

Tuesday Afternoon, October 19, 2010

Surface Science

Room: Picuris - Session SS-TuA

Chemical Dynamics at Surfaces

Moderator: I. Harrison, University of Virginia

2:00pm **SS-TuA1 Gently Lifting Gold's Herringbone Reconstruction by Tuning Adsorbate Chemistry**, A.D. Jewell, E.C.H. Sykes, Tufts University

Recently it was discovered that the structure of the molecule-metal interface in alkane thiol-based self-assembled monolayers (SAMs) is more complex than first believed. Thiols have been shown not only to lift the herringbone reconstruction of Au(111) but remove a significant fraction of the Au surface atoms. The etch pits formed by these vacancies are thought to be one of the weakest areas of the SAM films in terms of susceptibility to and degradation by oxidizing species.

In an effort to slightly weaken the molecule-metal interaction and prevent the formation of etch pits, we have chosen to study the interaction and assembly of trimethylphosphine (PMe₃) on Au(111) using a scanning tunneling microscope (STM). This is to our knowledge the first atomic-scale characterization of a phosphine species adsorbed on a metal surface.

At full monolayer coverage PMe₃, the molecules formed a hexagonally packed layer which exhibited a ($\sqrt{7} \times \sqrt{7}$)R19° unit cell. The interaction between PMe₃ and Au caused Au atoms to be ejected from the herringbone reconstruction, but not the substrate surface itself (as in the thiol case) and led to the formation of small Au islands. This effect manifested in the herringbone spacing increasing from that of native gold (6.33 nm) to 11.2 ± 0.9 nm. As this system was exposed to various annealing treatments, a fraction of the molecules desorbed, the Au islands coalesced, and the herringbones disappeared entirely, indicating that the underlying Au surface adopted a 1 x 1 reconstruction. The data indicate that the PMe₃/Au island formation is a kinetically limited process.

Finally, we have developed a mathematical equation that gives the theoretical island coverage (q) as a function of the maximum island coverage (q_{max}), the native herringbone spacing (x_0) and the experimental herringbone spacing (x): $q = q_{\text{max}}(1 - x_0/x)$. This should be useful in future studies of many types of SAMs on Au(111), or any similarly reconstructed surface.

2:20pm **SS-TuA2 Tunneling and Guidance in the Diffusion of Polyatomic Molecules at a Metal Surface**, Z.H. Cheng, E. Chu, D.Z. Sun, D.H. Kim, Y.M. Zhu, M. Luo, G. Pawin, K.L. Wong, K.-Y. Kwon, R. Carp, M. Marsella, L. Bartels, University of California at Riverside

Pentacene derivatives that have two and four carbonyl groups attached to them diffuse on a Cu(111) surface in a uniaxial fashion, i.e. exclusively along a substrate atomic row, despite the threefold symmetry of the substrate. In this, they resemble the behavior of dithioanthracene and anthraquinone, previously dubbed "molecular walkers", which move across Cu(111) sequentially stepping the thiol/carbonyl linkers on each side of the molecule. This poses the question of how a fourfold substituted, i.e. quadrupedal, molecule can accomplish uniaxial motion: will it move its substrate linkers on opposite ends of the molecule at the same time resembling the gait of trotting, or will it instead move both linkers on one side at the same time, resembling the gait of pacing? Density functional theory (DFT) suggests the latter. Variable temperature scanning tunneling microscopy (STM) monitoring of the molecular motion reveals a striking difference between the diffusion prefactors of the quadrupedal and bipedal species, with the latter being very low. Wentzel Kramers Brillouin-based modeling of the motion of the substrate linkers in the calculated diffusion barriers suggest that the origin of this discrepancy lies in the relevance of the tunneling of the substrate linkers, allowing bipedal species, which only need to move one substrate linker at a time, to accomplish motion through tunneling of the linker, whereas quadrupedal species, whose diffusion requires concerted motion of two substrate linkers, cannot move in this way, resulting in significantly higher diffusion temperatures.

2:40pm **SS-TuA3 Scanning Tunneling/Atomic Force Microscopy of Individual Atoms/Molecules on Insulating Films**, G. Meyer, L. Gross, F. Mohn, N. Moll, IBM Zurich Research Laboratory, Switzerland, P. Liljeroth, Utrecht University, Netherlands, J. Repp, University Regensburg, Germany
INVITED

Ultrathin insulating films on metal substrates are unique systems to use the scanning tunneling / atomic force microscope to study the electronic and structural properties of single atoms and molecules, which are electronically decoupled from the metallic substrate. Individual gold atoms on an ultrathin insulating sodium chloride film supported by a copper surface exhibit two different charge states, which are stabilized by the large ionic polarizability of the film [1]. The charge state and associated physical and chemical properties such as diffusion can be controlled by adding or removing a single electron to or from the adatom with a scanning tunneling microscope tip. The simple physical mechanism behind the charge bistability in this case suggests that this is a common phenomenon for adsorbates on polar insulating films. Employing a low temperature tuning fork AFM the different charge states can be observed directly in the force signal [2]. In the case of STM of molecules on ultrathin insulating films the electronic decoupling allows the direct imaging and manipulation of molecular orbitals [3]. As we have recently demonstrated detailed structural information can be attained by Atomic Force Microscopy which leads to the direct imaging of the molecular geometry. I.e. the complete chemical structure of single molecules can be accessed in scanning probe microscopy [4].

1. J. Repp, G. Meyer, F.E. Olsson, M. Persson, 'Controlling the Charge State of Individual Gold Adatoms', *Science* 305, 493 (2004)
2. L. Gross, F. Mohn, P. Liljeroth, J. Repp, F. J. Giessibl, G. Meyer, "Measuring the Charge State of an Adatom with Noncontact Atomic Force Microscopy" *Science*, 324, 1428-1431 (2009)
3. P. Liljeroth, J. Repp, G. Meyer, Current-Induced Hydrogen Tautomerization and Conductance Switching of Naphthalocyanine Molecules *Science*, 317, 1203-1206 (2007)
4. L. Gross, F. Mohn, N. Moll, P. Liljeroth, G. Meyer 'The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy', *Science*, 325, 1110-1114 (2009)

4:00pm **SS-TuA7 STM Tip Induced Chemistry of Anthracene Derivatives on TiO₂(110)**, D.V. Potapenko, R.M. Osgood, Columbia University

Surface chemistry in photocatalysis is driven by the charge carriers that are created in the bulk of the catalyst and then are transferred to the adsorbed molecules. Both electrons and holes can be injected into molecules from the scanning tunneling microscope tip thus allowing mechanistic studies of photocatalytic processes on a single-molecule basis. We have studied adsorption and tip-induced surface chemistry of anthracene, as well as a number of anthracene derivatives on the TiO₂(110) surface. These molecules form ordered monolayers on the surface at room temperature with their structure dictated by the surface-charge distribution on TiO₂(110). Passing the electric current pulses from the STM tip into molecules causes dissociation and in some cases desorption of the molecules as indicated by the changes in the STM images. Halogenated organic molecules were especially susceptible to electron-induced dissociation with an energy threshold of ~ 2.5 eV. We report on the conditions of the tip-induced chemistry and propose a mechanism for the observed phenomena.

4:20pm **SS-TuA8 A New Mechanism of Atomic Manipulation: Bond-Selective Molecular Dissociation via Thermally Activated Electron Attachment**, S. Sakulsermsuk, P.A. Sloan, R.E. Palmer, University of Birmingham, UK

We report a new mechanism of (bond-selective) atomic manipulation in the scanning tunneling microscope (STM). We demonstrate a channel for one-electron induced C-Cl bond dissociation in chlorobenzene molecules chemisorbed on the Si(111)-7x7 surface, at room temperature and above, which is thermally activated. We find an Arrhenius thermal energy barrier to one-electron dissociation of 0.8 ± 0.2 eV, which we correlate explicitly with the barrier between chemisorbed and physisorbed precursor states of the molecule. Thermal excitation promotes the target molecule from a state where one-electron dissociation is suppressed to a transient state where efficient one-electron dissociation, analogous to the gas phase negative ion resonance process, occurs. We expect the mechanism will obtain in many

surface systems, and not just in STM manipulation, but in photon and electron beam stimulated (selective) chemistry.

4:40pm **SS-TuA9 State-Resolved Molecular Beam Reflectivity Measurements of Methane Activation on Ni(111)**, *N. Chen, Y. Huang, V. Campbell, A. Utz*, Tufts University

5:00pm **SS-TuA10 Dynamical Heterogeneity in Surface Reactions**, *A. Utz, D.R. Killelea, V. Campbell, N. Chen*, Tufts University

The rates and pathways of energy flow within the reagent-surface complex play central roles in determining whether or not a given molecule will react during its encounter with the surface. State-resolved experimental studies, in combination with dynamical calculations, are beginning to paint a detailed picture of these energy flow dynamics, particularly for the model system of methane's dissociative chemisorption on low-index Ni surfaces. Four key features of the reaction dynamics have emerged. First, the barrier to reaction can depend very sensitively on bond lengths and bond angles in the reaction complex; second, vibrational motions and their phase can modulate transition state access and the resulting energy threshold for reaction; third, such motion can be slow relative to the duration of the reagent-surface encounter; and fourth, the extent of vibrational energy flow and redistribution within the reaction complex can range from very limited to significant depending on the details for the reactive system.

We will present a conceptual framework for understanding and predicting general energy flow propensities for surface reactions. State-resolved experimental measurements, including prior examples of mode- and bond-selective surface chemistry and very recent results that explore the generality of these results for a broader range of chemical systems, will illustrate these principles. We will also include data that clearly show the ability of surface phonon excitation to modulate the energy threshold for reaction and that support recent theoretical predictions. The data point to a significant role for surface atom displacement in promoting methane activation under thermal conditions. Taken together, these studies show that the dynamical vibrational motion of reagent and substrate and the relative phase of these motions for a particular encounter can modulate the energy threshold for reaction and introduce significant energetic heterogeneity at the single molecule level.

5:20pm **SS-TuA11 Adsorbate Distribution and Dynamics inside Nanometer-Scale Metal Facets**, *J. Wyrick, Z.H. Cheng, M. Luo, D.Z. Sun, D.H. Kim, Y.M. Zhu, W.H. Lu*, University of California at Riverside, *K. Kim, T.L. Einstein*, University of Maryland, *L. Bartels*, University of California at Riverside

We use low temperature scanning tunneling microscopy to investigate the diffusion and arrangement of CO molecules adsorbed on Cu(111) facets of ~4 nm diameter formed by self-assembly of a honeycomb network of anthraquinone molecules. CO molecules and adlayers exhibit properties under such nanoscale confinement that markedly depart from those of extended adlayers: a) the confinement stabilizes dislocation lines (anti-phase domain boundaries) in the adlayer that affect roughly 1/4 of the adsorbed molecules; b) confinement prevents the formation of dense islands of adsorbed molecules, depending on coverage either causing dispersion of vacancies in the adlayer or preventing the growth of molecular islands; c) at a coverage of just a few molecules on the facet, we observe that a molecular shell structure is formed, resembling in its underlying mathematics the atomic model. Confined structures are an ideal test bed for measurement of the coverage dependence of molecular diffusion and in this study we find a reduction of the diffusion barrier at a slope of 57%/ML.

5:40pm **SS-TuA12 Ab Initio Calculations of the Preexponential Factor for the Diffusion of CO on Ag(001): The Importance of Inclusion of the Full Phonon Dispersion**, *M. Alcántara Ortigoza, T.S. Rahman*, University of Central Florida, *K.P. Bohnen, R. Heid*, Karlsruhe Institute of Technology, Germany

Knowledge of factors that determine the diffusivity of CO on catalytic surfaces is of utmost importance for understanding why some surfaces render higher reaction rates (e.g. CO oxidation) than others. A rigorous calculation of the diffusion prefactor is not only the first approximation one should target to analyze diffusivity but also a prerequisite to adequately take into account dissipative anharmonic processes since calculation of both the prefactor and anharmonic processes rates require the full dispersion of all phonons in the system as input information. In this work, we obtain from first principles calculations the diffusion path of CO on Ag(001), the corresponding energy barrier, diffusion prefactors, and diffusion rate. The latter have been calculated via the total phonon density of states in the surface Brillouin zone from density functional perturbation theory calculations. Comparison of the results for the prefactors obtained using the full phonon dispersion curve with those confined only to the adsorbate modes on a frozen substrate point to significant differences and to the

importance of having a knowledge of the full vibrational dynamics of the system, particularly at (low) temperatures which are relevant to experimental measurements.

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