

Thursday Afternoon, October 23, 2008

Surface Science

Room: 207 - Session SS1+NC-ThA

Water-Surface Interactions

Moderator: M. Salmeron, Lawrence Berkeley National Laboratory

2:00pm **SS1+NC-ThA1 Structure and Kinetics of Nanoscale Amorphous and Crystalline Ice Films on Various Substrates**, *B.D. Kay, J.L. Daschbach, Z. Dohnálek, G.A. Kimmel, J. Matthiesen, N.G. Petrik, R.S. Smith, T. Zubkov*, Pacific Northwest National Laboratory **INVITED**

Molecular beam scattering, programmed desorption (both TPD and isothermal), and vibrational spectroscopy are used to study the chemical kinetics and reaction dynamics of molecular processes occurring both on the surface and within the bulk of amorphous and crystalline ice films. Molecular beams are used to synthesize chemically and structurally tailored thin films on various substrates including Pt(111), Pd(111), C(111) and FeO(111). These films can have morphologies ranging from dense and smooth, to highly porous depending on growth conditions. The precise control of the film structure allows physicochemical processes such as densification, crystallization, diffusion, isotope exchange, solvation, and dewetting to be studied in detail. The experimental methods, results, and their relevance to supercooled water, astrophysical icy bodies, wetting phenomena and nanoporous materials will be presented. Pacific Northwest National Laboratory is a multiprogram national laboratory operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

2:40pm **SS1+NC-ThA3 Iron Phthalocyanines on Au(111) and their Interaction with Water**, *C. Isvoranu, E. Ataman, K. Schulte*, Lund University, Sweden, *A. Rienzo, G. Magnano, J.N. O'Shea*, University of Nottingham, UK, *J.N. Andersen, J. Schnadt*, Lund University, Sweden

Phthalocyanines are an extensively studied class of molecules due to their chemical and thermal stability and high polarizability. These characteristics make the phthalocyanines and related molecules interesting for a wide range of applications such as in molecular electronics, gas sensing devices, or as cathode and/or anode materials in fuel cells. Often, in such applications the molecules will be in contact with either liquid water as an important component of the application or with water from the ambient atmosphere. In spite of the ubiquity of the water – molecule interaction, investigations of the atomic-scale properties of the interaction of organic and organometallic molecules with water in general and of phthalocyanines with water in particular are scarce. Here, we have studied the adsorption of iron phthalocyanines on Au(111) by x-ray photoelectron and x-ray absorption spectroscopies at both sub- and full monolayer coverages and we have characterized the interaction of the different preparations with small amounts of water. For the water-free preparations, the results indicate that the full monolayer is dominated by a single molecular species, while several distinct species are observed for the submonolayer coverages. Tentatively, these different species are assigned to structures previously observed by scanning tunnelling microscopy (STM).¹ The present results show clearly that the interaction between the substrate and adsorbate differ strongly between the submonolayer and full monolayer structures, with the interaction appearing considerably stronger for the submonolayer structures. Iron phthalocyanine monolayers on Au(111) are inert to water with no change observed in the spectral characteristics of the molecular layer when exposed to water. Quite in contrast, the submonolayers exhibit strong modifications of the spectral appearances, which can be assigned to an interaction between the molecular adsorbates and water. Surprisingly, the observed chemical shifts point to a more subtle interaction of water with the iron phthalocyanines than a mere hydrogen bond formation between the water and the phthalocyanines.

¹ Z.H. Cheng, L. Gao, Z.T. Deng, N. Jiang, Q. Liu, D.X. Shi, S.X. Du, H.M. Guo, and H.-J. Gao, *J. Phys. Chem. C* 111 (2007) 9240.

3:00pm **SS1+NC-ThA4 Water Diffusion on Pt(111) Terrace, Kink and Steps: Density Functional Theory Study of Water Interaction and Diffusion**, *L. Arnadottir, E.M. Stuve*, University of Washington, *H. Jónsson*, University of Iceland

Density functional theory (DFT PW91) calculations were used to study diffusion of water molecule on a flat Pt(111) terrace as well as on kinks and step edges. Diffusion on the (111) terrace is predicted to become active on the time scale of seconds at 74 K in reasonable agreement with experimental results (Daschbach et al. *J. Chem. Phys.* 120 (2004) 1516). The binding of water at steps and kinks on Pt(111) surface is substantially

stronger than at the flat terrace, by 0.16 eV and 0.25 eV, respectively. The diffusion barriers of a single water molecule moving along the flat terrace up to a kink site or moving along the step edge are all comparable, while the barrier of diffusion up to a step edge is significantly lower than all of the other barriers calculated. Consequently, the barrier for diffusion from the step edge down to the terrace is substantially larger than for diffusion along the flat terrace. At low coverage, clusters of water molecules would, therefore, be expected to align along the upper side of step edges. This is consistent with experimental STM images taken by Morgenstern et al. (Morgenstern et al. *Phys. Rev. Lett.* 77 (1996) 703).

3:20pm **SS1+NC-ThA5 Growth of Ice Multilayers Studied with STM**, *K. Thürmer, N.C. Bartelt*, Sandia National Laboratories

Much progress has been made in the past few years in determining the structure and morphology of ice films on Pt(111). In our work we use STM to explore how metal-water interactions determine the ice–film morphology by tracking the film evolution during growth and annealing. We find that ice films as many as 30 molecular layers thick can be imaged with STM when negative sample biases of $<6(\pm 1)V$ and sub-picoamp tunneling currents are used. As reported before by others, we observe that water deposited onto Pt(111) below 120K forms amorphous films, whereas metastable cubic ice appears between 120 and 150K. At 140K the first layer of water wets the Pt(111) substrate. At a mean film thickness of $\sim 1\text{nm}$ the film consists of individual regularly-shaped 2-3 nm high crystallites, embedded in a one bilayer high wetting layer. We analyze the annealing behavior of these crystallites and report that their dewetting is limited by the nucleation of new molecular layers on their top facets. By measuring nucleation rates as a function of crystallite height we estimate the strength of the driving force for dewetting. Upon deposition of additional water the crystallites coalesce and eventually, at $\sim 5\text{-}10\text{ nm}$ mean thickness, the film becomes continuous, with the exception of a few remaining pinholes. A common, but not well understood observation is that ice grows between 120 and 150K in its metastable cubic 1c variant rather than in its equilibrium hexagonal form ice 1h. We find evidence for ice 1c in thicker films and suggest that it is a consequence of the mismatch in the atomic Pt-step height and the ice-bilayer separation. We propose a mechanism of cubic-ice formation via growth spirals around screw dislocations.

¹ K. Thürmer and N. Bartelt, *Phys. Rev. Lett.* 100, 186101 (2008).

4:00pm **SS1+NC-ThA7 Ice Nanoclusters on Au(111): Formation of a Unique Double Bilayer**, *D.J. Stacchiola, J.B. Park, S. Ma, P. Liu, J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

The nucleation of water into ice on solid surfaces has far reaching consequences in physical and biological systems. We have used ice multilayers grown on gold surfaces to prepare oxide nanoparticles. Profound differences on the nanoparticle nucleation pattern were observed when a different oxidant, such as NO₂ multilayers, was employed. To gain insight into the origin of this nucleation behavior we have studied the formation of ice nanoclusters on Au(111) combining STM, TPD and IRAS results with DFT calculations. The nucleation of single water molecules in the elbows of the herringbone reconstruction of Au(111) has been previously reported, as well as the study of the initial formation of small clusters, with 6 or more water molecules, on other hydrophobic surfaces such as Ag and Cu. However, not detail studies on the initial formation of water multilayers on Au(111) surfaces have been reported. In the case of a hydrophilic surface such as Pt(111), where a wetting bilayer is formed in the interface, it has been very recently shown that the growth of thicker layers leads to the formation of isolated ice islands on top of the interfacial bilayer, with 5 or more bilayers of water per island. We will show in this presentation that in the case of Au(111) no wetting interfacial bilayer is formed, due to the gold hydrophobic character and large lattice mismatch with ice 1h, and the initial growth of multilayers proceeds through the formation of isolated ice clusters with a unique double bilayer structure. An absence of dangling hydroxyl groups on the ice clusters points to participation of all hydrogens in hydrogen bonding within and between the two bilayers, and renders the surface of the double bilayer hydrophobic.

This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

4:20pm **SS1+NC-ThA8 Isotopic Effects in the Mixing Between Surface and Bulk Molecules at the Surface of Amorphous Solid Ice Studied by FTIR and DFT Calculations**, *P. Uvdal, J. Blomquist*, Lund University, Sweden

We have studied the exchange between surface and bulk molecules on amorphous solid ice using infrared vibrational spectroscopy. Intact molecules are grown in a layer by layer fashion, on Cu(100), allowing the formation of isotopically uniform layers at 84 K. A bulk layer consisting of

3-5 bilayers of ice of isotope A was exposed to 0.15 monolayers of isotope B. Three different water isotopes were used in this study, H₂¹⁶O, D₂¹⁶O and H₂¹⁸O. By studying the free O-H(D) stretch, present only at the ice surface, all isotopes could be spectroscopically identified. In particular, the decrease of isotope B could be monitored, along with the concomitant increase of isotope A, as a function of temperature. It is observed that mixing between surface and bulk water starts already at 100K. There are also a clear difference between the different isotopes. H/D exchange is observed and will be discussed. The vibrational data is interpreted with the aid of DFT cluster calculations.

4:40pm **SS1+NC-ThA9 The Adsorption of Water on Cu₂O and Al₂O₃ Thin Films**, X. Deng, T. Herranz, C. Weis, H. Bluhm, M. Salmeron, Lawrence Berkeley National Laboratory

The initial stages of water condensation, approximately 6 molecular layers, on two oxide surfaces, Cu₂O and Al₂O₃, have been investigated using ambient pressure x-ray photoelectron spectroscopy at relative humidity values (RH) from 0 to > 90%. Water adsorbs first dissociatively on oxygen vacancies producing adsorbed hydroxyl groups in a stoichiometric reaction: $\text{O}_{\text{vac}} + \text{H}_2\text{O} = 2\text{OH}$. The reaction is completed at ~ 1% RH and is followed by adsorption of molecular water. The thickness of the water film grows with increasing RH. The first monolayer is completed at ~ 15% RH on both oxides and is followed by a second layer at 35-40% RH. At 90% RH, about 6 layers of H₂O film have been formed on Al₂O₃. The wetting process and the essential role of OH on oxide surfaces will also be discussed.

5:00pm **SS1+NC-ThA10 The Reactive Uptake of Water and CO₂ on MgO(100) Monitored by Ambient Pressure XPS**, J.T. Newberg, D.E. Starr, Lawrence Berkeley National Lab., S. Yamamoto, S. Kaya, H. Ogasawara, Stanford Synchrotron Radiation Lab., T. Kendelewicz, Stanford University, M. Salmeron, Lawrence Berkeley National Lab., G.E. Brown, Stanford University, A.R. Nilsson, Stanford Synchrotron Radiation Lab., H. Bluhm, Lawrence Berkeley National Lab.

The MgO(100) substrate is one of the most widely studied surfaces for water adsorption.¹ However, fundamental questions about whether water adsorbs molecularly or dissociatively under ambient conditions remains unanswered. This has been due in part to the lack of an in situ, chemically specific, surface sensitive technique. CO₂ is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for CO₂ sequestration.² Here we present results from the investigation of the interaction of water with MgO(100)/Ag(100) films using ambient pressure XPS (AP XPS). With AP XPS we can quantitatively probe the water film thickness along with the chemical speciation of the solid substrate, while in equilibrium with water vapor. We have characterized the uptake of water on MgO at water pressures from 10⁻⁹ to 1 Torr, up to a maximum of 25% relative humidity (RH). In addition, we monitored the interaction of CO₂ with the metal-oxide surface. At room temperature, both MgO hydroxylation and molecular water adsorption were observed at < 10⁻⁶ Torr. At ~0.1% RH about 0.3 ML of molecular water was observed (1 ML = 0.31 nm). However, at this RH the surface of MgO was completely passivated with an overlayer of hydroxide that has a thickness similar to that of brucite (Mg(OH)₂, 1 ML = 0.48nm). As the RH was increased to 25% RH, the Mg-hydroxide overlayer thickness remained at ~1 ML, while the molecular water film increased to ~1.5 ML. Preliminary results for CO₂ showed some dependency of RH on the reactivity towards the metal-oxide surface. The formation of a brucite-like overlayer is consistent with a favorable Gibbs free energy for the bulk reaction of liquid and gas phase water with MgO (-27 and -36 kJ/mol, respectively). A similar phenomenon was observed with AP XPS for water on hematite (Fe₂O₃).³ These results indicate that even under the lowest ambient RH values in the environment, metal-oxides that have thermodynamically stable hydroxides are chemically transformed at the surface due to thin film water. Thus, the presence of thin film water can have implications for how mineral surfaces interact with organic, biological and inorganic species in the environment.

¹ M.A. Henderson 2002 Surf. Sci Rep. 46 1.

² T. Koljonen et al. 2004 Energy 29 1521.

³ S. Yamamoto et al. publication in preparation.

5:20pm **SS1+NC-ThA11 Water-Stabilized Reconstructions on Polar Surfaces of Rocksalt Oxides**, J. Ciston, L.D. Marks, Northwestern University

We have investigated the stabilizing effect of water on the $\sqrt{3}\times\sqrt{3}$ -R30° and 2x2 reconstructions of the MgO(111) and NiO(111) surfaces using a combination of x-ray photoelectron spectroscopy (XPS) and transmission electron diffraction (TED). Combined experimental analysis has confirmed that the MgO(111)- $\sqrt{3}\times\sqrt{3}$ -R30° is stable only in the presence of hydroxyl groups on the surface, which is contrary to previously published structures. Experimental refinements of the valence charge density at these surfaces will also be discussed. Our experimental studies have been coupled with

full-potential, all-electron density functional theory calculations to estimate surface energies and perform structural relaxations. The NiO system is particularly difficult to calculate due to highly localized and correlated 3d electrons. This has necessitated the use of a hybrid exchange-correlation functional in which the generalized gradient approximation is augmented with a 25% mixing of Hartree-Fock exact exchange for the 3d shell. This methodology substantially improves the accuracy of DFT-calculated surface energies, sometimes by several eV.

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