

## Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+NS+SS+VT-WeA

### Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces I

**Moderators:** Juan Yao, Pacific Northwest National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:20pm **CA+NS+SS+VT-WeA1 Chemical Analysis and Imaging of Environmental Interfaces, Vicki Grassian**, University of California at San Diego **INVITED**

Environmental interfaces, defined as any surface in equilibrium with its surrounding environment, are ubiquitous. From this broad definition, there are a myriad of different types of environmental interfaces that include atmospheric aerosols, nanomaterials and indoor surfaces. This talk will focus on the use of different molecular probes including various spectroscopic and imaging techniques to investigate interfaces relevant to outdoor and indoor environments.

3:00pm **CA+NS+SS+VT-WeA3 Liquid/Vapor Interfaces Investigated with Photoelectron Spectroscopy, Hendrik Bluhm**, Fritz Haber Institute of the MPG, Germany **INVITED**

Aqueous solution/vapor interfaces govern important phenomena in the environment and atmosphere, including the uptake and release of trace gases by aerosols and CO<sub>2</sub> sequestration by the oceans.[1] A detailed understanding of these processes requires the investigation of liquid/vapor interfaces with chemical sensitivity and interface specificity under ambient conditions, *i.e.*, temperatures above 200 K and water vapour pressures in the millibar to tens of millibar pressure range. This talk will discuss opportunities and challenges for investigations of liquid/vapor interfaces using X-ray photoelectron spectroscopy and describe some recent experiments that have focused on the propensity of certain ions and the role of surfactants at the liquid/vapor interface.

[1] O. Björneholm et al., Chem. Rev. **116**, 7698 (2016).

4:20pm **CA+NS+SS+VT-WeA7 Methanol Hydration Studied by Liquid  $\mu$ -jet XPS and DFT Simulations, Jordi Fraxedas**, Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC and BIST, Spain; *E. Pellegrin, V. Perez-Dieste, C. Escudero*, CELLS-ALBA, Spain; *P. Rejmak*, Institute of Physics PAS, Poland; *N. Gonzalez, A. Fontseré, J. Prat, S. Ferrer*, CELLS-ALBA, Spain

The advent of liquid  $\mu$ -jet setups, in conjunction with X-ray Photoemission Spectroscopy (XPS), has opened up a plethora of experimental possibilities in the field of atomic and molecular physics [1]. Here, we present a combined experimental and theoretical study of the hydration of methanol at the aqueous solution/vapor interface. These are first experimental results obtained from the new liquid  $\mu$ -jet setup at the Near Ambient Pressure Photoemission (NAPP) endstation of the CIRCE helical undulator beamline (100–2000 eV photon energy range) at the CELLS-ALBA synchrotron light source, using a differentially pumped SPECS PHOIBOS 150 hemispherical electron energy analyzer [2]. The experimental results are compared with simulations from density functional theory (DFT) regarding the electronic structure of single molecules and cluster configurations as well as with previous experimental studies.

Methanol is the simplest amphiphilic molecule capable of hydrogen bonding due to its apolar methyl and polar hydroxyl groups. The results obtained from pure water at 600 eV photon energy emphasize the short range tetrahedral distribution as previously observed for crystalline and amorphous ice. We also find indications for ordering phenomena in water/methanol mixtures by the reduced O1s XPS liquid line width (as compared to pure water), which could be ascribed to the amphiphilic character of the methanol molecule. Regarding the C1s XPS lines, the vapor/liquid peak ratios allow for a quantitative determination of the methanol volume concentrations in both the vapor as well as in the liquid phase, that are corroborated by an analogue analysis of the valence band (VB) spectra. A detailed quantitative analysis of the water/methanol liquid VB XPS spectrum accounting for the photon energy dependence of photoemission cross sections confirms the atomic/orbital characteristics of the methanol molecular orbitals involved in the transitions and their pertinent intensities. From the decomposition of the liquid VB spectrum of the water/methanol mixture together with finite XPS probing depth we derive a methanol volume fraction of 43% for the outer liquid layers as compared to the nominal bulk liquid value of 37.5%. Finally, from the different binding energy (BE) shifts of the water/methanol liquid VB

spectrum with respect to that of pure methanol, we develop a CH<sub>3</sub>OH-(H<sub>2</sub>O)<sub>3</sub> cluster-based model that relates these different BE shifts to the different MO hybridizations within that cluster.

[1] B. Winter, M. Faubel, Chem. Rev. **106** (2006) 1176.

[2] V. Pérez-Dieste, L. Aballe, S. Ferrer, J. Nicolàs, C. Escudero, A. Milán, E. Pellegrin, J. Phys. Conf. Ser. **425** (2013) 072023.

4:40pm **CA+NS+SS+VT-WeA8 Survey of Ionic Liquid Interfaces under Vacuum and Ambient Conditions: An XPS Perspective, Yehia Khalifa**, Ohio State University; *A. Broderick, J.T. Newberg*, University of Delaware; *Y. Zhang, E. Maginn*, University of Notre Dame

Properties and behavior of Ionic Liquid interfaces tend to behave differently from their bulk counterparts. In this study the preferential enhancement of the lower molar concentration anion [TFSI] in a mixture of [C2MIM][OAc] and [C2MIM][TFSI] is shown in the top 17 Å via angle-resolved X-ray photoemission spectroscopy under ultra high vacuum conditions. This is supported by molecular simulations where a quantitative relationship is also established between the two techniques. This interfacial enhancement is not only unique to mixtures but is also displayed in a pure ionic liquid with a hydrophilic anion such as [HMIM][Cl] studied via ambient pressure X-ray photoemission spectroscopy. The surface of [HMIM][Cl] under vacuum and increasing pressures of water vapor was evaluated (maximum of 5 Torr, 27% relative humidity). Our quantitative results indicate a significantly larger mole fraction of water at the interface compared to the bulk with increasing pressures when compared to previously published tandem differential mobility analysis results on [HMIM][Cl] nanodroplets. Furthermore the reverse isotherms has shown that the water uptake on the interface is a reversible process. These results highlight the unique behavior of ionic liquid interfaces that can be exploited for smart materials design and application.

5:00pm **CA+NS+SS+VT-WeA9 Ambient Pressure XPS Study of Gallium-Indium Eutectic (EGaIn) Surface under Oxygen and Water Vapor, Meng Jia**, J.T. Newberg, University of Delaware

Liquid metals (LMs) have a combination of high thermal/electrical conductivity and excellent deformability. The application of LMs in the field of electronics has identified many opportunities for their use as stretchable electronics, self-healing conductors and interconnects. Gallium-Indium eutectic (EGaIn) is one of the leading alternatives to toxic liquid mercury because of its low vapor pressure, low viscosity, low toxicity and high conductivity. A surface oxide layer is known to form when EGaIn is exposed to ambient conditions. However, surface sensitive measurements of this chemistry occurring under ambient conditions are strongly lacking. Herein we present results from the interaction of oxygen and water vapor with the liquid-gas interface of an EGaIn droplet deposited on an W foil using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). EGaIn was examined up to a maximum of 1 Torr pressure at 550 K. Results reveal that under ambient conditions both oxygen and water vapor form a Ga(3+) oxide (Ga<sub>2</sub>O<sub>3</sub>) as an outer layer, while a thin layer of Ga(1+) oxide (Ga<sub>2</sub>O) resides between metallic EGaIn and the outer Ga(3+) oxide. Both gases were unreactive towards Indium under our experimental conditions. The oxidation kinetics in the presence of water vapor were much faster compared oxygen. Proposed reaction mechanisms will be discussed.

5:20pm **CA+NS+SS+VT-WeA10 Laboratory-based Hard X-ray Photoelectron System for the study of Interfaces, S. Eriksson**, Scienta Omicron; *Henrik Bergersen*, Scienta Omicron, Sweden

Hard X-ray photoelectron spectroscopy (HAXPES) has traditionally found its application in the core topics of condensed matter physics, but the slowly growing number of beamlines worldwide has widened its appeal to other interest groups. HAXPES uses X-rays in the 2-10 keV range to excite photoelectrons, which are used to non-destructively study the chemical environment and electronic structure of materials.

In contrast to the very surface-sensitive XPS, HAXPES is much more bulk sensitive. This makes it applicable to bulk materials and structured samples, e.g. layered samples and heterostructures. In addition, its bulk sensitivity means that realistic samples can be investigated without the need of prior surface preparation. However, the number of existing HAXPES systems is very small and they are predominantly located at synchrotrons (approx. 20 beamlines worldwide) due to low photoionization cross sections necessitating high X-ray intensities, limiting their availability to users and applications.

This work presents a new laboratory-based instrument capable of delivering monochromated hard X-rays with an energy of 9.25 keV and a focused 30x45  $\mu$ m<sup>2</sup> X-ray spot, giving excellent energy resolution of <0.5

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eV. Systematic reference measurements are presented outlining the systems capability as well as the latest results from various application fields including energy related materials such as batteries.

Ultimately, this spectrometer presents an alternative to synchrotron-based endstations and will help to expand the number and range of HAXPES experiments performed in the future. HAXPES is a cutting edge characterisation method and the advancement of this technique will tremendously increase the potential to study an ever increasing range of inorganic materials and beyond.

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