Surface Science
Room 210B - Session SS1-MoM

Electronic Structure and Excitations
Moderator: P.S. Weiss, The Pennsylvania State University

8:20am **SS1-MoM1 Electronic Stablization of Nanophase Separation Along Si Atomic Chains***, **J.L. McChesney**[1],* University of Wisconsin*; J.N. Crain,* NIST*; V. Perez-Dieste, F. Zheng,* University of Wisconsin*; M.C. Gallagher,* Lakehead University, Canada*; F.J. Himpsel,* University of Wisconsin

One-dimensional surface structures have received a great deal of interest both for probing the fundamental physics phenomena of low-dimensions and for applications in nano-electronics. The Si(111)5x2-Au surface exhibits one-dimensional tracks with extra Si atoms on top, which have been used to demonstrate an atomic scale memory [1] and to probe the limits of storage density by studying the effects of inter-atomic coupling [2]. Atomic-interactions play a vital role in the determination of the electronic structure and vice versa. In an effort to elucidate this connection we used angle-resolved photoemission spectroscopy to probe the relevant electronic states in the vicinity of the Fermi level EF [3]. They are located at the zone boundaries of a 5x4 unit cell which explains the 5x4 periodicity of the inter-atomic potential [2]. This corresponds to the preferred spacing of the Si adatoms while the optimum chain doping would correspond to a 5x8 arrangement of the Si adatoms [4]. We propose that the nanoscale phase separation of this surface [5] into semiconducting 5x4 and metallic 5x2 sections is a way to accommodate these conflicting requirements. 1. R. Bennnewitz et.al., Nanotech. 13, 499 (2002). 2. A. Kirakosian et.al., Phys. Rev. B. 67, 205412 (2003). 3. J. L. McChesney et.al., submitted to Phys. Rev. B. 4. S. C. Erwin, Phys. Rev. Lett. 91, 206101 (2003). 5. H. S. Yoon et.al., Phys. Rev. Lett 92,096801 (2004). @FootnoteText@ .

8:40am **SS1-MoM2 The Hammett Equation in Single Molecule Chemistry: Probing a Linear Free Energy Relationship One Molecule at a Time***, B.V. Rao, K.-Y. Kwon, A. Liu, **L. Bartels**,* University of California, Riverside

Selective addressal of specific chemical bonds inside a molecule is at the heart of modern chemistry. With the advent of low-temperature scanning tunneling microscopy (STM), specific bonds of individual molecules became accessible in a controlled manner. Here we present how this technique may be applied to the study of a fundamental pillar of physical organic chemistry, the Hammett Equation, one molecule at a time. Thiophenol and its halo/alkyl-substituted derivates adsorb on Cu(111) at 15K in a horizontal fashion leaving the thiol (-SH) group intact. Excitation by electrons of several hundred meV energy from an STM tip can induce selective dissociation of the SH-bond. This process is confirmed by STM-based vibrational spectroscopy of the S-H stretch mode. We measured the rate of electron-stimulated hydrogen abstraction for p-Fluoro-, p-Chloro-, p-Bromo-, p- Methyl-, m-Fluoro-, and m-Chloro-Thiophenol as well as for the unsubstituted species. The observed dehydrogenation rates follow the @sigma@-values of the Hammett equation, which were derived by pKs measurements on solutions of substituted benzoic acids 70 years ago. The positive @rho@ value of our measurements of 1.4 corresponds qualitatively to the solution phase value for thiophenols suggesting that a negatively-charged transition state is at the core of the STM-based hydrogen abstraction mechanism.

9:00am **SS1-MoM3 Benzene on Au{111} at 4 K: Observation of Molecular Cascades and Substrate-Mediated Interactions***, **P. Han**[2], E.C.H. Sykes, B.A. Mantooth, Z.J. Donhauser, P.S. Weiss,* The Pennsylvania State University

The role of the surface electronic structure was previously shown to have important implications on the long-range intermolecular interactions, molecular alignment and dynamics through substrate-mediated interactions (SMI) [1]. To date, attempts at quantifying SMI using scanning tunneling microscopy (STM) involve statistical measurements of STM images of static systems [2]. Here we present the study of benzene monolayer growth on a Au{111} surface using low temperature STM at 4 K. In this study, the tip-induced motion in the benzene overlayer was observed with 600 time-lapse STM images and it allowed us to statistically quantify the forces involved in SMI from a kinetic stand point. These estimates helped us explain the kinetics of the benzene motion, as well as the thermodynamics that determine the packing structure over the various regions of the reconstructed Au{111} surface. We also report the observation of tip-induced molecular cascade motion, and demonstrate that this observed motion is concerted in nature, not a result of individual random movements [3]. @FootnoteText@ [1] E. C. H. Sykes, P. Han, S. A. Kandel, K. F. Kelly, G. S. McCarty, and P. S. Weiss, Accounts Chem. Res. 36 (12), 945 (2003). [2] J. Repp, F. Moresco, G. Meyer, K. H. Rieder, P. Hyldgaard, and M. Persson, Phys. Rev. Lett. 85 (14), 2981 (2000); N. Knorr, H. Brune, M. Epple, A. Hirstein, M. A. Schneider, and K. Kern, Phys. Rev. B 65 (11) (2002). [3] P. Han, B. A. Mantooth, E. C. H. Sykes, Z. J. Donhauser, and P. S. Weiss, Accepted for publication by J. Am. Chem. Soc; E. C. H. Sykes, B. A. Mantooth, P. Han, Z. J. Donhauser, and P. S. Weiss, in preparation for J. Am. Chem. Soc.

9:20am **SS1-MoM4 Listening to Atom Dynamics During Atomic Manipulation***, **J.A. Stroscio**, R.J. Celotta,* National Institute of Standards and Technology

The physics of atomic manipulation with the scanning tunneling microscope (STM) involves many processes that depend on the tip-adatom interaction. We discuss our work on using atom manipulation imaging and the noise characteristics of the tunneling current as probes of the physics of the atomic manipulation process. By scanning a single Co atom across a Cu(111) surface, along the same path we would use to image the Cu surface, we can obtain a highly detailed image, showing three distinctly different atom binding sites. If the Co atom is positioned over an hcp site, dynamic behavior is observed both in the STM image and the tunneling current. The site dependent noise in the tunneling current is in the audio range and can be heard as the atom is dragged over the surface. We show that this dynamic behavior corresponds to state fluctuations of the Co atom; the Co hops between the hcp site and adjacent fcc sites. This occurs by the creation of an ideal, tunable, multi-well potential by the tip-adatom interaction. An ideal double-well potential can be created by positioning the Co atom slightly off the hcp site. Two-state transfer rates between the hcp and fcc sites are obtained by measuring the distribution of residence times in each state. The transfer rates show two distinct regimes. A transfer rate independent of tunneling current, voltage and temperature that is ascribed to quantum tunneling between the two wells, followed by a transfer rate with a strong power law dependence on current or voltage, indicative of vibrational heating. The role of these effects in atomic manipulation applications will be discussed.

9:40am **SS1-MoM5 Electronic Structure and Excitations at the Atomic Scale***, **W. Ho**,* University of California, Irvine **INVITED**

This talk will highlight the use of scanning tunneling microscopes (STM) to measure the electronic structure and elementary excitations at solid surfaces. The unique capabilities of the STM enable these measurements to be carried out with atomic resolution on single atoms, molecules, and nanostructures on solid surfaces. Electronic, vibrational, vibronic, plasmonic, and magnetic excitations will be discussed. These results provide a fundamental understanding of nanoscale properties and phenomena.

10:20am **SS1-MoM7 Quantum Well States in Thin Films of Pb on Si(111)***, **J.H. Dil**, J.W. Kim,* Fritz-Haber-Institute der MPG, Germany*; A. Mans, A.R.H.F. Ettema,* Delft University of Technology, The Netherlands*; K. Horn,* Fritz-Haber-Institute der MPG, Germany

The Pb/Si(111) system shows a rich variety of interesting physical properties and phenomena, such as the magic height of islands, vertical Friedel oscillations @footnote 1@, a competition between classical and quantum mechanical effects in the shape relaxation @footnote 2@, anomalous optical absorption @footnote 3@ and an anomalous behaviour in the Hall effect as a function of thickness. Hence it is important to study the electronic structure of thin Pb films on Si(111) with a view to understanding the origin of these phenomena. Photoemission experiments carried out at the synchrotron radiation facilities of MAX-lab in Lund (Sweden) and BESSY in Berlin, from a large range of film thicknesses prepared under different conditions exhibit clear signatures of 2 D quantum well states. Their energy dispersion with parallel electron momentum show an anomalously large in-plane effective mass of the 2D quantum well state bands, with the highest effective masses for states near the Fermi level. This contrasts with effective masses of the bulk bands from which these states are derived, and with similar data from the Pb/Cu(111) system @footnote 4@; also, band structure calculations for bulk and thin film slabs predict bands with predominantly free electron character. Our analysis suggests that this phenomenon may be due to a strong electron correlation effect in the 2D bands of the Pb quantum well states. @FootnoteText@ @footnote 1@ W.B. Jian, W.B. Su, C.S. Chang, T.T.Tsong, Phys.Rev.Lett.90, 6603 (2003). @footnote 2@ H. Okamoto, D. Chen, T.

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[1] **Morton S. Traum Award Finalist**

[2] **Morton S. Traum Award Finalist**

Yamada , Physical Review Letters 89, 6101 (2002). @footnote 3@ M. Jalochowski et al., Physical Review B 66, 205417 (2002). @footnote 4@ J.H. Dil, J.W. Kim, S. Gokhale, M. Tallarida, K. Horn, PRB, in press.

10:40am **SS1-MoM8 Newns-Anderson Model for Chemicurrents***, **S. Holloway**,* University of Liverpool, UK*; D. Bird, M. Mizielinski,* University of Bath, UK*; M. Persson,* Chalmers University of Technology, Sweden

The excitation of electron-hole pairs when a reactive species adsorbs on a surface should invariably be expected but it has proved difficult to quantify the strength of the process. We have performed first principles calculations for the interaction of a hydrogen atom with a Cu surface to investigate the chemicurrent induced. This calculation involves calculating the electronic response to the adsorbate motion and then using a forced oscillator description for the energy dissipation. Results will be presented for hydrogen and deuterium and comparison made with recent experiments. The numerical results are consistent with values derived from experiment for the H-Cu system. Application of the standard spin-polarised DFT approach results in a phase transition that occurs as the resonance intercepts the Fermi level. This, in turn, gives rise to an infinitely strong dissipative force above the metal which results in unphysical dynamics even before the atom encounters the adsorption well. The origin of the problem has been traced back to the nearly adiabatic assumption that is made in the standard application of time dependent DFT to electronic friction. In this present work, we deploy the Newns-Anderson description and show that this rather unexpected behaviour can be quite straightforwardly understood. Furthermore, we present for the first time, results for the chemicurrent using a new theoretical approach based on the time-dependent Newns-Anderson model.

11:00am **SS1-MoM9 Direct Observation of Electron Emission from a Metal Surface Due to Scattering of Vibrationally Excited Molecules***, **J.D. White**, J. Chen, D. Matsiev,* University of California, Santa Barbara*; D.J. Auerbach,* Hitachi Global Storage Technologies*; A.M. Wodtke,* University of California, Santa Barbara

We report the observation of electron emission from low work function metal surfaces due to the scattering of highly vibrationally excited nitric oxide (NO) molecules. Using Stimulated Emission Pumping (SEP) and Franck Condon Pumping (FCP), we prepare NO in vibrational states ranging from v=1 to v=18. SEP allows us to control explicitly the final vibrational state (from v=4 to v=18) while FCP allows us to prepare a range of states (dependent on the Franck Condon Factors) from v=0 to v=5 in the Electronic Ground State. These molecules are then scattered off of a low work function surface (~1.3 - 1.6 eV), in our case submonolayer cesium on gold, and the emitted electrons are detected with a Multi Channel Plate assembly. Our experiments indicate that the observed particles are indeed electrons which are promptly emitted after collision of the vibrationally excited NO with the surface. Vibrational energy dependence experiments suggest a threshold for emission at roughly the work function of the surface. The maximum efficiency we have measured is approximately 0.02 electrons per molecule. Possible mechanisms for vibrationally induced electron emission are discussed. Our results are very important in determining the limitations of using the Born Oppenheimer Approximation (BOA) to model highly excited gas-surface reaction dynamics. The transition state for molecular dissociation very likely involves molecules stretched to large bond distances, which can be approximated by highly vibrationally excited molecules. Experiments along this vein will help to determine how accurate it is to use the BOA for modeling these systems.

11:20am **SS1-MoM10 Co-Adsorption of Polar Molecules with SF@sub6@ on Ru(0001): Effect on Adsorption Geometry, Ion Yields and Electron-Mediated Chemistry***, **D.O. Kusmierek**, N.S. Faradzhev, T.E. Madey,* Rutgers, the State University of New Jersey

SF@sub6@ is widely used as an electron scavenger for high voltage applications, and is a potent greenhouse gas; the electron-induced reactivity of gaseous and condensed SF@sub6@ is an environmentally important issue. The present work focuses on the effect of polar co-adsorbates H@sub2@O and NH@sub3@ on (1) adsorption geometry of SF@sub6@ on Ru(0001) at 25K, (2) formation and desorption probabilities of ions (F@super+@, F@super-@,) generated by electron stimulated desorption (ESD) of SF@sub6@, passing through condensed overlayers, and (3) chemical reactions activated by low-energy electrons. Electron stimulated desorption ion angular distribution (ESDIAD) and temperature programmed desorption (TPD) reveal predominantly molecular adsorption of SF@sub6@ on Ru(0001) via three F atoms, with the other three pointing away from the surface. Deposition of a polar molecule overlayer leads to changes in both intensities and trajectories of desorbing F@super+@ and F@super-@ ions. Low-energy electron-irradiation of SF@sub6@ films causes a step-wise decomposition of the molecules, and new chemical species are detected for electron-irradiated SF@sub6@ adsorbed on water (ice) surface. Analysis of the angular distributions of F@super+@ and F@super-@ as a function of temperature, co-adsorbate coverage and electron irradiation, in conjunction with TPD data, give insight into the structure of the molecular film, the ESD mechanisms, the ion/molecule scattering processes and the radiation chemistry observed here.

11:40am **SS1-MoM11 Spin-Resolved Plasmon Dispersion of Gd(0001)***, **H.-K. Jeong**, D.S. Wisbey, P.A. Dowben,* University of Nebraska-Lincoln

The spin-resolved plasmon dispersion, Ep(k//), of Gd(0001) on Mo(112) was investigated using spin-polarized electron energy loss spectroscopy. In spin polarized electron spectroscopy, the spin majority band structure of Gd(0001) exhibits different electron-phonon coupling than spin minority. There is some modest indirect evidence from the effective higher Debye temperature [1] derived from the spin minority bands than from the majority bands, but the compelling evidence arises from the spin dependence plasmon structure. Spin-polarized plasmon dispersion was observed. In addition to the spin-resolved plasmon dispersion, Ep(k//), we will show plasmon energies are dependent on primary energies and temperature. [1] Hae-Kyung Jeong, R. Skomski, C. Waldfried, Takashi Komesu, P. A. Dowben, E. Vescovo, "The Effective Spin Dependent Debye Temperature of Gd(0001)", accepted Physics Letters A (2004).

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