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Liquid-jet XPS study on the air-aqueous interfacial composition of mixed sodium bromide/citric acid solutions

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Bromide ions at the sea salt solution - air interface are implicated in ozone depleting reactions in marine environments. Driven by the relevance, we intend to use near ambient pressure X-ray photoelectron spectroscopy (NAPP) on a liquid microjet at the SIM Beamline in order to determine the surface concentration of bromide ions in mixed solutions containing bromide and citric acid to mimic the complex composition of natural sea water derived aqueous phases.

The results show three exemplary scans of the region of about 160 eV photoelectron kinetic energy, excited at 229 eV photon energy. Br 3d (doublet due to spin orbit splitting) and Na 2s of sodium bromide have a binding energy of about 73 eV and 68 eV, respectively. We therefore used the presence of the small amount of second order light available at 458 eV to obtain C1s photoelectrons from citric acid around 170 eV kinetic energy. The three peaks in the C1s region are due to the occurrence of the carbon atom in different electronic configuration, i.e., three carboxyls, one alcohol and two methyl carbons in the citric acid molecule. Along the same line, we used third order light (687 eV) to observe O1s around 148 eV. Taking the spectra in this way allows to obtain directly an internal reference for the overlap between photon beam and the jet via the O1s or the C1s signals without the need to change the photon energy at the beamline in between.

Furthermore, apparently Br 3d peaks were not clear from the interface for the conditions of low bromide and high citric acid concentrations in the solutions. At higher bromide concentrations, the bromide signal remained clearly visible in presence of 2.5 M citric acid.

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