Friday Morning, November 19, 2004

Surface Science
Room 210B - Session SS1-FrM
Hydrated Surface Phenomena

Moderator: E. Stuve, University of Washington

8:20am **SS1-FrM1 Wetting and Dissociation of Water on Cu(111) and Cu(110)**, ***T. Schiros***, *H. Öström, K. Andersson, O. Takahashi, L.G.M. Pettersson,* Stockholm University, Sweden; *A. Nilsson, H. Ogasawara,* Stanford Synchrotron Radiation Laboratory

A fundamental understanding of the factors that control the interaction of water metal surfaces is indispensable in predicting electrochemical interactions and pathways for dissociation. Here we address the adsorption of water on Cu(111) and Cu(110) using x-ray absorption and x-ray photoelectron spectroscopy experiments combined with density functional theory calculations. We have found that water adsorbs intact on both surfaces, and wets Cu(110) by forming a monolayer prior to ice formation. In contrast, water does not wet Cu(111), but rather forms three-dimensional ice-like clusters upon adsorption. Our calculations show a much weaker electrostatic interaction and a stronger Pauli repulsion with the oxygen lone pair on Cu(111) compared to Cu(110). We have also investigated how these factors affect the wetting capabilities of water on other metals. We discuss the influence of the d-band density of states with respect to the Fermi level.

8:40am **SS1-FrM2 Point Defects in a Partially Dissociated Wetting Layer: D@sub 2@O/Ru(0001)@footnote 1@**, ***P.J. Feibelman,*** Sandia National Laboratories

Ab-initio total energies imply that about 43% of the D@sub 2@O molecules in a first layer on Ru(0001) optimally dissociate to adsorbed OD+D. This compares favorably to new x-ray photoemission measurements,@footnote 2@ which say that (3Â±0.25)/8 of them do. In the optimal wetting layer structure, atop sites on roughly 6% of the outer-layer Ru atoms are available as a natural pathway for D-adatom transport. They represent a surface analog of L-type, Bjerrum defects.@footnote 3@ An equal percentage of the wetting layer's H-bonds, disrupted by the presence of a second D atom, represent the corresponding D-type defects. @FootnoteText@ @footnote 1@ Supported by the USDOE, Office of Basic Energy Sciences, Division of Materials Sciences. Sandia is operated by the Lockheed-Martin Company under USDOE Contract No. DE-AC04-94AL85000.@footnote 2@ J. Weissenrieder, A. Mikkelsen, J.N. Andersen and P. J. Feibelman and G. Held (unpublished).@footnote 3@ N. Bjerrum, Kong. Dansk. Vid. Sels.Mat.-fys. Medd. 27, 1(1951).

9:00am **SS1-FrM3 Diffusion of He in Amorphous Solid Water: Observation of an Inverse H/d Lattice Isotope Effect**, ***J.L. Daschbach***, *G.K. Schenter,* Pacific Northwest National Laboratory; *P. Ayotte,* University of Sherbrooke, Canada; *R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The diffusion of He through amorphous solid water (ASW) has been measured in H@sub 2@O and D@sub 2@O between 50 K and 125 K. He is embedded in a thin layer of ASW grown on Pt(111) at 25 K by molecular beam techniques and subsequently capped with an ASW cap of precise thickness. Linear temperature programmed desorption of the embedded He diffusing through the ASW cap is measured by mass spectroscopy. We find that He diffuses more rapidly in D@sub 2@O than in H@sub 2@O ASW. To our knowledge, this is the first observation of a lattice isotope effect in diffusion. A microscopic kinetic model for He hopping between cage sites in the ASW, reflecting at the Pt(111) interface, and desorbing at the vacuum interface closely fits the data. The diffusion kinetic parameters are found to be D@sub 0@ = 1.3 ± 0.3 x 10@super -3@ cm@super 2@/s, E@sub a@ = 11.9 ± 0.17 kJ/mole and D@sub 0@ = 0.8 ± 0.2 x 10@super -3@ cm@super 2@/s, E@sub a@ = 11.2 ± 0.17 kJ/mole, for H@sub 2@O and D@sub 2@O respectively. The origin of this inverse isotope effect in the host lattice has been studied using transition state theory. These results indicate the inverse isotope effect arises predominantly from the frustrated rotations of the lattice water molecules.

9:20am **SS1-FrM4 H@sub 2@O/D@sub 2@O Dimer Formation on Pd (111) Studied by STM**, ***E. Fomin***, *M. Tatarkhanov,* University of California at Berkeley; *D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory

We have studied the adsorption and dynamics of H@sub 2@O and D@sub 2@O molecules and dimers on Pd(111) using variable low temperature (@>=@ 25 K) scanning tunneling microscopy (STM). At higher temperatures (>35K) dimers are formed by thermally activated diffusion. At lower temperatures dimer formation was induced by inelastic ecletron tunneling. We measured the hopping rate of single molecules and dimers and discovered that diffusion coefficients differ by 4 orders of magnitude. Recent theoretical analysis@footnote 1@, proposed to explain this effect implies isotopic change in a diffusion coefficient for D@sub 2@O dimers compared to H@sub 2@O ones. In our experiments we were unable to detect this difference. @FootnoteText@ @footnote 1@Ranea VA. Michaelides A. Ramirez R. de Andres PL. Verges JA. King DA. Water dimer diffusion on Pd{111} assisted by an H-bond donor-acceptor tunneling exchange - art. no. 136104. [Article] Physical Review Letters. 9213(13):6104, 2004 Apr 2.

9:40am **SS1-FrM5 Ultrafast Electron Solvation Dynamics and Structure of the Water/Metal Interface**, ***M. Wolf,*** Free University Berlin, Germany **INVITED**

The dynamics of excess electrons in water is of fundamental importance for charge transfer and solvation processes in chemistry and biology. We have studied the ultrafast dynamics of photoinjected electrons into thin layers of amorphous ice grown on metal surfaces (Cu(111) and Ru(0001)) and probe the subsequent electron localization, solvation and transfer processes by femtosecond time- and angle-resolved photoemission spectroscopy.@footnote 1@ The solvation dynamics is observed directly through a transient increase of the electron binding energy, which occurs on a 100 fs to 1 ps time-scale and depends critically on the structure of the ice. On the other hand, exceptionally long-lived and highly localized electrons are formed in crystalline ice. As the structure of the solvent can be modified in a controlled way by the growth conditions and substrate our approach provides insights on the relation between structure and solvation dynamics in low dimensional systems. We have also used vibrational sum-frequency generation (SFG) spectroscopy, isotope scrambling experiments and work function measurements to investigate the structure of D@sub 2@O on Ru(0001).@footnote 2@ Our results suggest that the first bilayer consists of intact water molecules, while density functional theory predicts a half-dissociated structure as energetically most favourable state.@footnote 3@ Some explanations for these controversial findings will be discussed. @FootnoteText@ @footnote 1@C. Gahl et. al, Phys. Rev. Lett. 89, 107402 (2002); U. Bovensiepen et al., J. Phys. Chem. B 107, 8706 (2003); Israel. J. Chem. (in press)@footnote 2@D.N. Denzler et al, Chem. Phys. Lett. 376, 618 (2003).@footnote 3@P.J. Feibelman, Science 295, 99 (2002).

10:20am **SS1-FrM7 Interfacial Segregation of Halogen Ions in Alkali Halide Solutions**, ***S. Ghosal***, University of California, Irvine; *B.S. Mun, D.F. Ogletree, M. Salmeron,* Lawrence Berkeley National Laboratory; *J.C. Hemminger,* University of California, Irvine

In recent years Molecular Dynamics (MD) Simulations@footnote 1, 2@ of alkali halide solutions have predicted the surface segregation of polarizable halogen ions. This is of particular interest since the composition of the liquid/vapor interface of salt solutions has implications for heterogeneous atmospheric chemistry involving sea salt aerosols@footnote 3@. We present here results from our studies of the surface composition of saturated salt solutions. Using a novel high pressure photoelectron spectroscopy (HPPES) system at beamline 9.3.2 of the ALS synchrotron radiation source, we have compared the surface composition of KBr and NaCl crystals cleaved in vacuum with the surface composition of the saturated solutions formed at the deliquescence point, in equilibrium with water vapor. Our results show that the anion/cation ratio in the saturated solution is significantly enhanced within one nanometer of the surface. This is consistent with the predictions of Jungwirth et al@footnote 1, 2@ regarding halogen surface segregation. @FootnoteText@ @footnote 1@ Jungwirth, P.; Tobias, D. J. J. Physical Chemistry 2002, 106(2), 379.@footnote 2@ Jungwirth, P.; Tobias, D. J. J. Phys. Chem. B 2002, 106, 6361.@footnote 3@ Finlayson-Pitts, B. J.; Hemminger, J. C. J. Phys. Chem. 2000, 104(49), 11463 .

10:40am **SS1-FrM8 Measurements of Interfacial Water Properties as a Function of Surface Functionalization Using the IFM**, ***G.E. Thayer,*** Sandia National Laboratories, US; *A.K. Boal, B.I. Kim, J.E. Houston, B.C. Bunker,* Sandia National Laboratories

Water exhibits dramatically different structures and properties near interfaces, impacting a wide range of activities including the assembly and properties of nano- and bio-materials, microfluidic and sensor systems. In this work, we use the interfacial force microscope (IFM) to study forces generated by hydrophobic/hydrophilic surfaces in contact with water and the resulting properties of the near-surface water region. The IFM measures force-distance curves between a scanning probe tip and substrate surfaces, providing quantitative measurements of adhesion, long-range (electrical double layer) and short-range (Van der Waals and hydration) forces, and fluid properties such as viscosity. Measurements are performed at the water-solid interface as a function of surface and tip functionalization using self-assembled monolayers (SAMs), temperature, speed, and tip size. Our results indicate that in extreme cases a viscous water layer can form which extends greater than 5 nm from the surface is 6 orders of magnitude more viscous than bulk water. This remarkable effect is due to the interaction of surface hydration forces with the hydrogen-bonding network of water. Such forces are capable of controlling phenomena such as protein adsorption, for example we find forces generated by ordered interfacial water are large enough to resist adsorption of the motor protein kinesin.

11:00am **SS1-FrM9 Light-Induced Contact Angle Switching on Nanowire Surfaces***, **S.T. Picraux**, R. Rosario, T. Clement, J.L. Taraci, J.W. Dailey, D. Gust, A.A. Garcia, M. Hayes,* Arizona State University

We combine monolayer surface chemistry with silicon nanowire substrates to create a lotus leaf like surface, and for the first time demonstrate the amplification of light-induced water contact angle switching. Si nanowires are grown by the vapor-liquid-solid growth technique and the air oxidized surfaces are functionalized with tert-butyldiphenylchlorosilane and perfluorooctyltrichlorosilane, followed by 3-aminopropyldiethoxymethylsilane, to which a photochromic spiropyran molecule was attached. Measurements of the contact angle for water on both the smooth and nanowire surfaces allow direct estimation of the effects of surface morphology on hydrophobicity. Functionalized nanowire surfaces with contact angles above 90° on the smooth surface exhibit superhydrophobic behavior, whereas those with smooth surface angles below 90° exhibit superhydrophilic behavior. Spiropyran-functionalized surfaces show reversible photoswitching of the contact angles. When irradiated with UV light (366nm) the spiropyran is converted from a closed, nonpolar form to a highly polar open form. Visible light (450-550 nm) irradiation of the spiropyran coating yields a relatively hydrophobic surface (higher contact angle) that can be reversibly converted into a more hydrophilic surface (lower contact angle) with UV light irradiation. The nanowire surfaces are observed to exhibit a significant amplification in the contact angle change over that for smooth surfaces (from 12° to 23°). The roughness induced amplification of contact angle switching was accurately predicted using a Wenzel model for contact angles on fractal surfaces. These results, based on a biomimetic approach to nanotechnology, have wide ranging implications for the design of microfluidic systems.

11:20am **SS1-FrM10 Interaction of Glycine with Ice Nanolayers@footnote *@***, **G. Tzvetkov**, M.G. Ramsey, F.P. Netzer,* University of Graz, Austria

The interaction of amino acids with ice surfaces is of interest in a variety of scientific disciplines, ranging from the chemistry in interstellar space and in stratospheric clouds to processes in the geosphere and biosphere. Thin films of ice grown on crystalline substrates under ultrahigh vacuum conditions have been recognised as excellent model systems to study the surface chemistry of molecules on ice. Here we report a study of the interaction of glycine, the simplest amino acid, with ultrathin films of amorphous and polycrystalline ice, as obtained by TPD, XPS, and work function measurements. Thin ice films (@<=@50 layers) have been condensed at 110 K and at 150 K on a hydrophilic single crystalline aluminium oxide surface to produce nanolayers of low-density amorphous and polycrystalline cubic ice, respectively. Glycine overlayers have been prepared by physical vapour deposition at 110 K onto the ice surfaces and mixed glycine-ice layers by codeposition of water and glycine. Whereas the TPD of glycine at 300-350 K remains unaltered by its previous history on ice, the desorption kinetics of water in the temperature range 155-200 K is significantly influenced by the presence of glycine on the ice surfaces, with TPD peaks shifting to lower and higher temperatures with respect to those from the pristine ice surfaces. It is proposed that, on the one hand, the glycine molecules restrict the crystallisation tendency of amorphous to crystalline ice at around 140-160K, and that, on the other hand, the glycine overlayers stabilise the ice surface. The N 1s XPS spectra of the glycine molecules in the monolayer show evidence of a H-bonding interaction of the glycine amino groups with the surface O-H species. The work functions of pristine amorphous and crystalline ice surfaces and the work function changes during glycine adsorption are reported and discussed. @FootnoteText@ @footnote *@ Supported by the Austrian Science Funds.

11:40am **SS1-FrM11 H@sub 2@O-Induced Instabilities at Alumina Surfaces Under Non-UHV Conditions***, F. Qin, N.P. Magtoto, **J.A. Kelber**,* University of North Texas*; D.R. Jennison,* Sandia National Labs

We report that ordered, transitional phase Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al single crystal substrates undergo dramatic reorganization and morphological changes upon exposure to H@sub 2@O under non-UHV conditions at room temperature. Notably, the reconstruction does not involve the formation of an UHV-stable hydroxide. STM, AES, LEED and XPS have been used to probe the reactivities of 7 Å - 20 Å thick, ordered Al@sub 2@O@sub 3@ films grown on Ni@sub 3@Al(110) and on Ni@sub 3@Al(111) substrates for 10@super-8@ Torr < P@sub H2O@ < 1 Torr at 300 K. STM near-atomic resolution image of the surface of an as-grown Al@sub 2@O@sub 3@/Ni@sub 3@Al(110) oxide film (estimated thickness, ~ 7 Å) indicates a 10 Å repeat distance between rows, in excellent agreement with the results of a first-principles DFT calculation of an ultrathin kappa-phase film. LEED pattern of this film with a 2 x 1 unit cell confirms this structure. Both films are inert toward H@sub 2@O under UHV conditions. We demonstrate that (a) both films undergo severe surface reorganization to a rough, irregular morphology upon exposure to H@sub 2@O at pressures above 10@super-5@ Torr, 300 K, although Al(OH)@sub 3@ formation is only observed above 1 Torr, as predicted by thermodynamics and observed on sapphire(0001); (b) the film grown on the (110) substrate (Al@sub2@O@sub 3@/Ni@sub 3@Al(110)) is significantly more sensitive to H@sub 2@O vapor than the Al@sub 2@O@sub 3@/Ni@sub 3@Al(111) film, and this may be due to the incommensurate nature of the oxide/Ni@sub 3@Al(110) interface; (c) the degree of reconstruction increases with time at constant P@sub H2O@; (d) bias-dependent STM indicates that this reaction is initiated at surface terrace sites, rather than at defect sites or by diffusion to the interface; and (e) the reaction is pressure-dependent, rather than exposure-dependent, indicating that this reaction is cooperative in nature.

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