Surface Science
Room 326 - Session SS1-TuA

Water at Interfaces II: Adsorbed Layers

Moderator: C.J. Hirschmugl, University of Wisconsin-Milwaukee

2:00pm **SS1-TuA1 Why Water Wets Precious Metals@footnote 1@***, **P.J. Feibelman,*** Sandia National Laboratories **INVITED**

To categorize surfaces as hydrophobic or hydrophilic by measuring contact-angles is a step toward understanding water-solid interactions, but a small one. To predict wetting, control aqueous surface chemistry or design nanofluidic systems, atomic-scale understanding of water-adlayer structure and dynamics is wanted. The research involved is risky -- systematic error is an ever-present concern in dealing with weakly interacting species, like water, which are commonplace in the natural world. To explore the limits of current ab initio methods for water on solids, I have been applying first principles Density Functional Calculations to the simplest examples: periodic water adlayers on close-packed, precious metal surfaces. On Ru(0001), the calculations invite the inference that wetting involves forming a half-dissociated monolayer with water molecules and hydroxyl fragments hydrogen-bonded in a hexagonal structure and hydrogen atoms bound directly to the metal. Refinements of this idea are needed, however, to make contact with measured vibration spectra. New understanding is also necessary to explain the occurrence of periodic adlayers on surfaces like Rh(111) and Pt(111), too unreactive to make dissociation energetically favorable, and to give meaning to beautiful STM images of water clusters obtained at LBNL on Pd(111). @FootnoteText@ @footnote 1@Work supported in part by the DOE Office of Basic Energy Sciences, Division of Material Sciences and Engineering. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE- AC04-94AL85000.

2:40pm **SS1-TuA3 Absence of Surface Water Crystallization***, E. Backus, M. Grecea,* ***A.W. Kleyn,*** *M. Bonn,* Leiden University, The Netherlands

For the transition from amorphous solid water to crystalline ice, it has been proposed that the required hydrogen bond rearrangement may occur more readily for the less coordinated water molecules at the surface so that the amorphous-crystalline transition would be expected to nucleate at the solid-air interface. By simultaneously monitoring the phase state of the bulk and the surface passing through this transition, we demonstrate conclusively that crystallization commences in the bulk. In our experiments, water is deposited on a low-temperature Pt substrate by means of a molecular beam in Ultra High Vacuum (UHV), on which it forms a layer of amorphous solid water. By slowly heating the substrate, the water crystallizes. Using RAIRS (reflectance absorption infrared spectroscopy), we can follow the crystallization kinetics real-time, since the RAIRS spectra for crystalline and amorphous ice are very different. Hence by measuring RAIRS spectra while we are heating the crystal, we can deduce the spatially averaged, i.e. bulk fraction of crystalline ice in the water layer throughout the crystallization process. We can also determine surface fraction of crystalline ice in the water layer by monitoring chloroform desorption from the (partially crystallized) ice layer: the desorption of chloroform occurs at temperatures well below the water phase transition, and the desorption temperature from amorphous solid water and crystalline ice differ by 15 K. Therefore chloroform is a good probe for study the crystallinity of the surface of the water layer. In this manner we can correlate surface to bulk crystallinity. We find that the surface crystallinity is always lagging compared to the bulk. We can therefore unequivocally conclude that the crystallization of water nucleates in the bulk and not on the substrate-water interface or on the water-vacuum interface. We further find that initiation of the crystallization process (the nucleation grain) involves ~100 water molecules.

3:00pm **SS1-TuA4 Surface Science - A New Tool for Laboratory Astrophysics***, M.P. Collings, J.W. Dever,* University of Nottingham, UK*; H.J. Fraser,* University of Leiden, The Netherlands*;* ***M.R.S. McCoustra,*** University of Nottingham, UK

The evolution of our galaxy, and that of others in the Universe, is subtley controlled by a combination of physics and chemistry. Molecules prevade the galaxy and are found to play a key role in controlling the very processes that give birth to new stars, their planetary systems, and potentially the precursors of life itself. Astronomical observations can give us much detail as to the nature of these molecules but laboratory measurements are necessary to understand the physics and chemistry that lead to their formation. Gas phase chemistry is important in this respect, but in recent years the molecular astrophysics community has come to realise that the interaction of the interstellar gas with solid grains plays a crucial role. Our laboratory effort has sought to apply surface science techniques and methodologies to understanding aspects of the gas-grain interaction. In particular, we will report on combined temperature-programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) measurements of the interaction of carbon monoxide (CO), carbon dioxide (CO@sub 2@) and molecular hydrogen (H@sub 2@) with vapour deposited ultrathin films of water (H@sub 2@O) ice under conditions that a closely mimic those in the denser regions of the interstellar medium where stars are known to form. Results will be presented that demonstrate a complex interplay of surface diffusion, substrate morphological change, pore trapping of gases and desorption that modifies the simple model of the behaviour of these systems currently utilised by the molecular astrophysics community.

3:20pm **SS1-TuA5 Formation and Dynamics of Water Clusters on Ru(001)***,* ***M. Asscher,*** Hebrew University, Israel

The adsorption kinetics of water on Ru(001) was simulated using molecular dynamics (MD) and equilibrium-model approach. The results nicely reproduce observations from STM imaging, work function change and IR measurements. The agreement with experimental results is based on the formation of stable clusters already at very low surface coverage and temperature. Tetramers are predicted to be relatively stable compared to smaller and larger clusters. The dipole moment per water molecule continuously decreases from 2.2D for the monomer down to 1.1D for pentamer and larger clusters. Dimers diffuse faster than monomers or larger clusters, in agreement with STM measurements. A unique mechanism for dimers diffusion is proposed. Photo-dissociation of H2O/Ru(001) with 193nm photons support recent DFT calculations that claim thermal decomposition.

3:40pm **SS1-TuA6 Comprehensive Structural Analysis of H@sub 2@O/MgO(111) using DLD-LEED and IR Spectroscopy***,* ***D.A. Human,*** *C.J. Hirschmugl,* University of Wisconsin-Milwaukee

The polar MgO(111) surface is predicted to be charged, and may dissociate water molecules or reconstruct to minimize its energy. Structural analysis using a powerful combination of Low Energy Electron Diffraction (LEED) and UHV infrared spectroscopy provides new insights into this water/oxide interface. A pico-ampere LEED study reveals a @sr@3x@sr@3 R30° structure, and IR transmission spectroscopy suggests the presence of OH and H@sub 2@O species. To perform the LEED study, a new instrument incorporating a delay line detector has been constructed to rapidly collect high-quality digital LEED images with low total electron exposures, thus reducing incident beam effects. The characteristics of the new LEED instrument and the structure and species identification of monolayer and bilayer water coverages will be discussed.

4:00pm **SS1-TuA7 The Growth of Water Monolayers on Pd(111)***, T. Mitsui, E. Fomin, M.K. Rose, D.F. Ogletree,* ***M. Salmeron,*** Lawrence Berkeley National Lab, University of California at Berkeley **INVITED**

Using STM at low temperature we have followed the structures formed by water growing on a clean Pd(111) substrate. Starting with the monomers the process of cluster formation proceeds via formation of dimers, trimers and so forth. We found a surprising increase in diffusivity for the small clusters (2 to 4 molecules), which we attribute to mismatch between the cluster's structure and the substrate. Cluster mobility decreases substantially when the sizes is 5 and above. Continued adsorption of water results in the formation of honeycomb-like structures reminiscent of ice-like hexagonal bilayers. These structures are limited in size below 90K approximately, indicating kinetic limitations to the growth. Above 100K more extensive honeycomb structures are formed. Above 130K new structures with larger periodicity are formed. The observations will be discussed in light of recent wetting models involving the possible partial dissociation of the first water layer.

4:40pm **SS1-TuA9 The Surface Chelate Effect***,* ***R. Major,*** *X.-Y. Zhu,* University of Minnesota

The adsorption of metal ions from a liquid phase to a molecularly functionalized solid surface is important in many disciplines, such as chemical sensing, environmental cleanup, protein purification, and "molecular beaker epitaxy". Few studies have investigated the kinetics and thermodynamics in adsorption at a such a liquid-solid interface. One distinguishing factor related to the coordination of metal ions to surfaces is that the surface functional groups can be arranged in a two-dimensional

array. We set out to explore how this two-dimensional arrangement may lead to an inherent chelate effect, using the model system of Cu2+ ions adsorption on self-assembled monolayers of 16-mercaptohexadecanoic acid (MHA) on Au. The formation constant of Cu2+ with the MHA surface was found to be two orders of magnitude greater than Cu2+ with succinic acid or glutaric acid in aqueous solutions. Both of these molecules are known to chelate to metal ions forming 7 and 8-membered rings. The greater surface chelate effect is attributed to the presence of the two-dimensional array of ligands on the surface. We believe the surface chelate effect demonstrated here is of general significance to adsorption on functional surfaces and should depend strongly on chemical functionality and monolayer structure.

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