

Monday Morning, October 31, 2011

Surface Science Division

Room: 109 - Session SS1-MoM

Water Films & Environmental Interfaces

Moderator: H. Fairbrother, Johns Hopkins University

8:20am **SS1-MoM1 Surface Science of Acetonitrile on Model Interstellar Ices and Grains**, *A. Abdulgalil, M. Collings, M. McCoustra*, Heriot-Watt University, UK

Physical and chemical processes occurring on the surfaces of icy dust grains in the cold, dense interstellar medium have a crucial role to play in the evolution of the modern Universe. The formation of simple hydrides, *e.g.* water, on grain surfaces explains the infrared astronomical observations of icy grain mantles and provides a reservoir of coolant molecules during the early stages of star formation that helps maintain the current rate of star formation and favours the formation of small, long-lived stars. Energetic processing of icy mixtures by short wavelength radiation and cosmic rays turns the icy grain mantles into chemical nanofactories producing increasingly complex organic molecules. Nitriles (RCN) represent a potential intermediate on the pathway to forming amino acids in these icy mantles. However, the formation of nitriles in and on icy grain mantles is not understood. Nor is the surface science of these simple species on models of the interstellar grain population. Acetonitrile (CH_3CN) is the simplest organic nitrile and is amongst the list of chemical species observed in the interstellar medium. This paper will report our recent investigations of the interaction of CH_3CN with model silica and water ice surfaces representative of bare and icy interstellar dust grains. We will report on the nature and strength of the interaction of CH_3CN with these substrates and on the thermal and non-thermal (electron-induced) desorption of CH_3CN from these surfaces as part of our on going programme in solid state and surface astrochemistry.

8:40am **SS1-MoM2 Energetic Xenon Sputtering and Embedding at Ice Surfaces**, *D.R. Killelea, K.D. Gibson, H. Yuan, S.J. Sibener*, University of Chicago

PLEASE NOTE YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY PRESENT ONE PAPER ONLY (ORAL OR POSTER) AT THE CONFERENCE. YOU ARE LISTED AS PRESENTER FOR ABSTRACT #278Energetic collisions between gas-phase atoms or molecules and ice surfaces are ubiquitous in nature. Such collisions occur under non-equilibrium conditions given the disparity between the temperature of the substrate and that of the incident species. Moreover, metastable absorption states can be accessed at sufficiently high collision energies, opening up enhanced channels for species collection and concentration. Here, we present results of a study where the energetically accessed absorption states of the network of molecules in an ice surface were probed with translationally activated gas-phase Xe atoms, focusing on sputtering, energy accommodation, and a new mechanism for the incorporation of volatile species into ice surfaces: collisionally activated embedding. Evidence for embedding comes from the observation of Xe desorption at temperatures nearly 100 K above the normal desorption temperature for xenon adsorbed onto an ice surface.

9:00am **SS1-MoM3 Composition and Chemistry at the Liquid/Vapor Interface of Aqueous Solutions: Liquid-Jet XPS Experiments Coupled with MD Simulations**, *J.C. Hemminger*, University of California, Irvine
INVITED

In spite of the importance of liquid/vapor interfaces to many real world problems our understanding of the composition and chemistry of liquid/vapor interfaces is limited. We have employed liquid micro-jet methods to obtain x-ray photoelectron spectra of the liquid/vapor interface of aqueous solutions at the BESSY II synchrotron. The variable photon energy characteristic of synchrotron light sources allows us to carry out experiments over a range of photoelectron kinetic energies—thus varying the probe depth of the experiment. The result is a depth profile of the composition of the liquid/vapor interface. We have focused our experiments on aqueous solutions. In this talk I will describe results from recent experiments on the following systems: (1) aqueous nitric acid solutions, in which we demonstrate a large difference in the degree of dissociation at the surface compared to bulk solution. We have also been able to determine the degree of dissociation at the interface and in the bulk solution for a range of temperatures sufficient to determine the enthalpy of the dissociation reaction for the interface and the bulk, (2) aqueous solutions of

monoethanolamine and monoethanolamine reacted with CO_2 —aqueous monoethanolamine is widely proposed for CO_2 capture processes, (3) aqueous solutions of the organosulfur compounds DMS, DMSO, DMSO_2 , DMSO_3 —DMS is a major source of environmental sulfur compounds including in the atmosphere. In these systems we have been able to determine the relative propensity of each molecule for the liquid/vapor interface, (4) carboxylic acid solutions where we have been able to determine the relative surface activity of the dissociated and undissociated acid. For each of the above systems we have carried out molecular dynamics simulations. These simulations combined with our experimental depth dependent measurements have provided molecular level insight into the behavior of molecular solutes in aqueous solution.

9:40am **SS1-MoM5 In Situ Studies of Sulfuric Acid Aqueous Solutions by X-ray Photoelectron Spectroscopy**, *A. Margarella, T. Lewis*, University of California, Irvine, *M. Faubel*, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *B. Winter*, Hemholtz-Zentrum Berlin für Materialien und Energie, Germany, *J.C. Hemminger*, University of California, Irvine

Sulfuric acid is amongst the most widely used acids in the chemical industry, as well as having an important presence in atmospheric aerosols. Using a micro-liquid jet, the chemistry at the liquid-vapor interface of aqueous solutions is explored in-situ by x-ray photoelectron spectroscopy (XPS). Experiments presented were performed at Beamline U41 at the BESSY II synchrotron facility. By tuning the energy of the incoming photons, the kinetic energy of the photoelectrons is varied, allowing measurements from different depths of solution. As a strong diprotic acid, an aqueous solution of sulfuric acid will have HSO_4^- and SO_4^{2-} present, and at high concentrations, (greater than 16M) undissociated H_2SO_4 is present. In XPS, all of these components are distinguishable using their S2p binding energy shifts. A series of sulfuric acid aqueous solutions with concentrations up to 16M is measured and using the peak areas in the XP spectra, the dissociation at the surface relative to the bulk can be determined for different solutions.

Additionally, the effect of solution temperature on the acid dissociation at the surface is explored.

10:00am **SS1-MoM6 Infrared Spectroscopy of Thin Water Films on $\text{TiO}_2(110)$: Anisotropy and the Hydrogen-Bonding Network**, *G.A. Kimmel, M. Baer, N.G. Petrik, C.J. Mundy, R.J. Rousseau*, Pacific Northwest National Laboratory

The structure of water at interfaces is crucial for processes ranging from photocatalysis to protein folding. We have investigated the structure of thin water films adsorbed on $\text{TiO}_2(110)$ using reflection-absorption infrared spectroscopy (RAIRS), temperature programmed desorption and *ab-initio* molecular dynamics simulations. Infrared spectra were obtained for light with the plane of incidence parallel and perpendicular to the [001] azimuth of $\text{TiO}_2(110)$ for water coverages ≤ 4 monolayers (ML). The spectra indicate strong anisotropy in the water structure along the two major azimuths. For both 1 and 2 ML coverages, the water films form “strings” of water molecules parallel to the bridging oxygen rows on the (110) surface. Within the strings, each molecule participates in 4 bonds, such that the films have no dangling hydrogen bonds. The vibrational densities of states predicted by the *ab-initio* simulations for 1 and 2 monolayer coverages agree well with the observations. Despite extensive prior research, the structure of water films on $\text{TiO}_2(110)$ has remained controversial. Our results provide crucial, molecular-level information about the structure of water films on this benchmark transition metal oxide.

11:20am **SS1-MoM10 Origins of the Molecular Volcano: Dewetting and Crystallization Effects Leading to Rapid Desorption from Amorphous Solid Water Overlayers**, *R.A. May, R.S. Smith, B.D. Kay*, Pacific Northwest National Laboratory

Amorphous solid water (ASW), a metastable phase of water occurring when water is deposited on a substrate cooled below 140K, is of fundamental interest for an array of applications including but not limited to desorption from interstellar ices and investigation of diffusion and solvation processes. When deposited over an immiscible substance, such as CCl_4 , the underlayer desorption is dictated by the morphology of the ASW overlayer. This desorption process culminates in the rapid release of the underlayer commensurate with the development of crystallization induced cracks through the ASW. This episodic release is termed the “molecular volcano”. Thus, the desorption event reports on changes in the structure of the ASW overlayer. Infrared spectroscopy combined with programmed desorption elucidates the complex interplay between the dewetting and crystallization processes which dominate the eruption event. The effects of the ASW

deposition temperature and overlayer thickness on the CCl₄ desorption process will be presented and discussed.

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.

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