

1 Introduction

Water is a substance so common we rarely take note of it, although we use it everyday. We drink water, cook with water, wash with water, swim and fish in water, and our bodies themselves are two-thirds water. Due to this omnipresence we continue to perceive water as pretty ordinary and we certainly take it for granted. However the fact is life, as we know it, could not have evolved without water. Together with its astonishing anomalies water is the crucial element for Earth's biosphere and all living organism survival. Despite all this, water is still surprisingly poorly understood.

The present work focuses on the electronic structure of liquid water and aqueous solutions as inferred from photoemission. This technique was for a long time hardly applicable to highly volatile liquids because of the difficulty to transfer photoelectrons originating from the liquid surface through the vapor phase to an electron detector. This problem has imposed serious limitations on the access to the electronic structure of liquids. Understanding the physical and chemical properties of liquid water and aqueous salt solutions is the main aspect of the present work. Eventually studies will be extended to other chemical and biological systems. Physical and chemical properties of any system are inherently determined by the electronic structure of matter. Chemical reactions occurring in liquid water are driving numerous electrochemical, biological and other processes [1]. The key to many properties of liquid water is the hydrogen bonding (H-bonding). H-bonding in liquid water can influence chemical processes by weakening specific chemical bonds. For instance, the formation of an $\text{O-H}\cdots\text{O}$ hydrogen bond weakens the O-H chemical bond, thereby enabling proton transfer via an exchange of these bonds [2].

Despite the importance of H-bonding there are many open questions as to the H-bonding structure, and not only in pure water. In the case of aqueous solvation the interplay of several processes leads to the formation of specific solvation shells, which requires a considerable reorganization of the water structure. Aqueous solvation forms one of the less understood interactions in chemical physics [2]. With respect to liquid water, a challenging question is

how H-bonding affects the electronic structure of the water molecule (e.g. [3]). Regarding solvation (here we will be particularly concerned with the solvation of simple alkali and halide ions) electronic structural information may be invaluable for better understanding the structure of solvation shells.

The initial step of the present work was to install a microjet apparatus, developed at the Max-Planck-Institut für Strömungsforschung (Göttingen) [4], at the Max-Born-Institut beamline at BESSY II. Earlier studies in the Göttingen laboratory, using HeI radiation, have already demonstrated that using a $6\ \mu\text{m}$ liquid jet, photoelectrons from the liquid can escape through the vapor [4]. In combination with high-intensity synchrotron photons appreciable photoemission signal is obtained. With photon energies in the range of 30-140 eV, electron binding energies of liquid species have been measured up to ca. 80 eV.

The first series of experiments was devoted to pure liquid water, mainly to determine the H_2O orbital binding energies, but also to look for liquid-specific extra features (electron energy losses). Measured electron binding energies, which are shifted with respect to gas-phase water, are discussed on the basis of a simple continuum (molecular cavity) model. Further effects, such as the role of oriented surface water or screening phenomena inherent to the photoemission process, will be also discussed. Moreover, by measuring photoemission spectra for different photon energies, differences in the relative photoionization partial cross sections are found for liquid vs. gas-phase water. Since synchrotron radiation is linearly polarized, for a given experimental geometry these changes can be qualitatively correlated with H_2O molecular changes due to H-bonding. Finally, understanding the photoemission spectrum of pure water is important for any subsequent aqueous solution studies.

Concerning solutions, two different groups of salts exhibiting entirely different solvation behavior were investigated. For the group of alkali-halide salts and a number of more complex salts, for various counter ion combinations, the ions are rather homogeneously dispersed throughout the bulk solution. The main focus is on possible near-surface structural effects, such as surface depletion or surface segregation, and the determination of electron binding energies of solvated ions as a function of concentration, including the effect of size and charge (in some cases also structure) of the counter ion. Iodide was preferentially used in this work due to its large photoionization cross section (I^- ($4d$) shape resonance) near 100 eV. As a representative of a hydrophobic (surface-active) type of salt, photoemission spectra were measured from aqueous tetrabutylammoniumiodide (But_4NI) solutions. The important question concerning this hydrophobic organic solute is how surface segregation, which gives rise to the formation of a monolayer of (paired) anions and cations (electric double layer) at the

surface, manifests in the photoemission spectra. Notice that photoemission for photoelectron kinetic energies in the 20-120 eV range is a very surface-sensitive technique. The data can be discussed, with some respect, similarly to adsorbate/single crystal systems. This refers to the identification of the completion of the surface segregation layer and also to spectral energy shifts associated with (adsorbate) dipoles on the liquid surface. Comparing the results for NaI and But₄NI aqueous solutions allows to infer specific structural information for both solutions.

A brief outlook proposes some future photoemission experiments for aqueous solutions. The role and potential of charge-transfer-to-solvent (CTTS) optical excitations, partly in the context of the generation of solvated electrons, will be addressed. Finally, the possibility to study chemical reactions in the liquid environment will be exemplified for aqueous triiodide. Both the formation and the laser-dissociation of this complex, probed by photoemission, is a great challenge.