

# Wednesday Morning, October 30, 2013

## Surface Science

Room: 202 A - Session SS+AS-WeM

### Catalysis in Prebiotic Chemistry (8:00-10:00 am)/Environmental Interfaces (10:40 am-12:00 pm)

Moderator: A.J. Gellman, Carnegie Mellon University

#### 8:00am SS+AS-WeM1 Models for the Origin of Biological Homochirality, D.G. Blackmond, The Scripps Research Institute INVITED

The single chirality of biological molecules has fascinated scientists and laymen alike since Pasteur's first painstaking separation of the enantiomorphic crystals of a tartrate salt over 150 years ago. In the past decade, a number of theoretical and experimental investigations have helped to delineate models for how one enantiomer might have come to dominate over the other from what presumably was a racemic prebiotic world. Our work has highlighted mechanisms that include either chemical or physical processes, or a combination of both. While much of the scientific driving force for this work arises from an interest in understanding the origin of life, research focusing on mechanisms for the enantioenrichment of chiral molecules has the potential to impact a wide range of applications, most notably in the synthesis and formulation of pharmaceuticals.

#### 8:40am SS+AS-WeM3 A New Catalytic RNA for the RNA World, J.E. Moretti, G.F. Dolan, U.F. Müller, University of California San Diego INVITED

The RNA world hypothesis describes a stage in the early origin of life in which RNA molecules served as genome and as the major genome-encoded catalyst. RNA world organisms must have existed more than 3.5 billion years ago, which makes it unlikely that direct evidence of them can be found. In contrast, researchers are trying to recapitulate these early stages of life in the lab. These efforts identified processes that can generate nucleosides under prebiotically plausible conditions, and have generated catalytic RNAs that are able to polymerize RNAs from nucleoside 5'-triphosphates. The latter would be the central activity in a self-replicating RNA organism. However, it has not been shown how nucleosides can be converted to nucleoside 5'-triphosphates in an RNA World scenario. Here we describe a new catalytic RNA that generates RNA 5'-triphosphates from RNAs with 5'-hydroxyl groups, using trimetaphosphate. Trimetaphosphate is a prebiotically plausible compound because it can be generated by volcanic processes and by the erosion of phosphide minerals. The catalytic RNAs were obtained by in vitro selection and work with pseudo-first order rate constants  $> 0.01 \text{ min}^{-1}$ . We are currently trying to identify variants of these catalytic RNAs that are able to triphosphorylate single nucleosides in multi-turnover reactions. In summary, our results show that catalytic RNAs can triphosphorylate RNA 5'-hydroxyl groups with trimetaphosphate and further the efforts to re-surrect RNA world organisms.

#### 9:40am SS+AS-WeM6 Chemical Mapping of Minerals and Meteorites for Origins of Life Research, R.D. Gann, C. Pirim, T.M. Orlando, Georgia Institute of Technology

Surface analytical techniques such as Raman, x-ray photoelectron spectroscopy, and two-step laser desorption/ionization stand to shed considerable light on the chemistry that occurs on mineral surfaces and the surfaces of meteorites. The results of Raman and XPS analysis of the meteorite schreibersite, for instance, show a rich surface with phosphate and several impurity metals. Because this surface is potentially prebiotic, the chemistry involved has implications for the origins of life, and recent results within our center show it is capable of phosphorylation of relatively simple molecules. Analysis of other potentially prebiotic minerals such as pyrite are also under investigation with these techniques. Toward this goal, we have built a xenon tripling cell for vacuum-ultra-violet (10.5 eV) photoionization and a basic rastering UV desorption laser for direct detection of organic molecular analytes over 40 amu photons. The rastering allows spatial resolution for investigation of different domains of a mineral. This provides a nondestructive means for meteorite chemical analysis without the intervention of wet chemistry, which would potentially introduce molecules via reactions that would not otherwise happen. It also allows for detection of extremely small amounts of mass analytes.

This work was jointly supported by NSF and the NASA Astrobiology Program, under the NSF Center for Chemical Evolution, CHE-1004570

#### 10:40am SS+AS-WeM9 Water at Interfaces under Realistic Conditions, A. Nilsson, SLAC National Accelerator Laboratory INVITED

I will present two classes of systems involving water at interfaces probed using ambient pressure XPS, water on  $\text{BaF}_2$  and the interaction of oxygenated species during electrocatalysis. The structure of thin-film water on a  $\text{BaF}_2(111)$  surface under ambient conditions was studied using Auger electron detected x-ray absorption spectroscopy (XAS) from ambient to supercooled temperatures at relative humidity up to 95 %. No ice-like structure was observed in spite of the expected templating effect of the lattice-matched (111) surface. The XAS spectrum of liquid thin-film water on  $\text{BaF}_2$  exhibits, at all temperatures, a strong resemblance to that of high-density ices for which the observed spectroscopic features correlate linearly with the density. Molecular dynamics simulations indicate that the first layer water on  $\text{BaF}_2(111)$  is indeed in a unique local structure that resembles high-density water, with a strongly collapsed second coordination shell.

The performance of fuel cells is limited by the sluggish kinetics of the oxygen reduction reaction (ORR) at the Pt cathode. An improved understanding of the catalytic steps of the ORR is thus essential for overcoming these limitations. By means of a PEM fuel cell designed to be compatible with our APXPS system, we have been able to identify the oxygenated intermediates of the ORR through their specific O 1s chemical shifts. Using XPS studies of well-defined model systems as spectroscopic references, we differentiate two types of OH intermediates whose population depends on cell voltage: hydrated and non-hydrated OH. We also establish that non-hydrated OH is the dominant surface species on a Pt cathode during ORR at high partial pressures of  $\text{O}_2(\text{g})$ . With the assistance of DFT calculations, we show that the reduction of non-hydrated OH requires less overpotential than that of hydrated OH. This indicates that tuning OH hydration through cathode or electrolyte design will be crucial for enhancing ORR activity.

#### 11:20am SS+AS-WeM11 pH Dependent Behavior of Ammonia and Ammonium at the Liquid-Vapor Interface of Aqueous Solutions, M.H.C. Van Spyk, A.M. Margarella, K.A. Perrine, University of California, Irvine, B. Winter, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, J.C. Hemminger, University of California, Irvine

The distribution of solutes near the air/water interface is known to affect chemical reactions occurring at the surface of aqueous atmospheric aerosols. Ammonia is a basic gas which is introduced into the air both naturally and biogenically, and is important for atmospheric reactions. Solvated ammonia ( $\text{NH}_3$ ) is in equilibrium with the protonated cation ammonium ( $\text{NH}_4^+$ ), and variation of the  $\text{NH}_4^+/\text{NH}_3$  ratio with pH for bulk solutions is reasonably well known. In contrast, little is known about the  $\text{NH}_4^+/\text{NH}_3$  ratio at the liquid/vapor interface, or how it varies with bulk solution pH. Understanding the interfacial chemistry of ammonia solutions is important because the  $\text{NH}_4^+/\text{NH}_3$  ratio may differ at the air/water interface leading to changes in reactivity that can influence air quality.

Liquid jet X-ray photoelectron spectroscopy (LJ-XPS) was used to investigate the interfacial behavior of aqueous ammonia in relation to pH at a solution temperature of 5 °C. For these studies, aqueous ammonium solutions were generated by dissolving ammonium hydroxide or ammonium chloride in water, and the pH was varied using hydrochloric acid or sodium hydroxide, respectively. A continuously renewed jet of solution was probed using photoelectron spectroscopy with synchrotron radiation which was tuned to produce various photoelectron kinetic energies corresponding to the desired sampling depth. Spectra were collected from the bulk solution by generating photoelectrons with high kinetic energies (600 eV) in which case the electron mean free path in solution is sufficiently large so that the experiment probes the bulk solution. Spectra were collected from the near-surface region by exciting photoelectrons with low kinetic energy (150 eV) so that signal from the bulk is attenuated. Nitrogen (N1s) and oxygen (O1s) photoelectron spectra were collected at two kinetic energies to study the relative amounts of each species at the surface versus the bulk for different bulk pH values. The N1s spectra were deconvolved into three peaks from aqueous  $\text{NH}_4^+$ , and  $\text{NH}_3$ , and gaseous  $\text{NH}_3$ , and since the spectra were recorded at the magic angle, the ratios of the integrated peak areas provide a comparison of the relative amounts of each species. It is observed that the  $\text{NH}_4^+/\text{NH}_3$  ratio decreases with increasing bulk solution pH for the surface and bulk of solution, and there is a reduction of the  $\text{NH}_4^+/\text{NH}_3$  ratio at the surface, compared to the bulk. The titrations of ammonium chloride and ammonium hydroxide may be contrasted to understand the impact of chloride concentration. This study illustrates that interfacial aqueous ammonia experiences a different equilibrium than that in the bulk.

11:40am **SS+AS-WeM12 Hydrogen Bonding – Probing its Role in Electron-promoted Desorption from Icy Films**, *D. Marchione, M.P. Collings, M.R.S. McCoustra*, Heriot-Watt University, UK

Previous work has demonstrated the efficiency of long range exciton transport to the vacuum/ice and substrate/ice interfaces in electron irradiation of solid water [1]. Building on this work, we have reported substantial enhancement of the cross-section for electron-promoted desorption (EPD) of benzene ( $C_6H_6$ ) that we know to interact with the surface through a weak form of hydrogen-bonding (pi-hydrogen bonding which is found to be common in biological systems) [2,3]. To probe the role of the hydrogen-bonding network in solid water in promoting the large enhancement of the EPD cross-section, we have undertaken studies on solid methanol (which possesses a one-dimensional hydrogen bonding network) and a simple ether, diethyl ether ( $C_2H_5OC_2H_5$ ), which present a similar electronic environment for exciton formation under electron irradiation yet have decreasing degrees of hydrogen bond interaction. We will report on our studies of the basic surface science of these thin films investigated using a combination of temperature programmed desorption (TPD) and reflection-absorption infrared spectroscopy (RAIRS) and our  $C_6H_6$  EPD measurements from these thin films. Comparisons with solid water as a substrate will be drawn.

[1] N.G. Petrik, and G.A. Kimmel, *J. Chem. Phys.* 123 (2005) 054702.

[2] J. D. Thrower, M. P. Collings, F. J. M. Rutten, and M. R. S. McCoustra, *Chem. Phys. Lett.* 505 (2011) 106.

[3] J. D. Thrower, A. G. M. Abdulgalil, M. P. Collings, M. R. S. McCoustra, D. J. Burke, W. A. Brown, A. Dawes, P. D. Holtom, P. Kendall, N. J. Mason, F. Jamme, H. J. Fraser and F. J. M. Rutten, *J. Vac. Sci. Technol. A* 28 (2010) 799.

# Authors Index

**Bold page numbers indicate the presenter**

**— B —**

Blackmond, D.G.: SS+AS-WeM1, **1**

**— C —**

Collings, M.P.: SS+AS-WeM12, **2**

**— D —**

Dolan, G.F.: SS+AS-WeM3, **1**

**— G —**

Gann, R.D.: SS+AS-WeM6, **1**

**— H —**

Hemminger, J.C.: SS+AS-WeM11, **1**

**— M —**

Marchione, D.: SS+AS-WeM12, **2**

Margarella, A.M.: SS+AS-WeM11, **1**

McCoustra, M.R.S.: SS+AS-WeM12, **2**

Moretti, J.E.: SS+AS-WeM3, **1**

Müller, U.F.: SS+AS-WeM3, **1**

**— N —**

Nilsson, A.: SS+AS-WeM9, **1**

**— O —**

Orlando, T.M.: SS+AS-WeM6, **1**

**— P —**

Perrine, K.A.: SS+AS-WeM11, **1**

Pirim, C.: SS+AS-WeM6, **1**

**— V —**

Van Spyk, M.H.C.: SS+AS-WeM11, **1**

**— W —**

Winter, B.: SS+AS-WeM11, **1**