Leaders in Energy and the Environment Focus Topic
Room On Demand - Session LD-Invited On Demand

Leaders in Energy and the Environment Invited On Demand Session

LD-Invited On Demand-1 Atomic-Scale Imaging of Optically-Active Nanoscale Systems*, Jeffrey R. Guest,* Argonne National Laboratory **INVITED**

Optical interactions and photophysical processes hinge on structure and the local environment in nanoscale systems, it is critically important to develop experimental approaches which can characterize these optical properties and correlate them with atomic-scale morphology and electronic structure. Over the past three decades, ultra-high vacuum (UHV) scanning tunneling microscopy/spectroscopy (STM/STS) and associated surface preparation techniques have demonstrated atomic-scale control over nanoscale structures.In parallel, single-particle laser spectroscopy has elucidated photophysics, quantum coherence, and optical properties with ultrahigh spectral resolution at the single quantum absorber and emitter level.

In this talk, I will focus on our efforts to extend these studies to the atomic scale on surfaces by combining UHV STM and single particle laser spectroscopy. I will discuss our work exploring the structural, electronic, and transport properties of donor-acceptor molecular heterojunctions (HJs) self-assembled from C60 and pentacene as a potential platform for exploring photophysics at the molecular scale. We have resolved a surprising structure and charge transfer in in-plane molecular HJs [1], and demonstrated extremely strong (and spatially dependent) current rectification in transport for a stacked molecular HJ at the monolayer level [2].I will discuss recent STM/STS measurements on defects in bilayer WSe_2, which may be related to the single-photon emitting defects observed in laser spectroscopy experiments, revealing the local electronic structure and demonstrate the ability to control the charge state of these defects [3]. Time permitting, I will discuss UHV STM measurements on Cu2O (111) and (110) surfaces and our efforts to understand their physical and electronic structure in light of their photocatalytic activity [4].

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1. J. A. Smerdon *et al.,* ACS Nano 7, 3086 (2013).
2. J. A. Smerdon *et al.,* Nano Letters 16, 2603 (2016).
3. R. Zhang *et al*., J. Phys. Chem. C, *in press.*
4. R. Zhang *et al.,* Phys. Chem. Chem. Phys*,* 20, 27456 (2018).

LD-Invited On Demand-7 Probing Molecule-Substrate Interactions at Angstrom Scale by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy*, Nan Jiang,* University of Illinois at Chicago **INVITED**

To demonstrate the effect of local environments on complex chemical systems, we designed a series of tip-enhanced Raman spectroscopy (TERS) experiments to study molecule-substrate interactions at angstrom scale. We chose subphthalocyanine molecules deposited on a Ag(100) surface as an example of weak interactions between the molecules and the substrate. We were able to ascertain subtle vibrational modes which showed an excellent agreement between experimental spectra and simulated Raman spectra of gas phase molecules. In another case, a strong interaction with the surroundings leads to symmetry breaking, allowing us to separately detect intermolecular interactions such as electrostatic attractions by using TERS. In combination with theory, we revealed the lifting of vibrational degeneracy inside a molecular self-assembly due to strong lateral intermolecular interactions. To address the inability of scanning tunneling microscopy (STM) to study the configurations of adsorbed non-planar molecules on surfaces, we used TERS to unambiguously determine the tilt or orientation of molecules on a surface. Due to the selection rules for TERS, vibrational modes that are perpendicular to the surface and parallel to the tip and enhanced EM field are the most strongly enhanced. Since TERS spectra rely upon molecular orientation, we identified multiple orientations of rubrene on a Ag(100) surface. The sensitivity of TERS to molecular orientation combined with our 5.5 angstrom spatial resolution demonstrates a unique analytical technique for similar non-planar molecules. We also reported the first demonstration of STM-TERS towards the study of isomeric nonplanar adsorbates on three different well-defined substrates, Ag(100), Cu(100) and Au(100). We demonstrated the effects of surface interactions on the vibrational modes of molecules, indicating that the substrate is an intriguing parameter to manipulate the self-assembly and configurations of ad-molecules. Together, our work allows the definitive identification of multiple orientations of individual molecules and their dependence upon highly localized chemical environments.

LD-Invited On Demand-13 HAXPES for Device Applications: From the Surface into the Bulk*, Anna Regoutz,* University College London, UK **INVITED**

X-ray photoelectron spectroscopy (XPS) is based on the photoelectric effect discovered and described by Planck, Einstein and Millikan, and has its beginnings in the ground breaking work of Kai Siegbahn, who received the Nobel Prize in Physics in 1981 for the development of the technique. XPS can non-destructively probe the chemical composition, local chemical environments, and electronic structure of matter, and since its invention it has been applied to a vast range of materials, including solids, liquids, and gases. The most common variety of XPS uses soft X-ray sources, e.g. Al Kα at 1.5 keV, giving extremely surface sensitive results probing only the first few nanometres of a sample’s surface.

Hard X-ray excitation sources with energies of up to 10 keV extend the probing capabilities of XPS beyond the outermost surface of materials by enabling photoelectrons from much deeper regions to be detected. Hard X-ray photoelectron spectroscopy (HAXPES) delivers much greater probing depths of tens of nanometres enabling the characterisation of buried layers and interfaces in structured materials, e.g. thin film stacks and core-shell nanoparticles, as well as bulk characteristics of homogeneous samples. Like XPS, HAXPES enables the study of both chemical states and electronic structure. Over the last decade the development of advanced beamlines at synchrotrons in parallel with the advent of laboratory-based spectrometers has opened up HAXPES for a much wider range of materials and applications.

This talk will give an introduction to the general capabilities of HAXPES. It will provide an overview of the additional challenges and opportunities that HAXPES presents and will cover recent developments and results of this emerging technique.

LD-Invited On Demand-19 Nanoparticle Size, Shape, Composition and Support Effects in the Hydrogenation of Carbon Dioxide*, Beatriz Roldan Cuenya,* Fritz-Haber Institute of the Max Planck Society, Germany **INVITED**

The selective hydrogenation of CO_2 to methanol and high-order hydrocarbons is a promising process for establishing a methanol economy and recycling CO_2. Although for the methanol synthesis there is a well-established industrial process based on a $Cu/ZnO/Al_2O_3$ catalyst, open questions still remain relative to the reaction mechanism and the active phases involved. The same applies to the “modified” Fischer-Tropsch process commonly catalyzed by Fe-based materials where the oxidation state of the active catalyst and the possible formation of carbide species is debated.

Since these reactions are catalyzed by nanostructured materials, tailoring their chemical reactivity at the atomic level will be the challenge to address. In order to accomplish this, we must first obtain a fundamental understanding of the structural and chemical properties of complex nanoscale systems. In addition, the dynamic nature of the nanoparticle (NP) catalysts and their response to the environment must be taken into consideration. To address the complexity of real-world nanocatalysts, a synergistic approach taking advantage of a variety of cutting-edge experimental methods (AFM, TEM, TPD, NAP-XPS, XAFS, MS/GC) has been undertaken.

Catalytically active size- and shape-controlled NPs (Fe, Cu, Cu-Zn, Cu-Ni, Cu-Ga) will be synthesized via colloidal chemistry and compared to model NP systems synthesized via physical vapor deposition. Structure/composition-reactivity correlations *in situ* and under realistic *operando* reaction conditions, i.e., at high pressure will be investigated. In particular, the role of the NP size, shape (spherical vs cubic NPs), surface composition (alloy, core-shell) and support (ZnO, Al_2O_3, ZnOAl, SiO_2, ZrO_2) in the activity and selectivity will be addressed. Our results are expected to provide the required fundamental understanding that might lead to new routes for the reutilization of CO_2 through its direct and selective conversion into valuable chemicals such as methanol or high order hydrocarbons.

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