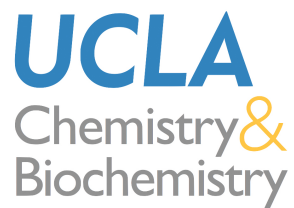


International Conference on Chemical Bonding

July 20-24, 2023
Lihue, Hawaii

Sponsors:



International Conference on Chemical Bonding

Technical Program

Wednesday, July 19

Arrival. Registration opens at 4 pm at the conference hotel lobby.

Thursday, July 20

Morning: Opening. Bonding appetizer plate.

Presiding: Anastassia Alexandrova

- 8:30 – 8:40 am Anastassia, Lai-Sheng - Introductory remarks
- 8:40 – 9:15 am Gernot Frenking (Nanjing Tech University, Philipps-Universität, DIPIC)
“Quest for a Genuine quadruple Bond Between two main-group atoms”
- 9:15 – 9:50 am Sergei Tretiak (Los Alamos National Laboratory, USA)
“Chemical bonding in photophysics and photochemistry of organic chromophores”
- 9:50 – 10:25 am Lai-Sheng Wang (Brown University, USA)
“Nanoclusters of Boron and Metal Borides”
- 10:25 – 10:40 am *Coffee Break*
- 10:40 – 11:15 am Roman Réocreux (ULC, UK)
“Ten-Electron Count Rule and Atomic Charges for the Binding of Adsorbates on Single-Atom Alloys”
- 11:15 – 11:50 am Dan Neumark (UC Berkeley, USA)
“High Resolution Photoelectron Spectra of Vibrationally Excited Anions”
- 11:50 – 12:25 pm Reinhard Maurer (University of Warwick, UK)
“Machine learning of electronic structure for quantum dynamics and molecular design”

Afternoon: Bonding for Quantum Technology

Presiding: Marissa Weichman

- 3:00 – 3:35 pm Eric Hudson (UCLA, USA)
“Phenol-menal Phun: Gaining quantum control of ever larger molecules”
- 3:35 – 4:10 pm Danna Freedman (Massachusetts Institute of Technology, USA)
“Molecular color centers”
- 4:10 – 4:25 pm *Coffee Break*
- 4:25-5:00 Anastassia Alexandrova (UCLA, USA)
“Toward liquid cell quantum sensing: Ytterbium complexes with ultra-narrow absorption”
- 5:00 – 5:35 pm Nicholas Hutzler (California Institute of Technology, USA)
“New approaches to engineering optical cycling in polyatomic molecules”
- 5:35 – 6:10 pm Xuenian Chen (Zhengzhou University, China)
“The different types of reactions of the B-H bond in L·BH₃ adducts”
- 07:00 – 10:00 pm **RECEPTION (conference hotel's ocean front)**

Friday, July 21

Morning: (Quantum) materials and interfaces

Presiding: Romain Réocreux

- 8:30 – 9:05 am Tyrel McQueen (Johns Hopkins University, USA)
"When is a bond not a bond? Unusual electronic bonding in solid state materials"
- 9:05 – 9:40 am Yulia Zaikina (Iowa State University, USA)
"Hard-to-make solids from unconventional synthetic routes"
- 9:40 – 10:15 am Francisco Munoz (Universidad de Chile)
"Single quantum emitters in hexagonal boron nitride"
- 10:15 – 10:30 am *Coffee Break*
- 10:30 – 11:05 am Joshua Goldberg (Ohio State University, USA)
"The Chemical Design Principles of Crystalline Materials with Anisotropic Conduction Polarities"
- 11:05 – 11:40 am Harry Morgan (UCLA, USA)
"Chemical origins of topology and the Fermi surface in SrAg₄Sb₂"
- 11:40 – 12:15 pm Wei Kong (Oregon State University, USA)
"Structures of nanoclusters formed in superfluid helium droplets: crystalline or amorphous?"

12:20 pm CONFERENCE PHOTO

Afternoon: (Quantum) materials and interfaces

Presiding: Reinhard Maurer

- 3:00 – 3:35 pm Vladimiro Mujica (Arizona State University, USA)
"Electron-Transfer Reactions and the CISS Effect"
- 3:35 – 4:10 pm Louis Bouchard (UCLA, USA)
"Chirality Induced Spin Selectivity (CISS): Exploring Electron-Mediated Spin-Spin Coupling in Chiral Molecules"
- 4:10-4:25 pm *Coffee Break*
- 4:25 – 4:55 pm David Waldeck (University of Pittsburgh, USA)
"Investigations into chirality and spin-selective redox chemistry"
- 5:00 – 5:35 pm Paul Weiss (UCLA, USA)
"Understanding and Controlling Charge, Heat, and Spin at Atomically Precise Interfaces"
- 5:35 – 6:10 pm Dao-Fu Yuan (University of Science and Technology of China)
"High-resolution photoelectron spectroscopic study on dipole-bound states of cryogenic molecular anions"

Saturday, July 22

TOUR DAY

Sunday, July 23

Morning: Polaritonics: what are chemical bonds doing? *Presiding: Maksim Kulichenko*

- 8:30 – 9:05 am Yuen-Zhou (UCSD, USA)
“Polariton chemistry: challenges and prospects”
- 9:05 – 9:40 am Marissa Weichman (Princeton University, USA)
“New Platforms for Molecular Polaritonics”
- 9:40 – 10:15 am Wei Xiong (UCSD, USA)
“Ultrafast Dynamics of Molecular Vibrational Polaritons”
- 10:15 – 10:45 am Raphael Ribeiro (Emory University, USA)
“Theoretical perspectives on the control of chemical equilibrium and energy transfer with optical microcavities”
- 10:45 – 11:05 am *Coffee Break*

Surface reactivity and catalysis

- 11:05 – 11:40 am Philippe Sautet (UCLA, USA)
“A mechanistic view of the restructuring of Pt catalysts under a pressure of gas”
- 11:40 – 12:15 pm Boniface Fokwa (UC Riverside, USA)
“Earth-Abundant Boron-based Solid Solution Electrocatalysts for Hydrogen Production”
- 12:15 – 12:50 pm Enrique Batista (Los Alamos National Laboratory, USA)
“Surface reactivity of actinide dioxides”

Afternoon: Clusters and spectroscopy *Presiding: Nikita Fedik*

- 3:00 – 3:35 pm J. Mathias Weber (JILA and University of Colorado Boulder, USA)
“Host-Guest Interactions in Chelation and Molecular Recognition Probed by Cryogenic Ion Vibrational Spectroscopy”
- 3:35 – 4:10 pm Masaichi Saito (Saitama University, Japan)
“ σ -Delocalization Arising from Interactions between Lone-pairs of Non-bonded Heavy Atoms to Produce a Stable σ -Delocalized Radical”
- 4:10 – 4:45 pm Ling Jiang (Dalian Institute of Chemical Physics, China)
“Infrared Spectroscopy of Neutral Water Clusters Based on the Tunable Vacuum Ultraviolet Free Electron Laser”
- 4:45 – 5:00 pm *Coffee Break*
- 5:00 – 5:35 pm Han-Shi Hu (Tsinghua University, China)
“Unexpected Quadruple Chemical Bonds of Main-Group and Metal Elements”
- 5:35 – 6:10 pm Dong-Sheng Yang (University of Kentucky, USA)
“Threshold Ionization and Spin-Orbit Coupling of Lanthanide Oxides”

Monday, July 24

Morning: New methods and ML

Presiding: Raphael Ribeiro

- 8:30 – 9:05 am Martin Head-Gordon (UC Berkeley, USA)
“Recent developments in energy decomposition analysis: From components to observables and back again”
- 9:05 – 9:40 am Ben Nebgen (Los Alamos National Laboratory, USA)
“Treatments of bonding in large scale molecular dynamics simulations using machine learning interatomic potentials”
- 9:40 – 10:15 am Robert Paton (Colorado State University, USA)
“Data-driven predictions of organic reactivity and selectivity”
- 10:15-10:35 *Coffee Break*
- 10:35 – 11:10 am Maksim Kulichenko (Los Alamos National Laboratory, USA)
“Advancing Semiempirical Quantum Chemistry with Extended Lagrangian and Machine Learning”
- 11:10 – 11:45 am Teresa Head-Gordon (UC Berkeley, USA)
“Physics-Inspired Machine Learning Methods: Predictive Chemical Reactivity”
- 11:45 – 12:20 pm Nikita Fedik (Los Alamos National Laboratory, USA)
“Ground and Excited State Properties on Intersection of Machine Learning and Semiempirical Models”

Afternoon: Reactivity in gas phase

Presiding: Lai-Sheng Wang

- 3:00 – 3:35 pm Xiaopeng Xing (Tongji University, China)
“Exploring Bonding Interactions between Coinage Metal Clusters and Small Molecules”
- 3:35 – 4:10 pm Shan Xi Tian (University of Science and Technology of China)
“Dissociative electron attachments in the gas phase and liquid-vapor interface”

Adjourn

5:00 pm departure to Luau (transportation is not provided)

Abstracts

Thursday, July 20

Morning: Opening. Bonding appetizer plate.

Quest for a genuine quadruple bond between two main-group atoms

Gernot Frenking

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The maximum bond multiplicity between two main group atoms is generally assumed to be three. A few years ago, a quadruple bond was proposed for the ground state of C_2 , but this was disputed by several groups. I report theoretical studies of diatomic species AeE , where Ae is an alkaline earth atom Be -Ba and E is a neutral or charged main group atom. The results suggest that in some systems there are four attractive orbital interactions that have unusual features.

Chemical bonding in photophysics and photochemistry of organic chromophores

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Chemical bonding patterns fundamentally change when molecules dynamically evolve in electronically excited states created by optical excitations. These dynamics give rise to many useful properties and functionalities. In this talk I will overview some applications of Non-adiabatic EXcited-state Molecular Dynamics (NEXMD) framework developed at several institutions and released to public. The NEXMD code is able to simulate tens of picoseconds photoinduced dynamics in large molecular systems and dense manifold of interacting and crossing excited states. As a first application, I will exemplify ultrafast excitonic dynamics through conical intersections (CoIns). In some systems these processes lead to large structural changes and chemical reactions. Other so-called intermolecular CoIns occur in a complete absence of chemical bonds. Here both simulations and time-resolved two-dimensional electronic spectroscopy track the coherent motion of a vibronic wave packet passing through CoIns within 40 fs, a process that governs the ultrafast energy transfer dynamics in molecular aggregates. In the second example, we use dynamical simulations to compute X-ray Raman signals, which are able to monitor the coherence evolution in molecular photoswitches. These spectroscopic signals are possible to measure at XFEL facilities, paving the way for detailed coherence measurements in functional organic materials. Finally, potential energy surfaces and chemical reactivity of molecules can be modified by strong interactions with quantum light in a cavity. As such, photochemical reactions (such as photoisomerization) can be controlled by specially designed photonic or plasmonic cavities.

Nanoclusters of Boron and Metal Borides

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Photoelectron spectroscopy in combination with computational studies has shown that bare boron clusters possess planar structures,¹ in contrast to that of bulk boron, which is dominated by three-dimensional polyhedral building blocks. The propensity for planarity has been found to be a result of both a and n electron delocalization over the molecular plane.² The B_{36} cluster was found to have a highly stable planar structure with a central hexagonal vacancy, providing the first experimental evidence that single-atom boron-sheets with hexagonal vacancies, named borophenes,³ are viable. Borophenes have since been synthesized and

characterized on inert substrates, forming a new class of synthetic 2D materials.⁴ We have found recently that the B_{48}^- cluster possesses a bilayer structure,⁵ suggesting the feasibility of bilayer borophenes. Furthermore, we have observed that transition metals can be doped into the plane of boron clusters, indicating the possibility of metallo-borophenes.⁶ However, lanthanide doped boron clusters form half-sandwich complexes, leading to the concept of “borozene”.⁷ Recent work on new borozene complexes,⁸ as well as novel lanthanide boron cage clusters ($Ln_3B_{18}^-$), will also be discussed.⁹

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Chemical bonds on the surface and quantum photon emission from carbon nanotubes Ten-Electron Count Rule and Atomic Charges for the Binding of Adsorbates on Single-Atom Alloys

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Embedding single atoms of transition metals into the surface of coinage metals (Cu, Ag and Au) has emerged as an effective atom-efficient approach to create active and selective catalysts. These so-called Single-Atom Alloys (SAAs) have proven to perform chemistries deemed as unattainable with pure transition metal catalysts [1]. This unique behaviour results from the SAAs' ability to escape decades-old models (d-band model, scaling relationships) that have successfully predicted the reactivity of more traditional metal catalysts [1]. With no predictive models, however, the design of new SAA catalysts is confined to trial-and-error approaches. Via two high throughput campaigns, we show here that atomic charges and electron count rules are better suited for the identification of potentially active SAA catalysts [2-3].

Following the (yet-scarce) experimental evidence of the existence of localised electrostatic charges on the dopant of SAAs [1], we have first determined the dopant charges of Cu, Ag and Au surfaces doped with Rh, Ni, Pd and Pt. Computed dopant charges show large differences among SAAs (-0.63e on PtCu vs +0.32e on NiAu) and could play a role in the binding of adsorbates [2]. To test this hypothesis, we have computed the binding energies of a large range of catalytically relevant adsorbates (H, CO, CH_x , OH_y , NH_z , CH_3OH). We have shown that the binding energies correlate with the dopant charges for a subset of adsorbates, namely electron rich Lewis bases such as H_2O , OH, and NH_3 , suggesting that the binding energy can be decomposed into an electrostatic contribution (dominating in this subset) and a covalent contribution. By linearly combining the dopant charge (descriptor of the electrostatic term) and the binding energy for carbon (proxy for the covalent term), we reproduce the DFT data within 0.06 eV mean absolute error and 0.07 eV standard deviation. We also propose an adsorbate classification based on the relative importance of the two identified terms.

Although this classification already provides a very intuitive theoretical framework for the rationalisation of reactivity trends on SAA catalysts, the covalency descriptor only gives indirect information about the dopants and ignores their electronic structure [3]. In our attempt to identify an electronic descriptor for the covalent

contribution, we have extended our high throughput approach to most of the d-block elements as potential dopants (3d, 4d and 5d). The obtained periodic trends reveal that the optimal binding energy is reached when the total number of valence electrons of both the dopant and the adsorbate reach 10. Further electronic structure analyses show that this corresponds to the saturation of the d-orbitals of the dopant. Finally, we illustrate how this 10-electron count rule can be used for the identification of promising SAA catalysts (in particular Mo, W and Re based SAAs) for the reduction of nitrogen to ammonia, a reaction of industrial significance.

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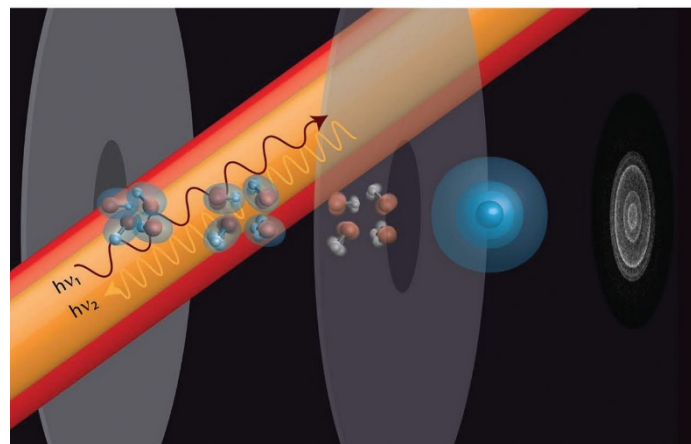
Chemical bonds on the surface and quantum photon emission from carbon nanotubes

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The method of slow-electron velocity-map imaging of cryogenically-cooled anions (cryo-SEVI) has been developed over the last several years in our laboratory.¹ This experiment is a high resolution variant of anion photoelectron spectroscopy and yields well-resolved photoelectron spectra for polyatomic molecular and cluster anions for which more conventional methods show little or no resolved vibrational structure. Cryo-SEVI has been shown to be a powerful spectroscopic probe of bare and complexed metal oxide clusters that serve as model systems for a range of catalytic reactions. In addition, it has been applied to the transition state spectroscopy of benchmark bimolecular and unimolecular chemical reactions. We have recently incorporated a tunable infrared laser into this experiment that can vibrationally excite anions prior to photodetachment. This new implementation, IR cryo-SEVI, enables one to access neutral vibrational levels that cannot be reached from the anion ground state. It also provides a novel probe of anharmonic coupling in both the anion and neutral. Moreover, IR cryo-SEVI provides a means of obtaining anion vibrational frequencies in the gas phase without rare-gas tagging. Hence, both anion and neutral vibrational frequencies can be obtained from a single experimental protocol. Examples will be presented for OH⁻, CH₂CHO⁻ (vinoxide), and H₂CC⁻ (vinylidene).^{2,3} The extension of this method to more complex species including metal oxide clusters will be discussed.



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Machine learning of electronic structure for quantum dynamics and molecular design

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Atomistic simulation based on quantum mechanics (QM) is currently being revolutionized by machine-learning (ML) methods. Many existing approaches use ML to predict molecular properties from quantum chemical calculations. This has enabled molecular property prediction within vast chemical compound spaces and high-dimensional parametrization of energy landscapes for the efficient simulation of measurable observables. However, as all properties derive from the QM wave function, an ML model that can predict the wave function also has the potential to predict other properties. In this talk, I will explore ML approaches that directly represent wave functions and QM Hamiltonians and their derivatives for developing methods that use ML and QM in synergy. Using example systems from heterogeneous catalysis and organic electronics, I will discuss the challenges associated with encoding physical symmetries and invariance properties into machine learning models of electronic structure. Upon overcoming these challenges, integrated ML-QM methods offer the combined benefits of data-driven parametrization and first-principles-based methods. I will discuss several opportunities associated with building ML-augmented quantum chemical methods, including Inverse Chemical Design based on ML-predicted wave functions and the development of efficient and accurate surrogate models to study materials chemistry.

Afternoon: Bonding for Quantum Technology

Phenol-menal Phun: Gaining quantum control of ever larger molecules

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Functionalizing molecules with optical-cycling centers could allow for both new molecule-based resources for quantum information science and new insights into chemical bonding. We will discuss recent work functionalizing phenol and its derivatives with optical cycling centers with an eye towards establishing design principles for creating even larger systems. We will also show work towards larger systems that highlights how an optical-cycling center can be used as a witness of chemical bonding. I will end with a call to arms in hopes of recruiting chemists, and their chemical intuition, to the cause!

Molecular color centers

Danna Freedman

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The unique combination of atomic-scale tunability, reproducibility, and chemical specificity make paramagnetic molecules a paradigm-shifting category of materials for quantum information science. Our team imbued molecular qubits with the same read-out approach as defect-based systems. To achieve this, we envisioned an inverse design problem whereby we mimicked the electronic structure with an orthogonal physical structure. Using transition metal chemistry, we designed the ground state, excited states and dynamics based on straightforward ligand field analysis. By coupling optical read-out with spatial precision, we seamlessly integrated a new class of materials with existing read-out technology. This work has potential in the area of quantum sensing.

Toward liquid cell quantum sensing: Ytterbium complexes with ultra-narrow absorption

Claire Dickerson, Ashley Shin, Changling Zhao, Yi Shen, Barry Li, Paula Diaconescu, Wesley Campbell, Justin Caram, Anastassia Alexandrova

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In quantum technology (such as atomic vapor cells used in precision magnetometry), the energetic disorder induced by a fluctuating liquid environment acts in direct opposition to the precise control required for coherence-based sensing. Overcoming fluctuations requires a protected quantum subspace that only weakly interacts with the local environment. We report a ferrocene-supported ytterbium complex ((thiolfan)YbCl(THF), thiolfan = 1,1'-bis(2,4-di-tert-butyl-6-thiomethylenephenoxy)ferrocene) that exhibits an extraordinarily narrow absorption linewidth in solution at room temperature with a full-width at half-maximum of 0.625 ± 0.006 meV. A detailed spectroscopic analysis allows us to assign all near infrared (NIR) transitions to atom-centered f-f transitions, protected from the solvent environment. A combination of density functional theory and multireference methods match experimental transition energies and oscillator strengths, illustrating the role of spin-orbit coupling and asymmetric ligand field in enhancing absorption and pointing toward molecular design principles that create well-protected yet observable electronic transitions in lanthanide complexes. Narrow linewidths allow for a demonstration of extremely low-field magnetic circular dichroism at room temperature, employed to sense and image magnetic fields, down to Earth scale. We term this system an 'atom-like molecular sensor' (ALMS), and propose approaches to improve its performance.

New approaches to engineering optical cycling in polyatomic molecules

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Optical control of molecules via cycling of photons promises new opportunities in precision metrology, fundamental chemistry, quantum information, and many-body science. Contemporary experimental and theoretical efforts have mostly focused excitation of a single electron localized to an alkaline earth-like metal bonded to a (pseudo-)halogen; the bond induces polarization of the electron wavefunction away from the bonding region, decoupling the electronic and vibrational degrees of freedom, and enabling optical control of the electron without unwanted excitation of vibrational modes. This motif for creating optical cycling centers has been hugely successful; it has a thorough, broad theoretical understanding and has resulted in several experimental breakthroughs. However, there is interest in extending optical control beyond the alkaline-earth-pseudohalogen paradigm. In this talk, I will discuss two additional, different approaches to realizing photon cycling in molecules. First, p-block post-transition metal and metalloid atoms bonded to SH result in molecules with photon cycling transitions not necessarily due to relying on atom-like excitations of the metal, but instead because the geometry is stabilized by the unique properties of the sulfur bond. These molecules have multiple valence electrons, and therefore have very different electronic structures than molecules which have been laser cooled. Second, transition metals bonded to "pseudochalcogenide" species, which bond like oxygen, can result in optical cycling centers with higher order, more complex bonds. We will discuss the theoretical ideas behind these motifs, as well as prospects for experimental studies.

The different types of reactions of the B-H bond in L·BH₃ adducts

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The B-H bond of borane molecules is active and participates in many types of reactions, which is different from the C-H bond of alkanes. The typical borane, BH₃, could not be existed alone because of the electron

deficiency of the B atom, thus, a borane Lewis base adduct ($L\cdot BH_3$) is formed. The activity and reactivity of the B-H bond are greatly dependent on the properties of the Lewis base in the adducts. This topic will discuss the relationship between the reaction types and the properties of Lewis base (L), and further present several examples of such reactions of different borane Lewis base adducts, including ionic reactions and boryl radical reactions.

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Friday, July 21

Morning: (Quantum) materials and interfaces

When is a bond not a bond? Unusual electronic bonding in solid state materials

Tyrel McQueen

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Analysis of bond making and breaking is central to chemical science, and crucial to the development of new chemistries to drive green chemistry, sustainable energy, and new technologies. Consequently, a multitude of tools and approaches exist to examine and explain bonding in systems ranging from diatomic molecules to extended solids, and connect that bonding to the ultimate usefulness. Yet there are cases of bonding -- or changes in bonding with temperature or pressure -- that seem to defy explanation. In this talk, I will highlight several such examples, drawn from diverse classes of quantum materials ranging from misfits and two dimensional van der Waals materials to mixed valent structures, and point out places where the bonding and changes in bonding is well understood, and where new insights are still needed to understand bonding in solid state chemical systems.

Hard-to-make solids from unconventional synthetic routes

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The search for new materials can be expedited by developing synthesis methods and real-time monitoring techniques that allow for faster screening of complex systems. Theoretical predictions of a new compound stability and structure can provide the necessary roadmap for targeted synthesis. However, the synthesis of solids can be challenging due to the slow reaction kinetics, necessitating high temperatures and lengthy annealing times, and oftentimes leads to thermodynamically stable products. We're exploring unconventional ways of synthesizing solid-state materials using reactive, salt-like precursors. Our process involves a combination of real-time reaction monitoring and theoretical predictions. Through our approach, we've discovered new, alkali-metal-containing (Li, Na, and K) compounds that are metastable or kinetically stabilized. I'll delve into their unique structural features, established through comprehensive diffraction methods, chemical bonding and physical properties.

Single quantum emitters in hexagonal boron nitride

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Luminescent atomic defects (color centers) are a promising alternative for quantum technologies and metrology applications. During the last decade such emitters were detected in hexagonal boron nitride, exhibiting marked differences with more studied emitters such as color centers in diamond. High-energy phonon replicas on the luminescence spectrum are incompatible with atomic vacancies, the most common type of defects in bulk emitters. On the other hand, some single emitters found in this material are spin-active, which are commonly associated with vacancies. In this contribution, we will elaborate on the identification and manipulation of the atomic defects associated with single emitters in this material.

The Chemical Design Principles of Crystalline Materials with Anisotropic Conduction Polarities Joshua Goldberg

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Electronic materials generally exhibit a single majority carrier type, either electrons or holes, uniformly along all directions of the crystal, which are then integrated together to separate and control the flow of charge to create virtually all modern electronic and energy harvesting devices. Here we will describe our recent work in the synthesis, properties, and applications of “goniopolar materials”, which are materials that exhibit either n-type or p-type conduction behavior depending on the crystallographic direction. We will establish the origin of this behavior, and the chemical design and bonding principles for identifying new goniopolar materials, which has led to the significant expansion in the number of systems that have been experimentally demonstrated to exhibit this effect. Finally, we will show that the inherent charge separation ability in goniopolar materials can overcome inefficiencies in energy-harvesting technologies including thermoelectrics and photocatalysis.

Chemical origins of topology and the Fermi surface in SrAg₄Sb₂

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Topological materials have erupted as a field of study in the solid state sciences since the publication of several databases which enumerate and classify real materials according to their topological properties. Greater chemical understanding of band topology and transport properties is required for us to rationally design new materials which maximize the benefits of topology, such as symmetry-protected metallic surface states for use in electrocatalysis. Here we investigate SrAg₄Sb₂, a layered topological crystalline insulator and a Fermi pocket material, with orbital projection techniques to understand the orbital origin of its non-trivial band topology. Orbital projection techniques reveal a band inversion along c^* , a signature of a topological insulator, in which the band composition changes from s to $d_{xy}/d_{x^2-y^2}$. The elemental and orbital characters of the Fermi pockets are determined, and we compute quantum oscillation data for comparison to experiments. Future directions including chemical modification and surface chemistry will be discussed.

Structures of nanoclusters formed in superfluid helium droplets: crystalline or amorphous?

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Superfluid helium droplets are known scavengers collecting dopants along their traveling path. The structures of the thus formed dopant clusters are of interest not just for scientific curiosity, but also for potential applications in synthesis of catalysts.¹ Using electron diffraction, we have determined that dimers and trimers are typically formed with gas phase structures,² different from any cuts from the crystalline structures. Given the fast rate of cooling of superfluid helium droplets, it is also reasonable to suspect that large nanoclusters formed in droplets are amorphous. On the other hand, evidence of crystalline structures of rare gas clusters has been reported.³ We compare structures of large benzene clusters and large argon clusters formed in superfluid helium droplets, and discuss the conditions for forming crystalline nanoclusters inside helium droplets.

Acknowledgments: This work was supported by the National Institutes of Health.

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Afternoon: (Quantum) materials and interfaces

Single quantum emitters in hexagonal boron nitride

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In this contribution, we will analyze how the Chirality-Induced Spin Selectivity (CISS) effect can be used to understand certain aspects of electron transfer (ET) reactions. Specifically, we will concentrate in the emergence of anomalous distance and temperature behavior in photo-induced ET reactions. In Marcus theory of ET reactions, exponentially decaying distance behavior, is determined by the fact that tunneling is the dominant transport mechanism, whereas the conventional Arrhenius-type temperature dependence emerges as a consequence of electron-vibration coupling via the Franck-Condon factors that intervene in the calculation of the reaction rate. The explicit inclusion of spin-orbit interaction in chiral molecules, and the onset of the CISS effect, have profound consequences insofar distance and temperature behavior, particularly in photo-induced ET reactions. The main reason for this remarkable change is that spin-polarized electrons interact with phonons exchanging linear momentum but not spin angular momentum. The inclusion of spin-orbit interaction affects the tunneling transmission probability, intimately connected with the efficiency of tunneling and the distance dependence of the ET reaction. In a different direction, the conservation of angular momentum imposes restrictions on the decoherence mechanisms due to electron-phonon interactions responsible for the temperature behavior of the reaction, weakening the exponential Arrhenius-type behavior of the rate constant. We will analyze different models for the inclusion of these effects and compare our theoretical models with some relevant experimental work

Chirality Induced Spin Selectivity (CISS): Exploring Electron-Mediated Spin-Spin Coupling in Chiral Molecules

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Spin selectivity in macromolecules, within the framework of CISS, has been hypothesized to arise from the interplay of atomic spin-orbit coupling (SOC) and the chiral symmetry exhibited by these molecules. In this study, a previously established analytical tight-binding model will be employed that has been used to investigate electron transport in helicoidal DNA structures. In this model, each base is represented by a p-like orbital projected perpendicular to the double helix, while the molecular base plane features bonded s and p orbitals representing the outer shell of carbon atoms. By utilizing the resulting tight-binding Bloch wavefunctions associated with the discrete modes created by the longitudinal confinement within the helix, an effective spin-Hamiltonian describing an indirect coupling between distant localized spins can be derived. The implications of these findings for experiments involving long-range spin-spin couplings will be discussed.

Investigations into chirality and spin-selective redox chemistry

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I will describe recent studies that investigate the effects of electron spin in electron transfer and electron initiated chemical reactions of supramolecular assemblies and at electrodes. I will discuss how charge polarization and charge transfer in chiral molecules and assemblies is accompanied by spin polarization and spin transfer, because of the chiral induced spin selectivity (CISS) effect. I will report on recent studies which show how the CISS effect modulates electron transfer rates in chiral assemblies and how spin polarized electron currents can be used to enhance the selectivity of electrochemical reactions.

Understanding and Controlling Charge, Heat, and Spin at Atomically Precise Interfaces

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One of the key advances in nanoscience and nanotechnology has been our increasing ability to reach the limits of atomically precise structures. By having developed the “eyes” to see, to record spectra, and to measure function at the nanoscale, we have been able to fabricate structures with precision as well as to understand the important and intrinsic heterogeneity of function found in these assemblies. The physical, electronic, mechanical, and chemical connections that materials make to one another and to the outside world are critical. Just as the properties and applications of conventional semiconductor devices depend on these contacts, so do nanomaterials, many nanoscale measurements, and devices of the future. We explore the important roles that these contacts can play in preserving key transport and other properties. Initial nanoscale connections and measurements guide the path to future opportunities and challenges ahead. Band alignment, minimally disruptive connections, and control of spin and heat are all targets and can be characterized in both experiment and theory. I discuss our initial forays into this area in a number of materials systems.

High-resolution photoelectron spectroscopic study on dipole-bound states of cryogenic molecular anions

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Polar molecules with sufficiently large dipole moments can form highly diffuse dipole-bound anions, and possess noncovalent dipole-bound states (DBSs) just below the electron detachment threshold by the long-range electron-dipole interaction. DBSs have been proposed as the “doorway” to the formation of valence-bound anions, and exploited as a means to develop high-resolution resonant photoelectron spectroscopy. We have developed an experimental technique coupling electrospray ionization (ESI), cryogenic ion cooling in a

3D Paul trap, and high-resolution photoelectron imaging. Using this third generation ESI-PES apparatus, DBSs of a wide variety of cryogenically cooled anions have been investigated. Some fundamental properties of DBS have been study in depth, including experimental confirmation of the existence of π -type DBS with one additional angular node in the wave function, the observation of polarization-assisted DBS providing decisive information about the role that polarization plays in the formation of DBSs, and the complete unravel of the complex vibronic levels of radicals with strong nonadiabatic effects involved in.

Sunday, July 23

Morning: Polaritonics: what are chemical bonds doing?

Polariton chemistry: challenges and prospects

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I will discuss the prospects and challenges of polariton chemistry, namely, the effort of controlling physicochemical processes and properties using strong light-matter coupling. The main challenge is the "large N problem," where in the collective strong coupling regime, a macroscopic number N of molecules couple to each photon mode in a microcavity, rendering the equilibrium effects negligible on a per-molecule basis. Way to ameliorate this problem include polariton condensation, molecular optomechanics, and non-equilibrium effects. I will outline our theoretical efforts along these lines, together with experimental works done with experimental collaborators.

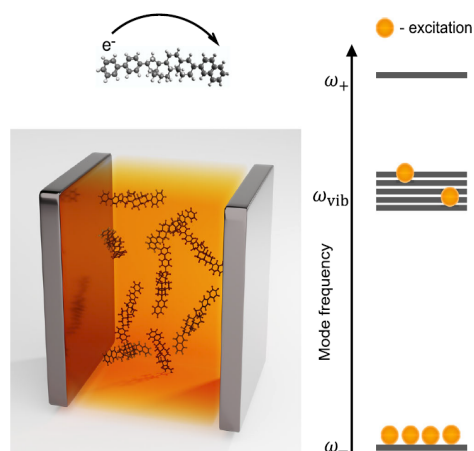


Fig. 1. An electron transfer reaction can be dramatically accelerated in the presence of a vibrational polariton condensate. Adapted from Ref. 3.

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New Platforms for Molecular Polaritonics

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Polaritons are hybrid light-matter states with unusual properties that arise from strong interactions between a molecular ensemble and the confined electromagnetic field of an optical cavity. Cavity-coupled molecules can demonstrate energetics, reactivity, and photophysics dramatically distinct from their free-space counterparts, but the mechanisms and scope of these phenomena remain open questions. I will discuss new platforms we are developing to investigate molecular reaction dynamics under vibrational strong coupling. While polaritons are now well-established in solution-phase and solid-state systems, they have not yet been reported in isolated gas-phase molecules, where attaining sufficiently strong light-matter interactions is a challenge. We access the strong coupling regime in an intracavity cryogenic buffer gas cell optimized for the preparation of simultaneously cold and dense ensembles and report a proof-of-principle demonstration in gas-phase methane. We strongly cavity-couple individual rovibrational transitions and probe a range of coupling strengths and detunings. We will use this infrastructure as a new testbed for future fundamental studies of polariton physics and chemistry. We are also searching for signatures of cavity-altered dynamics in solution-phase systems. We first focus on radical hydrogen-abstraction processes, which have well-characterized reactive surfaces and can be initiated with photolysis and tracked directly on ultrafast timescales. We use ultrafast transient absorption to examine intracavity reaction rates with the goal of better understanding how and when reactive trajectories may be influenced by strong light-matter interactions.

Ultrafast Dynamics of Molecular Vibrational Polaritons

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When the vibrational modes of molecules strongly couple with virtual states of photonic modes, they give rise to new states called molecular vibrational polaritons, accompanied by a significant population of dark reservoir modes. Similar to how atomic orbitals combine to form bonding and antibonding molecular orbitals in molecular bonding, polaritons resemble these orbitals, while the dark modes are akin to nonbonding orbitals. As polariton states are a hybrid of matter and light, their energy is shifted from the original states. This unique characteristic of polaritons leads to predictions that they can induce changes in chemistry under thermally activated conditions, giving rise to an exciting and emerging field called polariton chemistry, which has the potential to revolutionize the field of chemistry. However, despite some published results supporting this concept, the precise chemical physics and mechanisms underlying polariton chemistry are still not fully understood. My group recently used 2D IR spectroscopy to address the mechanics challenge by differentiate the dynamics of polaritons and dark modes. Specifically, our findings are twofold. Firstly, we discovered that polaritons can facilitate the transfer of vibrational energy within and between molecules. This paves the way for controlling the flow of vibrational energy in liquid-phase molecular systems. Secondly, by studying a single-step isomerization event, we confirmed that polaritons indeed have the ability to modify the dynamics of chemical reactions under conditions of strong coupling. In contrast, the dark modes behave similarly to uncoupled molecules and do not influence the reaction dynamics. This discovery affirms the central concept of polariton chemistry: polaritons can alter the potential energy landscape of reactions. Moreover, it provides a clear understanding of the role played by dark modes, establishing a critical foundation for the design of cavities in future polariton chemistry endeavors.

Theoretical perspectives on the control of chemical equilibrium and energy

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Molecular polaritons are exotic hybrid light-matter states formed via strong interactions between optical microcavities and molecular materials. Recent experiments have reported that polaritons enable modulation of various physicochemical phenomena including chemical reactions, charge conductivity, and intermolecular energy transfer, but many open questions remain on the operating mechanisms. In this talk, I will describe our recent investigations of polariton effects on chemical equilibrium and excited-state transport in optical microcavities. Focus will be given to the collective strong coupling regime within a theoretical framework that includes hybridization of a large density of molecular excitations with multiple confined electromagnetic modes. Connections to recent experiments and current questions in the field of polariton chemistry will be made throughout the talk.

Surface reactivity and catalysis

A mechanistic view of the restructuring of Pt catalysts under a pressure of gas

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Understanding how catalyst active sites dynamically evolve at the atomic scale under reaction conditions is a key challenge and a prerequisite for accurate determination of catalytic mechanisms and predictably developing catalysts. We combine in-situ time-dependent observation with scanning tunneling microscopy and machine learning-accelerated first-principle atomistic simulations to uncover the mechanism of restructuring for the surface of Pt catalysts under a pressure of carbon monoxide (CO). We show that a high CO coverage at a Pt step edge triggers the formation of atomic protrusions of low-coordination Pt atoms, which then detach from the step edge to create subnano-islands on the terraces, where undercoordinated sites are stabilized by the CO adsorbates. A fast and accurate machine learning potential is key to enable the exploration of tens of thousands of configurations for the CO covered restructuring catalyst. These studies open an avenue to achieve atom-scale understanding of structural dynamics of more complex metal nanoparticle catalysts under reaction conditions.

Earth-Abundant Boron-based Solid Solution Electrocatalysts for Hydrogen Production

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The large-scale production of hydrogen is hindered by the high cost and scarcity of noble metal catalysts such as Pt. Recently, non-noble metal materials have emerged as highly active electrocatalysts for the hydrogen evolution reaction (HER) to produce hydrogen.[1] Our recent experimental and theoretical investigations show that metal diboride are excellent HER electrocatalysts in bulk and nanoscale forms, as summarized in an invited account.[2]-[5] Our results indicate that the H-surface binding energy decreases as the

electronegativity of the metal increases. Therefore, the electron transfer between metal and boron is one of the key parameters to control the HER activity of MB₂ electrocatalysts. Furthermore, an unexpected boron-chain dependency of the HER activity was discovered in the V-B system,[6] that even allows for the prediction of unknown active HER electrocatalysts. In addition, we have also recently found an unexpected lattice parameter-dependency on HER of ternary solid solution variants crystallizing with the AlB₂-type structure that allowed some members to overpower Pt/C at high current density.[7,8]

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Surface reactivity of actinide dioxides

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Actinide compounds, especially actinide oxides, play a critical role in many stages of the nuclear fuel cycle. The behavior of these materials under different conditions dictate aspects from crystal growth to disposal of spent fuels, and much of those properties start at the surface. In that way, catalytic reactions that can lead to unstable storage conditions stem from surface interactions with environmental species. Similarly, the morphology of crystal growth conditions is dictated by the stabilization or destabilization of different surfaces by ligands present in the solution environment. We have recently been focusing on surface properties induced by the presence of surface defects and surface interactions with environmental and non-environmental molecules. In this talk we present results of these studies for a series of actinide dioxides (AnO₂). We show how, under predicted conditions, one can control the morphology of growth, starting from nanoparticles to solids. The effect of surface defects is also analyzed as they can significantly affect the outcome, not only in morphology but also on the catalytic properties of the different exposed surfaces.

Afternoon: Clusters and spectroscopy

Host-Guest Interactions in Chelation and Molecular Recognition Probed by Cryogenic Ion Vibrational Spectroscopy

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The binding of ions in chelation and in molecular recognition is governed by their interaction with charged and/or neutral residues of the molecular host. These interactions are encoded in the vibrational signatures of the complex, and they can be used to probe the structural properties and intermolecular forces in the host-guest complexes. We show investigations of two classes of such complexes, using cryogenic ion vibrational spectroscopy in concert with density functional theory.

Ethylenediaminetetraacetic acid (EDTA) is used as a chelating agent for binding metal ions in solution. In addition, its binding pocket is a model for the interactions between carboxylate groups and the divalent ions

they often bind in some biological systems. With its four carboxyl/carboxylate groups and two nitrogen atoms, EDTA can chelate nearly any metal cation to form water-soluble complexes, making it a robust model system for studying biologically relevant divalent ion-carboxylate interactions. Here, we present infrared spectra of a series of cryogenically prepared alkaline earth metal-EDTA complexes of the form $[M(\text{II})\cdot\text{EDTA}]^{2-}$. The vibrational spectra encode structural and electrostatic information, reflecting the geometry of each metal ion within the EDTA binding pocket and its relation to ionic radius. The evolution of the spectra by interaction with water molecules shows how water binds to the pocket, and how the structure of the pocket reacts to hydration.

Octamethyl calix[4]pyrrole (omC4P), is a prototypical receptor for small anions in aqueous solution chemistry. We present cryogenic gas-phase infrared spectra of a series of anion-omC4P complexes of the form $[X\cdot\text{omC4P}]$ (X = fluoride, chloride, bromide, formate, nitrate), and assign spectral features using density functional theory calculations. The vibrational spectra encode the structures of and intermolecular forces in each complex, revealing the binding motif and interplay of each ion with the NH groups that form the binding site in omC4P. The NH stretching modes show a clear spectral response to changes in the guest ion.

σ -Delocalization Arising from Interactions between Lone-pairs of Non-bonded Heavy Atoms to Produce a Stable σ -Delocalized Radical

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The extension of electronic delocalization has long been one of the important research topics in various fields of chemistry, and π -delocalization in double-bond conjugation and σ -delocalization in polysilanes have mainly been investigated. On the other hand, σ -delocalization is also possible between non-bonded atoms. In a geometric constraint, lone-pair interactions on non-bonded atoms can produce σ -delocalization without a bonding framework.¹ To closely orient lone pairs on non-bonded atoms, the utilization of rigid platforms such as aromatic skeletons is of great use.² We have focused on a benzene platform and synthesized multi-arylselenenyl-substituted benzenes. As the number of adjacent selenium atoms increases, the HOMO energy level increases (Figure 1).³ Increase in steric congestion makes the HOMOs composed of σ -symmetric delocalized orbitals with anti-bonding interactions. Oxidation of the hexa-substituted compound affords a dication bearing ($\sigma+\pi$)-double aromaticity,⁴ while that of the penta-substituted one provides a stable σ -delocalized cation radical, stable in the solid state.

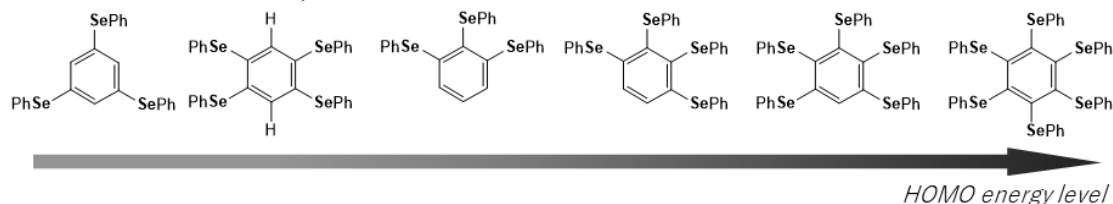


Figure 1 The multi-arylselenenyl-substituted benzenes in this study.

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High-resolution molecular scattering experiments using the velocity map ion imaging technique

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Crossed molecular beams method is a mature technique in the study of molecular physics and chemical reaction dynamics. With the development of high-resolution laser detection techniques, various interesting quantum effects have been investigated in detail in crossed molecular beam scattering experiments over the past decade [1-3], which are of great value in understanding molecular quantum dynamics.

Here we report the studies of reactive collisions by using time-sliced velocity map ion imaging technique together with the near threshold ionization method. We acquired quantum state resolved ion images for the F+HD [4], H+HD/D₂ and D+CH₄ reactions. The high-resolution results are beneficial in the study of detailed reaction mechanism of elementary chemical reactions.

Acknowledgements: This work was supported by the National Natural Science Foundation of China (Grant No. 22125302), Strategic Priority Research Program of the Chinese Academy of Sciences, and the Ministry of Science and Technology of China.

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Unexpected Quadruple Chemical Bonds of Main-Group and Metal Elements

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Multiple chemical bonds are important in chemistry. For a long time, main group elements (such as B, C, N) can only form triple bonds at most. We proposed the four-fold chemical bond of carbon-uranium in 2012 and found that in the C \equiv UO molecule, in which the terminal C atom forms a new type of quadruple chemical bond between the four unhybridized 2p and 2s atomic orbitals of C and the 5f and 6d atomic orbitals in U.¹ This discovery breaks through the traditional concept that the highest bond order of the main group p-block elements is three. In recent years, we have extended this concept to B element, and found that the BFe(CO)₃⁻ molecule contains a B \equiv Fe quadruple chemical bond.² Based on our previous research, we further extended the concept of the formation of quadruple bonds by the third main group B elements to the third subgroup rare earth elements (Fig. 1), and discovered the first rare-earth-transition metal quadruple bond compounds RE \equiv Fe(CO)₃⁻ (RE = Sc, Y, La).³ This series of studies reveals that a variety of such quadruple-bonded systems of main-group and metal elements may exist in inorganic and organometallic chemistry.

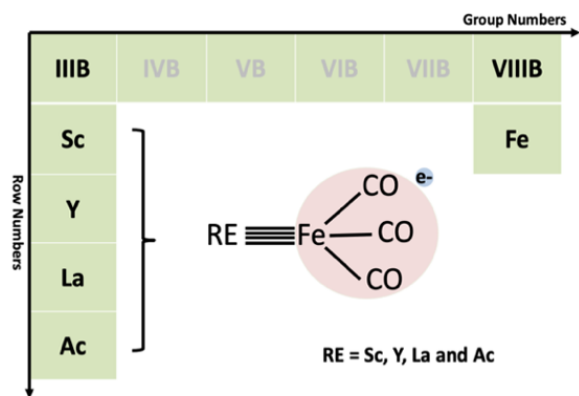


Figure 1. Schematic diagram of the binuclear metal quadruple bond compound $\text{RE}\equiv\text{Fe}(\text{CO})_3^-$.

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Threshold Ionization and Spin-Orbit Coupling of Lanthanide Oxides

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Spin-orbit (SO) coupling makes spin forbidden transitions or reactions possible. Thus, quantification of such interactions has important implications in photophysics and chemical catalysis. Our work aims to quantify SO interactions using lanthanide (Ln) oxides as target molecular systems. Through these systems, we examine the impact on the SO coupling by electron configurations and 4f orbital occupancies of Ln elements and sizes of the metal oxides. By examining these factors, we explore how SO coupling is affected by the number of Ln 4f electrons for a given size of molecules and if the Ln 4f orbitals stay atomic in nature in these molecules. Ln oxides are produced in laser ablation molecular beams, identified with time-of-flight mass spectrometry, and characterized with threshold ionization and relativistic quantum chemical computations. Measured ionization energies are two-fold improvements over previously reported values where the comparison is available and are used to evaluate literature reaction enthalpies of chemical ionization reactions. Most of low-lying electronic states of the neutral molecules and ions that have at least one 4f electrons are identified as SO coupled states consisting of two or more electron spins. Examples of Ln oxides for discussion include LnO and Ln_2O_2 (Ln = La, Ce, Pr, and Lu).

Infrared Spectroscopy of Neutral Water Clusters Based on the Tunable Vacuum Ultraviolet Free Electron Laser

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Dalian Coherent Light Source (DCLS) delivers the Vacuum Ultraviolet Free Electron Laser (VUV-FEL) with high brightness and ultrafast laser pulses in the 50-150 nm wavelength region in picoseconds or 100 femtoseconds, which is an ideal light source for the ionization of molecular systems and the excitation of valence electrons with very high efficiency. Very recently, we set up an infrared spectroscopic facility based

on threshold photoionization using the VUV-FEL, which allows for size selection of neutral clusters. Here, we report the size-specific infrared spectra of neutral water clusters $(\text{H}_2\text{O})_n$ ($n = 2-10$) based on the tunable VUV-FEL near-threshold single-photon ionization, providing key microscopic information for systematic understanding of the growth mechanism of dynamical hydrogen-bonding networks and benchmarks for accurate description of the water intermolecular potentials.

Monday, July 24

Morning: New methods and ML

Recent developments in energy decomposition analysis: From components to observables and back again.

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Energy decomposition analysis (EDA) is increasingly used for applications such understanding non-covalent interactions, chemical bonds, and even aspects of chemical catalysis and reactivity. Yet EDAs themselves cannot be considered entirely mature themselves. With this in mind, I will discuss the current status of the Absolutely Localized MO (ALMO) EDA, which attempts to decompose supermolecular calculations on molecular clusters into underlying physical driving forces, such as Pauli repulsions, permanent and induced electrostatics, dispersion, and charge-transfer [1]. Recent developments to refine the DFT-based ALMO-EDA, particularly for controversial questions such as charge-transfer versus polarization will be discussed. An important frontier is linking EDA components to observable properties, and I will discuss examples of how this can be accomplished, with a focus on the newly introduced Force Decomposition Analysis (FDA).

[1] Y. Mao, M. Loipersberger, P. R. Horn, A. Das, O. Demerdash, D. S. Levine, S. P. Veccham, T. Head-Gordon, and M. Head-Gordon, "From intermolecular interaction energies and observable shifts to component contributions and back again: A tale of variational energy decomposition analysis", *Annu. Rev. Phys. Chem.* **72**, 641–666 (2021).

Treatments of bonding in large scale molecular dynamics simulaons using machine learning interatomic potenals

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Machine learning interatomic potentials (MLIAPs) have enabled large scale, reactive, molecular dynamics simulations on the order millions to billions of atoms. However, the accuracy of these simulations is dictated by the underlying Electronic Structure simulations used to train the MLIAP. Due to the challenges associated with finite resources, frequently Density Functional Theory is utilized to build training datasets for these models. Many of these DFT methods, however, exhibit poor performance when computing the energies and forces associated which bond breaking, which usually exhibit open shell and multi-reference character. In this talk, we will examine recent efforts at constructing an MLIAP for reactive systems, as well as the errors associated with using DFT methods for building reference training sets. Using these preliminary results, we will explore possible avenues for enhancing the quality of MLIAP training data.

Advancing Semiempirical Quantum Chemistry with Extended Lagrangian and Machine Learning

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Direct Born-Oppenheimer Molecular Dynamics (BOMD) simulations often suffer from the computational bottleneck of iterative self-consistent field (SCF) optimization, limiting their applicability to large-scale simulations. In this work, I will introduce an advanced formulation of Extended Lagrangian Born–Oppenheimer Molecular Dynamics (XL-BOMD) implemented in the PySeQM software, a PyTorch-based semiempirical quantum chemistry package.

The new XL-BOMD method eliminates the need for SCF optimization by simultaneously propagating the electronic degrees of freedom along with the nuclear motion. The implementation incorporates several key features, including consideration of finite electronic temperatures, the use of canonical density matrix perturbation theory, and an adaptive Krylov subspace approximation. Leveraging the power of machine learning hardware accelerators, the PyTorch implementation enables efficient simulations by interfacing reduced semiempirical Hamiltonians with machine-learned models, achieving higher accuracy.

With the new XL-BOMD formulation, we can now study challenging chemical systems characterized by charge instabilities and low HOMO-LUMO gaps. Applied to molecular dynamics, simulation of 840 carbon atoms, one integration time step executes in 4 s on a single GPU.

[1] M. Kulichenko, K. Barros, N. Lubbers, N. Fedik, G. Zhou, S. Tretiak, B. Nebgen, A. M. N. Niklasson. “*Semi-Empirical Shadow Molecular Dynamics: A PyTorch Implementation*”. *J. Chem. Theory Comput.* (2023).

[2] A. M. N. Niklasson. “*Density-Matrix Based Extended Lagrangian Born–Oppenheimer Molecular Dynamics*”. *J. Chem. Theory Comput.* **6**, 6, 3628 (2020).

[3] G. Zhou, N. Lubbers, K. Barros, S. Tretiak, B. Nebgen. “*Deep learning of dynamically responsive chemical Hamiltonians with semiempirical quantum mechanics*”. *PNAS* **119**, 27, e2120333119 (2022).

[4] <https://github.com/lanl/PYSEQM/tree/develop>

Physics-Inspired Machine Learning Methods: Predictive Chemical Reactivity

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At present, the application of machine learning (ML) to chemical reactivity is still in its infancy. The challenge of ML-learned potential energy surfaces (PESs) is that they are always incomplete because the ab initio data used to inform them is always small-scale and overly reliant on chemical intuition of what data is important for training. Instead a “negative design” data acquisition strategy is necessary to create a more complete ML model of the PES, since it must also learn avoidance of unforeseen high energy intermediates or even unphysical energy configurations. Because this type of data is unintuitive to create, we introduce an active learning workflow based on metadynamics that samples a lower dimensional manifold within collective variables that efficiently creates highly variable energy configurations for further ML training. This strategy more rapidly completes the ML PES such that deviations among query by committee ML models helps to now signal occasional calls to the external ab initio data source to further molecular dynamics in time without need for retraining the ML model. With the hybrid ML-physics model we predict the change in transition state and/or reaction mechanism at finite temperature and pressure for hydrogen combustion, thereby delivering on the promise of real application work using ML trained models of an ab initio PES with two orders of magnitude reduction in cost.

Ground and Excited State Properties on Intersection of Machine Learning and Semiempirical Models

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Pure machine learning approaches have achieved remarkable success in chemistry and material science, but their performance often decreases when applied to new regions of chemical space far from the training set. Models such as interatomic potentials neglect electronic structure information, limiting their transferability. Moreover, many relevant processes take place beyond the ground electronic state which is particularly hard

to model without electronic structure information. To overcome these limitations, our group has been focusing on the development of PYSEQM (Pytorch-based Semiempirical Quantum Mechanics), differentiable physics model that combines domain knowledge of reduced quantum mechanics with machine learning as a corrective tool. Semiempirical models, specifically the AMx and PMx families, encompass numerous static parameters, primarily accounting for Coulomb interactions. Employing ML tools, we demonstrate that structure-aware on-the-fly reoptimization of semiempirical constants yields better accuracy, particularly in extreme conditions that drive systems away from equilibrium. In the last part, we will overview the latest work in progress focusing on the development of the excited states capability based in CIS and RPA approaches solved in a reduced space through Davidson diagonalization routine.

Data-driven predictions of organic reactivity and selectivity

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Quantum chemical models of reaction mechanism and selectivity provide a powerful tool to explain the outcome of laboratory experiments. However, since many reactions involve several steps and multiple conformers, the computational expense of QM approaches often prevent their application to predict reaction outcomes more broadly. Surrogate machine-learning models with quantum chemical accuracy at a fraction of the computational cost are set to transform the accessibility of computational predictions of reactivity and selectivity. I will discuss machine learning efforts utilizing knowledge and data from QM studies to generate surrogate models for the large-scale prediction of various atomic and molecular properties. We have developed graph neural networks to predict computational and experimental observables such as spin density, chemical shift, thermochemistry and reactivity. In this talk I discuss the performance of these models in high-throughput predictions of reactivity and selectivity of heteroaromatics and in goal-directed molecular optimization of stable organic radicals, along with strategies to improve model transferability.

Afternoon: Reactivity in gas phase

Exploring Bonding Interactions between Coinage Metal Clusters and Small Molecules

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Coinage metals have relatively simple electron configurations-- $(n-1)d^{10}ns^1$, and many of their clusters have distinctive geometries and electronic structures. At the same time, coinage metal clusters have special catalytic abilities and photoelectric characters, which make them have broad application prospects. In the past several years, we systematically studied the reactivity of pure and doped coinage metal clusters with small molecules using an instrument composed of a magnetron sputter cluster source, a micro flow reactor running at a low temperature, and a time-of-flight mass spectrometer. Combing the observed size-dependent or component-dependent reactivity and extensive theoretical calculations, we explored the bonding interactions between coinage metal clusters and small molecules like O₂ and NO. The effects of clusters' global electronic properties and local interaction sites were discussed. In the formed products, the general bonding patterns in small molecules, such as the electron-sharing bond, the dative bond, and the weak electrostatic interaction, can be distinguished in the interactions between coinage metal clusters and the adsorbed molecules.

Dissociative electron attachments in the gas phase and liquid-vapor interface

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In contrast to the neutral and cationic atoms and molecules, our current knowledge about anionic species is still deficient. An anion can be directly formed by electron attachment or capture. Differing from the stable anion, temporary negative ion(TNI) in electron-atom/molecule resonant states decay quickly via electron autodetachment or molecular dissociation. Recently, the application of velocity map imaging (VMI) technique in the dynamics of molecular dissociative electron attachment (DEA) remarkably facilitates the experimental studies of TNI's properties. In this presentation, I will give a brief review of our recent progresses using the VMI technique. Amazing features about the anionic properties and the DEA dynamics have been revealed for the gas-phase molecules and the liquid-vapor interface, and these findings will have profound impacts on some important issues in atmospheric, interstellar chemistry and radiation chemistry of bioorganic materials.