

Abstract

The present work is concerned with the electronic structure of liquid water and aqueous solutions as inferred from photoemission. Of central focus is a better understanding of the effect of hydrogen bonding. A specially designed liquid microjet, providing a free liquid surface in vacuum, enables the detection of photoelectrons from highly volatile liquid surfaces. In combination with high-intensity synchrotron light from an undulator (U125/1 at BESSY II) for photoexcitation, in the 30-140 eV range, electron binding energies of the liquid constituents are determined. This includes energies of liquid water's valence orbitals as well as of a number of solvated ions, particularly alkali cations and halide anions. Liquid-specific energy losses of photoelectrons will be also addressed. Measured binding energies for liquid water, which are about 1.4 eV lower than in the gas phase, are discussed in terms of surface dipoles, polarization screening after photoionization, and hydrogen bonding. The relative signal decrease of the H₂O $1b_2$ orbital results from a change of the respective anisotropy parameter β . Broadening of the $3a_1$ orbital feature correlates with peak splitting. Both effects are due to hydrogen bonding. Hydrogen bonding also plays a central role in ion solvation. Here, a number of salt solutions (XY for X = Li, Na, K, Cs, and Y = Cl, Br, I; CaI₂; MgCl₂; Na₂CO₃; Na₄[Fe(CN)₆]; K₃[Fe(CN)₆]; But₄NI; Prop₄NI), are systematically investigated by photoemission in order to address various aspects of ionic solvation. One focus is on correlating measured electron binding energies, obtained for different counter ions and concentrations, with solvation shell structural details. Experimental binding energies, which are considerably different from gas-phase values, are discussed within a dielectric continuum model and also with respect to comparative measurements performed for some gas-phase alkali halides. The other important topic, regarding photoemission from aqueous salt solutions, was the structure of the solution/vacuum interface. Two processes have been investigated, ion depletion near the solution surface for high-concentration NaI solutions, and the surface segregation of hydrophobic tetrabutylammoniumiodide, But₄NI (and also the smaller Prop₄NI). The former aspect is related to the question if for high NaI concentration surface ions are incompletely solvated, with the possibility of anion surface excess. Solutions of surface-active But₄N⁺I⁻ provide the opportunity to investigate the formation of a segregation monolayer (electric double layer) at the liquid surface. The resulting molecular surface dipoles correlate with spectral shifts of the photoemission features, due to work function changes of the solution as a function of the salt concentration.