

Thursday Afternoon, November 1, 2012

Surface Science

Room: 22 - Session SS-ThA

Liquid/Surface Interactions

Moderator: G.A. Kimmel, Pacific Northwest National Laboratory

2:00pm **SS-ThA1 Interface Properties of Aqueous Nitrile Solutions**, *K.A. Perrine, A. Margarella, M.H.C. Van Spyk*, University of California Irvine, *B. Winter*, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, *H. Bluhm*, Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California Irvine

It is important to understand the molecular-level properties of aqueous organic mixtures that can affect the environment as well as a variety of chemical systems. Mixtures of acetonitrile and water solutions have been shown to have different properties at the surface and in the bulk at different bulk acetonitrile concentrations. According to surface sensitive studies and molecular dynamic simulations, at 0.07 mole fraction, hydrogen bonding is lost at the interface with increasing acetonitrile concentration, leading to a reorientation of the acetonitrile at the surface. In addition, water and acetonitrile clusters have been shown to coexist and interact by dipole interactions between 0.2 and 0.8 mole fraction of acetonitrile. The reorientation of another nitrile at the surface, propionitrile, by hydrogen bonding has also been observed, but for this molecule, there is a lack of bulk studies of water-nitrile solutions.

In our studies, liquid-jet X-ray photoelectron spectroscopy was used to determine the nature of aqueous solutions of these two nitriles. The C1s, N1s and O1s regions suggest that clustering of the nitrile and water is apparent at the surface as well as the bulk. A full range of nitrile concentrations was studied. In addition, we made comparisons between experiments in which the liquid jet is in contact with a few torr of vapor and experiments in which the jet is exposed to high vacuum. The surface and bulk properties, as determined by XPS, are the same under these two experimental conditions. Our results also allow us to compare the differences between solubility of the two nitrile aqueous solutions and their hydrogen bonding properties at the surface and in the bulk.

2:20pm **SS-ThA2 Photoelectron Spectroscopy of Sulfuric Acid Aqueous Solutions**, *A. Margarella, K.A. Perrine*, University of California Irvine, *T. Lewis*, Lawrence Livermore National Laboratory, *M. Faubel*, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *B. Winter*, Helmholtz-Zentrum Berlin für Materialien und Energie and BESSY, Germany, *J.C. Hemminger*, University of California Irvine

The air-liquid interface of aerosols is an important site for heterogeneous chemistry in the atmosphere, associated, for instance, with the formation of reaction products relevant for ozone depletion. Concentrated (5-14 M) super-cooled aqueous solutions of sulfuric acid are known as sulfate aerosols and are one of the most abundant types of atmospheric aerosols. Fully understanding the dissociation of sulfuric acid, on the molecular level, is important because heterogeneous chemistry occurring on the surface of sulfate aerosols depends on the availability, speciation, location, and solvation structure of the species in solution. Aqueous solutions of sulfuric acid and the subsequent acid dissociation are useful models for sulfate aerosols. As a strong acid, the bulk of an aqueous solution of sulfuric acid will have H_3O^+ , HSO_4^- and SO_4^{2-} , and at high concentrations when the water concentration is very low, un-dissociated H_2SO_4 may be present. The bulk species composition is a function of the initial solution concentration, as well as temperature, and this composition as been well characterized by a variety of methods, such as sum frequency generation and Raman spectroscopy. Here, the chemistry of sulfuric acid aqueous solutions is explored by photoelectron spectroscopy on a liquid micro-jet. Experiments were performed at Beamline U41-PGM at the BESSY II synchrotron facility. A series of sulfuric acid aqueous solutions is measured at a low temperature of 6°C. Deconvolution of the photoelectron spectra yields electronic information on the ionization species of sulfuric acid.

2:40pm **SS-ThA3 Using Nanoscale Amorphous Solid Water Films to Create and Study Deeply Supercooled Liquid Water**, *S.R. Smith, B.D. Kay*, Pacific Northwest National Laboratory **INVITED**

Vapor deposition of water on cryogenic substrates is known to produce amorphous solid films. When heated above their glass transition (136 K) these films transform into deeply supercooled liquid water which subsequently crystallizes around 160 K. These nanoscale liquid films can be used to study processes such as diffusion, isotope exchange, and crystallization at cryogenic temperatures not attainable by conventional

supercooling of the bulk liquid. Molecular beam scattering, programmed desorption (both TPD and isothermal), and vibrational spectroscopy are used to study the thermodynamics and chemical kinetics of these processes in unprecedented detail. This talk will highlight our recent advances in this area. This work was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. The research was performed using EMSL, 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 by Battelle, operated for the U.S. DOE under Contract DE-AC05-76RL01830.

3:40pm **SS-ThA6 DFT Study of Water Dissociation and Diffusion on Metal Surfaces, Kinks and Step**, *L. Arnadottir*, Oregon State University

Surface defects play a critical role in many surface processes, for example in the formation of a water layer on Pt(111). In this DFT study, we describe water adsorption, diffusion, dissociation and early cluster formation on terrace, steps and kinks on Pt(111). The adsorption energy of a single water molecule increase as it moves from the flat terrace up to the step edge and then atop a kink atom. The highest activation barrier along this path is only 0.22 eV. The stronger binding on the step and kinks makes the reverse barriers much larger and, therefore, the diffusion from the step or kink back to the flat terrace less likely. This suggests that at approximately 100 K, water will diffuse to lower energy adsorption sites on the steps and kinks and form chains on step edges before wetting the lower terrace, in agreement with STM measurements by Morgenstern, M. et al. [1].

Surface defects also play an important role in the dissociation of water molecules. The calculated reaction energy for water dissociation, $\text{H}_2\text{Oads} \rightarrow \text{OHads} + \text{Hads}$, on flat terrace, step and kink shows an interesting trend where the reaction energy on the flat terrace is almost twice the energy at a kink and three times the energy on a step. Water molecule dissociation on flat Pt(111) terrace is therefore less likely than at defects. The reaction energy is 0.21 eV on the (221) step and 0.37 eV on the (854) kink, making the defect sites significantly more promising for water dissociation.

The activation energy for dissociation is also lowest at a step site, 0.80 eV. An oxygen assisted dissociation on the step ($\text{H}_2\text{Oads} + \text{Oads} \rightarrow 2 \text{OHads}$) has even lower reaction energy but the activation barrier is similar. Although the reaction energy at the kink was not so high, the activation barrier for dissociation is very high, 1.4 eV. The energy landscape is quite complicated around the kink but we consistently get this high barrier for the various dissociative pathways that have been tried. The high barrier may be the result of the strong adsorption at the kink sites.

1. Morgenstern, M., Michely, T. and Comsa, G., *Phys. Rev. Lett.* **77** 703 (1996).

4:20pm **SS-ThA8 Adsorption and One-Dimensional Chain Formation of Water on $\text{TiO}_2(110)$** , *J. Lee, D.C. Sorescu, X. Deng*, National Energy Technology Laboratory, *K.D. Jordan*, University of Pittsburgh

The adsorption of water molecule on a reduced rutile $\text{TiO}_2(110)$ - (1×1) surface has been investigated using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. STM results indicate that water monomer adsorbs on top of Ti(5f) atom on the Ti row. The DFT calculations show that the most stable configuration of adsorbed water on $\text{TiO}_2(110)$ has the binding energy of 23.6 kcal/mol. In this configuration, the oxygen atom is positioned on top of a Ti(5f) atom with one of the O-H bonds pointing toward a bridging oxygen via H-bonding and the other pointing along the Ti row direction. The water monomer can be dissociated by the electron injection from the STM tip into an oxygen adatom on Ti row. As the coverage increases, water molecules start to form one-dimensional chains via H-bonding along the Ti row direction. Thermal annealing after the adsorption of water at low temperature on $\text{TiO}_2(110)$ is also found to be effective in the formation of the one-dimensional water chain. The effects of other coadsorbates such as CO_2 and O_2 in the formation of water chain will also be discussed.

4:40pm **SS-ThA9 Characterization of Surface and Adsorbate Chemistry on TiO_2 ; Particle Ensembles and Atmospherically Prepared TiO_2 ; Single Crystalline Surfaces**, *C. Kunze, B. Torun, G. Grundmeier*, University of Paderborn, Germany

Titanium dioxide (TiO_2) plays a crucial role for modern technical applications such as the design of new catalysts or biomaterials. TiO_2 particles in the modifications of rutile or anatase are a widely used material as an inorganic white pigment. In particle processing the force interactions within particle collectives are of outmost interest in terms of bulk flow properties and agglomerate dispersibility. As the adhesion between small particles is mostly driven by capillarity- and van der Waals forces, the

investigation of surface chemistry plays a crucial role to understand interactions at TiO_2 particle surfaces. For studies of particle ensembles a new experimental setup was developed to investigate particle parameters under both control of relative humidity (capillary forces) and UV light exposure (hydrophobic to hydrophilic transition). By combined Fourier Transform Infrared Spectroscopy (FTIR) and quartz crystal microbalance (QCM) we studied the influence of surface hydroxyl densities and molecular adsorbates on the formation of surface water adsorbate films in environments of defined relative humidity.

To study the formation of adsorbates on a model surface, $\text{TiO}_2(100)$ and $\text{TiO}_2(110)$ single crystalline surfaces were prepared by a wet chemical etching procedure followed by an annealing step. The crystal surface and the native adsorbate layer were studied by means of angle resolved photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and atomic force microscopy (AFM).

The surface analysis by AFM and LEED revealed a single crystalline TiO_2 surface for both crystal orientations. An ad-layer of surface-hydroxides and specifically adsorbed water additionally to the native contamination layer of low-weight (hydro)carbon species formed under ambient conditions could be proven by angle resolved XPS experiments.

As a model of the carboxy-functional, (hydro)carbon contamination film the adsorption of nonadecylcarboxylic acid (NDCA) on the crystal surface was studied by AFM and angle resolved XPS experiments. Here a significantly different mechanism of adsorption was found comparing the $\text{TiO}_2(100)$ and $\text{TiO}_2(110)$ surfaces. AFM investigations showed a micellar adsorption of NDCA on the (100) surface forming a dense layer of NDCA micelles which could be removed from the surface by AFM based “nanoshaving”-experiments. In comparison the (110) surface showed very weak interactions with NDCA leading to a coverage of less than one monolayer as a result of different surface termination in comparison to the (100) crystal.

5:00pm **SS-ThA10 The Critical Marangoni Number Dependence with Different Aspect Ratio Comparing Microgravity Experiments and Numerical Simulation**, *S. Yoda*, ISAS, Japan, *S. Matsumoto*, IASA, Japan, *H. Kawasaki*, *I. Ueno*, Tokyo University of Science, Japan

Marangoni experiments with a large diameter, 50 mm, were carried out under microgravity condition in Japanese Experiment Module to make clear critical Marangoni number dependence in liquid bridge configuration such as liquid bridge aspect ratios (length/diameter of liquid bridge). The experiments with the different aspect ratios (length/diameter of liquid bridge) were changed from 0.25 to 1.2 which determined each critical Marangoni numbers. The critical Marangoni numbers decreased up to around 0.4, and after that the number increased monotonically up to 1.2. The most smallest number is observed at critical $\text{Mac}(20000)$ at 0.4 and the maximum is $\text{Mac}(50000)$ at 1.2. The large liquid bridge was vibrated by crew activity, so that all experiments were done during crew sleeping. This behavior can be qualitatively explained by considering thermal boundary layers which form at both heating and cooling desks of the liquid bridge. The experimental data were good agreement with the numerical results.

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