

Monday Afternoon, October 15, 2007

Surface Science

Room: 608 - Session SS1-MoA

Water-Surface Interactions

Moderator: M.A. Henderson, Pacific Northwest National Laboratory

2:00pm SS1-MoA1 Water Adsorption on Ruthenium (0001) Pre-covered with Atomic Oxygen Studied by Scanning Tunneling Microscopy, T.K. Shimizu, A. Mugarza, Lawrence Berkeley National Laboratory, **P. Cabrera-Sanfelix,** Donostia International Physics Center, Spain, **D.S. Portal,** Unidad de Física de Materiales, Centro Mixto CSIC-UPV, Spain, **A. Arnau,** Departamento de Física de Materiales UPV/EHU, Spain, **D.F. Ogletree, M. Salmeron,** Lawrence Berkeley National Laboratory

The adsorption of water on a Ru(0001) surface pre-covered with atomic oxygen forming a (2x2) structure was studied using low temperature scanning tunneling microscopy (STM). Below 0.25 ML, water adsorbs molecularly on top Ru sites within the (2x2) superstructure and forms two hydrogen bonds with pre-adsorbed O atoms. Because of the additional H-bonding, the water molecules are more strongly bound than those on the bare Ru metal. Water dissociation is completely blocked on the (2x2)-O/Ru surface and annealing results only in molecular desorption in the temperature range of 140-230 K. This is in contrast to the water adsorption on Ru with smaller pre-coverage of oxygen. These results will be discussed in light of current models relating water binding to the hydrophilicity and hydrophobicity of the underlying metal surfaces.

2:20pm SS1-MoA2 Vibrational Study of Individual Water Dimers on Pt(111) using Scanning Tunneling Microscope, K. Motobayashi, RIKEN, The University of Tokyo, Japan, **C. Matsumoto,** Gakushuin University, Japan, **Y. Kim,** RIKEN, Japan, **M. Kawai,** RIKEN, The University of Tokyo, Japan

The adsorption and diffusion of water molecules on metal surfaces play an important role in various fields of surface science, such as electrochemistry, heterogeneous catalysis, corrosion, and so on. Although the adsorption structure of water on a variety of metal surfaces at low coverage has been extensively investigated with various techniques, still unclear is the microscopic feature of adsorbed isolated water molecules. On the other hand, Vibrational spectroscopy methods have been used as powerful tools to get information of bond specific interactions, but in spite of that, the spatial resolution and sensitivity of conventional methods are not sufficient to detect vibrational signals from individual water monomers and dimers. To solve these problems, we investigated and report microscopic and vibrational study of adsorption behaviors of individual water molecules, especially water dimers, on Pt (111) by use of the scanning tunneling microscopy (STM) at 4.7 K. The Pt (111) single crystal surface was dosed with a small amount of water molecules (< 0.01 ML) at a temperature lower than 20 K. This temperature is low enough to prevent water molecules from thermal processes, such as diffusion, desorption and chemical reaction, on the surface, so that one can easily observe isolated water monomers and without forming large clusters. A water dimer appears as a flower like protrusion in the STM images, while a water monomer as a single protrusion as shown in Figure 1. It can be explained as one of the water molecules in a dimer rotating around the other. Indeed, we have succeeded in forming a dimer by manipulating two monomers with an STM tip, and also breaking a dimer into two monomers by inducing pulse bias. We obtained vibrational information by analyzing diffusion behavior of individual water dimers using STM, which method is so called "Action spectroscopy". The result of this measurement provides us not only the information of bond specific interaction but also the detailed features of adsorption structure. We found a kind of hydrogen bonding between one water molecule and Pt surface atoms in adsorption structure of a dimer.

2:40pm SS1-MoA3 Dissociation of Water on Modified Transition Metal Surfaces, G. Held, University of Reading, UK **INVITED**

Water dissociation on surfaces of late transition metals has been a topic of intense discussion in the last few years.¹⁻⁴ It is remarkable in this context that different members of the Pt group, which normally show very similar chemical behavior, cause water to react in very different ways. This could be caused by small differences in the surface lattices, affecting the (mis)match with ice-like water layers, or by electronic differences, affecting the balance between inter-molecular hydrogen bonds and water-substrate

bonds. Atomic or molecular coadsorbates are convenient means of modifying both types of bonds and were used in a systematic study to address this question. We compare the reactivity of water on clean and O-modified Pd{111}, Ir{111}, Pt{111} and Ru{0001} using LEED, TPD, high resolution XPS and NEXAFS. All four surfaces have the same surface symmetry and very similar lattice constants. Except for Ru{0001}, no dissociation is observed on the clean surfaces, even after prolonged irradiation with X-rays. Small amounts of oxygen, however, cause water to dissociate, whereas high coverages (> 0.25ML) tend to leave water intact with more stable surface bonds than for the clean surfaces.⁵ The exception here is Pt{111}, where water dissociates for all oxygen coverages up to saturation. Molecular co-adsorbates, such as CO and methanol tend to inhibit water dissociation. Possible geometrical effects were investigated using Pt{111}, {110} and {531}, these surfaces represent a series with increasing atomic roughness and coordination numbers decreasing from 9 to 6. We could not find any increased reactivity of low-coordinated Pt atoms with respect to the dissociation of water only an increase in the water-substrate bond strength. Small amounts of oxygen promote water dissociation on all three surfaces; a high coverage (exceeding half the saturation coverage) prevents dissociation on Pt{531} and Pt{110}, but not on Pt{111}. These results indicate that dissociation of water on Pt group surfaces depends more sensitively on electronic modifications, as induced by oxygen coadsorption, than on the surface geometry.

¹ A. Thiel, T.E.Madey, Surf. Sci. Rep. 7 (1987) 211; M.A. Henderson, Surf. Sci. Rep. 46 (2002) 1.

² P.J. Feibelman, Science 295 (2002) 58.

³ J. Weissenrieder, et al. PRL 93 (2004) 196102;

⁴ K. Andersson, et al. PRL 93 (2004) 196101.

⁵ M.J. Gladys, et al. CPL 414 (2005) 311.

3:40pm SS1-MoA6 Crystallization of Thin Amorphous Solid Water Films on Ru(0001) and on CO-precovered Ru(0001), T. Kondo, RIKEN and University of Tsukuba, Japan, **H.S. Kato,** RIKEN, Japan, **M. Bonn,** AMOLF, FOM, The Netherlands, **M. Kawai,** RIKEN and University of Tokyo, Japan

The deposition and the isothermal crystallization kinetics of thin amorphous solid water (ASW) films on both Ru(0001) and CO-precovered Ru(0001) have been investigated in real time by simultaneously employing helium atom scattering, infrared reflection absorption spectroscopy and isothermal temperature-programmed desorption. The modification of the Ru(0001) surface by the pre-adsorption of CO has been found to affect the deposition feature of water layers at the water coverage below ~5 ML: whereas an ordered first layer structure of water is formed on both the bare surface and the surface pre-adsorbed with 0.33 ML CO, a disordered structure is formed when 0.65 ML CO is pre-adsorbed. During ASW deposition, the interaction between water and the substrate depends critically on the amount of pre-adsorbed CO. However, the mechanism and kinetics of the crystallization of ~50 layers thick ASW film were found to be independent of the amount of pre-adsorbed CO. We demonstrate that crystallization occurs through random nucleation events in the bulk of the material, followed by homogeneous growth, for solid water on both substrates with an apparent activation energy of 650 ± 25 meV. The morphological change accompanying the formation of 3D grains of crystalline ice results in the exposure of the water monolayer just above the substrate to the vacuum. Remarkably enough, the appearance of this first water layer occurs already during the crystallization process, on both substrates.

4:00pm SS1-MoA7 Growth, Structure, and Dynamics of Nanoscale Water Films on Various Substrates, B.D. Kay, G.A. Kimmel, N.G. Petrik, Z. Dohnalek, R.S. Smith, Pacific Northwest National Laboratory

The growth of amorphous solid water and crystalline ice films on various substrates (Pt(111), Pd(111), C(0001) and FeO(111)) is investigated using temperature programmed desorption, rare gas physisorption, specular helium scattering, and infrared spectroscopy. At low temperatures water forms an amorphous film that wets all substrates studied. Heating the amorphous film, or growth at higher temperatures, results in the formation of crystalline ice. Concomitant with crystallization, the water films form non-wetting three dimensional crystallites on either the bare substrate or a substrate covered by only a single monolayer of water. The experimental results and their implications concerning hydrophobicity and the wetting-dewetting transition will be presented.

This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Chemical Science Division. The experiment and calculations were performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated for DOE by Battelle.

4:20pm **SS1-MoA8 The H/D Exchange in Water at Surfaces of Ice and on Cu(100) Studied by Infrared Vibrational Spectroscopy and DFT Calculations**, *P. Uvdal, J. Blomquist*, Lund University, Sweden

Proton transfer in water through the reaction $\text{H}_2\text{O} + \text{D}_2\text{O} \rightarrow 2\text{HDO}$ is one of many intriguing properties of water. We have studied the exchange in water at ice surfaces and on a Cu(100) surface using infrared vibrational spectroscopy. Intact molecules of H_2O and D_2O are observed up on adsorption at 84 K and no H/D exchange is observed in $\text{H}_2\text{O}/\text{D}_2\text{O}$ mixtures. By monitoring the O-H (3695 cm^{-1}) and O-D (2730 cm^{-1}) stretches assigned to none-hydrogen bonded water molecules at the surface of the ice we have followed the H/D exchange in the temperature region 84 - 145 K. A clear isotope effect is observed in 4/1 mixtures of $\text{H}_2\text{O}/\text{D}_2\text{O}$ or $\text{D}_2\text{O}/\text{H}_2\text{O}$. The majority isotope governs the exchange efficiency. The exchange is completed at 140 K resulting in a total scrambling of the isotopes. The vibrational data is interpreted with the aid of DFT calculations of small water complexes.

4:40pm **SS1-MoA9 Hydrogen Bonding, H/D Exchange and Molecular Mobility in Thin Water Films on $\text{TiO}_2(110)$** , *G.A. Kimmel, N.G. Petrik*, Pacific Northwest National Laboratory

We use the electron-stimulated desorption (ESD) of water from films of D_2O , H_2^{16}O and H_2^{18}O to investigate hydrogen bonding, H/D exchange and molecular mixing in water films on $\text{TiO}_2(110)$ for coverages $\leq 2\text{ ML}$. By depositing water on the Ti^{4+} adsorption sites ($\text{H}_2\text{O}_{\text{Ti}}$) at 190 K using one water isotope and water on the bridge bonded oxygen sites ($\text{H}_2\text{O}_{\text{BBO}}$) at $T \leq 70\text{ K}$ using a different isotope, films with no appreciable mixing of the isotopes between the layers can be prepared. When $\text{H}_2\text{O}_{\text{BBO}}$ is deposited at $T > 70\text{ K}$, partial or complete mixing of the layers occurs depending on the temperature and time. H/D exchange between the first and second water layers occurs at $\sim 15\text{ K}$ lower temperatures than $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$ exchange. Isothermal experiments demonstrate that the mixing occurs with a distribution of activation energies centered on $0.29 \pm 0.07\text{ eV}$ ($0.26 \pm 0.07\text{ eV}$) for $\text{H}_2^{16}\text{O}/\text{H}_2^{18}\text{O}$ (H/D) exchange. While these distributions of activation energies are relatively narrow, they have a profound effect on the kinetics. The results demonstrate that $\text{H}_2\text{O}_{\text{BBO}}$ is hydrogen bonded to $\text{H}_2\text{O}_{\text{Ti}}$. Since the lateral distance (0.325 nm) for atop adsorption at these sites is too large for hydrogen bonding, one (or both) of the adsorbates must be laterally displaced toward the other in agreement with theoretical predictions.

5:00pm **SS1-MoA10 Vicinal and Interfacial Water Structure of Non-Fouling Poly(ethylene glycol) and Sulphobetaine Self Assembled Monolayers**, *M.J. Stein, B.D. Ratner*, University of Washington

Poly(ethylene glycol) (PEG) and sulphobetaine (SB) are currently used in the formation of non-fouling surfaces. As yet, an understanding of the water phase effects in the vicinal realm of these surfaces and their impact on protein resistance remains imperfect. In this work, we present analysis of mixed self-assembled monolayers (SAMs) with either the PEG or SB functionality and the impact of hydration on both monolayer and vicinal water structure using multiple surface analytical techniques. The degree of protein resistance in the SAMs was modified through successive addition of diluent hydrophobic thiols to achieve a broader spectrum of protein resistant surfaces as measured through radio-labeled protein adsorption. The hydrophilic diluents yielded lower amounts of protein adsorption overall for both PEG and SB surfaces. However, the overall trends in protein adsorption differed for the two non-fouling thiols. SB yielded lowest adsorbed fg, alb, and lys when assembled in a 50:50V concentration with 11-mercaptoundecan-1-ol; whereas, pure PEG SAMs yielded the lowest levels of adsorbed protein. The packing density and chemical composition of the SAMs were examined by XPS, as well as ToF-SIMS. The orientation of the SB head groups was confirmed through angular XPS revealing a nearly horizontal head group. This contradicted ellipsometric thickness measurements. PEG data showed no similar contradictions. The terminal hydrophilicity of the groups was characterized through contact angle measurements and followed protein adsorption trends. Unpolarized infrared spectroscopy (FTIR) showed that the stretching frequencies, $\nu\text{CH}_2_{\text{asym}}$ and $\nu\text{CH}_2_{\text{sym}}$, of the ultra-nonfouling SB and PEG SAMs decreased and approached 2918 and 2850 cm^{-1} , indicative of a crystalline phase, when hydrated. To study hydration effects, each SAM was exposed to a series of timed D_2O soaks. Band shapes of the composite ν_{OH} band of H_2O obtained were fitted to individual peak components and a ratio of the component band areas from the 3400 and 3200 cm^{-1} regions was utilized to cross-compare samples. A single linear trend between the water peak ratio minima and protein adsorption was obtained for both the PEG and SB SAMs with lower ratios corresponding to higher levels of protein resistance. Using this method, FTIR has been used for the first time to demonstrate a correlation between strongly-bound water structure and protein adsorption.

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