Surface Science
Room: M - Session SS1-WeA

Water/Surface Interactions & Environmental Chemistry II

Moderator: V. Grassian, University of Iowa

2:00pm **SS1-WeA1 Towards Understanding the Formation of Water in the Interstellar Medium**, ***V.L. Frankland***, *M.P. Collings, M.R.S. McCoustra*, Heriot-Watt University, UK

Exposed to the harsh radiation fields of interstellar space, few molecules can escape photodestruction. However, the vast clouds of gas and dust that accumulate in the gulfs of space between the stars (known as the interstellar medium) have been observed to contain more than 120 different molecular species[1]. The low temperature (10-100 K) and pressure (10^{-14} mbar) conditions within the interstellar medium limit the range of viable gas-phase reactions resulting in the gas-phase chemistry alone being insufficient to explain the observed abundances of some key chemical species (for example, H_2 and H_2O). Dust grains provide a surface on which adsorbed species can react[2] and hence an alternative pathway to key interstellar molecules. Indeed, this has been proven for the efficient formation of H_2 both experimentally[3-6] and computationally[7-9].

Surface chemistry within an ultrahigh vacuum chamber is being used to explore the surface irradiation reactions of O on a range of astrophysically relevant surfaces using atomic beam methods. In these experiments, the products are identified using temperature programmed desorption. The results of the experiments are interpreted using kinetic analysis of a simple surface mechanism. Analogous experiments will be conducted using an atomic H beam. The ultimate aim of this research will be to combine the two beams to study *in situ* H_2O formation on a grain surface.

References

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2:20pm **SS1-WeA2 Photon- and Electron-stimulated Desorption from Laboratory Models of Interstellar Ice Grains**, *J.D. Thrower, A.G.M. Abdulgalil, M.P. Collings,* ***M.R.S. McCoustra,*** Heriot-Watt University, UK, *F.J.M. Rutten*, Keele University, UK

Dense molecular clouds, in our own and other galaxies throughout the Universe, are the seats of evolution in the present day Universe. New stars and their planetary systems are born in such environments from the chemically rich soup of gas and icy dust from which these environments are made. In the last decade or so, astronomers have turned to the surface science community to help explain the role played by physical and chemical processes in coupling of the gas and solid (dust grain) phases in these crucially important regions of space.

We have recently been investigating one key aspect of that gas-grain interaction; the role played by non-thermal (photon- and low energy electron-driven) processes in returning components of the icy grain mantle to the gaseous interstellar medium. Ultrathin layers of predominantly water (H_2O) ice grow reactively on dust grains; such layers can accumulate adsorbed volatiles such as carbon monoxide (CO) from the gaseous interstellar medium and are observed with sufficient ease in the infrared to be mapped. Indeed such icy mixtures are firmly believed to be the home of chemical evolution in these dense environments as the simple ices (H_2O, CO, NH_3 *etc.*) are converted by a combination of thermal and non-thermal processes into more complex species (*e.g.* CO_2, CH_3OH, CH_3NH_2 *etc.*). Further processing of these complex icy mixtures may lead to the formation of prototypical molecules which may, following exogenous delivery to a nascent planet, provide the raw materials for biological evolution. However such a drive towards increasing chemical complexity takes time; time in which competition from non-thermal desorption processes may in fact remove the icy mantle from its substrate exposing the fragile molecular contents to the harsher environment of the gaseous interstellar medium. We describe preliminary studies of both photon- and low energy electron-driven desorption from a model interstellar ice deposited on model grain surfaces under UHV conditions. We will report on the rates of desorption mediated by photon- and electron-stimulated interactions and, where known, outline the dynamical consequences of such desorption.

2:40pm **SS1-WeA3 Structure-Property Relationships of Water Interfaces 200° Beyond the Boiling Point**, ***S. Putnam***, *L. Gschwender*, Thermal and Materials Sciences Branch - WPAFB

In cooling technologies that utilize the latent heat of vaporization (e.g. pool boiling and spray cooling), knowledge of the critical heat flux is "critical." Beyond the critical heat flux, a continuous vapor layer forms at the solid-liquid interface that impedes heat transfer. The formation of this chaotic, thermally-resistive vapor layer" is well known. However, our recent research has demonstrated that a new, unique, and stable water interface is formed beyond the critical heat flux for surface temperatures 100+ degrees above the boiling point. At this point, film boiling stops, forming a smooth, highly light reflective, high surface energy water interface that further impedes heat transfer. We present our efforts in correlating the thermal, mechanical, and structural properties of this unique water interface using high-speed imaging, Raman spectroscopy, and numerical modeling. Critical heat flux data as a function of vapor pressure is also presented for water boiling on patterned surfaces of carbon nanotubes and nanowire whisker arrays.

3:00pm **SS1-WeA4 Proton and Water Self-diffusion in Thin Layers of Amorphous Solid Ice Studied by FTIR and DFT Calculations**, ***P.E. Uvdal***, *J.E. Blomquist*, Lund University, Sweden

We have studied the H/D exchange in both two- and three-dimensional thin layers of 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 sandwiched layers at 84 K. By careful pretreatment of the surface we can control the proton diffusion, thereby allowing for a separation and a characterization of the two diffusion processes. The role of the Grotthuss mechanism for the observed H/D exchange will be discussed. Using infrared vibrational spectroscopy we can monitor the isotopic mix of water molecules both at the ice surface as well as in the solid ice. A detailed understanding of the vibrational data is obtained with the aid of DFT cluster calculations.

4:00pm **SS1-WeA7 Surface Science Studies of Environmentally Relevant Chemistry on Some Metal Sulfide and Oxide Minerals**, ***D.R. Strongin***, Temple University **INVITED**

Studies are presented that investigated environmentally relevant chemistry on pyrite (FeS_2), birnessite (MnO_2), and nanocrystalline ferrihydrite. Photoelectron spectroscopy, in situ atomic force microscopy, and in situ infrared spectroscopy studies will be presented that address the oxidation of pyrite, arsenite adsorption on birnessite, and carbonate formation of ferrihydrite. Selected results from these studies will bring forward important issues related to the understanding of complex environmental chemistry occurring on mineral surfaces. In the arsenite/birnessite circumstance, for example, batch reaction measurements determined the extent of the conversion of the arsenite to arsenate and the amount of Mn(II) formed during this reductive dissolution process. Atomic force microscopy (AFM) investigated morphology changes during the reactions associated with birnessite as well as the nature of any precipitate phases by using phase imaging. The microscopy was complemented by X-ray photoelectron spectroscopy (XPS) that was able to determine the relative distribution of Mn(IV), Mn(III) and Mn(II) after reaction with As(III). Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was also used to determine the nature of the arsenic-species on the Mn oxide and oxyhydroxide surfaces.

4:40pm **SS1-WeA9 Water Growth on a Hydrophobic Substrate: Observation of a Metastable, Two-Layer Crystalline Ice on Graphene**, ***G.A. Kimmel***, *J. Matthiesen,* Pacific Northwest National Laboratory, *M. Baer,* Ruhr-Universität Bochum, Germany, *C. Mundy, N.G. Petrik, R.S. Smith, Z. Dohnálek, B. Kay*, Pacific Northwest National Laboratory

The structure of water at interfaces is crucial for processes ranging from photocatalysis to protein folding. Here, we investigate the structure and lattice dynamics of two-layer crystalline ice films grown on a hydrophobic substrate – graphene on Pt(111) – with low energy electron diffraction, reflection-absorption infrared spectroscopy, rare-gas adsorption/desorption, and *ab-initio* molecular dynamics. Unlike hexagonal ice, which consists of stacks of *puckered* hexagonal "bilayers", this new ice polymorph consists of two *flat* hexagonal sheets of water molecules in which the hexagons in each sheet are stacked directly on top of each other. Such two-layer ices have been predicted for water confined between hydrophobic slits, but not previously observed. Our results show that the two-layer ice forms even at zero pressure at a single hydrophobic interface by maximizing the number of hydrogen bonds at the expense of adopting a non-tetrahedral geometry with weakened bonds.

5:00pm **SS1-WeA10 SrTiO$_3$(001) Surface Structure Stabilization Via Water Mediation**, ***A.E. Becerra-Toledo***, *D.M. Kienzle, L.D. Marks*, Northwestern University

Strontium titanate, SrTiO$_3$, has been largely studied as the quintessential model system for perovskite oxides. In the field of surface science, the presence of multiple cation valence states has allowed for insights into the stabilization mechanisms in mixed-metal oxides. Multiple SrTiO$_3$ surface structures have been conclusively described at the atomic scale, which lets us go beyond bulk-like caricature descriptions of oxide surfaces. In turn, this allows for a more realistic study of the interaction of oxide surfaces with foreign species such as water, whose ubiquity makes such analysis inescapable.

Density functional theory (DFT) calculations were performed to study the surface energetics of several observed and theoretical SrTiO$_3$(001) surface reconstructions, both dry and with chemisorbed water. A repeated slab configuration was used to model all surface structures, which include not only bulk-like truncations, but also the 2x1, c(4x2), (√13x√13)R33.7º reconstructions, as well as the theoretically predicted low-energy (√2x√2)R45º structure. The use of an augmented plane wave plus local orbital (APW+lo) basis, coupled to the full-electron potential implementation, accurately reflects the character of single-particle wavefunctions. The TPSSh hybrid meta-GGA exchange-correlation functional [Tao et al., PRL 91,146401 (2003)] was employed, which allows for an improved treatment of strongly correlated systems. Both the molecular and dissociative water adsorption modalities were taken into account.

Our analysis suggests that water mediation is responsible for the fact that the thermodynamically favorable (√2x√2)R45º structure [Warschkow et al., Surf.Sci. 573, 446 (2004)] has never been detected while other reconstructions of identical stoichiometry and significantly higher surface energy, such as the 2x1, have been readily observed. In the latter, the adsorption of water is much more favorable, which insinuates that the formation of the (√2x√2)R45º reconstruction is kinetically limited if there is any exposure to water vapor. Several experimental results back up this observation.

5:20pm **SS1-WeA11 Water Adsorption on O(2x1)-Ru(0001)**, *S. Maier, I. Stass,* ***M. Salmeron***, Lawrence Berkeley National Laboratory

We studied the adsorption of water on the O(2x1) -Ru(0001) surface at submonolayer coverage by low temperature scanning tunneling microscopy. We found that water reconstructs the oxygen layer from a linear configuration to a honeycomb structure with the water molecules incorporated inside, confirming a model previously proposed by Gladys et al. based on XPS measurements [1]. In addition, we found that water monomers inside the oxygen hexagons can rotate through interaction with the tip, while dimers are more stable.

[1] M.J. Gladys et al. PRB 78, 035409 (2008).

5:40pm **SS1-WeA12 Structure and Dynamics of Liquid Water on Surfaces from Ab Initio Molecular Dynamics: Graphene/Water and Alumina/Water**, ***P. Huang***, *E. Schwegler*, Lawrence Livermore National Laboratory

Many important surface phenomena occur under aqueous conditions, where water plays a significant but poorly understood role in interfacial structure and reactivity. Atomic-scale information at solid/water interfaces is notoriously difficult to unravel, and thus simulations are an essential complement to experimental efforts. To date, such simulations typically rely on simple, empirical models for interatomic interactions. However, there is a great deal of ambiguity in the parameterization of these potentials; often they are fitted to bulk properties, and the transferability to complex interfacial systems is unclear. Here, we report atomic-scale simulations of solid/water interfaces via ab initio molecular dynamics, where interatomic interactions are derived on-the-fly from density functional theory. Unlike empirical models, this approach is generally applicable to both bulk and interfacial environments, without input from experiment. Two prototype examples are considered: graphene/water as a model hydrophobic surface, and alumina/water as a model oxide surface. In both cases, a bulk-like liquid water layer at ambient conditions is explicitly included. We examine interfacial structure and dynamics, relate these to spectroscopic observables (infrared spectroscopy, nuclear magnetic resonance). Comparison to predictions from common empirical potentials is given in order to gain insight into when such models fail, and how they can be improved.

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