Surface Science Division
Room D136 - Session SS-WeA

A Special Session Honoring Wilson Ho: 25 Years of Single-Molecule Vibrational Spectroscopy and Microscopy

Moderators: Xi Chen, Tsinghua University, **Xiaohui Qiu**, Nanocenter

2:20pm **SS-WeA-1 Development of Single-Molecule Spectroscopy Inspired by STM-IETS**, ***Yousoo Kim***, RIKEN, Japan **INVITED**

The scanning tunneling microscope (STM) is a versatile and powerful tool for investigating and controlling the chemistry of individual molecules on solid surfaces, mainly due to its extremely high spatial resolution. Using tunneling electrons from an STM tip, it is possible to excite various quantum states of single molecules on a surface, providing insights into the mechanisms of surface chemical reactions. Inspired by the pioneering work of Wilson Ho's group on single-molecule vibrational spectroscopy by inelastic electron tunneling spectroscopy combined with STM, we have been able to establish a dynamic approach to explore vibrational mode-selective chemistry in single-molecule reactions based on action spectroscopy with STM. Later, we developed an optical STM that combines the STM with light illumination and detection systems to probe molecular energetic processes such as energy transfer, conversion, and dissipation. In this talk, I will discuss some of our long-standing efforts to develop single-molecule spectroscopy using local excitation sources, such as tunneling electrons and localized surface plasmon, generated at the STM junction.

2:40pm **SS-WeA-2 Unraveling Orbital Magnetism Contributions to Landau Levels in Moiré Quantum Matter**, ***Joseph Stroscio***, NIST **INVITED**

Flat and narrow band physics in moiré quantum matter (MQM) has proven to be extremely rich with new emergent quantum phases which can be tuned with applied electric and magnetic fields. The topological properties of the eigenstates of the moiré Hamiltonian are critical for establishing the quantum phase of the system. In this talk, we use the quantum ruler of Landau levels to unravel the energy-resolved valley-contrasting orbital magnetism and large magnetic susceptibility that contribute to the energies of Landau levels of twisted double bilayer graphene. These orbital magnetism effects lead to significant deviations from the standard Onsager relation, which manifests as a breakdown in scaling of Landau level orbits. These substantial magnetic responses emerge from the nontrivial quantum geometry of the electronic structure and the large length scale of the moiré lattice potential. We show that this breakdown of the original Onsager relation is unique in MQM due to the typical superlattice length scales in these systems. Going beyond traditional measurements, STM-based Landau level spectroscopy offers a complete “quantum ruler” resolving the full energy dependence of orbital magnetic properties in moiré quantum matter.

3:00pm **SS-WeA-3 Sub-Nanometer Resolved Single-Molecule Optical Imaging**, *Z. Dong,* University of Science and Technology of China; ***Shaowei Li***, University of California, San Diego **INVITED**

Aspirations for reaching atomic resolution with light have been a major force in shaping nano-optics, whereby a central challenge is to achieve highly localized optical fields. The plasmonic nanocavity defined by the coinage-metal tip and substrate in a scanning tunneling microscope (STM) can provide highly confined and dramatically enhanced electromagnetic fields upon proper plasmonic resonant tuning, which can modify both the excitation and emission of a single molecule inside the nanocavity and produce intriguing new optoelectronic phenomena. In this talk, I shall demonstrate two recent STM-based phenomena related to single-molecule optical spectroscopy. The first is single-molecule Raman scattering closely associated with molecular vibrations. The spatial resolution of tip enhanced Raman spectroscopy (TERS) has been further driven down to the Angstrom scale at the single-bond level. Such a capability not only yields a new methodology called scanning Raman picoscopy for structural reconstruction and tracking bond breaking and forming of surface reactions, but also enables to clarify the chemical enhancement mechanism in TERS through well-controlled local contact environments. The second phenomenon is single-molecule electroluminescence. Through managements over molecular quenching and energy level alignment, we demonstrate clear single-molecule electroluminescence and even single-photon emission. Furthermore, by precisely controlling intermolecular distances, we can not only demonstrate coherent dipole-dipole coupling in homodimers, but also reveal intriguing transitions from incoherent hopping-like Forster energy transfer to coherent wavelike electronic energy transfer in donor-acceptor heterodimers. In addition, the wavelike quantum-coherent transfer channel is found three times more efficient than the incoherent channel in a one-step transfer process, highlighting the advantage of coherent channels in electronic energy transfer processes in large molecular networks. Our results provide new routes to optical imaging, spectroscopy and engineering of light–matter interactions and intermolecular coupling at the sub-nanometer scale.

3:20pm **SS-WeA-4 Magnetic Resonance Imaging of Individual Organic Radicals with sub-Molecular Resolution Using a Scanning Tunneling Microscope**, ***Christopher Lutz***, *G. Czap,* IBM Almaden Research Center **INVITED**

Scanning tunneling microscopy (STM) gives atomic-resolution detection of properties such as the electronic density of states, spin polarization, and spin and vibrational excitations. Electron spin resonance (ESR) of individual atoms and small molecules has extended these capabilities to give very high energy resolution and quantum control, transforming individual adsorbed atoms into sensitive detectors of the local magnetic field. Here we present spin resonance of individual organic radical molecules adsorbed on an ultra-thin MgO film grown on a silver crystal. We find that several nearly-planar fluorenone derivatives become charged to anions upon adsorption on the insulating film. This spontaneous charging quenches the spin of the radicals, and transforms stable molecules into radical anions. These radicals are driven spin-resonantly by the radio-frequency electric field from the tip and sensed locally by magnetoresistance. We found a g-factor of nearly 2 for each species and visualized the delocalized unpaired electron in these molecules by magnetic resonance imaging. We used conventional Fe-terminated tips as well as halogen-functionalized Fe tips in a 1-Kelvin microscope. Potential applications include the investigation of coupled molecular spins and graphene nanoribbon edge states, and the transfer of a spin-resonant molecule to the microscope tip in order to provide a versatile scanning ESR sensor.

4:20pm **SS-WeA-7 Revealing the Local Band Structures of Sharp WS_2/MoS_2 Heterojunction and Graded $W_xMo_{1-x}S_2$ Alloy by Near-Field Optical Imaging**, ***Chi Chen***, Academia Sinica, Taiwan **INVITED**

With the development of various chemical vapor deposition (CVD) methods [1], many artificial 2D semiconductors have been synthesized, which increase the chances of forming disrupted interfaces and non-periodic or small-sized systems (defects and grain boundaries). All such systems create local electronic band structures within a finite scale, which cannot be readily explained by solid-state band theory nor be probed easily by confocal microscopes and macroscopic transport.

In this study, we investigated abrupt heterojunctions and graded alloys between two transition metal dichalcogenides (TMD), which involve non-periodic band structures and require high spatial resolution. We employed near-field photoluminescence (NF-PL) imaging to study the atomically sharp 1D interfaces between WS_2 and MoS_2. With an optical resolution of 68 nm, a 105 nm-wide region for quenched PL was confirmed using NF-PL imaging [2]. Our NF-PL imaging resolved the narrowest quenching width and sharpest strain mapping because of the superior spatial resolution and stability of our home-built SNOM [3].

We further developed a near-field broadband absorption (or transmittance, NF-tr) imaging method to overcome the limitations of NF-PL for low-quantum-yield materials. The NF-tr technique provides abbreviation-free and nanoscale-resolution imaging capability of the entire conduction band over highly lateral inhomogeneity. We utilized NF-tr microscopy to investigate the varying bandgap and bowing factor of a single-layered $W_xMo_{1-x}S_2$ alloy [4]. For the bilayer $W_xMo_{1-x}S_2$ alloy, the energy contour maps present the bandgap evolution in the alloy and reveal bilayer coupling between the top and bottom layers. We can conclude that the bottom layer has an alloy nature, whereas the top layer is composed of pure WS_2. High-spatial-resolution spectral capability is essential for analyzing compositional and location-dependent bandgap evolutions.

[1] K.-C. Chiu and Y.-H. Lee *et al., Adv. Mater.* 30, 1704796 (2018)
[2] H.-C. Chou and C. Chen *et al.,Nanoscale* 14, 6323 (2022)
[3] J.-R. Yu and C. Chen*et al.,Rev. Sci. Instrum.* 91, 073703 (2020)
[4] P.-W. Tang and C. Chen *et al.,ACS Nano*, 16, 5, 7503 (2022)

4:40pm **SS-WeA-8 On-Surface Chemical Dynamics Probed with Concurrent In Situ STM, Infrared Spectroscopy, and Supersonic Molecular Beams**, ***Steven Sibener***, *J. Wagner, R. Edel, T. Grabnic, S. Brown, J. Sayler, J. Brown,* University of Chicago **INVITED**

We have developed the capability to elucidate interfacial reaction dynamics using an arguably unique combination of supersonic molecular beams combined with in situ STM and AFM visualization. These capabilities have been implemented in order to reveal the complex spatio-temporal correlations that govern heterogeneous reactions at their most fundamental level spanning atomic, nano, and meso length-scales. For example, time-lapse visualization of reacting interfaces is allowing us to probe the reactivity of specific sites at interfaces and how the presence of a reacted site or local region influences the subsequent reaction probability at proximal sites. Such correlations are important in chemisorption, catalysis, materials oxidation and erosion, and film processing. This capability also opens up a new view for interfacial reaction dynamics where incident beam kinetic energy and angle of incidence can be used for reaction control parameters with outcomes such as site-specific reactivity, changes for overall time-evolving mechanisms, and where the on-surface fate of chemisorbed species can be definitively ascertained. In this work the time-evolving interface can be probed either in real-time or, for reactions occurring under extreme thermal conditions, using time-lapse sequential imagery. This presentation will give illustrative examples from our recent work on the atomic and multiscale oxidative reactivity of HOPG graphite, H reactivity with SAMs, atomic oxygen interactions with single and multilayer graphene including moiré superlattices, and the energy disposal and geometric endpoint for molecular nitrogen chemisorption on Ru. Most recently, the ability to visualize single-molecule nitrogen dissociation events provides a new approach for assessing the importance of adiabatic vs. non-adiabatic interactions in chemisorption by examining the rate of energy disposal and ultimate atomic resting adsorption sites for the dissociatively adsorbed atoms from each individual molecular scattering event. Taken together, these results provide a direct and information-rich complement to traditional gas-surface scattering experiments which monitor volatile products, especially with respect to uncovering the important on-surface chemical events that inform multiscale spatio-temporal correlations that influence interfacial reaction pathways.

5:00pm **SS-WeA-9 Unravelling the Mysteries of Water and Ice: A Journey Starting from Single Water Molecule***, **Ying Jiang**,* International Center for Quantum Materials, School of Physics, Peking University, China **INVITED**

Despite its ubiquity in nature, water is one of most complicated condensed matters. The understanding of water structure and phase transition is far from satisfactory, and many unusual properties of water remain as puzzles. The main reason arises from the many-body hydrogen (H)-bonding interaction between the water molecules. Moreover, the light H nuclei can exhibit prominent quantum effects, in terms of tunneling and zero-point motion. The so-called nuclear quantum effects (NQEs) add additional complexity to water and ice. Therefore, it would be ideal to directly access the degree of freedom of H in water/ice. To this end, we have steadily continued to improve accuracies of imaging and spectroscopic methods based on scanning probe microscopy (SPM) (tip-enhanced inelastic electron tunneling spectroscopy and higher-order electrostatic force microscopy) [1,2], which acquire unprecedentedly high sensitivity to the H of single water molecule in a nearly non-invasive manner. In this talk, I will showcase the application of those techniques to probe water clusters, ion hydrates, 2D ice and even bulk ice surface [3-6], with increasing complexity. The possibility of combing SPM with quantum sensing technology to perform nanoscale NMR measurement of protons in ambient water will be also briefly discussed [7].

References:

[1] Guo *et al*., Science 352, 321 (2016)
[2] Peng *et al*., Nature Communications 9, 122 (2018)
[3] Meng *et al*., Nature Physics 11, 235 (2015)
[4] Peng *et al*., Nature 557, 701 (2018)
[5] Ma *et al*., Nature 577, 60 (2020)
[6] Tian *et al*., Science 377, 315 (2022)
[7] Zheng *et al*., Nature Physics 18, 1317 (2022)

5:20pm **SS-WeA-10 Probing Chemistry at the Angstrom-Scale via Tip-Enhanced Raman Spectroscopy***, **Nan Jiang**,* University of illinois Chicago **INVITED**

The chemical interrogation of individual atomic adsorbates on a surface significantly contributes to understanding the atomic-scale processes behind on-surface reactions. However, it remains highly challenging for current imaging or spectroscopic methods to achieve such a high chemical spatial resolution. Tip-enhanced Raman spectroscopy (TERS), which couples scanning tunneling microscopy (STM) and surface-enhanced Raman spectroscopy, provides such a powerful capability to concurrently harvest topographic and chemical information with single-bond sensitivity at the angstrom-scale. Herein, we use ultrahigh vacuum (UHV) TERS to measure the angstrom-scale interfacial interactions of a vertical Van der Waals heterostructure of borophene with tetraphenyldibenzoperiflanthene (DBP) molecules. TERS reveals subtle ripples and compressive strains of the borophene lattice underneath the molecular layer. The induced interfacial strain is demonstrated to extend in borophene by ∼1 nm beyond the molecular region by virtue of 5 Å chemical spatial resolution. Furthermore, we use our method to probe the local chemical properties of oxidized borophene. The results show that single oxygen adatoms on borophene can be identified and mapped with ~4.8 Å spatial resolution and single bond (B–O) sensitivity. In addition to offering atomic-level insights into the above-mentioned systems, our studies demonstrate UHV-TERS as a powerful tool to probe the local chemistry of surface adsorbates and interfacial structures in the atomic regime with widespread utilities in heterogeneous catalysis, on-surface molecular engineering, and low-dimensional materials.

5:40pm **SS-WeA-11 Single Molecule Characterization of Cobalt Phthalocyanine Co$_2$ Reduction Catalysts***, X. Wang,* Yale University*; P. Zahl,* Brookhaven National Laboratory*; H. Wang, **Eric Altman**, U. Schwarz,* Yale University

Immobilized cobalt phthalocyanine (CoPc) derivatives have been identified as promising catalysts for CO_2 electroreduction to methanol. The support as well as side chains attached to CoPc have a large effect on the activity and selectivity to methanol. CO adsorption strength is considered a key descriptor for CO_2 reduction activity and selectivity. Therefore, we have begun to study CO interactions with individual supported CoPc molecules using scanning probe methods. This talk focuses on a combined scanning tunneling microscopy, non-contact atomic force microscopy, and Kelvin probe force microscopy characterization of CoPc molecules on Ag(111) with CO functionalized tips. In addition to resolving the atomic structure, the data provides the three-dimensional force field acting between the tethered CO and supported CoPc molecules and the charge distribution across the CoPc that is responsible for it. Analysis of the force field yielded maps of the catalytically relevant equilibrium potential energy between the tethered CO and specific locations within the CoPc molecule. Surprisingly, the maps show that the strongest interaction is not directly above the Co atom, but rather in four nodes surrounding it. The results are being compared with amino-substituted CoPc where the amino groups have been shown to enhance catalytic activity.

6:00pm **SS-WeA-12 Switching Chemical Bonds by Mechanical Load at Single Molecule Level via Qplus Atomic Force Microscope***, **A.M. Shashika D. Wijerathna**, M. Zirnheld,* Old Dominion University*; Z. Win,* City University of Hong Kong, Hong Kong Special Administrative Region of China*; Y. Li,* Center for Nanoscale Materials, Argonne National Laboratory*; R. Zhang,* City University of Hong Kong, Hong Kong Special Administrative Region of China*; S. Hla,* Center for Nanoscale Materials, Argonne National Laboratory*; Y. Zhang,* Old Dominion University

Switching Chemical Bonds by Mechanical Load at Single Molecule Level via Qplus Atomic Force Microscope

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Abstract: Mechanical properties of molecules adsorbed on materials surfaces are increasingly vital for the applications of molecular thin films. Here, we induce molecule conformational change by switching chemical bonds on a single molecule by mechanical load, and quantify the force and energy required for such switch via a low temperature (~ 5K) Scanning Tunneling Microscope (STM) and Qplus Atomic Force Microscope (Q+AFM). Molecule TBrPP-Co (a cobalt porphyrin) deposited on an atomically clean gold substrate typically has two of its pentagon rings tilted upward and the other two downward. An atomically sharp tip of the STM/Q+AFM, which vibrates with a high frequency (~ 30kHz), is employed to run over single TBrPP-Co molecule at different heights with 0.1Å as increment and meanwhile to record tip-molecule interaction strength in the form of tip frequency change. When tip approaches to the threshold distance to the molecule, mechanical load by the tip becomes large enough to switch chemical bonds of the molecule and cause pentagon rings flip their direction. Due to the sensitive nature of tip-molecule interaction, the rings flipping can be directly visualized by STM, as rings tilting upward exhibit two bright protrusions in contrast to rings downward in image. By processing frequency change, we obtain a three-dimensional mechanical potential and force map for the single molecule TBrPP-Co with the resolution of angstrom level in three dimensions. Our preliminary results indicate that an energy barrier of ~67meV for switching between covalent and coordinated bonds to cause rings flipping of TBrPP-Co.

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