

Thursday Afternoon, October 18, 2007

Surface Science

Room: 608 - Session SS1-ThA

Environmental Surfaces

Moderator: J.T. Dickinson, Washington State University

2:00pm **SS1-ThA1 Influence of Surface Oxides on the Colloidal Stability, Mobility and Sorption Properties of Carbon Nanotubes in Aquatic Environments.** *H. Fairbrother, B. Smith, H.-H. Cho, F.K. Bangash, M. Shin, W.P. Ball*, Johns Hopkins University **INVITED**

Carbon nanotubes (CNTs) are a unique and versatile class of nanomaterials with enormous commercial potential. This has been responsible for a rapid increase in their production rates and, as a result, larger quantities of CNTs will inevitably find their way into the environment. The ecological and toxicological impacts of these nanomaterials are, however, still poorly understood. Many purification and functionalization strategies incorporate oxygen-containing functional groups into the surface of CNTs, and similar modifications can occur after CNTs are released into the environment through exposure to oxidizing agents. To address this issue surface analytical techniques have been developed to quantify both the concentration of oxygen and distribution of surface oxides produced on CNTs by different oxidative treatments. In this presentation the effect of oxidation and the introduction of surface oxides on the colloidal stability and sorption properties of CNTs in aquatic environments will also be discussed. A suite of CNTs with different levels of oxygen content were prepared by refluxing pristine CNTs in HNO_3 solutions of various concentrations; X-ray photoelectron spectroscopy (XPS) showed that the surface oxide concentration increased from 3% for the pristine nanomaterials to 12.5% for CNTs treated in $\sim 16\text{M}$ HNO_3 . The corresponding variation in oxide distribution has been probed using chemical derivatization in conjunction with XPS. UV-vis spectroscopy shows that well-defined relationships exist between the level of CNT surface oxidation and their colloidal stability; specifically, more highly oxidized CNTs remain stable over a wider range of aquatic conditions. The sorption properties of CNTs also display systematic variations as the level of surface oxidation increases: adsorption of ^{14}C labeled-naphthalene, a hydrophobic organic chemical, decreased linearly while divalent heavy metal contaminants like Zn^{2+} showed an increasing affinity towards more highly oxidized CNTs. Relationships that exist between specific types of surface oxides, particularly carboxylic acid groups, and CNT behavior in aquatic environments will also be discussed. In general, our studies highlight the fact that even comparatively small changes in surface oxygen concentration are responsible for pronounced changes in CNT properties.

2:40pm **SS1-ThA3 Reactions of Sulfur Dioxide on Calcium Carbonate and Iron Oxide Single Crystal and Particles Surfaces under Ambient Conditions.** *J. Baltrusaitis, V.H. Grassian*, University of Iowa

Reactions of sulfur dioxide under ambient conditions on environmentally important interfaces - calcium carbonate and iron oxide - single crystal and particle surfaces - have been investigated. A custom-designed X-ray Photoelectron Spectroscopy (XPS) ultra-high vacuum chamber is coupled to an environmental reaction chamber so that the effects of adsorbed water and molecular oxygen on the reaction chemistry can be followed. Atomic force microscopy provides additional spatial details about the reaction chemistry. It is determined that both the extent of reaction, the chemical speciation, which includes adsorbed sulfite and adsorbed sulfate, and reaction mechanisms are controlled by the environmental conditions. In addition, the two interfaces behave quite differently. Adsorbed water plays a key role in reactions of sulfur dioxide on calcium carbonate but not on iron oxide whereas molecular oxygen enhances the extent of reaction of sulfur dioxide on iron oxide but not calcium carbonate. Mechanisms to explain the reaction chemistry of sulfur dioxide on these two important environmental interfaces under different conditions are proposed. Atmospheric and environmental implications of these reactions are also discussed.

3:00pm **SS1-ThA4 pH Dependent X-ray Photoemission Studies of Hexylamine at the Aqueous-Vapor Interface.** *M.A. Brown*, University of California, Irvine, *B. Winter*, Max-Born-Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Germany, *M. Faubel*, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, *J.C. Hemminger*, University of California, Irvine

The understanding of molecular arrangements and interactions at the aqueous-vapor interface is important in many chemical and biological systems where the pH dependent chemistry may vary greatly from that of the bulk. We examine the surfactant properties of hexylamine ($\text{C}_6\text{H}_{13}\text{NH}_2$) and the protonated hexylamine ion ($\text{C}_6\text{H}_{13}\text{NH}_3^+$) at the aqueous-vapor interface. The state of this acid/base equilibrium couple should shed light on the local pH of the aqueous interface, as well as the relative aqueous solvation of the two species. Chemical shifts are observed in the N (1s) and C (1s) photoemission spectra due to protonation of the amine, allowing us to clearly identify and quantify the two species. The experiments use a 15 μm liquid micro-jet free vacuum surface at a micro-focus x-ray beamline of the BESSY synchrotron radiation facility. The bulk pH of solution is varied by addition of HCl in order to vary the degree of hexylamine protonation. Varying the energy of the ejected photoelectrons by carrying out experiments as a function of x-ray wavelength allows us to generate a depth profile of the aqueous-vapor interface. The core level O (1s), N (1s) and C (1s) photoemission spectra were collected as a function of photoelectron kinetic energy, creating a molecular level picture of the entire interfacial region. Results show that the concentration of hexylamine ($\text{C}_6\text{H}_{13}\text{NH}_2$) is greatly enhanced at the interface relative to the protonated hexylamine ion ($\text{C}_6\text{H}_{13}\text{NH}_3^+$). Peak broadening, and relative peak intensities vary with bulk pH, and are attributed to changes in molecular packing.

3:40pm **SS1-ThA6 Heterogeneous Uptake of Ozone on Solid Potassium Iodide.** *M.A. Brown, J.T. Newberg, M.J. Krisch*, University of California, Irvine, *B.S. Mun*, Advanced Light Source, LBNL, *P. Ashby*, Molecular Foundry, LBNL, *J.C. Hemminger*, University of California, Irvine

Ozone, a powerful oxidant trace gas found throughout both the troposphere and stratosphere is believed to oxidize alkali halides in the form of sea-salt aerosols and is considered to be a significant candidate for the formation of reactive gas phase molecular halogens. Recent studies suggest that although iodide is a minor component of sea-salt spray its concentration at the interface of aqueous solutions and at the interface of dried solid crystalline sea-salt particles is greatly enhanced relative to the bulk concentration. X-ray photoelectron studies described here show, under conditions in which a low defect density KI surface is completely devoid of adsorbed water molecules the surface oxidation by ozone results in a thin molecular layer of KIO_3 that is self-passivating. We report for the first time the reaction probability (?) at room temperature for the reaction $\text{KI(s)} + \text{O}_3(\text{g}) \rightarrow \text{KIO}_3(\text{s})$ of $? = 1.4 (\pm 0.7) \times 10^{-4}$. Results of the low defect density system are compared with the results of a high defect density polycrystalline KI surface. In-situ SPFM imaging provides molecular insight into the site specificity of the chemical reaction on the surface of KI (100).

4:00pm **SS1-ThA7 Surface Science Investigations of Photoprocesses in Model Interstellar Ices.** *J.D. Throver*, Heriot-Watt Univ., UK, *D.J. Burke*, Univ. College London, UK, *M.P. Collings*, Heriot-Watt Univ., UK, *A. Dawes*, P.J. Holtom, The Open Univ., UK, *F. Jamme*, Univ. of Nottingham, UK, *P. Kendall*, The Open Univ., UK, *W.A. Brown*, Univ. College London, UK, *I.P. Clark*, Central Laser Facility, CCLRC, UK, *H.J. Fraser*, Strathclyde Univ., UK, *M.R.S. McCoustra*, Heriot-Watt Univ., UK, *N.J. Mason*, The Open Univ., UK, *A.W. Parker*, Central Laser Facility, CCLRC, UK

In the last decade or so, the astronomy and astrophysics communities have come to realise that physical and chemical processes occurring at the surfaces of interstellar dust grains play a key role in the chemical evolution of the Universe. Grain surfaces promote the formation of molecular hydrogen and simple hydride species such as water, ammonia and methane. As such, at the temperatures found in the most chemically rich regions of the interstellar medium (ISM), typically 20 K or less, they reactively accrete icy mantles containing these species. Condensation of molecules from the gaseous ISM occurs in parallel, producing water-rich icy mantles that are readily observed in the infrared in many lines of sight towards star-forming regions. These mantles play a crucial role as reservoirs for small molecular coolants during the earliest phases of star formation, promoting the formation of small, long-lived stars such as our own Sun. They also act as chemical nanofactories driven by energy from photons and cosmic rays to produce increasingly complex chemical species from simple ice mixtures, hence seeding the Universe with a complex chemical soup. While numerous studies exist in the literature seeking to understand the chemical evolution

of water-rich icy mixtures during irradiation by light and charged particles, the majority of these high vacuum studies have failed to address the fundamental question of the disposition of the incident energy. How much of the photon or charged particle's energy goes into driving physical processes (morphological change, desorption, etc.) as opposed to driving chemical processes? Here we will report on recent surface science investigations aimed at addressing this most fundamental of questions in laboratory astrochemistry.

4:20pm SS1-ThA8 Monolayer Etch Pits Produced by Pulsed 248-nm Irradiation of Cleaved Alkali Halide Surfaces in 10^{-5} Pa Water Vapor¹, S.C. Langford, K. Kimura, J.T. Dickinson, Washington State University

On single crystal NaCl, 248-nm laser radiation can roughen steps and produce monolayer islands and etch pits at fluences well below the macroscopic damage threshold.² These effects are dramatically altered by the presence of 10^{-5} Pa water vapor. In this work, we extend these observations to single crystal KCl and KBr. Atomic force microscopy (AFM) images of NaCl, KCl, and KBr cleavage surfaces exposed to pulsed 248-nm laser radiation in ultrahigh vacuum show monolayer islands; the island density increases with increasing laser fluence. We attribute island formation to the aggregation of alkali halide monomers desorbed from steps onto terrace sites as a consequence of UV exposure; this desorption accounts for the observed step roughening. In the presence of water vapor at pressures of 10^{-5} to 10^{-3} Pa, fifty 248-nm pulses at 100 mJ/cm² produce monolayer etch pits on KCl and KBr. Higher fluences are required for NaCl. Quadrupole mass spectrometry on the products emitted during laser irradiation show much more intense alkali and halogen emissions in the presence of water vapor, consistent with the observed etching. Although the mechanism for enhanced etching in the presence of water vapor is not clear, the erosion of alkali halides during electron irradiation at room temperature is hindered by the accumulation of alkali metal.³ Water vapor may hinder alkali aggregation, perhaps by dissociative adsorption at halogen vacancies. We show that water vapor at similar partial pressures has comparable effects on alkali halide surfaces exposed to 2 keV electrons.

¹This work was supported by the U.S. Department of Energy—under Grant DE-FG02-04ER-15618.

²K.H. Nwe, S.C. Langford, and J.T. Dickinson, J. Appl. Phys. 97, 043502 (2005).

³B.M. Szymonski, J. Ruthowski, A. Poradzisz, Z. Postawa, and B. Jørgensen, in Desorption Induced by Electronic Transitions—DIET II (Springer, Berlin, 1985), p. 160-168.

4:40pm SS1-ThA9 The Adsorption and Desorption of H₂O, H₂S and SO₂ on Amorphous Carbon Films, E. Broitman, W. Michalak, J.B. Miller, A.J. Gellman, Carnegie Mellon University, M.A. Alvin, U.S. Department of Energy

There is a renewed interest in the development of efficient catalyst-sorbents for the capture and conversion of sulfur containing compounds that poison the catalysts and separation membranes, often used in modern processes for hydrogen generation. It is well known that sulfur-containing molecules interact with activated carbon surfaces by both physisorption and chemisorption, where surface chemistry and pore structure appear to contribute to the strength of the interaction. However, because it is difficult to control and characterize their surface properties, the fundamental nature of the adsorption onto activated carbons is still not well understood. In this work, we obtain precise control of surface properties by modeling activated carbons with amorphous carbon (a-C) films deposited under ultra high vacuum conditions. Carbon films with controlled and defined microstructure (sp²/sp³ ratio), surface chemistry (dangling bonds, oxidation state), and morphology (roughness, porosity) were deposited by DC magnetron sputtering. Temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) were used to study H₂O, H₂S and SO₂ surface chemistry on these films. For comparison, experiments were also carried out on a highly oriented pyrolytic graphite (HOPG) surface. H₂O, H₂S and SO₂ physisorb on HOPG and on a-C films by a cluster growth mechanism. At lower coverages, the molecules adsorbed in the first two-dimensional layer and on the edges of the three dimensional (3D) islands have a weaker interaction (lower binding energy) than molecules within 3D islands. Water desorbs from a-C with one peak, while H₂S and SO₂ desorb with two features, corresponding desorption from the monolayer and the multilayer. The three adsorbates interact with the a-C surface with different strengths: at low coverage, energies of desorption, E_{des}, from a-C films were 11.3, 8.2 and 10.2 kcal/mol for H₂O, H₂S and SO₂, respectively. XPS analysis after TPD experiments on HOPG and a-C films revealed no reactions between the carbon surfaces and the adsorbates. On the other hand, H₂S adsorption on oxidized films, a-CO_x, revealed the presence of residual elemental sulfur, thereby indicating that the oxygen of the films had reacted with the adsorbate.

5:00pm SS1-ThA10 Atomic Scale Features on Air Exposed Mica Surfaces Revealed By UHV Dynamic SFM, F. Ostendorf, C. Schmitz, S. Hirth, M. Reichling, University of Osnabrueck, Germany

Mineral surfaces play a key role in many reactions regarding mineral dissolution, precipitation and crystal growth. The most prominent of this type of surfaces in nano biology and material science is Muscovite mica. Air cleaved mica surfaces have been investigated by dynamic force microscopy operated in the non-contact mode (NC-AFM) under ultra-high vacuum (UHV) conditions with atomic resolution. In contrast to the common assumption that a simple degas under UHV conditions leads to a true atomically flat and clean surface, we demonstrate that the sample surface always exhibits a high density of small defects and clusters. In addition to these defective features we find flat and layered, hexagonally shaped islands exhibiting two different types of atomic scale patterns on different length scales: namely a rectangular pattern and a Moiré superstructure. In general one can consider that potassium ions of a mica surface - when cleaved in air - react with water and carbon dioxide. This composes potassium carbonate. By detailed measurements with atomic precision we clearly identify the unit cells of both patterns. The rectangular pattern is associated with the potassium carbonate unit cell. For growing potassium carbonate crystallites on mica surfaces the slight lattice mismatch needs to be compensated. This compensation is reflected by the observed Moiré superstructure. Finally we yield strong evidences that crystallites of potassium carbonate emerge due to the reaction with water and carbon dioxide and grow by Ostwald ripening on mica surfaces.

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