

Surface Science

Room 120 - Session SS1-MoM

Aerosol and Related Chemistry

Moderator: T.E. Madey, Rutgers, The State University of New Jersey

9:40am **SS1-MoM1 Great Enhancements in Dissociative Electron Attachment to Chlorofluorocarbons Adsorbed on Polar Molecular Ices: A New Pathway for the Formation of the Ozone Hole, Q.-B. Lu**, University of Sherbrooke, Canada; T.E. Madey, Rutgers University; L. Sanche, University of Sherbrooke, Canada

INVITED

Atmospheric ozone depletion is an issue of global concern. It is generally accepted that the Earth's ozone layer is depleted by chlorine atoms produced via photolysis of chlorofluorocarbons (CFCs) in the upper stratosphere, and the formation of the Antarctic / Arctic ozone hole has been attributed to heterogeneous reactions occurring on surfaces of ice particles in polar stratosphere clouds (PSCs). Based on measurements of anion yields in (~250 eV) electron stimulated desorption (ESD) from a submonolayer of CFCs coadsorbed with polar molecules, we find evidence for an unrecognized process: dissociative electron attachment (DEA) to CFCs by low energy secondary electrons is enhanced by several orders of magnitude when CFCs are adsorbed on polar molecular ices, such as water and ammonia. This enhancement has been identified to be due to transfer of ~ 0 eV electrons temporarily trapped in polar molecular ices to CFCs that then dissociate via DEA, based on measurements of electron trapping cross sections as a function of electron energy in the range of 0-10 eV. This enhancement effect should be very efficient in the stratosphere, where low-energy electrons can be produced by cosmic-ray ionization and trapped in PSCs. In this talk, we present our laboratory measurements on anion yield enhancements in ESD and on absolute DEA cross sections of CFCs adsorbed on polar molecular ices, and discuss the physics of these processes. The implications of these observations for the formation of Antarctic / Arctic ozone holes, and correlations with data obtained by field measurements (satellite, balloon and ground station), will also be discussed. Q.-B. Lu and T.E. Madey, Phys. Rev. Lett. 82, 4122(1999); J. Chem. Phys. 111, 2861(1999). T.E. Madey and Q.-B. Lu, Surf. Sci. 451, 238(2000); J. Phys. Chem. B105, 2779(2001). L. Sanche and Q.-B. Lu, Phys. Rev. B63, 153403(2001).

10:20am **SS1-MoM3 Electron Stimulated Reactions of Chlorocarbons in Ice Films, H. Fairbrother, A.J. Wagner**, Johns Hopkins University

Electron stimulated reactions of chlorocarbons adsorbed in ice films are of importance in atmospheric processes as well as in understanding the mechanisms of glow discharge chlorocarbon remediation. We present results on the electron -induced reactivity of carbon tetrachloride (CCl₄) adsorbed in ice films at 100K studied using a combination of reflection absorption infrared spectroscopy and mass spectrometry. Both mass spectrometry and infrared measurements indicate that CCl₄ is converted to a mixture of phosgene (COCl₂) and CO and HCl as a result of electron mediated reactions within the ice/chlorocarbon film, supported by separate experiments using CCl₄. The product branching between COCl₂ and CO@SUB 2@ and H@sub 2@O-rich films favoring CO@SUB 2@ production. Results will also be presented on the electron-stimulated reactions of CHCl₃ adsorbed in ice films.

10:40am **SS1-MoM4 Study of CO@sub 2@ Adsorption on Ice using High-pressure X-ray Photoelectron Spectroscopy, F. Requejo**, Lawrence Berkeley National Laboratory; H. Bluhm, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany; D.F. Ogletree, M. Luna, Z. Hussain, Lawrence Berkeley National Laboratory; C.S. Fadley, University of California, Davis; M. Salmeron, Lawrence Berkeley National Laboratory

Water at surfaces plays a fundamental role in atmospheric science, chemistry and biology. A new generation of experimental and theoretical tools are actually revisited this subject. Many interesting properties of water still remain unexplained at molecular level, even though it has been a capital subject of research for decades. Interaction between ice surfaces and adsorbed molecules emerges as a very attractive topic. Macroscopic studies have investigated the adsorption of CO@sub 2@ on ice, showing the existence of a quasi-liquid layer on ice. On the other hand, new studies confirm that CO@sub 2@ is the main driver in global warming and glaciation changes. Recently, by

means of surface X-ray absorption spectroscopy, we have studied the premelting of ice trough to the Auger electron yield NEXAFS from its surface. This methodology has proven to be capable of detecting and measuring the thickness of the liquid layer on ice. In the present contribution, we have applied the same methodology to study the effect of atmosphere CO@sub 2@ on the premelting of ice. Samples of ice and water were condensed from vapor onto a cooled substrate, which was placed inside a cell. In equilibrium conditions between the water vapor and the sample at different temperatures, CO@sub 2@ gas was introduced into the cell at different pressures in the range of 0 to 1 Torr. Afterwards, surface-sensitive XPS measurements and Auger electron-yield NEXAFS experiments at O K-edge in the energy range of 530 to 620 eV were performed. Our results indicate unambiguously that the amount of liquid water on the surface of ice increases with the pressure of CO@sub 2@. This effect becomes more evident when the temperature is also increased. F. Bensebaa and T.H. Ellis. Progr. in Surf. Sc., 50, 1-4 (1995) 173. J. Ocampo and J. Klinger. J. Coll. Interf. Sci. 86, 2 (1982) 377. N.J. Shackleton. Science, 298 (2000) 1897. F.G. Requejo - Postdoctoral Fellow at MSD, LBNL, Berkeley, CA. Permanent address: Dept. Physics, FCE, UNLP and IFILP(CONICET), La Plata, Argentina.

11:00am **SS1-MoM5 Sea Salt Aerosol Reactions: Quantitative Single Particle Studies, A.J. Laskin, M.J. Iedema, J.P. Cowin**, Pacific Northwest National Laboratory

Sea salt from ocean wave action is a very common aerosol. This aerosol is far from inert, with several papers in recent years looking at how it can react with HNO₃ to form sodium nitrate (releasing HCl), or hydroxyl radicals to form Cl₂. We present highly quantitative, time resolved studies of sea salt aerosols observed during the fall 2000 Texas Air Quality Study. We used a novel automated sampler to preserve 3000 samples (10 minute intervals) for nearly a month of continuous observation. These were preserved for automated laboratory analysis with scanning electron microscopy/energy dispersed x-ray analysis. We analyze particles down to 0.2 micron in size for elements from carbon upward. We are able to follow these reactions in detail, and relate them to the time-resolved atmospheric gases seen by other researchers there. We are able to show that nitration occurs preferentially to sulfating (until later in the daily cycle). We are able to follow the size-resolved reaction, with as expected faster reactions for the smaller particles. We used the archived samples for other techniques too. High resolution time of flight secondary ion mass spectrometry gave important molecular speciation information, on a single particle basis (0.2 micron resolution).

11:20am **SS1-MoM6 Surface Chemistry of Size-Selected, Gas-Phase Nanoparticles, J.T. Roberts, K. Higgins, M.R. Zachariah, H. Jung**, University of Minnesota

A method has been developed to conduct surface chemistry and extract surface kinetic rates from size-selected aerosol nanoparticles. The measurements encompass broad ranges of particle size, phase, and composition. Results will be presented on the growth and oxidation of soot nanoparticles (particle radius between 10 and 40 nm). The particles are investigated for changes in surface area using on-line nanoparticle characterization instrumentation. Experiments emphasize two classes of reactive conditions: high temperature oxidation by O@sub 2@ and NO@sub x@, and room temperature addition of hydrocarbons. We believe these to be the first measurements of soot oxidation and condensation kinetics that have been conducted on size-selected particles. The results are important because soot emission from combustion sources is dictated by the competing surface processes of growth and oxidation. More generally, the results represent one of the first kinetic and mechanistic studies of gas-phase particle reactivity.

11:40am **SS1-MoM7 Scanning Electron Microscopy Studies of the Hydration of Mixed Alkali Halide Aerosols, S.A. Joyce**, Los Alamos National Laboratory; J.P. Cowin, J.T. Atherley, Pacific Northwest National Laboratory

The morphologies of aerosols generated from pure NaCl, NaBr, and MgCl₂ solutions and from NaCl/NaBr and NaCl/MgCl₂ mixtures have been studied using an environmental scanning electron microscope (ESEM). For aerosols produced by nebulizing pure NaCl solutions, nearly perfect cubic crystals with widths of a few microns are normally observed. Upon raising the water vapor pressure in the specimen chamber, these pure NaCl aerosols are observed to dissolve at relative humidities consistent with previous studies. For aerosols produced by nebulizing NaCl/NaBr mixtures, ranging from 0.1 to 0.5 mole fraction NaBr, polycrystalline particles are often observed. For these polycrystalline

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samples, deliquescence of individual crystallites occurs at two different relative humidities. The central or core crystallite typically dissolves at relative humidities similar to that for pure NaCl, whereas the outer crystallites dissolve at humidities lower than that for either pure NaCl or NaBr. The deliquescence pressure for these crystallites is independent of the mole fraction of starting solution. The outer region, which dehydrates last, is composed of the NaCl/NaBr eutonic (0.9 mole fraction NaBr), with the inner region composed of nearly pure NaCl. For the aerosols produced by nebulizing NaCl/MgCl₂ mixtures, a crystalline core surrounded by a featureless outer region is typically observed. X-ray fluorescence measurements show that this outer region is largely magnesium-based while the inner crystallite is sodium-based. Based on available thermodynamic data, no eutonic of NaCl/MgCl₂ exists, and so phase separation into the pure components is expected. The implication of the phase-separation to surface enrichment of minority components and its potential role in heterogeneous atmospheric chemistry will be discussed. * Pacific Northwest National Laboratory is operated for the Department of Energy by Battelle under Contract DE-AC06-76RLO 1830.

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