Monday Morning, October 25, 1999

Surface Science Division Room 612 - Session SS3-MoM

Water-Surface Interactions

Moderator: E.M. Stuve, University of Washington

8:20am SS3-MoM1 Surface Chemistry of Organic Aerosols, G.B. Ellison, University of Colorado, Boulder INVITED

Organic aerosols are believed to be important cloud condensation nuclei in the earth's atmosphere. We suggest a chemical model for the composition, structure, and atmospheric processing of these organic aerosols. This model is stimulated by recent field measurements showing that organic compounds are a significant component of atmospheric aerosols. The proposed model organic aerosol is an "inverted micelle" consisting of an aqueous core that is encapsulated in an inert, hydrophobic organic monolayer. We propose a chemical mechanism by which the organic surface layer will be processed by reactions with atmospheric radicals. Surface reactions of the hydrocarbon film with atmospheric species such as OH, Cl, O3, and NO3 will transform the organic film. The net result is the transformation of an inert hydrophobic film to a reactive hydrophilic layer.

9:00am SS3-MoM3 Water Adsorption Structures on Flat and Stepped Ru(0001)-Surfaces, W. Hoffmann, C. Benndorf, University of Hamburg, Germany

We investigated the structural influence of vicinal Ru(0001) surfaces to water adsorption and desorption kinetics. Flat Ru(0001) surfaces show a unique behavior in the difference of H@sub2@O and D@sub2@O desorption spectra - referred to as the isotope effect. In accordance with other authors we observed on Ru(0001) three desorption peaks for H@sub2@O denoted as C, A@sub2@ and A@sub1@ (C, 155 K / A@sub2@, 190 K / A@sub1@, 212 K).The isotope effect for D@sub2@O on Ru(0001) is characterized by a missing A@sub1@ peak. Isothermal desorption measurements were performed using @Delta@@phi@, in order to determine the different kinetics for H@sub2@O and D@sub2@O. Neither for D@sub2@O nor for H@sub2@O the desorption of the A@sub2@-state can be described by 1st order kinetics. Especially for the A@sub2@ peak of H@sub2@O we observed an initial range of 1st order kinetics followed by a strong deviation, which could be described by Avrami kinetics or lateral interactions.@footnote 1@ Stepped Ru surfaces were used for comparison and @Delta@@phi@ measurements were complemented by ARUPS measurements of H@sub2@O and D@sub2@O adsorption. Further we performed LEED structure calculations of the clean stepped hcp(0001)-surfaces using a spherical wave model approach and single scattering theory.@footnote 2@ In experiments the vicinal Ru(0001) surfaces show a triplet spot splitting due to the alternating step width with different atomic arrangements at the steps, in agreement with our calculations. Regarding the adsorption phenomena on low indexed stepped surfaces, the diffraction pattern do not show ordered structures of water molecules. Higher indexed surfaces allow to built ordered water super structures as observed for flat Ru(0001) surfaces.@footnote 3@ @FootnoteText@ @footnote 1@ W. Hoffmann, C. Benndorf, Surface Sci. 377-379 (1997) 681-686. @footnote 2@ W.P. Ellis and R.L. Schwoebel, Surface Sci. 11 (1968) 82-98. @footnote 3@ D. L. Doering and T. E. Madey, Surface Sci. 123 (1982) 305-337.

9:20am SS3-MoM4 Kinetics of Water Uptake on a Hydrophobic Surface Studied by UHV-TPD, *T.R. Linderoth*, *P. Löfgren*, Chalmers University of Technology, Sweden; *V.P. Zhdanov*, Boreskov Institute of Catalysis, Russia; *B. Kasemo*, Chalmers University of Technology, Sweden

Thin water (ice) films are currently receiving much attention. The motivations are both intrinsic scientific interest and their importance in areas such as astrophysics, biology and atmospheric chemistry. As a model of water adsorption on a very hydrophobic surface, we have investigated the uptake of water onto an octane (C@sub 8@H@sub 18@) covered Pt(111) surface and compared the results with previous studies on hydrophilic clean Pt(111). Our adsorption experiments were executed at substrate temperatures (T) in the range 100-120 K. A water-doser provided precise control of dosage flux (F) and exposure time (t). The adsorbed amount of water (@theta@) was determined by thermal desorption spectroscopy (TDS). In contrast to the case of hydrophilic metal substrates, we find that the apparent sticking (condensation) coefficient is well below unity for adsorption on the octane film (typically <<1 ML is adsorbed for exposures up to 10 ML). Furthermore, the adsorbed amount of water at a given exposure is strongly dependent on dosage flux and substrate

temperature, being larger for higher F or lower T. Qualitatively, these findings can be understood if the binding of a single water molecule to the octane surface is so weak that adsorbed, diffusing water molecules can redesorb before they manage to nucleate with other adsorbed molecules or incorporate into already stable water islands. A quantitative treatment of the corresponding kinetic equations yields: @theta@(t)~F@sup 3@exp[(3E@sub d@-2E@sub a@)/k@sub B@T]t@sup 2@ (E@sub d@/E@sub a@ are activation energies for desorption/surface diffusion of water molecules). The experimental data agree well with the predicted time and temperature dependences: We find that @theta@~t@sup 2.3@ and from the Ahrrenius analysis 3E@sub d@-2E@sub a@=0.20 eV is obtained. The observed flux-dependence of @theta@~F@sup 0.6@ is not in agreement with the model, however. Further investigations of the system are currently being undertaken.

9:40am SS3-MoM5 Soft-Landed Ion Study of a Liquid-Liquid-Solid Interface, J.P. Cowin, K. Wu, M.J. Iedema, Pacific Northwest National Laboratory

Ion beams with energies of about 1 eV allow one to gently land, without damage, molecular ions important to aqueous/organic liquid chemistry. We have used these soft-landed ions to probe the transfer of hydronium ions from non-aqueous to organic media. Molecular beam epitaxy is used to create aqueous/organic interfaces with monolayer precision, and the motion of the ions is detected with a non-contact work function probe, in UHV environments. Amorphous vapor- deposited films become true liquids above their glass temperatures (135 for water, 85 K for methyl cyclohexane (MCH)). We find hydrating the hydronium strongly effects its ability to enter the organic phase. We also see strong non-linear electric field effects. When a "dry" 30 monolayer MCH film is ramped at 0.2 K/s, we find that the ions traverse a film at about 97 K, under their self-induced field on order of 6 volts/(10.2 nm). We then added water with the ions on top of the MCH film. The temperature for ion transport shifts linearly with added water to 100 K at 0.4 monolayer, and is constant at @DELTA@T of 3K from 0.4 to 1.0 monolayer. This is consistent with an increase of ion size due a large hydration "sphere" (or pancake) being dragged through the organic film. Above 1 monolayer of added water the temperature shifts as much as 15 K, and is consistent with the expected @DELTA@G difference for transferring a solvated ions from this nano-aqueous environment to the organic phase. At electric fields from 0.01 to 0.1 V/angstrom, we see considerable deviations from simple viscosity-based ion transport models.

10:00am SS3-MoM6 The Molecular Volcano: Release of Trapped Volatile Gases by Amorphous Solid Water, *K.P. Stevenson, Z. Dohnálek, G.A. Kimmel, R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

The trapping and release of volatile gases by amorphous solid water (ASW) has important astrophysical implications, predominately for the adsorption of gases on icy planetary surfaces and the outgassing behavior of cometary bodies. A previous study involving ASW and CCl@sub 4@ introduced the concept of the molecular volcano,@footnote 1@ wherein the abrupt release of trapped CCI@sub 4@ was driven by the amorphous to crystalline ice phase transition. The mechanism for the release of gas was postulated to be the formation of connected pathways in the ASW film during the nucleation and growth of the crystalline ice. We have investigated the mechanisms for trapping and release of volatile gases by ASW using temperature programmed desorption (TPD) from N@sub 2@, O@sub 2@, and Ar adsorbed underneath thin ASW films. The TPD of physisorbed N@sub 2@ monolayers from the ASW surfaces was used to probe the crystalline ice surface fractions and surface area changes during crystallization of the ASW films. The isothermal desorption and TPD of N@sub 2@, O@sub 2@, and Ar deposited beneath thin ASW overlayers results in the desorption of the trapped gas at the onset of crystallization in the ASW. During crystallization, the trapped gas escapes in concert with a cracking of the ASW film as observed by a significant change in film surface area. For thicker ASW overlayers (~600 BL), the gas release is delayed until after the ASW film has crystallized. A comparison with the isothermal desorption of pure ASW films, reveals that the amorphous to crystalline ice phase transition kinetics are independent of the trapped gas in the ASW films. @FootnoteText@ *Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. @footnote 1@ R. S. Smith, C. Huang, E. K. L. Wong, and B. D. Kay, PRL, 79, (1997) 909.

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10:20am SS3-MoM7 The Effect of Water on the Nitric Acid Pressure Dependence of the Reaction Between Gas Phase Nitric Acid and NaCl Surfaces.@footnote 1@, J.C. Hemminger, S. Ghosal, University of California, Irvine

The reactions of oxides of nitrogen with sea salt particles, that liberate halogenated compounds into the gas phase, may play an important role in the chemistry of the marine troposphere. Recent laboratory measurements have shown that the reactive sticking coefficient of HNO@sub 3@ on NaCl particles exhibits a significant dependence on the HNO@sub 3@ pressure. when the measurements are carried out under conditions of steady state reaction. This pressure dependence has been rationalized in terms of a two-site Langmuir model for dissociative adsorption of the HNO@sub 3@. However, our XPS experiments show that the dissociative adsorption of HNO@sub 3@(g) on NaCl to form NaNO@sub 3@(s) and HCl(g) follows single-site Langmuir adsorption behavior. We also used XPS to show that the amount of "strongly adsorbed water" on the surfaces of NaCl particles strongly depends on the particle size. Particles of 1-10 micron diameter show large quantities of adsorbed water that remain on the sample up to temperatures of 200 degrees C. Particles in the size range of 500 micron diameter have less, but still easily measurable, amounts of strongly adsorbed water. We present a model for the HNO@sub 3@ pressure dependence of the reactive sticking coefficient of HNO@sub 3@ on NaCl under steady state reaction conditions. The origin of the pressure dependence in the model is the competition between site blocking on the surface by the build-up of the NaNO@sub 3@ reaction product and the water induced 3-d recrystallization of the NaNO@sub 3@ that frees up reactive sites for further reaction. @FootnoteText@ @footnote 1@ This work was supported by the National Science Foundation Grant ATM-9707285.

10:40am SS3-MoM8 Giant Cl@super-@ and F@super-@ Enhancements in Electron-Stimulated Desorption of CF@sub2@Cl@sub2@ Coadsorbed with Water or Ammonia Ices: Implications for Atmospheric Ozone Depletion, *T.E. Madey*, *Q.-B. Lu*, Rutgers, The State University of New Jersey

Dissociative electron attachment to form Cl@super-@ and F@super-@ can be an important process for the destruction of ozone-depleting chlorofluorocarbons (CFCs) in the upper atmosphere, because of their extremely large electron attachment cross sections.We have observed giant Cl@super-@ and F@super-@ enhancements by several orders of magnitude in electron-stimulated desorption of a fractional monolayer of CF@sub2@Cl@sub2@ coadsorbed with water ice and ammonia ice on a Ru(0001) surface at ~25 K, respectively. The yields of negative ions are measured by an electron-stimulated-desorption ion angular distribution (ESDIAD) detector with time-of-flight capability. The enhancement of Cl@super-@ is much stronger than that of F@super-@, and the enhancements for both ion species by NH@sub3@ coadsorbate are stronger than by H@sub2@O. Moreover, all magnitudes of enhancement increase strongly with decreasing CF@sub2@Cl@sub2@ concentration; for 0.3 ML CF@sub2@Cl@sub2@, the largest Cl@super-@ enhancements are ~3x10@super4@ for NH@sub3@ and ~10@super2@ for H@sub2@O. In contrast, the enhancements are much smaller for CF@sub2@Cl@sub2@ coadsorption with rare-gas atoms or nonpolar molecules. Whereas the primary electron beam energy is 250 eV, the giant negative-ion enhancements are attributed to dissociation of CF@sub2@Cl@sub2@ by capture of low-energy secondary electrons self-trapped (solvated) in polar water or ammonia clusters. This process may be an important sink for chlorofluorocarbons (CFCs) in the atmosphere, where low-energy electrons created by cosmic ray ionization can be trapped in clouds. Cl@super-@ ions produced may be directly or indirectly converted to Cl atoms, which then destroy ozone.

11:00am SS3-MoM9 Cation Trapping Effects on HCl Diffusion in Ice Measured Using a New Laser Resonant Desorption Depth-Profiling Technique, F.E. Livingston, S.M. George, University of Colorado, Boulder

HCI diffusion in ice is important for an understanding of heterogeneous atmospheric chemistry on ice particles and may influence the interpretation of ice core data. The diffusion of alkali metals in ice is also relevant for the evaluation of ice core samples and alkali cations may interact strongly with coadsorbates in ice. Novel laser resonant desorption depth-profiling techniques were used to measure HCI and Na diffusion in ice. The diffusion was monitored using a Q-switched Er:YAG laser to depth-profile the ice multilayer. The Er:YAG laser emits infrared light at 2.94 microns. This light can be resonantly absorbed by the O-H stretching vibration of H@sub2@O and thermalized to induce resonant desorption. HCI diffusion was monitored in ice multilayers containing a thin HCI

interlayer. The HCl spatial coverages at various diffusion times and temperatures were used to extract the diffusion coefficients. The measured HCl diffusion coefficients ranged from D= $(3.8\pm2.8)\times10@$ super-13@ cm@super2@/s at T=169 K to D= $(2.0\pm1.5)\times10@$ super-10@ cm@super2@/s at T=197 K. Arrhenius analysis yielded diffusion kinetic parameters of E=14.6±1.6 kcal/mol and D@subo@= $(2.9\pm2.0)\times10@$ super6@ cm@super2@/s. Na was also observed to diffuse in the ice multilayers. In addition, coadsorbed Na decreased the HCl diffusion rate by a factor of ~5-85 for Na/Cl ratios ranging from 0.05-0.5. The Na-induced decrease in the HCl diffusion rate may be attributed to cation trapping manifested by NaCl formation in the ice.

11:20am SS3-MoM10 The Effect of Porosity on the Crystallization of Amorphous Solid Water, Z. Dohnálek, G.A. Kimmel, K.P. Stevenson, R.S. Smith, B.D. Kay, Pacific Northwest National Laboratory

The annealing and crystallization of amorphous solid water (ASW) is important to understand the properties of ice in extraterrestrial environments. Here we show a dramatic effect of the initial porosity of the ASW films on their crystallization kinetics. The porosity of the films was varied by changing the incident angle of the H@sub 2@O molecules during the deposition.@footnote 1@ The crystallization kinetics were followed using the temperature programmed desorption (TPD) of N@sub 2@(g) monolayers from the ASW film surface. Despite the fact that the films densify upon annealing, before any crystallization takes place, a strong dependence of the crystallization kinetics on the initial porosity exists. The crystallization of dense ASW films (grown at zero angle of incidence) proceeds via classical bulk nucleation and 3-dimensional growth. In the case of porous films (grown at high angles of incidence) the crystallization half time is reduced by more than an order of magnitude and the apparent activation energy decreases to a value that corresponds to the growth of the crystalline phase in the absence of nucleation. We propose that the lowering of the activation energy is due to seeding of the porous films that is likely to occur during the densification. This conclusion is supported by detailed Monte Carlo simulations of the effect of seeding on the crystallization kinetics. @FootnoteText@ * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830. @footnote 1@ K. P. Stevenson, G. A. Kimmel, Z. Dohnálek, R. S. Smith, and B. D. Kay, Science 283 (1999) 1505.

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