

SLS Symposium on Liquids and Gases

Tuesday, August 3, 2010

10:00 to 11:45, WBGB/019

10:00 Mapping morphology upon water uptake in single particles using X-ray microspectroscopy

Veronika Zelenay, A. Křepelová, Y. Rudich, T. Huthwelker, M. Ammann

10:30 Imaging Photoelectron Photoion Coincidence for High Accuracy Thermochemistry and Fundamental Ion Processes

Andras Bodi, William R. Stevens, Tom Baer, Sampada Borkar, Bálint Sztáray

11:00 Coffee

11:15–11:45 X-ray reflectivity studies of liquids under nanometer confinement

Shirish Chodankar, Edith Perret, Kim Nygård, Tobias Balmer, Oliver Bunk, Manfred Heuberger & J. F. van der Veen

Mapping morphology upon water uptake in single particles using X-ray microspectroscopy

V. Zelenay¹, A. Křepelová¹, Y. Rudich², T. Huthwelker¹, M. Ammann¹

¹ Paul Scherrer Institut, 5232 Villigen, Switzerland

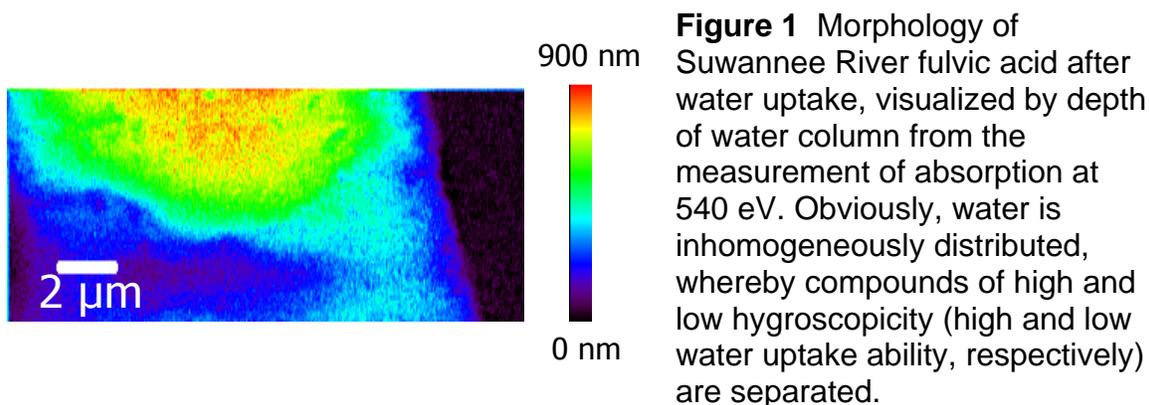
² Weizmann Institute, Rehovot, Israel

veronika.zelenay@psi.ch

Aerosols directly affect the radiation balance of the earth by absorbing and scattering radiation. This important property is strongly influenced by the hygroscopic properties of the aerosol particles, which strongly depends on the chemical composition of the aerosol. While the overall chemical composition of the aerosol particles is known to some degree, the complex interplay between individual components as a function of humidity including the formation of separate phases is just poorly understood. Therefore, accurate identification of the behaviour of the single components or phases within individual particles during the uptake and release of water is necessary.

We use X-ray microspectroscopy to follow the water uptake in single particles. To establish a stable microenvironment around the particles a new device – a microreactor – was developed. Using this reactor, the samples can be kept in an environment with controlled temperature and humidity ranging from 0 to 95 % while being analyzed in the X-ray microscope.

The samples were deposited either as droplets with a microdispenser or as aerosol particles on the sample holder of the microreactor. Using this setup we could obtain unique images showing the microstructure of model substances as ammonium sulfate and mixtures of ammonium sulfate and adipic acid as well as images from heterogeneous mixture like the Suwannee River Fulvic Acid (see Figure 1).



Imaging Photoelectron Photoion Coincidence for High Accuracy Thermochemistry and Fundamental Ion Processes

Andras Bodi,¹ William R. Stevens,² Tom Baer,² Sampada Borkar,³ Bálint Sztáray³

¹Molecular Dynamics Group, Paul Scherrer Institut, Villigen, Switzerland

²University of North Carolina at Chapel Hill, Chapel Hill NC, USA

³University of the Pacific, Stockton CA, USA

andras.boedi@psi.ch

The VUV Beamline delivers high-flux monochromatic vacuum ultraviolet radiation primarily in the 5–30 eV range, which corresponds to valence ionization of gas phase samples. By tuning the photon energy, the dissociative photoionization processes are recorded as a function of the ion internal energy. The breakdown diagram shows the fractional abundances of the parent and daughter ions resulting from the dissociation of energy selected parent ions. Time-of-flight distributions are used to measure unimolecular dissociation rates in the $10^3 \text{ s}^{-1} < k < 10^7 \text{ s}^{-1}$ range. Determining highly accurate 0 K onset energies, *i.e.* dissociative photoionization reaction energies, makes it possible to obtain thermochemical information on the studied neutrals.

The three possible isomers for dichloroethylenes, the 1,2-*Z*, 1,2-*E* and 1,1 ones, have different enthalpies of formation. However, when one halogen atom is lost upon dissociative photoionization, all three isomers give rise to the same monohalogenated $\text{C}_2\text{H}_2\text{Cl}^+$ cation. As shown in Figure 1, the 0 K onset energies can thus be used to obtain the isomerization heats. The mechanism of dissociative photoionization as well as higher energy processes will also be discussed.

Methanol cations lose an H-atom in the lowest energy dissociative photoionization process, which produces the CH_2OH^+ cation, *i.e.* protonated formaldehyde. By measuring the onset energy, the proton affinity of formaldehyde can be deduced. In higher energy processes, further H-atoms, an H_2 molecule or an OH radical may be lost. Deuterated isotopologues, namely CD_3OD , CD_3OH and CH_3OD were also studied to understand the mechanism of these higher energy processes, and the zero-point effects. The breakdown diagram and the threshold photoelectron spectra help understand the non-statistical nature of the competition between H and OH losses, which is also supported by quantum chemical calculations.

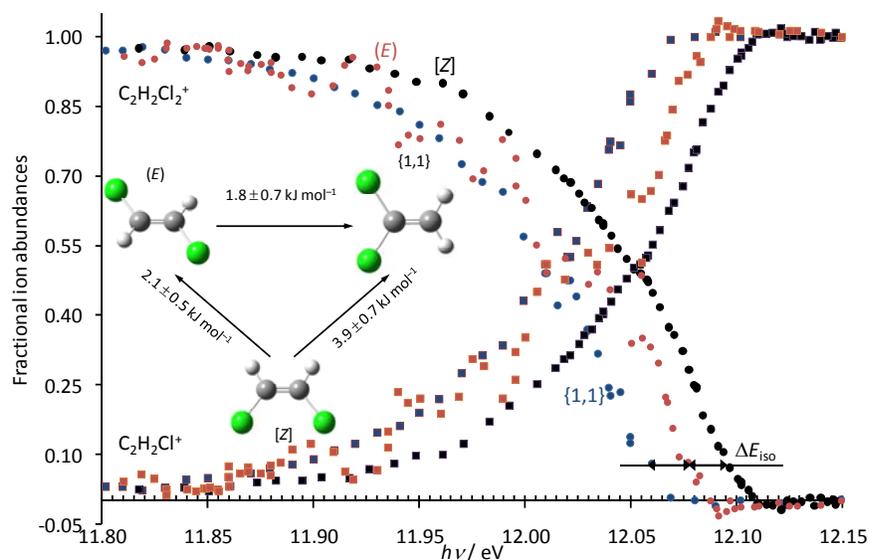


Figure 1. The breakdown diagram of Cl-loss in $\text{C}_2\text{H}_2\text{Cl}_2$ isomers. Although this process is slow, it occurs along a shared reaction coordinate in all three ions. Therefore, the breakdown diagram can be used to deduce accurate isomerization heats as shown in the inset.

X-ray reflectivity studies of liquids under nanometer confinement

S. Chodankar¹, Edith Perret¹, Kim Nygård¹, Tobias Balmer², Oliver Bunk¹, Manfred Heuberger³ & J. F. van der Veen^{1,2}

¹Research Department of Synchrotron Radiation and Nanotechnology,

Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

²ETH Zürich, 8093 Zürich, Switzerland

³EMPA, 9014 St. Gallen, Switzerland

Shirish.chodankar@psi.ch

The lubricating properties of a molecular liquid between two surfaces may change if the surfaces approach each other to within a few molecular diameters¹. The question arises whether the liquid remains 'liquid' in this case². Measurements of the normal force between two approaching surfaces show oscillations which correspond to the squeezing-out of consecutive molecular layers³. On the other hand a solid-like ordering of the confined liquid has been predicted⁴, which may preclude such mobility. These issues call for an experimental determination of the liquid's structure under extreme confinement. Israelachvili designed an x-ray surface force apparatus for x-ray transmission experiments on confined fluids under shear⁵. However, a design to determine the liquid's density profile along the confinement direction is missing. We present a novel x-ray surface force apparatus for synchrotron x-ray reflectivity (XRR) experiments on confined liquid thin films. We show the electron density profiles of water under confinement have been obtained. The distance between two opposing mica membranes was determined to be on average 1.7 nm at zero relative humidity and 4.5 nm at 50% relative humidity. The determined electron density profiles of confined water between nominally dry mica membranes along the confinement direction show distinct peaks, indicating layering of water molecules. The electron density profiles for 50% relative humidity suggest the formation of trapped water nano-droplets.

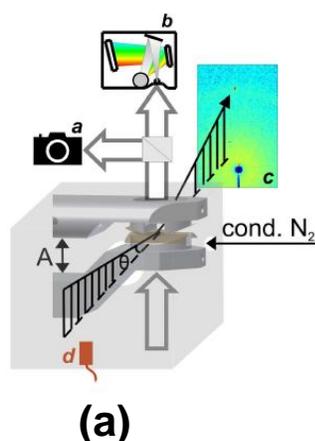


Fig (a) Schematic representation of a specular X-ray reflectivity experiment on a confined liquid. The gap width is controlled by the actuator A and measured through white-light interferometer. The momentum transfer dependence of the reflected intensity is measured in a θ -2 θ scan. Where the scattered beam is detected by a PILATUS 100K detector.

References:

- [1] Persson, B. N. J. & Tosatti, E. Physical Review B 50, 5590-5599 (1994).
- [2] Jinesh, K. B. & Frenken, J. W. M. Physical Review Letters 96 (2006).
- [3] Israelachvili, J. N. Intermolecular and Surface Forces (Academic Press, London, 1991).
- [4] Bhushan, B., Israelachvili, J. N. & Landman, U. Nature 374, 607-616 (1995).
- [5] Idziak, S.H.J., Koltover, I., Israelachvili, J.N. & Safinya, C.R. Physical review letters 76, 1477-1480 (1996).