

TEMPO

Near ambient pressure photoemission and environmental science

Where do the ions go at vapor water interface?

Using an original setup designed on the TEMPO beamline by scientists from Laboratory of Physical Chemistry- Matter and Radiation (UPMC, Paris), it becomes possible to carry out x-ray photoemission spectroscopy measurements at pressures that can reach 20 mbars, far from ultra-high vacuum conditions. This bridges the pressure gap with “real-life” conditions, and allows applications in environmental sciences, for instance.

Since the work of Kai Siegbahn (Nobel prize 1981) we know that when X-rays impinges on a sample, energy is conserved in the photoemission process. Besides, the measurement of electron energy distribution gives important information not only on which atomic species are observed but also on their chemical bonding. As the inelastic mean free path of electrons in the kinetic energy range 50-1000 eV is short in condensed matter, with a minimum of a few atomic layers at 50 eV, the information extracted with this technique is extremely surface sensitive.

Usually experiments are performed in ultra-high vacuum conditions needed to operate soft X-rays beamlines and electron energy analyzers. To bridge the pressure gap with “real-life” surfaces, for instance those of catalysis or environmental chemistry, new X-ray photoemission spectrometers were designed, capable to reach working pressures of ~20 mbar.

For the pressure to rise up...

The design involves a very short distance between the surface under

study and the analyzer (~1mm) to minimize the inelastic scattering of the photoelectrons by the gas phase and a highly efficient pumping of the analyzer lenses. The latter point implies that the photoelectrons are collected through a pinhole of diameter ~0.3 mm drilled in the conical skimmer shown in figure 1.

Because of the small dimension of the X-ray spot (~0.1 mm for Branch n°2 of TEMPO beamline), these geometrical constraints make that the best performances are obtained at synchrotron sources. The high photon flux also balances the signal attenuation by the gas phase.

A unique and specific setup

With respect to other setups installed in the world, one specificity of the Laboratory of Physical Chemistry-Matter and Radiation (LCPMR) installation at SOLEIL is the absence of window to confine the near ambient pressure region under study. Indeed, the soft X-rays photons beam at TEMPO beamline goes through a differential pumping system whose final diameter is 300 microns. In consequence,



Figure 1: Water droplets on a gold coated silicon surface in the analysis chamber during the acquisition. The soft X-ray beam of TEMPO beamline impinges on the sample from the right. The cone pointing to the droplet is the 300 microns diameter entrance of the electron energy analyzer.

the incoming photon flux is not damped by the absorption edges of silicon nitride or aluminum windows. Therefore, experiments can be performed at all photon energies between 50 and 1500 eV (the energy range of TEMPO beamline). The specially designed lens system has no negative impact on photoelectron collection, and photoelectrons are measured with high energy and angular resolution as efficiently as in any “regular” UHV setup. Studies of catalytic reactions at partial pressures equivalent to those of real devices are one of the main applications. However, the example presented below is an original application to environmental science.

Reproducing marine aerosols on TEMPO

Experiments are performed on liquid water and we can learn about ion distribution at the water surface by using the tunability of the photon energy and hence by changing the probed depth. The sample environment during the experiment is presented in fig. 1. Some salt is deposited on a metallic substrate (gold in our case), and then the sample is cooled down to 8°C. When water vapor is introduced in the experimental station under a pressure of 8 mbar, one assists to the deliquescence of the salt crystals until liquid droplets form. The prepared solution can now be studied.

The conventional view of electrolyte solution surfaces was essentially the one of ion-depleted surfaces, similar to the surface of neat water (the Onsager-Samaras model). However, in the last decade, theory and experiments have shown a very different picture, pointing to the segregation of ions at the water surface. Naturally, this observation is highly relevant to environmental systems: the segregation of halide ions at the surface of marine

aerosol has a relevant impact on atmospheric chemistry.

The Na 2p/O 2s energy window is shown in fig. 3. We can identify the electrons from sodium atoms and oxygen atoms of water. The same experiment can be repeated changing the photon energy (the electron kinetic energy) and then the probing depth. This procedure that is currently used in surface science to obtain atomic distribution in a solid can be readily applied to solutions. It is observed that the intensity ratio between the Na 2p level and the O 2s changes as the photoelectron kinetic energy increases (i.e. as the probing depth increases). After taking into account photoemission cross section variations, the analysis of the data comes to the conclusion that this change in relative intensity is mainly due to an accumulation of Na⁺ close to the surface for the NaI solution. This is also true for the NaBr solution, but this trend is not seen for the NaCl one.

In agreement with molecular dynamics results, when the anion polarizability increases, a cation plane is formed below the anion one near the liquid surface, to recover the electro neutrality of the solution. This is an important result. It is the first time that an experimental measurement proves the existence of an increase of cation concentration below the surface.

Looking in another kinetic energy region, photoelectrons from the salt anions, such as the chlorine atoms of the NaCl solution or iodine atoms of the NaI one, can be observed (see fig. 3). Ions at the surface have different coordination than in the bulk solution, for instance less water molecules around them. This has a sizeable impact on their binding energy.

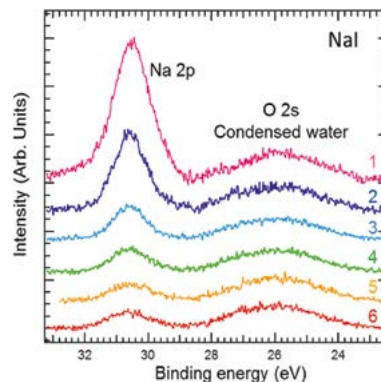


Figure 2: Na 2p and O 2s XPS spectra of a saturated sodium iodide solution surface measured at several photon energies with the gold substrate biased at -40 V at relative humidity (RH) = 95% (P = 8 mbar, T = 278 K). The spectra are normalized to the O 2s peak intensity and a vertical offset is added to make the figure clear. The binding energy (BE) is referenced with respect to the Fermi level measured on the gold substrate. (1) $h\nu = 200$ eV, $\lambda \approx 13$ Å; (2) $h\nu = 400$ eV, $\lambda \approx 17$ Å; (3) $h\nu = 600$ eV, $\lambda \approx 20$ Å; (4) $h\nu = 800$ eV, $\lambda \approx 23$ Å; (5) $h\nu = 1000$ eV, $\lambda \approx 33$ Å; and (6) $h\nu = 1200$ eV, $\lambda \approx 50$ Å are theoretically determined for pure liquid water. The sample was biased to -40 V with respect to the spectrometer to get rid of the O 2s gas phase contribution.

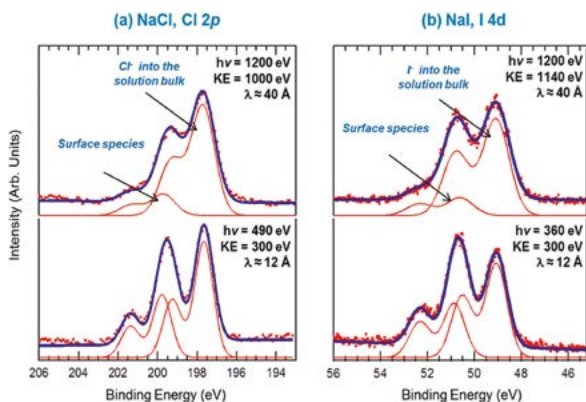


Figure 3: (a) Cl 2p spectra of a saturated NaCl (6M) solution surface and (b) I 4d spectra of a saturated NaI (11M) solution surface measured with two photon energies at RH = 95% (P = 8 mbar, T = 278 K). The BE is referenced with respect to the Fermi level of the gold substrate. Inelastic mean free paths (λ) are theoretically determined for pure liquid water.

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