

Surface Science

Room 2004 - Session SS2-TuM

Water-Surface Interactions

Moderators: A.A. Baski, Virginia Commonwealth University, M. Salmeron, Lawrence Berkeley National Laboratory

8:20am **SS2-TuM2 Reactions of Ozone with the Constituents of Sea Salt Particles**, *M.A. Brown, M.J. Krisch, J.T. Newberg*, University of California, Irvine and AirUCI; *B.S. Mun*, Lawrence Berkeley National Laboratory; *J.C. Hemminger*, University of California, Irvine and AirUCI

The uptake and then destruction of ozone on the surface of alkali halides is thought to play an important role in the chemistry of the troposphere and is believed to generate gas phase molecular halogens in the atmosphere. We present the results from both lab based UHV XPS and ambient pressure XPS at LBNL Advance Light Source beamline 9.3.2 on the reactive uptake of ozone at both the vapor solid and vapor liquid interfaces of alkali halide salts. Ozone proves to be a strong oxidizer and iodide salts are surface oxidized to iodates. Uptake measurements for both the bromide and chloride salts will also be presented. Through the use of surface imaging techniques at the Molecular Foundry of LBNL insights into the site specificity of the reaction are explored.

8:40am **SS2-TuM3 Nanocarpenter Effect: Formation and Characterization of Watermarks on Aligned Silicon Nanorod Arrays**, *Y.P. Zhao, J.G. Fan*, University of Georgia

When a water drop spreads on an aligned silicon nanorod surface prepared by glancing angle deposition, a watermark developed on the surface after water evaporated due to the bundling of nanorods. The watermark radius R follows a simple power law relationship with the water volume V as $R \sim V^n$. The scaling exponent n , in the vicinity of $1/3$, increases when the nanorods height decreases. This behavior is attributed to the competition of evaporation and spreading of a water droplet during the spreading process. The size of the bundled nanorod cluster depends not only on the nanorod height, but also on the location in the watermark. The cluster size almost remains as a constant near the center, and then it decreases with the distance from the center. This phenomenon can be qualitatively interpreted through the change of the total free energy during the precursor invading the nanorod array, by considering the contribution from the mechanical energy change due to the bending and clustering of nanorods.

9:00am **SS2-TuM4 Lateral Water Ordering at Reconstructed MgO(111) Surfaces**, *P.F. Lyman, S.S. Parihar, H.T. Johnson-Steigleman, V.L. Shneerson, R. Jung, D.K. Saldin*, University of Wisconsin-Milwaukee; *F.U. Renner, T.-L. Lee, J. Zegenhagen*, ESRF, Grenoble, France

The polar oxide surface MgO(111) is known to undergo several air-stable reconstructions, including $p(2 \times 2)$ and $(\sqrt{3} \times \sqrt{3})R30^\circ$ phases. The observed structure depends on O partial pressure and temperature. We report on a study of stability and structure of these reconstructions at an aqueous interface. The interface between the bulk water layer (5 μm) and the reconstructed MgO(111) was probed using surface x-ray diffraction. For other substrates, previous measurements of the specular surface truncation rod had revealed that a surface can induce layered ordering in the interfacial water, but measurements of off-specular rods indicated that only weak lateral ordering was present.¹ Our study addressed the additional effect of a corrugated, reconstructed interface. Moreover, reflections with smaller in-plane momentum transfers are available when using a reconstructed surface, allowing more sensitive studies of any lateral ordering. For the $(\sqrt{3} \times \sqrt{3})R30^\circ$ phase, the reconstruction was stable in contact with water for many hours. Changes (between wet and dry interfaces) in the non-specular rods closest to the origin (in reciprocal space) reveal changes in the ordered lateral electron density, presumably due to lateral ordering in the water layer. The $p(2 \times 2)$ surface roughened and de-reconstructed almost immediately upon immersion in water. ¹FootnoteText@ footnote 1@M.F. Reedijk et al., Phys. Rev. Lett. 90, 066103 (2003).

9:20am **SS2-TuM5 2006 Medard W. Welch Award Lecture - Surface Composition and Surface Chemistry of Alkali Halide Solids and Aqueous Solutions**, *J.C. Hemminger*¹, UC, Irvine; *M.J. Krisch, M.A. Brown*, UC, Irvine and AirUCI; *S. Ghosal*, LLNL; *H. Bluhm, B.S. Mun*, LBNL; *A. Verdaguer*, Institut Catala de Nanotecnologia, Spain; *F. Ogletree, M. Salmeron*, LBNL
INVITED

Chemistry at the surfaces of aerosol particles in the troposphere has become a topic of considerable interest recently. Reactions between gas phase molecules in the atmosphere and aerosol particles and droplets may modify the properties of the aerosol (such as hydrophobicity or chemical composition). In addition, components of the aerosol may be converted into volatile compounds that can then be active in gas phase reactions in the troposphere. Clearly, the composition of the surfaces of such particles will control their surface reactivity. We have studied models for sea salt aerosols, which are abundant in the marine region world-wide. We have shown that adsorbed water is critical to the surface chemistry of salt surfaces. In addition, recent molecular dynamics simulations of alkali halide solutions have suggested that the surfaces of alkali halide solutions are enriched in halide species. Our experiments quantitatively confirm that the surfaces of aqueous KI, KBr and KCl solutions have enhanced halide ion concentrations. Additionally, experiments on Br doped NaCl samples show conclusively that Br strongly segregates to the liquid-vapor interface of such mixed solutions. A combination of data from scanning polarization force microscopy experiments and x-ray photoelectron spectroscopy experiments will be shown to illustrate these phenomena. The importance of these results to atmospheric chemistry will be illustrated through a discussion of bromine segregation in sea salt aerosols and the importance of the subsequent bromine chemistry in the arctic marine troposphere.

10:40am **SS2-TuM9 Growth and Structure of Water on Amorphous SiO₂ Investigated by Kelvin Probe Microscopy and In Situ X-ray Photoelectron Spectroscopy**, *M. Salmeron*, Lawrence Berkeley National Laboratory; *A. Verdaguer*, Institut Catala de Nanotecnologia, Spain; *G. Ketteler, Ch. Weiss, H. Bluhm, D.E. Starr*, Lawrence Berkeley National Laboratory

The growth and structure of water layers on SiO₂ on Si wafers at pressures between 1 and 4 torr and temperatures between -10 and 21 C has been studied using Kelvin Probe Microscopy and in situ X-ray photoelectron spectroscopy. As the relative humidity (RH) increases from 0 to 75% water adsorbs forming a uniform film up to a thickness of 4 to 5 layers. The surface potential increases in that range by about 120 mV and remains constant afterwards. Above 75% RH the film grows rapidly reaching 6 to 7 monolayers at 90%. The near-edge X-ray adsorption spectra is similar to that of liquid water (imperfect H-bonding coordination) after the first four layers. At all stages the presence of unsaturated dangling H-bonds in the outermost layer in contact with the vapor is visible.

11:00am **SS2-TuM10 A Combined Droplet Train / Photoemission Spectroscopy Experiment for the Investigation of Heterogeneous Reactions on Liquid Surfaces**, *D.E. Starr, K.R. Wilson, H. Bluhm*, Lawrence Berkeley National Laboratory

The properties of liquid/vapor interfaces strongly influence the abundance and reactivity of trace gas molecules that are important for many heterogeneous processes in atmospheric and environmental chemistry. A direct measurement of the liquid/vapor interface under atmospherically and environmentally relevant conditions is difficult due to the lack of quantitative experimental techniques that are surface-sensitive, chemically specific and can operate at elevated pressures in the Torr range. Here we describe a novel experimental setup that is operating at beamline 11.0.2 at the Advanced Light Source in Berkeley. The instrument combines synchrotron-based ambient pressure photoemission spectroscopy (APPE), operating at pressures of more than 5 Torr) and a liquid droplet train produced by a vibrating orifice aerosol generator (VOAG). In a VOAG, droplets of uniform size (5-100 μm) are generated by forcing the liquid under investigation through a vibrating orifice. The short time (milliseconds) between the generation of the droplets at the vibrating orifice and their measurement in the spectrometer minimizes the level of contamination of the surface. Beam damage is kept at a minimum since each droplet is irradiated only for a few microseconds by the incident X-rays. In addition, the interaction time of the droplet surface with gas molecules can be varied over a range from about 1 to 20 ms, allowing for measurements of the reaction kinetics at liquid surfaces as a function of exposure time to a gaseous environment. Studies of the role of liquid surface species in the transport of gas molecules across the liquid/vapor

¹ Medard W. Welch Award Winner

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interface, as well as studies of surface-mediated chemical reactions at the liquid/vapor interface are also possible.

11:20am **SS2-TuM11 Ion Depth Profiles at the Liquid - Vapor Interface of Electrolytes in Mixtures of Water and Alcohol**, *M.J. Krisch, M.A. Brown, R. D'Auria, K.M. Callahan, D.J. Tobias, J.C. Hemminger*, University of California at Irvine; *M. Ammann*, Paul Scherrer Institute; *H. Bluhm*, Lawrence Berkeley National Laboratory

We find that organic compounds modify the interfacial profile of electrolytes in aqueous solutions. Our experiments probe atomic composition at the liquid surface with ambient pressure x-ray photoelectron spectroscopy at the Advanced Light Source. Photoelectron kinetic energies are varied to produce a depth profile of the liquid - vapor interface. Surface enhancement of iodide anions, an effect observed in aqueous potassium iodide solution, disappears in the presence of a surface active alcohol such as 1-butanol. Results are compared to molecular dynamics simulations of the same system. Insight into ion behavior at mixed liquid surfaces is crucial for understanding the chemistry of atmospheric aerosols, which frequently contain ternary mixtures of water, electrolytes, and organics.

11:40am **SS2-TuM12 Interfacial Water Structure and Dynamics Probed with Chemical Force Microscopy**, *P.D. Ashby, M. Salmeron*, Lawrence Berkeley National Laboratory

Understanding the structure and energetics of water at interfaces is important for many diverse fields of study including self-assembly of nanostructures, protein folding, tribology, and catalysis. Two novel methods for investigating interfacial water structure with the Atomic Force Microscope will be presented. First, Brownian Force Profile Reconstruction harnesses cantilever thermal motion to accurately and precisely reconstruct equilibrium force profiles. Experiments between solvated hydroxyl terminated self-assembled monolayers revealed highly oriented water structure which decayed into the bulk within three molecular layers. Second, Tapping Mode Force Profile Reconstruction computes the forces experienced by the advancing and receding tip surface during high frequency oscillation. Investigation of solvated hydrophilic surfaces revealed slow reordering dynamics in electrostatic double layers and fast reordering for less long range interactions.

12:00pm **SS2-TuM13 The Adsorption and Uptake of Acetone on Ice Studied with Ambient Pressure Photoemission Spectroscopy**, *D.E. Starr*, Lawrence Berkeley National Laboratory; *M. Ammann*, Paul Scherrer Institute; *H. Bluhm*, Lawrence Berkeley National Laboratory

The interaction between small molecules and ice particles has broad implications in atmospheric chemistry. While many experimental techniques, such as flow tube and Knudsen cell measurements and laser based spectroscopic techniques, have provided a great deal of insight into the kinetics and mechanisms associated with these reactions, most of these techniques lack the ability to chemically identify the species directly adsorbed on the ice surface. On the other hand, surface science techniques are particularly well-suited for exactly this purpose but generally require Ultra-High Vacuum to be utilized, precluding their use under atmospherically relevant conditions where the vapor pressure of ice is in the mTorr to Torr range. With the development of synchrotron-based Ambient Pressure Photoemission Spectroscopy (APPES) the chemical identification of adsorbed molecules on the ice surface at atmospherically relevant conditions becomes possible. As an initial step in these studies we have investigated the adsorption and uptake of acetone on the ice surface. The sequestering of acetone by ice particles in the atmosphere and polar snowpack may play an important role in atmospheric chemistry due to acetone's role as a radical source in the upper troposphere and radical chemistry in polar snowpack. In addition, the acetone/ice system is believed to be a fairly simple, reversible adsorption system. Uptake measurements using the integrated C1s peak area as a function of acetone partial pressure indicate an adsorption energy of approximately 45 kJ/mol. In addition, high resolution C1s spectra as well as O K-edge Near Edge X-ray Absorption Fine Structure (NEXAFS) both show little to no modification of the acetone molecule or the ice surface upon adsorption. The combined results indicate a weak interaction between the acetone molecule and ice surface under ambient conditions.

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