrotating) pulse polarizations are suppressed by approximately 90% when using perpendicular (corotating) beams. Similar results have been reported using linearly polarized pulses in atomic He [3], in which the p-to-s type couplings observed using parallel pulses are eliminated when using perpendicular pump and probe polarizations. The interpretation of the nature of the s-like dark state in LiF is supported by simulation with a few-level model system, along with DFT calculations of the LiF band structure. In addition to validating rigorous alignment / orientation dynamics in solids by the XUV - NIR polarization investigations, the timing of the NIR pulse also allows the coherence decay of the exciton states to be obtained. The observed ultrashort 2.4 ± 0.4 fs coherence lifetime is attributed to a phonon-mediated dephasing mechanism [4], similar to conclusions in other time-resolved core exciton reports [5-7].

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

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Hydrocarbon pyrolysis chemistry at extreme pressures and temperatures is relevant to the thermal decomposition of aviation fuel, which is the primary thermal management fluid onboard aircraft. At such conditions, destructive coke deposits can form, which can foul system components (*e.g.*, injector nozzles). We have developed a novel experimental technique to characterize the reaction progress of a neat hydrocarbon fluid undergoing pyrolysis in a quartz tube reactor. Using optical absorption spectroscopy, we sensitively measure the onset and rate of amorphous carbon deposition. Simultaneously, we catalog the chemical speciation of the fluid by online quadrupole mass spectrometry (MS) with 15 eV ionization. For hydrocarbon fuel surrogates (*e.g.*, *n*-hexane and *n*-dodecane) we have observed three chemical regimes with increasing temperature: (1) cracking with little or no coking, (2) cracking with steady coke deposition, and (3) rapid and severe coking. In regime (1), lighter hydrocarbons (*e.g.*, ethane, ethylene, and methane) are observed with little-to-no aromatic compounds or optical absorption. In regime (2), there is also a steady increase in the optical absorbance at 405 nm. Finally, in regime (3) aromatics appear in the mass spectrum while the absorbance rapidly increases. Using this tool, we will develop empirical models to predict supercritical hydrocarbon chemistry and carbon deposition rates at pyrolysis conditions.

Electrical Double Layer Modulation of Cation Radical Reaction Kinetics

Prof. Jesse McDaniel, Georgia Tech

Harnessing electrochemistry via the development and optimization of electrochemical reaction mechanisms often involves key kinetic processes within the electrical double layer (EDL) formed at the working electrode/electrolyte interface. In many cases, altering the EDL environment by changes in solvent, electrolyte, and/or overpotential can substantially modulate kinetic rate constants which manifest in practically important changes in reaction yield/selectivity. Computational studies complement experimental characterization by providing an atomistic description of intermolecular interactions of reactive intermediates within the EDL environment, and prediction of rate constants for fast kinetic processes that are difficult to interrogate experimentally. We will present computational work highlighting examples of how the EDL environment can substantially modulate kinetic rate constants for nucleophilic coupling and deprotonation reactions of electrogenerated organic cation radical intermediates. We focus on organic cation radical intermediates formed by oxidation of olefin or aromatic functional groups generated via outer-sphere electron transfer at working electrodes held at moderate anodic potentials (e.g. 1.5 V vs Ag/AgCl). We illustrate several paradigms for how the EDL environment modulates reactivity of these intermediates, including 1) electrostatic catalysis, in which strong electric fields from the electrode and/or double layer ions substantially stabilize key intermediates; 2) deprotonation mechanisms, in which the EDL environment alters transition state character from a "homolytic" to "heterolytic" bond cleavage; 3) solvation effects, in which the unique solvation environment provides advantageous selectivity as compared with homogeneous reactions. Our computational studies rely heavily on DFT-QM/MM molecular dynamics, free energy simulations, and we will highlight method, algorithm, and software development work from our group that has made these studies possible.

Project Abstract

“Coherent Transport of Energy and Information in 2D Superatomic Crystals”

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

PI: Colin Nuckolls

Co-PIs: Milan Delor, Xavier Roy, and Xiaoyang Zhu

This poster will discuss our efforts to engineer quantum properties in two-dimensional (2D) superatomic materials, a new class of ultra-manipulable and hierarchical systems whose functional building blocks can be individually addressed to tune their properties. We investigate the unique properties of 2D superatomic materials and develop methods to tune their electronic structures, magnetic properties, and vibrational properties. We develop techniques to deterministically dope or functionalize the surfaces of 2D superatomic materials with high positional precision reaching atomic-level control. We control the dimensionality and strain in 2D superatomic materials to realize massive changes in their inter-superatom electronic, vibrational, and magnetic coupling. Furthermore, we functionalize the surface of 2D superatomic materials with molecules that will direct the assembly of new moiré lattices with predictable and uniform twist angles as a platform for studying chirality induced spin selection. We utilize designer 2D superatomic materials to achieve coherent and directional transport of electrons and excitons (electron-hole pairs) by making these electronic excitations ‘surf’ on optically-generated coherent phonons that propagate as waves. 2D superatomic materials support exceptionally strong coupling between phonons and electronic quasiparticles, far beyond traditional atomic semiconductors. This strong coupling will help sustain wavelike transport of electronic excitations over macroscopic distances. We develop superatom-based quantum materials for coherent magnons. We study the 2D C_{60} frameworks, which can be exfoliated down to the monolayer limit and stacked with 2D magnetic materials. We create and study 2D superatomic magnetic semiconductors with large magnetic moment on each superatom, tunable inter-superatom exchange coupling for magnetic order, and controlled electronic band formation from linking chemistry and symmetry. Using this approach, we tune the spin waves to be in resonance with those of interesting qubits for strong coupling and remote entanglement.

Evaluation of IP and EA of Transition Metal systems: A comparison of IP/EA-EOM/CCSD and DFT/QTP Functionals

Hyunsik Kim, Ajith Perera and Rodney J. Bartlett

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Accurate determination of the ionization potential (IP) and electron affinity (EA) is essential for understanding the electronic properties and reactivity of transition metal systems. In this study, we compare the performance of several advanced quantum mechanical methods, including Δ CCSD, IP/EA-EOM/CCSD, and DFT calculations using Quantum Theory Project (QTP) functionals (QTP00, QTP01, QTP02, LC-QTP) and other conventional functionals for predicting these key properties.

The IP/EA-EOM/CCSD method consistently provides the most accurate predictions. Among the QTP functionals, LC-QTP shows the best performance, closely matching experimental results whereas QTP00 consistently underperforms. A comparison of results from QTP functionals to other DFT results shows the enhanced accuracy in predicting IPs and EAs of QTP functionals than other conventional functionals.

The Δ CCSD method, which computes the difference between the coupled-cluster energies of the cation and neutral species, provides a direct measure of IP and EA and accounts for the orbital relaxation effect. This effect plays a significant role in accurate IP/EA predictions, particularly in transition metal systems where electronic correlations are more pronounced.

By benchmarking these methods against experimental data and other theoretical studies, this work emphasizes the superior predictive accuracy of IP/EA-EOM/CCSD and selected QTP functionals and the importance of incorporating orbital relaxation effects for transition metal systems.

Spin Relaxation and Chiral-optical properties of Solids from First-principles Density-Matrix Dynamics

Yuan Ping

University of Wisconsin-Madison

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

In this presentation we will introduce our recently developed real-time first-principles density-matrix dynamics (FPDMD) approach with electron-electron, electron-phonon, electron-impurity scatterings and self-consistent spin-orbit couplings[1-3]. The electron-electron interactions can be rigorously derived through nonequilibrium Green's function plus generalized Kadanoff-Baym ansatz [4]. We further extend this framework with Wigner functions for simulating spatial-temporal quantum dynamics and transport accounting for a range of quantum degrees of freedom (e.g., charge, spin, orbital, lattice).

We show our methods can accurately predict spin and carrier lifetime, spin diffusion length, and pump-probe Kerr-rotation signatures for disparate solids, with examples of Si, GaAs, 2D materials[5], and hybrid halide perovskites[6-7]. In particular, we show our recent study of how g factor fluctuations lead to spin dephasing in halide perovskites under external magnetic field, and the distinct electron-phonon contributions to spin and carrier relaxations and crucial dependence on crystal symmetry[7]. We next will introduce our recent progress of developing methodology for spin-optotronic signatures, such as circular dichroism [8,9] and circular photogalvanic effect [10] to chiral and broken-inversion-symmetry solids, and how they are correlated with continuous chirality measure for structural-property relations[10].

We then will show our recent progress on orbital relaxation and orbital transport in systems with and without inversion symmetry, which shows distinct mechanism from spin relaxation in semiconductors, which are critical for orbitronics applications. Finally, we will present recent work on first-principles prediction of spatial-temporal spin transport properties in graphene[11] and chiral materials, where we show spin generation and dephasing in both coherent and incoherent transport, and discuss the distinction between chirality induced spin selectivity and Edelstein effects. Our results provide important insights for spin-optotronic properties and spin and orbital transport in chiral and non-centrosymmetric systems.

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Engineering photosynthetic energy transfer using polariton light-matter interactions

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Coupling between light and matter in an optical cavity creates hybrid states known as polaritons. The light-matter coupling splits the molecular states into polariton states with new energy levels, thereby providing a new way to modulate the energy landscape and, in turn, the photophysical pathways of molecular and materials systems. We incorporate photosynthetic light-harvesting systems into a polariton microcavity as a tool to selectively and systematically tune their energy transfer dynamics. I will present broadband pump-probe spectra measured on a Fabry-Perot microcavity incorporating a thin film layer of chlorophyll, the primary light-harvesting pigments in photosynthesis. Comparison of the ultrafast photophysics of chlorophyll inside and outside the cavity reveals that the energy relaxation accelerates by several orders of magnitude in the presence of light-matter coupling, highlighting the active role of the cavity photon mode in determining the mechanisms of energy transfer in these systems.

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

FA9550-22-1-0445

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We will present an update on our studies relevant to plasma formation in hypersonic flows. These are pursued along two distinct directions: In the first, we have combined velocity map imaging with stimulated emission pumping to prepare NO in highly excited vibrational levels for collision with rare gases and molecular oxygen. This allows us to study state-to-state scattering dynamics from arbitrary initial states to selected final states. This approach is employed in a near-counterpropagating crossed-beam geometry that allows us to access collision energies up to 1.4 eV. We are currently applying this method in an effort to obtain differential cross sections for vibrationally inelastic scattering for the near-resonant process $\text{NO}(v = 12) + \text{O}_2(v = 0) \rightarrow \text{NO}(v = 11) + \text{O}_2(v = 1)$ which is 12 cm^{-1} endoergic. Progress in this effort will be presented along with results for rotationally inelastic but vibrationally elastic collisions in the same system.

The second project thrust involves development of a new instrument using electron-ion coincidence detection to reveal the electronic states of atoms involved in associative ionization. We are pursuing a new experimental approach that involves intrabeam scattering of fast (1-3 kV) atomic beams formed by charge transfer of atomic ions, one of which is formed in a slightly delayed second discharge in the same beam. In the N + O reaction, for example, we have demonstrated selective acceleration of the second O⁺ beam allowing for matching velocities of the neutral O and N beams in the interaction region to give controllable relative energies. A complete description of the instrument and the latest progress will be presented.

Chiroptical cavities for asymmetric synthesis with circularly polarized light

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Despite the advances in the pharmaceutical, agrochemical, beauty and flavoring industry, the *synthesis of chiral small molecule targets is resource- and energy- intensive and generates significant toxic waste*. This process requires expertise in the design of **asymmetric ligands** that physically create a structurally handed environment for enantioselective bond formation – a synthetic process that is non-trivial and generally not scalable across the vast array of structurally diverse target chiral molecules.

We present preliminary data on the photochromism of molecular photoswitches on optical metasurfaces, which bodes well for the use of photocatalysts derived from metal stereocenters for asymmetric synthesis. We focus on the diarylethenes, a class of compounds which have a pair of thermally stable isomers that interconvert in response to light. Our preliminary results suggest that the amplified optical chirality at the metasurface selectively enhances the absorption of circularly polarized light of one enantiomer compared to the other. Circular dichroism (CD) measurements show a big change from CD= +12 to -5 mdeg at 552 nm (**Figure 1a**), obtained from the CD spectrum in **Figure 1b**. This closed-ring isomer is then irradiated with right-handed CW green circularly polarized light (CPL), which selectively ring-opens one stereoisomer compared to the other, as reflected by the change in the CD spectra. Further experimental evidence supporting these assignments is the fact that equal and opposite CD spectra is obtained when left CW green CPL is used for the ring-opening reaction instead. In order to relate this CD spectra to photoisomerization and chemical changes, we will isolate both ring-closed DAE stereoisomers with chiral HPLC, to obtain the basis spectra of each enantiomer both in solution and also on the metasurface, so we can optically track any enantioselectivity in the photochromism induced by the metasurface

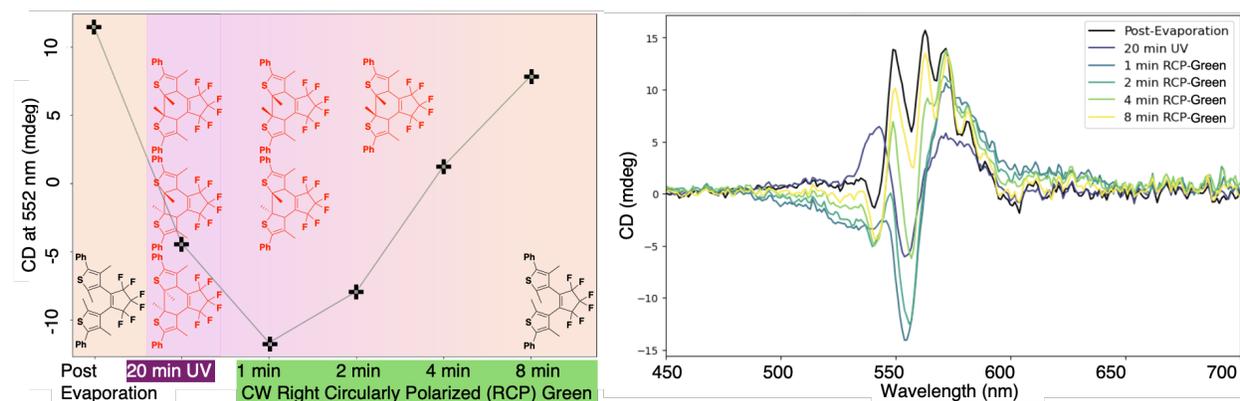


Figure 1. Circular dichroism (CD) of the DAE molecule evaporated on the metasurface shows that one enantiomer can be selectively ring-opened depending on the circular polarization of the green light impinging on the substrate. The experimental CD spectra is shown on the right, while the CD signal at 552 nm is isolated for clarity on the left.

Probing molecular mutual neutralization reactions of atmospheric importance using the ion storage facility DESIREE

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The evolution of plasma environments is defined and governed by intricate balances between ionizing processes, chemical rearrangements, and neutralisation reactions such as mutual neutralisation (MN) and dissociative recombination (DR). Measuring and explaining these processes in detail is fundamental to understanding and modelling non-local thermal equilibrium (non-LTE) environments, such as atmospheric plasmas.

Until recently, experimental studies of MN involving molecular ions in flow tubes and merged-beams experiments were limited to measurements of overall reactivities without detailed information of the mechanism or of the final states formed. The Double ElectroStatic Ion Ring ExpERiment (DESIREE) facility [1-5], with its combination of stored and merged ion beams and coincident imaging detection, has now made such studies possible [6-9]. With the cryogenic ion-beams storage ring DESIREE it is possible to control and manipulate the internal energies of the ions before they react. Furthermore, the ion-ion collision energy may be fine-tuned in small steps, and it is possible to identify the reaction products and the states they are in. This opens possibilities to reach new insights on balances between different MN reaction pathways and the related dynamics.

We aim for a better understanding of how molecules are formed and processed where we combine novel experimental methods to build a fundamental picture of the transfer of charge-, energy- and mass in gas phase collisional reactions. Here I focus on MN relevant to atmospheric non-LTE phenomenon such as sprites, looking at reactions involving molecular oxygen and nitrogen ions. Starting with $O^- + NO^+$ [6] and $O^- + O_2^+$ [9] to $NO_2^- + NO^+$, I illustrate the power of the techniques available at DESIREE to elucidate competition between two- and three-body product channels and unravel effects of rovibrational energy on the reaction.

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This material is based upon work supported by the Air Force Office of Scientific Research under award numbers FA9550-19-1-7012; FA8655-24-1-700.

Multicomponent Oxides for High-Temperature Catalysis

Abstract

Multicomponent oxides, especially those with the perovskite structure, have a range of redox and other properties that make them attractive for use as heterogeneous catalysts, especially for reactions at high temperatures and other severe conditions. One such application is the endothermic dehydrogenation of hydrocarbon-based fuels which is used as a component in the thermal management of hypersonic vehicles. This thermal management strategy requires a highly active, coking-resistant, heterogeneous catalyst that remains stable during the mission duration. In this poster we will give an overview of our research program on the development of such catalysts, which focuses on the use of perovskite (ABO_3) type metal oxides as both catalysts and as a support for transition metal catalysts. Experimental studies of the structure of thin films of $CaFeO_3$ and $BaZrO_3$ perovskites grown by ALD on a high surface area alumina and their synergistic interactions with supported Pt that enhance their performance as reforming catalysts will be presented. Density functional theory (DFT) calculations which provide insight into bonding interactions between the Pt and the perovskite support that affect the metal stability and reactivity will also be presented.

New Platforms for Molecular Polariton Dynamics

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Polaritons are hybrid light-matter states that arise from strong interactions between a molecular ensemble and the confined electromagnetic field of an optical cavity. Cavity-coupled molecules can demonstrate reactivity and photophysics distinct from their free-space counterparts, but the mechanisms and scope of these phenomena remain uncertain. I will discuss new experimental platforms that we are developing to observe and understand molecular dynamics under cavity strong coupling.

While polaritons are well-established in solution-phase and solid-state systems, they had not been previously reported in isolated gas-phase molecules, where attaining sufficiently strong light-matter interactions is a challenge. We are able to access the strong coupling regime in an intracavity cryogenic buffer gas cell optimized for the preparation of simultaneously cold and dense ensembles. We recently reported a proof-of-principle demonstration in methane where we strongly cavity-coupled individual rovibrational transitions and explored a range of conditions, including coupling strengths and detunings. We are now extending this platform to achieve state-resolved electronic strong coupling (ESC) in molecular iodine and perform nonlinear spectroscopy of strongly-coupled systems when optically pumped either along the cavity axis or orthogonal to it. We will harness this setup as a testbed for fundamental studies of polariton photophysics and chemistry.

We are also searching for signatures of cavity-altered dynamics in benchmark condensed-phase systems with the goal of understanding how and when reactive trajectories may be influenced by strong light-matter interactions. We recently examined ultrafast radical hydrogen (H)-abstraction processes under vibrational strong coupling and found a conspicuous absence of cavity-altered dynamics in these low-barrier reactions. We are now targeting reactions with higher barriers where vibrational dynamics may be more likely to be perturbed by cavity coupling. We are also examining ultrafast dynamics in molecules under ESC in order to examine prospects for cavity control of photochemistry. We engineer ESC in chlorin molecules embedded in dichroic cavities, which allow us to directly track excited state absorption signatures spectrally separated from the cavity-coupled region. This direct readout of excited state signatures allows us to disentangle whether any cavity-altered dynamics we observe derive from classical optical cavity interference effects versus emergent strong light-matter coupling phenomena.

Nucleation at solid–liquid interfaces is accompanied by the reconfiguration of electrical double layers

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In electrochemical systems, the structure of electrical double layers (EDLs) near electrode surfaces is crucial for energy conversion and storage functions. While the electrodes in real-world systems are usually heterogeneous, to date the investigation of EDLs is mainly limited to planar, homogeneous substrates. To bridge this gap, here we image the EDL structure of an ionic liquid/graphite system in the initial stage of interfacial nucleation and growth using our recently developed electrochemical 3D atomic force microscopy. Upon surface nucleation of lithium-containing compounds, the local EDL layers exhibit pronounced restructuring, featuring bending, breaking, and/or reconnecting patterns that switch when the size of the local interphase cluster changes. These EDL reconfiguration patterns are likely universal during nucleation and growth, calling into attention the hitherto hidden contribution of EDL heterogeneity on electrochemical processes.

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