4 Photoemission from Liquids: Results and Discussion

4.1 Pure Liquid Water

The electronic structure of liquid water is not well understood even though this property holds the key to understanding the chemical and physical properties of matter. Furthermore, the study of the electronic states in hydrogen bonded (H-bonded) systems is of great interdisciplinary importance. A well suited technique by which this information may be accessed is photoelectron spectroscopy [24]. The only valence photoemission experiment from liquid water reported to date, which extends beyond the top of the valence band [22], was performed with focused HeI (21.2 eV) radiation using a similar microjet setup as in the present work [28]. With this laboratory photon source the outer three valence orbital energies of liquid water were measured for the first time, however, on a large background of secondary electrons [4, 26, 47]. For the present study the microjet apparatus has been modified for the use at a synchrotron radiation source (see 3.2.1). This enables for systematic studies of the dependence of the photoemission spectra on photon energy, flux, and polarization. The wide tunability of synchrotron radiation allows excitation at maximum photoionization cross section, which is particularly advantageous if low-concentration aqueous solutions are examined. Assessing resonances, e.g. charge-transfer-to-solvent excitation in the case of aqueous ions, is of great fundamental importance [48, 49, 50]). Furthermore, the use of polarized photons of tunable energies not only enables to map but also to reasonably interpret photoionization cross sections.

Here the first full range (inner and outer) valence photoemission spectra of liquid water will be presented. The photon energy range from 30 to 140 eV enables the investigation of previously inaccessible electronic structural features. Liquid-specific photoelectron scattering



Figure 4.1: Photoemission spectrum of pure water obtained after photoexcitation of the water jet using 100 eV photon energy. The spectrum was optimized for maximum liquid-to-gas-phase intensity ratio (see text). $1b_{1g}$ refers to the respective gas-phase orbital; the other gas-phase contributions strongly overlap with the liquid features. Labels denote the water orbitals, single numbers 1, 1', 2 partly denote the electron energy-loss features (see section 4.1.4). The emission between 90-100 eV is the low-kinetic energy cutoff region.

processes are addressed, and partial ionization cross sections, $d\sigma/d\Omega$, of the liquid water molecular orbitals for some selected photon energies are reported. The role of surface species and the effect of hydrogen bonding will be discussed.

4.1.1 General Features, Spectral Assignment and Analysis

Fig. 4.1 shows a typical full-range photoemission spectrum from pure liquid water obtained for 100 eV excitation photon energy (acquisition time was about 30 minutes). The energies in the figure are binding energies calibrated to the gas-phase water $1b_1$ orbital¹ ionization threshold (set to 12.60 eV [51] as discussed below).

Unlike in the case of metal samples where the Fermi energy (E_F) provides an internal energy reference, in liquids and solutions, energies are related to a reference potential (ref-

¹hereafter the $1b_1$ gas-phase orbital will be denoted $1b_{1q}$.

erence electrode). In aqueous solutions one typically defines the free energies and enthalpies of the hydrogen ion, and of the elements in their standard states, as energy zero [52]. This is technically difficult for the free jet, which may be treated in many respects similarly to free clusters (which may be of very large size with aggregation states being liquid or solidlike). In cluster photoemission studies absolute ionization potentials are typically obtained by calibration using a gaseous species of known threshold energy. Generally not relevant in cluster studies is the presence of surface potentials caused by oriented surface species, giving rise to a surface dipole. Whether or not this exists for water is still debated. For the present case, the $1b_{1g}$ gas-phase binding energy was chosen as an external energy reference. Its peak position and width is found to remain constant in the photoemission spectra as the jet was moved out of the spectrometer acceptance angle by 50-100 μ m. This implies that all gas-phase water is sampled from the identical potential between the jet and the spectrometer skimmer, which makes the measured $1b_{1g}$ energy a convenient and precise reference.

For a more detailed discussion of the photoemission spectrum in Fig. 4.1 it will be useful to consider the low kinetic energy part (I), the medium range (II), and the valence orbital region (III) separately. The latter region (III), between ca. 10-35 eV binding energy, is characterized by distinct emission features predominantly arising from the four outer orbitals of the H₂O molecule, $2a_1$, $1b_2$, $3a_1$, $1b_1$ as introduced in section 2.2. Gas-phase contributions, denoted by the subscript g in Fig. 4.1, result from the continuous evaporation of the liquid surface; only $1b_{1g}$ in labeled since it can be best distinguished (see also Fig. 4.2). Binding energies and peak width are different for liquid and gas-phase water as will be discussed in detail below. Broad emission features observed in the center part (II) of the spectrum (label 2), but also some weaker features at lower binding energy (e.g. features 1, 1'), are in part assigned to electron energy losses in the liquid. They arise from photoelectrons initially emitted from the various molecular orbitals of water which subsequently excite the same transitions known from optical absorption of liquid water [53,54]. This part of the spectrum also contains rather unspecific electron bulk scattering contributions which give rise to a broad background.

The assignment of features within the near cutoff region (I) is unclear, and further studies are required to better understand the issue. In general, this low-kinetic energy region is found to be extremely sensitive to minor experimental changes (particularly jet position). In fact, the cutoff features may change considerably from one aligning adjustment to another, at least, as far as relative intensities are concerned; the energies remain fixed.

4.1.2 H₂O Gas-Liquid Phase Binding Energy Shift

As mentioned in the previous paragraph, quite a large amount of gas-phase water molecules is detected in the measurement due to the larger focal size of the synchrotron radiation as compared to the jet diameter. Hence, the analysis of the liquid water properties requires the separation of the liquid from the gas-phase contributions in the spectra. Fig. 4.2 presents valence band photoemission spectra of water obtained for 60 eV photons. The abscissa in



Figure 4.2: Photoemission spectra sampled for maximum liquid signal (top), from gas-phase water sampled > $100 \,\mu\text{m}$ aside the liquid jet (center), and difference spectrum (bottom), obtained for $60 \,\text{eV}$ photon energy. Labels denote the water orbitals. From the top spectrum a Shirley-type background [55] was subtracted.

the figure is the electron binding energy relative to vacuum and the axis is fixed with respect



Figure 4.3: Gas-phase subtraction from the measured (maximum liquid) photoemission spectrum. (1) Photoemission spectrum (background subtracted) obtained for 60 eV photon energy. (2) and (3) exemplify incorrect subtraction, corresponding to too little or too much gas-phase subtraction (as judged by the $1b_{1g}$ peak or dip, respectively). (4) Optimum difference spectrum.

to the $1b_{1g}$ (gas phase) molecular orbital (see 4.1.1).

The center spectrum in Fig. 4.2 is a pure gas-phase spectrum (obtained by moving the jet aside relative to the spectrometer entrance by some hundred microns), and the top spectrum displays the measured liquid spectrum characterized by a maximum liquid-to-gas phase intensity ratio. Qualitatively similar results were obtained for other photon energies. The labels in the figure denote the molecular orbitals (MOs) of the water molecule (see section 2.2).

Since identical binding energies and peak widths are obtained for the gas-phase lone pair orbital, $1b_{1g}$, for both the (maximum) liquid and the gas-phase photoemission spectra, one may subtract, with proper scaling of the relative intensities (as illustrated in Fig. 4.3), the gas from the liquid spectrum. The difference spectrum, bottom curve in Figs. 4.2 and 4.3, is our best experimental approach to the valence photoemission spectrum from pure *liquid* water. The main difference between the pure liquid and the pure gas-phase spectra is a binding energy shift of the liquid water orbitals to lower values, accompanied by considerable liquid



Figure 4.4: Gas-phase subtracted photoemission spectra for 60, 80 and 100 eV. Constant peak positions are indicated by vertical lines. The inset is a zoom into the low binding energy onset of the liquid-water $1b_1$ emission, showing the ionization threshold.

peak broadening as summarized in Table 4.1. The values in the table result from Gaussian peak fitting averaged over a number of spectra. No dependence of the excitation photon energy (60, 80, 100 eV) on both width and binding energy has been observed. Representative gas-phase subtracted photoemission spectra for 60, 80 and 100 eV are presented in Fig. 4.4. The spectra are normalized to the $1b_1$ liquid water feature. Constant peak positions are indicated by vertical lines. The differences of the relative photoemission intensities, as a function of the photon energy, are discussed in section 4.1.3, which is concerned with the relative partial photoionization cross section of liquid water in detail.

Fig. 4.5 is a presentation of the spectral analysis (60 eV photon energy), which was used to derive both peak energies and widths, shown in Table 4.1. Prior to subtracting the measured gas-phase spectrum (center Fig. 4.2) from the measured maximum liquid spectrum (top Fig. 4.2) a background (Shirley-type [55]) was subtracted from the latter. The result is shown in Fig. 4.5 along with the corresponding Gaussian peak fits. As will be discussed below (4.1.4), in addition to the main peak for the $2a_1$ feature, two further peaks of identical height and width on either side of the main peak were introduced. Also for fitting the $3a_1$



Figure 4.5: Representative Gaussian peak fitting shown for a photoemission spectrum of pure liquid water (here obtained for 60 eV photon energy). The extra peaks required for fitting the $2a_1$ feature account for distinct electron energy losses. A double-peak structure has been assumed for the $3a_1$ feature in order to account for possible Davydov splitting.

feature two peaks were used, however, for a different reason (see 4.1.3).

The observed differential gas-liquid peak shifts are 1.72 ± 0.16 , 1.46 ± 0.06 , 1.34 ± 0.12 , and $1.45 \pm 0.05 \text{ eV}$ for the $2a_1$, $1b_2$, $3a_1$, and $1b_1$ orbitals, respectively (see Table 4.1). As the statistical error is smaller than the mean relative energy differences, the observed differential shifts are considered to be significant. Notice that simple Gaussian fitting neglects possible differential shifts due to altered vibronic spectra of liquid water as a consequence of modified molecular structures.

Origin of gas-liquid energy shift. The observed gas-liquid peak shifts of water are the net result of different contributions: electronic polarization, surface dipoles, and H-bonding induced orbital changes. The two former contributions would be expected to make up for the observed mean shift, which is supposed to be identical for all orbitals. The polarization term refers to the fact that the emitted photoelectron may sense the fast (on the time scale of the photoemission process) polarization screening by the (liquid) environment around the photo-generated charge. Such a *final state* effect is common in photoemission of condensed molecular systems, where electron binding energy shifts are on the order of $1-2 \,\text{eV}$ just as in the present case [57]. For liquids, (fast) polarization screening may be treated similarly to the static electronic polarization of the solvent [25]. Traditionally, such shifts are derived

Orbital	$E_g \; [eV]$	$E_{aq} [eV]$	FWHM [eV]	FWHM [eV]	Shift(g-l)	broadening
MO_i	Gas	Liquid	Gas	Liquid	[eV]	factor (liq)
		(this work)		(this work)		(this work)
$1b_1$	12.60	11.16(4)	0.30(1)	1.45(8)	1.45(5)	4.03
			$0.09^{ m a}$			
$3a_1$	14.84(2)	13.50(10)	1.18(2)	2.52(10)	1.34(12)	2.14
	14.85^{a}		$1.03^{\rm a}$			
$1b_2$	18.78(2)	17.34(4)	1.74(2)	2.28(8)	1.46(6)	1.31
	18.76^{a}		$1.62^{\rm a}$			
$2a_1$	32.62(10)	30.90(6)	2.82(4)	3.30(6)	1.72(16)	1.17
	32.52 ^a		2.34 ^a			

Table 4.1: Experimental electron binding energies (E_g, E_{aq}) , peak widths (FWHM) and experimental gas-to-liquid energy shifts of the four H₂O (gas and liquid) valence orbitals. For comparison respective literature high-resolution data for gas-phase water are also shown: ^a [56]

from the Gibbs free energy of solvation 2 based on the Born equation [12]:

$$\Delta G^{Born} = -\frac{Z^2 e^2}{8\pi\epsilon_0 R} (1 - \frac{1}{\epsilon}) \,. \tag{4.1}$$

The model assumes electronic polarization (typically static polarization) of a continuum solvent around an ion with charge Ze and radius R; ϵ_0 is the vacuum permittivity and ϵ is the relative permittivity of the solvent. For the case of photoemission, only the fast process contributes, while the rearrangement of the solvation structure can be neglected [25]. Therefore, the optical macroscopic relative permittivity of liquid water, ϵ_{opt} , is used to describe the response. This accounts for the electronically polarized but *not* for reoriented surrounding in terms of nuclear positions of water molecules. In section 4.2.5 it will be seen that for aqueous ions, on the other hand, the slow (static) response, ϵ_{st} , is the most important (see also Fig. 4.38).

Since the solvation process for any solute is its transfer from a fixed point in vacuum to a fixed point in solution, one can obtain the Gibbs free energy of solvation of an ion from the difference of the Gibbs energy of the aqueous and of the gaseous ion. As mentioned in

²Terminology varies considerably: Gibbs free energy, Gibbs function or free enthalpy [16,58]. In Ref. [58] one also finds: 'The partial molar Gibbs free energy G is equivalent to the chemical potential μ '.

section 2.3 (see Born cycle diagram; Fig. 2.6), ΔG^{Born} (equation 4.1) needs to be evaluated for both the initial and the final state, i.e. for the neutral and the ionized liquid, respectively (see also section 4.2.5). The ion electron binding energy difference between liquid and gas phase, which equals the liquid phase shift, is obtained by $E_{aq}^{Born} - E_g = \Delta G$. Here E_g and E_{aq} denote the respective gaseous and aqueous electron binding energies, and $\Delta G =$ $\Delta G_f^{Born} - \Delta G_i^{Born}$ accounts for the ionization state of the system before (initial) and after (final) photoionization. It is noted that even though the Born model is primarily applied for solvated ions (see section 4.2.5), formally the concept may be applicable for the pure solvent as well. The main difference is the absence of an initial hydration shell for the latter case, and hence orientational contributions to the gas-liquid phase shift are of no concern. As we will see below, this also explains the considerably smaller energy shifts observed for pure water as compared to aqueous ions. Using an effective (theoretical) solute cavity radius $R_{eff} = 2.24 \text{ Å}$ of pure water [14], and an optical permittivity $\epsilon_{opt} \simeq 1.78$ [8], one obtains $-\Delta G^{Born} = 1.41 \,\mathrm{eV}$ from equation 4.1 (for removing the outermost electron). The good agreement with the experimental shift is attributed to the small size of the water molecule as this allows for the assignment of a well-defined cavity radius [25]. On the other hand, as no structural details are taken into account in this continuum model, this value only constitutes a rough estimate. The limits of the model will be discussed in further detail in section 4.2.5.

As mentioned above, polarization screening is not the only possible contribution to the measured shifts. The surface potential of water, due to oriented surface dipoles, would also cause a spectral shift in photoemission. The magnitude of this potential is not well known, but it is likely to be some ten mV. With a voltaic cell the surface potential of pure water was determined to be about 25 mV [59]. Depending on the detailed structure of the water-vacuum interface, especially the density and the orientation of the intrinsic water dipole moments at the surface, the electrostatic contributions to the surface work function could range from a few meV³ (moments parallel to the surface) up to approximately 1 eV (assuming the O-H bond being perpendicular to the surface, which, however, seems unlikely).

³It is interesting to compare this number with surface structural data obtained by vibrational spectroscopy of water at the vapor/water interface [60]. With the free OH pointing out of the liquid, the bonded OH must point into the liquid (H-bonded). In fact the permanent dipoles of water are suggested to lie close to the surface plane [60]. The result indicated that the surface density of this species is more than 20% of a full monolayer, i.e. $n > 2.7 \times 10^{14} \,\mathrm{cm}^{-2}$. Based on these data, assuming the OH bond being *perpendicular* to the water surface, one obtains $m_{\perp} = 1.13 \,\mathrm{D}$ for the normal component of the surface dipole per water

51

Understanding differential binding energy shifts requires some theoretical treatment of the electronic structure of bulk liquid water which, however, generally suffers from an inadequate description of the H-bonding and the relevant interaction potentials [3]. Most of present electronic (band) structure theories of liquid water are crude, besides, only a few reports are available [62,63,64]. In fact, band energy positions of liquid water are still subject of continuing debate [65] with the only consensus being the assignment of 10.06 eV below the vacuum level for the top of the valence band [65,66]. This value has been known from rather early threshold photoemission experiments using photon energies near 10 eV [22]. A value of about 9.9 eV is obtained for the onset of the $1b_1$ photoemission feature as shown in the inset of Fig. 4.4. The water ionization threshold energy, including the possibility of autoionization contributions in the context of the generation of solvated electrons, is discussed in Refs. [22, 67].

Very recently, evidence for water molecular orbital structural changes, if the water molecule is brought into the liquid environment, was reported both by experiment [2, 9] and theory [3]. In the latter study it was found that, with respect to the case of the isolated molecule, in bulk water the lone pair orbitals are pulled out due to the formation of H-bonds, while the covalent bond orbitals are pulled in. These changes correlate with the existence of distinct molecular species, characterized by varying H-bonding, and also with an increase of the average O-H bond length. This increase can be viewed as a charge-transfer process in which the hydrogen atoms lose electrons in favor of the oxygen atoms [3]. As a consequence, in the liquid the electronic charge is more spherically distributed around the oxygen atoms [3]. Regarding the orbital *energies*, no obvious correlation between measured binding energy shifts and theoretically expected trends [3] could be found. Presumably, this reflects the multiple contributions to the experimental gas-liquid binding energy shift. To make this point more clear, photoemission from liquid water is a much more complex task than for typical gaseous or solid samples. This is partly due to the nature of volatile liquids; it is simply impossible to separate liquid water from its vapor. Another difficulty is how to

$$\Delta \Phi = \frac{enm_{\perp}}{\epsilon_r \epsilon_0} \,, \tag{4.2}$$

molecule, which is an upper bound. Using the Helmholz equation [61]:

with $\epsilon_r = 1$ (in order to account for the liquid/vacuum interface), we obtain 1.14 eV for the work function change. This value might seem large, but one has to realize that the OH bond being fully perpendicular to the surface is a rather unrealistic assumption [60]. Clearly, for dipole moments almost in the surface plane smaller values for $\Delta\Phi$ would be obtained (some ten meV).

account for the role of the surface potential. As mentioned above, this issue still needs to be understood, and consequently, also for the present results, the mean contributions to the energy shift by surface dipoles cannot be quantified. The interesting result, at this point, is the fact that differential contributions in addition to polarization screening and surface potential were identified, which reflects the effect of H-bonding on water's electronic structure. In section 4.1.3 it will be argued that the influence of H-bonding is also responsible for the peculiar behavior of the $H_2O \ 1b_2$ orbital photoionization cross section measured here. In fact the photoionization cross section appears to be a more sensitive tool for probing differences of the electronic structure of water in its different aggregation states.

Peak broadening. Peak widths of all valence orbitals are increased as compared to the gas phase, however, not by the same relative amount as presented in Table 4.1. For comparison, the table also contains the widths of the respective gas-phase water orbitals of both the present spectra and high-resolution photoemission studies [56] (see Fig. 4.6). The latter correspond to the widths of the envelope of the vibrational structure of the bands, which is not resolved in the present experiment. The differential broadening of the liquid



Figure 4.6: High-resolution photoemission spectra of gas-phase H_2O [56] obtained for 100 eV photon energy. The photoemission spectra in the inset, covering a shorter energy range, was measured at increased resolution. Arrows indicate features the origin of which is discussed in the text.

Orbital	$E_{ice} [eV]$	$E_{aq} \; [eV]$	FWHM [eV]	FWHM [eV]
MO_i	Ice	Liquid	Ice	Liquid
		(this work)		(this work)
$1b_1$	$12.3^{\rm c,d}$	11.16(4)	1.3 ^g	1.45(5)
	$11.8^{\text{ e}}$		$1.28^{\rm h}$	
$3a_1$	14.2 ^{c,d}	13.50(10)	2.5 - $3.0^{\mathrm{g,h}}$	2.52(10)
$1b_2$	17.6 ^{c,d}	17.34(4)	$2.0^{ m g}$	2.28(8)
	18.0 ^e		$1.82^{\rm h}$	
$2a_1$	$31.0^{\rm f}$	30.90(6)	$3.3^{ m f}$	3.30(6)

Table 4.2: Experimental electron binding energies (E_{aq}) and peak widths (FWHM) of the four H_2O valence orbitals obtained from liquid water photoemission spectra. For comparison respective data for ice $(E_{ice}, FWHM)$ are shown: ^c [69], ^d [7], ^e [70], ^f [71], ^g [72], ^h [73]

with respect to the gas phase peaks is by a factor of about 1.17, 1.31, 2.14 and 4.03 for the $2a_1$, $1b_2$, $3a_1$, and $1b_1$ orbital, respectively. Hence, also the widths of individual orbitals are differently affected as the water molecule is brought into the liquid environment. Most likely, the main broadening effect can be associated with the presence of a distribution of different local environments (and hence slightly different energies) of a given water molecule within the H-bonding network [9]. Particularly, structural network differences of surface vs. near-surface water, located within the first few layers, may be important in our experiment. Also lifetimes of electronic states are likely to differ for surface water, which could be another source of peak broadening. Finally, it is pointed out that the measured $1b_1$ (liquid) peak width well agrees with the conduction bandwidth of water, $1.45 \pm 0.25 \text{ eV}$ [68], which would suggest that the measured value is close to the true intrinsic bandwidth.

The narrowest peak width is observed for the $1b_1$ orbital of the liquid-water molecule, which is also true for gas-phase water. In the latter case the small width results from the non-bonding character of this orbital. Similarly, in liquid water the $1b_1$ contribution to Hbonding would seem the smallest among the valence orbitals. In the next section it will be shown that the broadening of the $3a_1$ feature correlates with an apparent signal loss as compared to the gas phase. In fact, this feature needs special consideration as it seems to be split in two components, which points to the importance of this orbital in H-bonding. Notice that the $3a_1$ orbital was predicted to lose its original character [1] as mentioned above.

Liquid water versus ice. As both the liquid and the solid H_2O phase structures are

governed by hydrogen bonding, the question to be asked is how similar the water and the ice surfaces actually are. The differences appear to be small as the overall spectral features of liquid and ice photoemission are very similar as shown in Fig. 4.10 (see next paragraph). Hence, no clear answer to this question can be given. Yet, electron binding energies tend to be slightly *larger* in ice, by about 0.1 - 1.0 eV. The corresponding values, obtained for adsorbed H₂O multilayers on single-crystal surfaces [69, 72, 73, 74, 75] or for crystalline ice [70, 71], are presented in Table 4.2. Regarding the $3a_1$ and $1b_2$ orbitals, the observed energy shifts would be qualitatively consistent with the expected larger O-O and O-H distances in liquid water [71]. Notice that the $3a_1$ orbital also plays a central role in bonding water to single-crystal surfaces (as it does in H-bonding mentioned above), specifically in binding water to cation sites on oxides [7]. Moreover, the relative orbital binding energy shifts for adsorbed water correlate with the strength of the adsorption bond to the cation site on the oxide; consequently the effect decreases for subsequent water layers. The dependence of the differential binding energy shifts on the nature of the substrate has been evaluated in detail in Ref. [7].

Linewidth differences for liquid water and ice cannot be discerned. Quantifying this effect is difficult since experimental widths for ice have generally not been explicitly reported. Hence, widths for ice, as shown in Table 4.2, are based on a rather crude analysis of published spectra (see caption in Table 4.2 for references). Notice also that the assignment of precise values to the widths is complicated due to substantial band overlap, which particularly applies to the $3a_1$ feature. In addition, the latter feature seems to even split in two components in solid ice. Splitting of this feature in solid ice has in fact been considered earlier, even though the data were not conclusive [57, 72, 75]. In Ref. [57] it was argued that for H_2O multilayers the broadening, attenuation, and splitting of this peak arise from H-bonding. For the present case it is also not possible to resolve if this feature is split in two components for liquid water. Even though it is unclear how to accurately account for both peak energy and width of this feature, for the analysis of the present photoemission spectra a two-component feature (of identical peak height and width) consistent with Davydov split $ting^4$ was assumed. This is demonstrated in Fig. 4.5, which represents a typical fit to our data, and from which the values presented here are inferred. Similarly, in a theoretical study of the electronic band structure of cubic ice, the splitting of the $3a_1$ orbital was interpreted

⁴A given molecular energy level may split into as many components as there are translationally inequivalent molecules per unit cell [76]. This splitting is in addition to the level splitting produced by the interaction energy between two adjacent identical molecules.



Figure 4.7: Comparison of electron binding energies of water orbitals in liquid, gas-phase, and ice. Binding energies for liquid and gas-phase were determined in the present work (see Table 4.1). Ice values were obtained from the literature (see Table 4.2).

to also arise from the Davydov interaction between two molecules of different orientation in the unit cell [71]. Considerable energy level splitting has been also found in very recent calculations of the influence of H-bonding on the local electronic structure [1].

In conclusion, noticeable parallels are found between the bonding of water in bulk water (H-bonding) as compared to water binding to single crystals. This particularly refers to the behavior of the water $3a_1$ orbital. Yet, there might be small binding energy differences, reflecting electronic structural differences for H-bonded water and ice. Certainly further experiments, including photoemission from condensed water films, would be useful.

4.1.3 Relative Partial Photoionization Cross Sections of Liquid Water

In the following section the relative partial photoionization cross sections of liquid water will be discussed. The results for the measured differential relative photoionization cross sections, $d\sigma_i/d\Omega$, are displayed in Table 4.3 for the four water orbitals. Shown are the raw peak integrals (normalized to the $1b_1$ liquid feature) as obtained by fitting each (pure liquid) photoemission spectrum to Gaussians. No attempt was made to determine *absolute* partial ionization cross sections in the present work.

The indicated scatter of the values was inferred by comparing different fitting procedures, i.e. with constant vs. variable peak width at fixed (averaged) orbital binding energy. The errors obtained for the same method, but evaluating different spectra, are smaller than the ones given in Table 4.3. Rather large deviations for the $3a_1$ orbital, in the case of liquid water, arise from the strong spectral overlap with the $1b_1$ orbital. The relatively large uncertainty in determining the $2a_1$ integral arises from the difficulty to properly account for the low and high-energy *wings* of this feature (see sections 4.1.1 and 4.1.4). For reference, the corresponding gas-phase integrals are displayed in the table as well. These latter values can be determined more accurately due to both the strongly reduced background and the fact that the peaks do not overlap.

Orbital	Intensity liquid			Intensity gas phase		
MO_i	$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$	$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$
$1b_1$	1.00	1.00	1.00	1.00	1.00	1.00
$3a_1$	0.96(6)	0.99(6)	1.06(6)	1.16(3)	1.23(3)	1.12(3)
$1b_2$	0.83(3)	0.76(3)	0.80(3)	1.68(4)	1.67(4)	1.50(4)
$2a_1$	0.43(8)	0.38(8)	0.36(8)	0.41(10)	0.40(10)	0.36(10)

Table 4.3: Experimental liquid and gas-phase relative photoemission intensities (as measured) of the four H_2O valence orbitals for three photon energies 60, 80, 100 eV, obtained in the present study.

From Table 4.3 significant differences with respect to the relative intensities for liquid and gas-phase water can be observed (see Fig. 4.8a). Relative intensity changes are particularly noticeable for the $1b_2$ orbital, which is about 50% smaller than in the gas phase. For $3a_1$ the effect is smaller, but difficult to be quantified due to the peak splitting (see above); the relative decrease is no more than 10%. This behavior seems to be one of the keys to the



Figure 4.8: Measured differential partial photoionization cross sections, $d\sigma_i/d\Omega$, of water orbitals for liquid H₂O and D₂O, obtained for 60, 80, 100 eV photon energies. Data are normalized to the 1b₁ value. The H₂O data were taken from Table 4.3, and the data for D₂O from Table 4.6. Photoelectron detection is perpendicular to the light polarization vector $(\Theta = 90^{\circ})$.

Orbital		σ_i liqui	d	σ_i gas phase		
MO_i	$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$	$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$
$1b_1$	1.00	1.00	1.00	1.00	1.00	1.00
$3a_1$	0.69	0.84	0.96	0.84	1.03	1.02
$1b_2$	0.39	0.36	0.41	0.79	0.80	0.78
$2a_1$	0.46	0.47	0.51	0.44	0.50	0.51

Table 4.4: Relative partial photoionization cross sections σ_i of H₂O calculated using data from Table 4.3 and 4.5 (gas-phase β_i) in equation 4.4.

variation of the water molecular orbital structure due to H-bonding. On the other hand, oriented species at the water surface might contribute to cross section changes as well. Both aspects will be discussed in the following.

Photoionization cross section measurements in the gas phase (statistically oriented molecules) are usually performed at the magic angle [43] (see section 3.1.3) as this allows for determining cross sections independent of the experimental geometry. However, from the measured quantity $d\sigma_i/d\Omega$, obtained for a given geometry, the integrated cross sections (relative partial photoionization cross sections) σ_i may be calculated using [41,51] (for linear polarization):

$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} \left[1 + \frac{\beta_i}{4} (1 + 3P_1 \cos 2\Theta)\right]. \tag{4.3}$$

It will be shown below that this presentation, in fact, better suits the interpretation of the origin of the different cross sections between liquid and gas-phase water. In equation 4.3, β_i denotes the energy-dependent asymmetry (anisotropy) parameter ($2 \ge \beta \ge -1$), P_1 is the Stokes parameter (degree of linear polarization), and Θ measures the angle between the direction of the ejected electron and the polarization of the incident light. For this experiment $P_1 = 1$ (synchrotron light is 100% horizontally polarized), $\Theta = 90^{\circ}$ (detection normal to the polarization) and thus from the equation 4.3 one obtains:

$$\sigma_i = \frac{4\pi}{(1 - \frac{\beta_i}{2})} \left(\frac{d\sigma_i}{d\Omega}\right). \tag{4.4}$$

For liquid water one then has two unknown parameters for each orbital; notice that the β_i are known for gas-phase water only. As the present experimental setup did not allow for measuring photoemission spectra from the liquid jet either at the magic angle or for another geometry different than depicted in Figs. 3.7 and 3.10, the corresponding β_i for liquid water

Orbital	β_i liquid	β_i gas phase			
MO_i		$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$	
$1b_1$		1.53	1.58	1.59	
$3a_1$		1.35	1.50	1.55	
$1b_2$		1.00	1.12	1.21	
$2a_1$		1.56	1.66	1.71	

Table 4.5: Anisotropy parameters β_i of gas-phase H_2O [51] used in equation 4.4. Data for liquid water are not available.

could not be determined here. Consequently, σ_i can be calculated for the gas-phase spectra only; gas-phase β_i were taken from Ref. [51] (see Table 4.5). The corresponding plot of σ_i for gas-phase water, for the four valence orbitals, is presented as an inset in Fig. 4.9 for three different photon energies. Values are normalized to σ_{1b_1} ; both sets of gas-phase data agree well. The main figure (Fig. 4.9) displays calculated σ_i for liquid water, where the corresponding $d\sigma_i/d\Omega$ values together with gas-phase β_i have been used in equation 4.4. As noticed above the relative cross sections σ_{1b_2} (and σ_{3a_1}) are found to be smaller. The decrease is by about 50% (and 10%, respectively), for liquid water. However, with β_i for the liquid being only approximate, the observed changes might principally result from the variation of σ_i as well. On the other hand the effect of β_i would seem more important, because β_i not only depends on the amplitude but also on the phase shift of the outgoing partial electron waves. Then, within our simple model, according to equation 4.4, the σ_{1b_2} decrease in Fig. 4.9 can be attributed to a smaller β_{1b_2} for the liquid than for gas-phase water. Apparently the difference of β_{1b_2} as compared to the other β_i , in the gas-phase case⁵, is even enhanced in

⁵Notice that here the change of the β_{1b_2} value was interpreted in terms of a decrease for liquid water. It is not clear, however, if rather β for the other orbitals decreases or possibly all values change. The answer to that is difficult as no photoemission investigations of the angular distribution from liquids exist. It is important to realize that for photoionization of liquids (or solids) photoelectrons experience considerable inelastic scattering, which reduces the anisotropy of the angular distribution. This may be associated with a decrease of β . The effect would depend on the probing depth and thus on the photon energy and on the experimental geometry. In section 4.2.1 it will be shown that considerably intense *s* photoemission lines can be observed in the present experiment. This contradicts the expectations for pure atomic *s* photoionization, i.e. $\beta = 2$, in which case no emission intensity would be detected in the direction perpendicular to the polarization vector of the synchrotron light (see Fig. 3.5). This shows the importance of determining β values for liquids using a suitable experimental setup.

the presence of H-bonding. In fact this quantity will change if the orbital structure changes. The reason for the small β_{1b_2} in the gas phase is related to the strong bonding character of this orbital [51]. As mentioned above, H-bonding affects the covalent bond orbitals causing a more spherical distribution of electron charge around the oxygen atom [3]. Perhaps this decreases β_{1b_2} even more for liquid water.

These results show that apparently the relative photoionization cross section is a sensitive probe of water's molecular changes in the liquid environment which otherwise are very difficult to be accessed experimentally. Notice that the geometry being used in the present photoemission experiments (Fig. 3.10) enables the detection of β changes. Specifically, at Θ = 90 ° the electron emission probability is about 50 % smaller for $\beta = 1.5$ than for 1.0.

Possible surface-specific contributions to the cross-sectional behavior will be considered in the following. This aspect relates to the very surface sensitivity of photoemission for photoelectron kinetic energies on the order of 20-120 eV, which is about the range of the present experiment. Since the electron mean free path, λ_e , should be similar for the solid and the liquid phase, the information depth accessed for pure liquid water is about 2-4 layers (see Fig. 3.4), which corresponds to about $\lambda_e = 1$ nm assuming the size of a water molecule being ca. 0.3 nm (see section 4.1.2). Experimental mean free paths for liquid water have been reported for considerably lower kinetic energies only. The value obtained for 0.1-2.0 eV electrons, injected in water, is $\lambda_e = 3-4$ nm (or 10-15 monolayers of water), which seems somewhat small according to Fig. 3.4. For low-density amorphous ice theory predicts values of about 3-5 nm for 1-20 eV electrons [77], which better agrees with the present assumption.

The liquid-water surface is assumed to be hydrogen terminated with one free OH projecting into the vapor [60]. Also for adsorbed water, for instance on metal surfaces, the first two layers of water molecules are arranged similarly to the molecules in the most dense layer of ice [78]. In this structure the higher-lying H₂O molecules have one OH bond oriented along the surface normal and contribute *one* H atom to the hydrogen bonding network (compare above discussion on oriented H₂O on the liquid water). Notice that for liquid water the OH axis pointing into the vacuum is likely to be sufficiently inclined towards the surface in order to stabilize the dipoles within the water surface plane (see discussion footnote, page 50). For adsorbed water the OH bond may be oriented more upright with respect to the surface. It then appears feasible that the relative photoemission intensity of a given orbital may vary based on symmetry arguments and orientational effects. Relative photoemission intensity differences of the outer valence band orbitals, $1b_2$, $3a_1$ and $1b_1$, have indeed been observed



Figure 4.9: Relative partial photoionization cross section σ_i of the four water valence orbitals for three photon energies, 60, 80, 100 eV (from Table 4.4). Data are presented for liquid and gas-phase water (using gas-phase β_i), with the intensities being normalized to the 1b₁ value. Also shown are reported gas-phase σ_i [51] (inset) for comparison.

for monolayer versus multilayer water [72, 73, 74, 75]. This implies that the overall orientation of water molecules in the monolayer is different from those in the multilayer, consistent with the influence of surfaces in orienting water monolayers. A quantitative explanation of the intensity variations has not yet been reported. A striking common feature to all multilayer studies, but also to results reported for bulk ice, is the relative intensity decrease of the $3a_1$ orbital [72, 73, 74, 75]. Generally, the multilayer spectra are almost identical irrespective of the surface used [7, 75], and moreover, the multilayer spectra turn out to exhibit similar relative intensities as found for liquid water in the present study. This is best confirmed by comparison with Ref. [73] (see Fig. 4.10), which reports photoemission spectra from 10 bilayers hexagonal ice grown on Pt(111), and using a similar excitation photon energy, 75 eV. In



Figure 4.10: Photoemission spectra from 10 bilayers hexagonal ice grown on Pt(111) [73] and liquid water obtained for 75 eV and 80 eV, respectively.

Fig. 4.10 the spectra are normalized to the $1b_1$ (liquid) peak height, and the binding energy axis is fixed with respect to the $1b_1$ (liquid) binding energy.

The present results, in fact agree well with very recent results from a X-ray emission study of liquid water, in which the character of the $3a_1$ state was also found to be changed entirely upon H-bonding [1]. The authors interpret their result in terms of electron density transfer from the hydrogen site to the oxygen site leading to polarization increase and hybridization of the $3a_1$ orbital. The following comment would seem useful in order to not confuse several aspects of our interpretation. As mentioned above one has to distinguish between relative intensity changes which correlate with a change of σ , and apparent signal changes associated with peak splitting, which are not associated with σ changes. To summarize this, the present data indicate a change of β for the $1b_2$ orbital.

With respect to the observed cross section variation, the particular geometry of the present experiment would, however, seem rather unfavorable to detect contributions due to oriented surface species. Given the curved surface of the microjet such an effect is likely to average out. As the jet radius is much smaller than both the synchrotron radiation focal size and the detector entrance of the spectrometer (compare section 3.2.1), the effective

orientation of water molecules varies by up to 90° with respect to both the polarization axis of the light and the detection angle. In conclusion, in spite of the inherent surface sensitivity of photoelectron spectroscopy, the present results suggest that the prevailing effect responsible for the cross sectional behavior of liquid water is due to the random Hbonding network. The observed change of σ_{1b_2} for liquid water is proposed to arise from the decrease of β_{1b_2} relative to the gas-phase values.

 H_2O versus D_2O . The measured relative photoionization cross sections, $d\sigma_i/d\Omega$, for liquid H_2O and D_2O show no significant differences as can be inferred from Fig. 4.8b. The figure is a plot of measured $d\sigma_i/d\Omega$, normalized to the $1b_1$ value, for three photon energies (60, 80, 100 eV). The corresponding data for D_2O are shown in Table 4.6. Notice that also the photoemission spectra are identical for the two isotopes, as shown in the Fig. 4.11.

Orbital	Intensity liquid			Intensity gas phase		
MO _i	$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$	$60\mathrm{eV}$	$80\mathrm{eV}$	$100\mathrm{eV}$
$1b_1$	1.00	1.00	1.00	1.00	1.00	1.00
$3a_1$	0.90(6)	0.93(6)	0.98(6)	1.15(3)	1.14(3)	1.01(3)
$1b_2$	0.80(3)	0.77(3)	0.83(3)	1.66(4)	1.50(4)	1.38(4)
$2a_1$	0.34(8)	0.35(8)	0.41(8)	0.28(10)	0.41(10)	0.33(10)

Table 4.6: Experimental liquid and gas-phase relative photoemission intensities (as measured) of the four D_2O valence orbitals for three photon energies 60, 80, 100 eV, obtained in the present study.

Thus, within the limits of the present experiment, the electronic structure of liquid H_2O and D_2O is indistinguishable.



Figure 4.11: Photoemission spectra of liquid H_2O and D_2O , respectively, obtained for 100 eV photon energy. Spectra are as measured.

4.1.4 Electron Energy Losses in Liquid Water

The electronic configuration of the ground state of the H_2O molecule is (see section 2.2):

$$(1a_1)^2 (2a_1)^2 (1b_2)^2 (3a_1)^2 (1b_1)^2$$

Since the $1b_1$ and $3a_1$ orbitals have the lowest and second lowest ionization potentials, the low-lying excited states are expected to arise from these orbitals [79]. As initially suggested by Mulliken [80] and confirmed by recent calculations [79], the simplest view of the excited orbitals is to consider them arising from an $n \ge 3$ Rydberg atomic orbital modified by the molecular field. Thus, the sequence of states obtained by exciting from either the $1b_1$ or $3a_1$ is 3s, 3p, 4s, 3d, 4p, 5s, ... with splitting of each degenerate atomic orbital in the molecular field.

The VUV absorption spectrum of H₂O vapor [81,82] shows a first absorption maximum at around 7.45 eV and an absorption threshold near 6.6 eV. After an absorption minimum around 8.6 eV, maxima at 9.75, 9.81, 10.0 and 10.17 eV follow. The first band is attributed to a transition into the 3s Rydberg state $1b_1 \rightarrow 3sa_1$, while the transition bands near 10 eV terminate in the 3p Rydberg states $(1b_1 \rightarrow 3pb_2, 1b_1 \rightarrow 3pb_1, 1b_1 \rightarrow 3pa_1)$ or in states arising from excitation of an electron from the lower $3a_1$ orbital $(3a_1 \rightarrow 3sa_1, 3a_1 \rightarrow 3pb_2)$. At higher energies 3d, 4p Rydberg states are also attainable [67]. The first band leading to a 3s Rydberg state is structure-less, while the transitions leading to the p-type states exhibit vibrational and rotational structure [79, 81, 82].



Figure 4.12: Absorption cross section of liquid water as a function of the incident photon energy [53]. The inset shows the exponential tail of the lowest transition maximum, which extends down to about $5.9 \, \text{eV}$ [63].

In the case of *liquid* water the absorption bands are considerably broadened and blueshifted [66] with respect to the gas-phase spectra. The VUV absorption spectra of liquid water, as reproduced from Refs. [53, 63], is presented in Fig. 4.12.

The lowest transition maximum appears at 8.2 eV. This is a rather narrow feature having, however, an exponential tail, which extends down to 5.9 eV [63] (see inset in Fig. 4.12). Bands at higher energy overlap, but the shoulder at 10 eV indicates that the energies of the 3p Rydberg states are not changed by much. Another band is found at about 14 eV [53], and largest absorption occurs at 18.5 eV.

The pronounced background in the liquid water photoelectron spectra, which has no counterpart in the gas phase, immediately points to photoelectron interaction processes intrinsic to liquid water. High-energy (photo)electrons passing through the liquid medium appear to excite the molecules through processes similar to photoexcitation [83]; the selection rules, as far as one is concerned about long-range dipole scattering, have been suggested to be the same as for optical excitation [67], and the excitation probability is likely to be the



Figure 4.13: Photoemission spectra of liquid water (as measured) obtained for 80, 100, 120 eV photon energy. Electron energy losses, assigned to features 1, 1', and 2 are characterized by their constant electron binding energies as a function of the photon energy.

highest in the region of the optical absorption band. Hence, strong *optical* absorption bands of liquid water (in the region of 14 eV and above) may be expected to provide efficient energy-loss channels also for fast electrons [67].

This would be in agreement with the present experimental findings, as best represented by the broad feature near 50 eV (label 2 in Fig. 4.13) constant binding energy. In the present experiment, typically using 100 eV photons, a broad distribution of photoelectron kinetic energies is generated. For instance, photoelectrons generated from $2a_1$, have about 68 eV initial kinetic energy, which would give rise to a satellite near 50 eV binding energy due to the 18 eV optical channel. In order to demonstrate that this is a constant binding energy feature Fig. 4.13 displays the respective photoemission spectra obtained for three photon energies, 80, 100, and 120 eV. As such a specific energy loss appears on a large secondary electron background from non-specific electron scattering processes (down to the zero kinetic energy cutoff) the data are once again displayed in Fig. 4.14, however for subtracted background. Similarly, one might, in part, attribute the *wings* of the original $2a_1$ peak (labels 1, 1' in Figs. 4.13 and 4.14) as well as the large width of the 50 eV feature to the respective



Figure 4.14: Photoemission spectra of liquid water (background subtracted) obtained for 80, 100, 120 eV photon energy. Electron energy losses, assigned to features 1, 1', and 2 are characterized by their constant electron binding energies as a function of the photon energy.

energy losses associated with the lower binding water orbitals. I.e., the initial $1b_2$, $3a_1$, $1b_1$ photoelectrons could contribute to the shoulders in the $2a_1$ region by the same mechanism. Likewise, are 14 eV losses from initial $2a_1$ photoelectrons assumed to contribute to the lowbinding energy side of the 50 eV feature, extending up to ca. 54 eV. The various transitions are indicated in Fig. 4.13 by arrows.

Despite much stronger electron-loss contributions to the photoemission in the case of liquid water a number of features may be of different origin, as they also exist for the gas phase. This particularly applies to the $2a_1$ wings, which have been observed for gas-phase water as well (see Fig. 4.6). Generally, their origin is not well understood [51,82,84]. The feature near 27 eV has been shown to be associated with the $2a_1$ ionization process [51,84], but its assignment is controversial. Another feature at about 22 eV binding energy has been suggested to contain contributions from one or more of the $1b_2$, $3a_1$, and $1b_1$ orbitals [84]. Hence, the lower-energy transitions (for the liquid) proposed here are difficult to be distinguished from the processes reported for the gas phase. The emission in the near 50 eV range is, however, likely to arise predominantly from the electron energy losses as discussed here. Notice that a



Figure 4.15: The loss function, $\text{Im}(-1/\epsilon(q, E))$, of liquid water for $0.19 \leq 0.69$; q denotes the momentum and E the energy (from [54]).

deeper discussion of this subject would require a detailed theoretical treatment of the energy loss function of liquid water, as this is the more relevant quantity to be considered (rather than the optical absorption). Experimentally, the loss function of liquid water, which is the imaginary part of the inverse dielectric response function $\text{Im}(-1/\epsilon(q, E))^6$, has been determined by optical reflectance measurements [53] and by inelastic X-ray scattering [54]. The latter study reports the loss function for up to 50 eV energy losses as shown in Fig. 4.15 (from Ref. [54]). The important result is the fact that $\text{Im}(-1/\epsilon)$ peaks at about 20 eV, but there is also considerable intensity for larger energies. Values for < 10 eV are much smaller, by about a factor of five and more. This behavior qualitatively agrees with the occurrence of the rather distinguished 50 eV binding energy feature in the present photoemission spectra. One may even speculate if the weak loss feature occurring near 82 eV in Fig. 4.14 correlates with the shallow hump at ca. 30 eV energy loss of $\text{Im}(-1/\epsilon)$ shown in Fig. 4.15.

⁶The imaginary part of the reciprocal dielectric constant, i.e. $-\text{Im}(1/\epsilon) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$, is called the energy loss function [85]. Here $\epsilon = \epsilon_1 - i\epsilon_2 = n^2$ is the complex dielectric function with ϵ_1 and ϵ_2 being the real and imaginary part, respectively. n is the complex index of refraction.

4.2 Aqueous Salt Solutions

It has long been established that water, both the intrinsic liquid and the solvent, is of complex nature giving rise to some unusual if not unique properties [86]. The complexity of liquid water is due to a combination of the small size and distinct polar charge distribution of the water molecules. As mentioned above (see section 2.2) the charge distribution allows water to form highly organized intermolecular networks through H-bonding and makes it sufficiently ionic to separate and insulate the cations from corresponding anions producing a solution. In the case of salt solutions, this typically leads to ions being surrounded by a cage of water molecules, the solvation (hydration) shell (see section 2.3). Even though research on hydration of ions has a long history and the field is still very active, the understanding of such systems is far from being complete [87,88,89]. One reason for the difficulties is to correctly account for the polarizability of water and aqueous systems, including the polarizability of the solvated ions, as this property is crucial for describing the respective interaction energies [89].

The present experiment is aimed to identify solvation structural changes by both spectral peak shifts or relative changes of the photoemission spectra. The results will be discussed in terms of the specific interactions (such as ion pairing) of solvation complexes, in the case of moderately low to saturation concentrations (i.e. beyond the low-concentration solutions well described by the Debye-Hückel model [90].)

For the simple solvation, the case of an alkali-halide salt dissolved in water, the situation is certainly less complex than for the biological molecules but still, it has generally not been possible to directly measure the electron binding energy of solvated ions in water (compare section 2.3). The first photoemission studies of inorganic anions and cations in aqueous solutions were performed by Delahay [91,92] using a rotating target (see section 3.1.1) and monochromatized light from a hydrogen lamp (up to 10.5 eV). Lower-vapor-pressure liquid substitutes were studied primarily by ESCA [24]. Ever since, not much progress in photoelectron spectroscopy on highly volatile targets has been made. There seem to be two main reasons for that: the experiments mentioned above are threshold measurements ($6.1 < E_t <$ 9.1 eV) in which the total yield for electron photoemission is detected by an electron collector electrode as a function of the photon energy. Such a method it actually predestinated for ionization threshold studies since no energy resolution for the electrons is required. In order to go beyond threshold detection, a method being sufficiently energy-sensitive is needed. Another major concern is surface contamination.

The only photoemission experiments from water and aqueous salt solutions reported to

date, which extend beyond the very threshold photoemission energy, were performed with focused HeI (21.2 eV) radiation using a similar microjet setup as in the present work [26]. With this source the three outer valence orbital energies of liquid water as well as binding energies of solvated ions up to ca. 8 eV were measured for the first time [4,93].

Note that many aqueous cations of interest (released in salt solutions), e.g. solvated alkali ions with their closed shell configuration, possess electron binding energies larger than 20 eV, which is on the order of the second ionization potential of their neutral counterpart. Thus suitable high-energy photon sources are required. The importance of synchrotron radiation in taking advantage of resonance phenomena has been already addressed in section 4.1.

In this chapter full-range photoemission spectra from aqueous alkali-halide solutions, aimed to better understand the electronic structure of hydrated anions and cations will be presented. Photon energies up to 130 eV were used. This energy range not only allows to determine relatively large binding energies (well beyond the first ionization potential of the solvated ion) but also to accesses characteristic Auger energies in the liquid environment. The effect of the counter ion size, charge, and complexity, but also salt concentration, on the electron binding energy is systematically evaluated. Experimental binding energies will be discussed within the continuum Born model. In addition, results for aqueous NaI solutions for near-saturation concentrations will be presented in the context of ion surface vs. bulk solution concentration, and its implication for solvation structural details at the surface. Photoexcitation near 100 eV, which corresponds to the maximum of the aqueous $I^{-}(4d)$ ionization cross section due to a shape resonance [94] (see also section 4.2.4), turns out to be valuable for investigating iodide (which is one of the central components of this work) solutions as low as 0.1 molal. The remainder of the section is dedicated to hydrophobic (surface-active) organic salts. The results will be discussed in terms of surface structural information, including the built-up of an electric double layer at the surface, and ion exchange phenomena.

4.2.1 Solvent and Solute Features

Photoelectron spectra of pure liquid water (bottom) and of 1 molal^{7,8} aqueous NaI solution (top), are displayed in Fig. 4.16. The spectra were obtained for 100 eV excitation photon energy. Typical acquisition time per spectrum is about 30 minutes. For clarity the two spectra are vertically displaced relative to each other, with the intensities being normalized to the $1b_1$ (liquid) peak height. The abscissa in the figure is the electron binding energy relative to vacuum. For solutions one may observe an *apparent* energy shift of the liquid features as will be discussed in section 4.3.1. Therefore the solution spectra will be given with respect to the liquid water $1b_1$ orbital binding energy, which is 11.16 eV (see section 4.1.2).

Comparing the photoemission spectra obtained for 1 m salt solution with the one for pure water, one can recognize the underlying water features along with the new peaks arising from the respective alkali-metal and iodide ions. Iodide photoemission gives rise to the weak low-energy doublet feature at $7.7 \pm 0.2 / 8.8 \pm 0.2 \text{ eV}$, the strong doublet at $53.8 \pm 0.03 / 55.5 \pm 0.03 \text{ eV}$, and in part, to the broad feature near 68 eV. These peaks can be assigned to I⁻(5p), I⁻(4d_{5/2, 3/2}) direct emission, and Auger electrons (for details see next section), respectively. The large I⁻(4d) photoemission signal is due to a shape resonance with maximum near 100 eV, similar to the gas-phase iodide anion [94,95] (to be discussed in section 4.2.4). The features at $35.4 \pm 0.04 \text{ eV}$ and at about $68.0 \pm 0.15 \text{ eV}$ originate from Na⁺(2p) and Na⁺(2s) emission, respectively.

Indicated by dotted vertical lines are the corresponding gas-phase binding energies of the ions as found in the literature [96, 97, 98]. Notice that the measured values in the liquid are shifted, the effect of the solvation being an increase in the anions' binding energies and a decrease in the cations' binding energies. The experimental binding energies are fairly well reproduced within a simple continuum model (Born continuum model) which accounts for the difference in total energies of the respective species (neutral, cation, anion) in the liquid vs. gas phase. Details will be discussed below.

⁷Molality: the number of moles of a solute dissolved in one kilogram of solvent. For example: preparation of 1 molal aqueous (water) solution of sodium iodide (NaI) corresponds to adding 1 mole of the solute to 1 kilogram of water. The molar weight for NaI is 149.89 and therefore 149.89 grams of NaI dissolved in 1 kilogram water would result in a 1 molal solution of NaCl. For 2 molal concentration, the amount of solute will be doubled, and the number of solute molecule respectively, while the number of water molecules stays the same. Thus, the relative photoemission signal directly scales with the molal concentration.

 $^{^{8}\}mathrm{hereafter}\;1\,\mathrm{molal}$ will be denoted $1\,\mathrm{m}.$



Figure 4.16: Photoemission spectra of pure liquid water (bottom) and of 1 m NaI aqueous solution (top), obtained for 100 eV photon energy. The vertical dotted lines indicate the binding energy of the respective gas-phase ion and the arrows indicate the direction of the energy shift. The emission from ions is labeled. The inset shows a zoom into the $I^{-}(5p)$ region.

The observed larger peak width for solvated ions as compared to gas-phase species (see Tables 4.8 and 4.9) is thought to arise from the distribution of different environments of the ions within the complex H-bonding network. No change of the peak width was observed as a function of excitation photon energy in these experiments.

4.2.2 Electron Binding Energy Dependence on Counter Ion

Alkali-metal halide salts dissociate in water by forming a solvation shell surrounding the ions. The energetics, i.e. the balance between salt crystal energy and solvation energy, was briefly addressed in the introduction (see section 2.3). For sufficiently low salt concentrations (very dilute solutions), the simple ions are in fact known to be completely solvated (hydrated) by non-shared water molecules, in accord with the Debye-Hückel theory [90]. Yet, as simple as this may sound, many of the details governing solvation on the microscopic level, particular for high concentrations, are not well understood. Some of the difficulties are related to properly accounting for the polarizability of both ions and water in order to describe the complex interactions eventually stabilizing a specific hydration shell structure. The latter

itself is the result of a number of competitive interactions including water-ion interaction, water-water repulsion within the first solvation shell and others [10]. Part of the interest to this aspect, within the present work, is to investigate whether a change of the solvation shell structure, for instance induced by a different counter-ion size/charge or by changing the salt concentration, may be detectable by photoemission (particularly by electron binding energy shifts). It is anticipated, however, that the counter-ion effect, for a sufficiently dilute system, would be expected to be small as the interaction of the solvation complexes (for ions of opposite charge) is small. For very high salt concentrations additional interactions may occur as a consequence of decreasing distances between solvate complexes (of opposite charge). One aspect of particular interest concerns the ion concentration profile at the surface as compared to bulk solution, and related to that the possible consequences for the solvation shell structure. This will lead to a brief discussion on the possibility of ion pairing for simple salts, and to the question of how large solvation shells (for simple ions) are.

With that in mind systematic measurements of alkali-halide salt solutions, while keeping either the cation or the anion constant (XCl, XBr, XI, NaX), were performed. In the same context photoemission spectra of CaI₂, MgCl₂, MgBr₂, Na₂CO₃ aqueous solutions were measured as well. As an example of complex ions in solution, sodium hexacyanoferrate (II) Na₄[Fe(CN₆)], potassium hexacyanoferrate (II) K₄[Fe(CN₆)], and potassium hexacyanoferrate (III) K₃[Fe(CN₆)] were chosen.

Aqueous XCl solutions, X = Li, Na, K, Cs. Photoemission spectra of aqueous solutions of 3 m LiCl, 3 m NaCl, 3 m KCl, and 3 m CsCl, respectively, obtained using 100 eV photons, are displayed in Fig. 4.17. Spectra are vertically displaced relative to each other, and the intensities are normalized to the $1b_1$ liquid peak height. In each spectrum shown in the Fig. 4.17 one clearly recognizes the underlying water features (indicated by dotted lines) along with the extra peaks arising from the solvated ions. Chloride photoemission gives rise to a weak feature at about $9.6 \pm 0.07 \,\text{eV}$, originating from the 3p level. The peak position could not be precisely determined due to the strong overlap with the $1b_1$ liquid water orbital.

The features originating from the alkali-metal cations are found at following values: Li⁺(1s) emission at 60.4 \pm 0.07 eV binding energy, and the two features corresponding to Na⁺(2p), Na⁺(2s) appear at 35.4 \pm 0.04 eV and at 68.0 \pm 0.15 eV. In the case of aqueous KCl solution the peak at 22.2 \pm 0.06 eV arises from K⁺(3p). For aqueous CsCl solution the doublet at 80.6 \pm 0.03 /82.9 \pm 0.04 eV is assigned to Cs⁺(4d) emission. The extra features near 58 eV are attributed to a Cs 4d - 5p5p Auger emission process. Here a Cs⁺(5p) electron fills the initial Cs⁺(4d) hole and the simultaneous emission of a 5p electron leads to a two-



Figure 4.17: Photoemission spectra of aqueous alkali-chloride solutions XCl (X = Li, Na, K, Cs) obtained for 100 eV. The concentrations are indicated and characteristic ion emission is labeled. The inset shows a zoom into $Cl^{-}(3p)$ region.

hole final state. The Auger character is evidenced by varying the excitation energy, 90 eV vs. 100 eV, as shown in the Fig. 4.18. Note that the Auger signal obtained for 90 eV photons is lower as compared to the signal obtained for 100 eV photons. This is consistent with the



Figure 4.18: Photoemission spectra of aqueous CsCl solutions (concentration as indicated) for 90 and 100 eV photon energies as labeled. Electron energies are displayed on the kinetic energy scale. Cesium 4d - 5p5p Auger features, at constant kinetic energy (near 40 eV), are marked by the dashed vertical lines. The inset schematically shows the transitions involved in the Auger process.

lower $Cs^+(4d)$ photoionization cross section in the former case.

It is noted that the relative photoemission intensities for a given solvated ion in Fig. 4.17 directly correlate with the corresponding salt concentration (see footnote on page 71). This is also true for most of the solutions studied here; exceptions will be discussed.

Aqueous XBr solutions, $\mathbf{X} = \mathbf{Na}$, \mathbf{K} , \mathbf{Cs} . Fig. 4.19 shows photoemission spectra of solutions of 1 m NaBr, 1 m KBr and 1 m CsBr, respectively, obtained for 100 eV photons, i.e. similarly to the compounds presented in the previous paragraph, except that the Cl is replaced by Br. Spectra are vertically displaced relative to each other, and the intensities are normalized to the $1b_1$ liquid peak height, as described before. The emission from water valence orbitals is indicated by dotted lines. The extra peaks at $73.2 \pm 0.07 / 74.3 \pm 0.09 \text{ eV}$ and $8.8 \pm 0.06 \text{ eV}$ binding energy arise form the Br⁻(3d) and Br⁻(4p), respectively. The features originating from the Na⁺, K⁺ and Cs⁺ cations are found at the same binding energy as for XCl aqueous solution series.



Figure 4.19: Photoemission spectra of aqueous alkali-bromide solutions XBr (X = Na, K, Cs) obtained for 100 eV. The concentrations are indicated and ion emission is labeled. The lower $Br^{-}(3d)$ signal in the center spectrum indicates that the actual concentration was smaller than labeled. The inset shows a zoom into $Br^{-}(4d)$ region.

Aqueous XI solutions, $\mathbf{X} = \mathbf{Li}$, Na, K, Cs. Photoemission spectra of aqueous solutions of 3 m LiI, 3 m NaI, 3 m KI, and 2 m CsI, respectively, obtained for 100 eV photons, are displayed in Fig. 4.20. Spectra are vertically displaced relative to each other, and the intensities are normalized to the $1b_1$ liquid peak height. As specified in the previous section, iodide photoemission gives rise to the weak low-energy doublet feature at 7.7 ± 0.20 / 8.8 $\pm 0.20 \text{ eV}$, the strong doublet at 53.8 ± 0.03 / $55.5 \pm 0.03 \text{ eV}$, and in part, to the broad feature near 68 eV. These peaks are assigned to $I^-(5p)$, $I^-(4d_{5/2,3/2})$ direct emission, and Auger electrons (AE), respectively. The partial Auger character of the feature near 68 eV is confirmed by constant kinetic energy contributions as inferred from excitation-energy variation (100 and 110 eV), see Fig. 4.21.



Figure 4.20: Photoemission spectra of aqueous alkali-iodide solutions XI (X = Li, Na, K, Cs) obtained for 100 eV. The concentrations are indicated and ion emission is labeled.



Figure 4.21: Photoemission spectra of aqueous NaI solutions (concentrations as shown) for 100 and 110 eV photon energies as labeled. Electron energies are displayed on the kinetic energy scale. iodide 4d - 5p5p Auger features (AE), at constant kinetic energy (near 32 eV), are marked by the dashed vertical line. The inset schematically shows the transitions involved in the Auger process.


Figure 4.22: Photoemission spectra of aqueous-sodium halides solutions NaX (X = Cl, I, Br) obtained for 100 eV. The concentrations are indicated and ion emission is labeled.

The Auger process is assigned to the filling of the $I^-(4d)$ hole by a $I^-(5p)$ electron, and simultaneous emission of a 5p electron leading to a two-hole final state (4d - 5p5p), see sketch in the inset Fig. 4.21). The constant binding energy contribution was attributed to Na⁺(2s) emission. The alkali-metal ion derived features (see Fig. 4.20) are found at the same binding energies as for the XCl and XBr aqueous solution series as summarized in Table 4.8. The additional weak features in the CsI spectrum near 58 eV binding energy is attributed to an Cs 4d - 5p5p Auger emission process, being described above; see Fig. 4.18.

Aqueous NaX solutions, X = Cl, Br, I. Fig. 4.22 displays photoemission spectra of 3 m NaCl, 2 m NaBr and 2 m NaI salt solutions obtained for 100 eV photon energy. As opposed to the preceding aqueous-solution spectra, this time the anions are exchanged, while the cation is the same. The figure is thus a different presentation of the respective NaX spectra from Figs. 4.17, 4.19, 4.20 in order to emphasize that there is also no shift of the alkali cation binding energy as a function of the counter anion. Photoemission threshold energies for aqueous halide anions. Threshold ionization energies, E_t , for halide ions solvated in water have been known for a long time [91,92]. Note that E_t corresponds to the low-binding-energy onset of the photoemission feature. To compare the measured values with the respective literature ones, a blow-up of the low binding energy region of Fig. 4.22 is displayed in the Fig. 4.23. The threshold energies are inferred from Fig. 4.23 by linear extrapolation (compare caption Table 4.7). The obtained values are summarized in Table 4.7 along with the respective values reported in the literature [91].



Figure 4.23: Zoom into the photoemission spectra shown in Fig. 4.22. Photoemission threshold energies for halide ions solvated in water are indicated by arrows.

ANION	$Cl^-(3p)$	$Br^{-}(4p)$	$I^{-}(5p)$
$E_t \; [eV]$	8.7 ± 0.1	8.1 ± 0.1	7.3 ± 0.1
$E_t \; [eV] \; [91]$	8.77	7.95	7.21

Table 4.7: Photoemission threshold energies for halide ions solvated in water (from Fig. 4.23) compared with literature values [91]. Experimental values were obtained by simple linear extrapolation of the rising low-binding energy edge from Fig. 4.23.



Figure 4.24: Photoemission spectra of 2 m NaI and 2 m CaI₂ aqueous solutions obtained for 100 eV. There is reason to believe that the CaI₂ concentration was considerably lower than 2.0 m (see text). The spectra are normalized to the $1b_1$ liquid water emission intensity. Ion emission is labeled.

Divalent ions. The following paragraph addresses the effect of a counter cation other than an alkali-metal ion on the respective anion binding energies. Specifically, aqueous CaI₂, MgCl₂, MgBr₂, Na₂CO₃ have been chosen as representative test cases for divalent cations. Typical photoemission spectra of the respective salt solutions are shown in Figs. 4.24, 4.25, 4.26 and 4.27. For comparison photoemission spectra of a suitably chosen alkali-metal halide aqueous solution are also presented. Fig. 4.24 displays the photoemission spectra of a 2 m CaI₂ (bottom) along with 2 m NaI (top) aqueous solutions. The spectra were obtained for 100 eV photon energy. Emission from aqueous Ca^{2+} contributes weakly in the region of the $2a_1$ water orbital. The identical binding energy for aqueous I⁻ is measured in both spectra, within the limit of the experiment, which implies an identical structure of the iodide-anion solvation complex in NaI as compared to aqueous CaI₂ solution. The noticeable observation about Fig. 4.24 is almost identical intensity of the I⁻(4d) peak. For the CaI₂ solution this peak should be about twice as large. The reason for this discrepancy is not understood; it may be that this particular solution was of lower concentration than assumed. Fig. 4.25 compares the photoemission spectra of 3 m MgCl₂ and 3 m NaCl aqueous solutions, both



Figure 4.25: Photoemission spectra of 3 m NaCl and 3 m MgCl_2 aqueous solutions obtained for 100 eV. The concentrations are indicated and ion emission is labeled.



Figure 4.26: Photoemission spectra of 2 m NaBr and 3 m MgBr₂ aqueous solutions obtained for 100 eV. The concentrations are indicated and ion emission is labeled.



Figure 4.27: Photoemission spectra of 1 m NaI and 0.75 m Na₂CO₃ aqueous solutions obtained for 100 eV. The concentrations are indicated and ion emission is labeled. Spectra are normalized to the liquid water $1b_1$ peak height, which overestimates the relative Na⁺(2p) intensity increase in the upper spectrum.

obtained for 100 eV excitation energy. The extra photoemission peak at $55.5 \pm 0.03 \text{ eV}$ originates from the Mg²⁺(2*p*) emission. Similarly, Fig. 4.26 compares the photoemission of 3 m MgBr₂ and 2 m NaBr aqueous solutions. No relative peak shifts could be detected. Also for sodium carbonate (Na₂CO₃) no shifts of the Na⁺ photoemission features, relative to the energies found for the previous solutions, were observed. Notice that in Fig. 4.27 the intensity ratio of the Na⁺(2*p*) peak does not scale with the concentration. In the absence of any structural effect the peak should be 1.5 times larger (not 2.5) in the upper spectrum. This apparent discrepancy arises from improper normalization of the spectra, which in Fig. 4.27 was with respect to the liquid water $1b_1$ orbital. Due to the larger size of the CO₃⁻ anion as compared to the I⁻ anion, more water molecules would be replaced per given solution volume in the former case. Hence, water intensities would be expected to be different for the concentrations used in Fig. 4.27.



Figure 4.28: Photoemission spectra of 1 m NaI and 0.6 m Na₄[Fe(CN)₆] aqueous solutions obtained for 100 eV. The concentrations are indicated and ion emission is labeled.

Salts with complex structure. $Na_4[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, and $K_3[Fe(CN)_6]$ were chosen as representatives of bulky and complex anions ($[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$) in solutions. Moreover, these systems were proposed to not fully dissociate in water. The interesting question is whether the solvated alkali cation would sense the different environment. Photo emission spectra of the respective aqueous solutions (almost saturation) are presented in Figs. 4.28 and 4.29. In Fig. 4.28 the photoemission spectra of $0.6 \text{ m Na}_4[\text{Fe}(\text{CN})_6]$ and 1 mNaI aqueous solution are compared. The $Na^+(2p)$ intensities are consistent with the number of Na atoms per water molecules, i.e. 0.0432 in latter solution, and 0.018 in the former. As for other salts, no binding energy shift of the $Na^+(2p)$ line can be observed in the experiment. Fig. 4.29 compares the photoemission spectrum from $0.5 \text{ m K}_4[\text{Fe}(\text{CN})_6]$ solution with 1 m $K_3[Fe(CN)_6]$ and 3 m KI aqueous solutions. Signal from Fe^{2+} and Fe^{3+} in $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ gives rise to small features at $6.2 \pm 0.03 \, eV$ and $7.5 \pm 0.03 \, eV$, respectively. The important information from both figures is that identical binding energies, within 0.03 eV, are observed for both aqueous Na⁺ and K⁺, respectively, as indicated by the dashed vertical lines. This result suggests that, within the limit of this experiment, identical hydration shells exist for Na⁺ / K⁺ in NaI / KI and in Na₄[Fe(CN)₆] / K₄[Fe(CN)₆] / K₃[Fe(CN)₆] aqueous so-



Figure 4.29: Photoemission spectra of 3 m KI, $1 \text{ m } K_3[\text{Fe}(\text{CN})_6]$ and $0.5 \text{ m } K_4[\text{Fe}(\text{CN})_6]$ aqueous solutions obtained for 100 eV. The concentrations are indicated and ion emission is labeled.

lutions. Furthermore, the absence of any extra feature in the upper spectrum suggests that non-dissociated species either do not exist or their number is negligibly small.

In conclusion, the constant electron binding energy of aqueous iodide in different alkalimetal salt solutions, but also in the case of a divalent ion or the more complex sodium ferricyanide ion, is consistent with the absence of structural changes of the solvation complex. The same result was inferred by different experimental methods [88,99] as well. The results also suggest that the solvating water molecules efficiently shield any ion-ion interactions. Concerning the water binding energies, no significant effect of the interaction of a solvating water molecule with the ion could be inferred. Thus within the limits of the present experiment (30 meV), the electronic structure is indistinguishable for solvate water (both anion and cation solvation) and bulk water. It is worthwhile to mention that the potential barrier between the energy well of the hydration shell and the bulk is rather low so that it can be surmounted by the thermal energy of water molecules [87]. This together with the continuous breaking and making of H-bonds within the H-bonding network in water would in fact suggest only small differences of the electronic structure between hydrate and bulk water. This result matches the observation made in section 4.1.3, where it has been shown that also the electronic structure of D_2O water is not distinguishable from H_2O water.

Summary of electron binding energies of aqueous cations and anions. Tables 4.8 and 4.9 summarize the measured electron binding energies and peak widths for cations and anions, obtained for the various salt solutions discussed in this paragraph. Also contained are, for comparison, the relevant gas-phase energies (electron binding energies of both neutrals and the respective ions) as reported in the literature. Literature data include the first $(X^0 + h\nu \rightarrow X^+ + e^-)$ and second $(X^+ + h\nu \rightarrow X^{2+} + e^-)$ ionization potential (IP) of the corresponding gas-phase alkali atom X⁰ (see Table 4.8). The relevant quantity for the halides would be the first IP of the respective negative atom, Y⁻ (Y⁻ + h $\nu \rightarrow Y^0 + e^-$; see Table 4.9). Finally the energy required to remove a deeper electron from the respective singly charged atom, i.e. from X⁺ and Y⁻ if available, was included. Notice that the experimental binding energies of aqueous ions to be reported in the following result from individual Gauss-



Figure 4.30: Gauss fits to $I^{-}(4d)$ and $Na^{+}(2p)$ emission features for 4 m NaI aqueous solution.

ATOM X	$E_g(\mathbf{X}^0)$	⁰) [eV]	$E_g(\mathbf{X}^+)$ [eV]	$E_{aq}(\mathbf{X}^+)$ [eV]	FWHM [eV]
	2s	5.39			
Li	$1s^{a}$	64.42	$75.64^{\rm e}$	60.4 ± 0.07	1.4 ± 0.20
		66.31			
	3s	5.14			
	$2p^{\mathrm{b}}$	37.98	47.28^{e}	35.4 ± 0.04	1.1 ± 0.03
Na		38.07	$47.45^{\rm \ e}$		
		38.14			
		38.45			
	2s	71.03	80.07 ^e	68.0 ± 0.15	3.1 ± 0.50
	4s	4.34			
	$3p^{\rm b}$	24.48			
Κ		24.57	$31.62^{\text{ e}}$	22.2 ± 0.06	1.4 ± 0.20
		24.81	$31.89^{\text{ e}}$		
		24.97			
	$3s^{\mathrm{c}}$	41.00	47.81 ^e		
	6s	3.89			
	5p	17.23	$23.14^{\rm f}$		
		17.64			
Cs^{d}		19.06			
		19.12			
	5s	30.65			
	$4d_{5/2}$	82.74	$88.55^{\rm f}$	80.6 ± 0.03	1.1 ± 0.05
	$4d_{3/2}$	85.01		82.9 ± 0.04	1.3 ± 0.06

Table 4.8: Electron binding energies for aqueous cations obtained from the present photoemission study (E_{aq}) , and the corresponding gas-phase values (E_g) , as reported in the literature. ^a [100], ^b [96], ^c [101], ^d [56], ^e [102], ^f [103]. Indicated errors are statistical errors.



Figure 4.31: Comparison of electron binding energies for a given solvated cation $E_{aq}(X^+)$, with the respective gas-phase binding energy, $E_g(X^+)$. Binding energies of the solvated species were determined in the present work (see Table 4.8). Gas-phase values were obtained from the literature (see Table 4.8).

peak fitting averaged over a number of spectra. A typical fit, exemplified for Na⁺ and I⁻ features in the case of 4 m aqueous NaI solution, is presented in Fig. 4.30. Binding energy errors given in Tables 4.8 and 4.9 are statistical errors. These numbers are smaller than the overall experimental resolution of the present experiment, which is about 200 meV (see section 3.2.1).

The experimental binding energies reported here are independent of the excitation photon energy used (typically 60, 80, 100 eV). Furthermore, identical energies have been confirmed irrespective of the salt concentration. Also the binding energies of the solvated ions were found to be independent of the counter ion. For solvated alkali cations the observed energies exhibit solvation energy shifts up to 16 eV towards lower binding energies as compared to the gas-phase singly charged cations (column 4 vs. 3 in Table 4.8). Contrary, the halide anion binding energies are shifted in solution towards higher energy by ca. 3 eV with respect to the corresponding gas-phase value (column 4 vs. 3 in Table 4.9). The different behavior of electron binding energies of gas-phase vs. aqueous species, for cations and anions, is

ATOM Y	$E_g(\mathbf{Y}^0$) [eV]	$E_g(\mathbf{Y}^-)$ [eV]	$E_{aq}(\mathbf{Y}^{-})$ [eV]	FWHM [eV]
	$3p^{\mathrm{a}}$	12.96	$3.61^{\rm f}$	9.6 ± 0.07	0.6 ± 0.20
Cl		13.82			
	$3s^{\mathrm{a}}$	24.54			
		25.33			
	$4p^{\mathrm{b}}$	11.81	$3.36^{\rm \; f}$	8.8 ± 0.06	0.9 ± 0.20
		12.20			
		12.29			
		13.31			
Br		15.27			
	$4s^{\mathrm{c}}$	23.77			
		24.06			
		24.24			
		25.86			
	$3d_{5/2}$			73.2 ± 0.07	1.2 ± 0.10
	$3d_{3/2}$			74.3 ± 0.09	1.1 ± 0.10
	$5p^{\mathrm{d}}$	10.50	$3.06^{\rm f}$	7.7 ± 0.20	0.8 ± 0.30
		11.31		8.8 ± 0.20	1.1 ± 0.30
Ι		12.17			
		14.11			
	$5s^{\mathrm{d}}$	20.80	15.10*		
		21.30			
	$4d_{5/2}^{e}$	57.83	57.41*	53.8 ± 0.03	1.0 ± 0.02
	$4d_{3/2}$	59.73		55.5 ± 0.03	1.0 ± 0.03

Table 4.9: Electron binding energies for halide anions in water obtained from the present photoemission study (E_{aq}) , and the corresponding gas-phase values (E_g) , as reported in the literature. ^a [104], ^b [105], ^c [102], ^d [97], ^e [98], ^f [8]. The values marked with * are calculated [94]. Indicated errors are statistical errors.



Figure 4.32: Comparison of electron binding energy for a given solvated anion $E_{aq}(Y^-)$ with the respective gas-phase binding energy $E_g(Y^-)$. Binding energies of the solvated species were determined in the present work (see Table 4.9). Gas-phase values were obtained from literature (see Table 4.9). No experimental gas-phase values reported for $I^-(4d)$.

displayed within an energy level diagram in Figs. 4.31 and 4.32, respectively (with the values from Tables 4.8 and 4.9). In conclusion, no electron binding energy shifts, which could be correlated with a change of the solvation shell structure, were observed as a function of the counter ion size, charge and complexity. Since the ions considered here can be assumed to be completely solvated by water molecules, expected energy changes should in fact be small. One might argue that the effect is on the order of the spectral width of the ionic feature. In other words, the observed peak width may well reflect a distribution of solvation situations, which energetically differ by no more than the peak width. In section 6.1 it will be shown that $I^-(4d)$ electron binding energy changes can be observed for the I_3^- aqueous complex.

A comparison of the values reported here with the values predicted within a continuum model (Born model) will be presented in section 4.2.5.

4.2.3 Selected Data of Gas-Phase Alkali Halides

The following described gas-phase experiments on alkali-halide salts were motivated by various aspects. A first idea was to compare electron binding energies and Auger energies of free molecules/atoms with the respective solvated ions. The subject is also concerned with energy shifts of the photoemission lines as a function of the ionic character of a given bond (molecule). The latter is known to vary with different environments of the atom (chemical shift). This aspect is, however, beyond the main line of the present work and it will be touched upon only briefly. In addition, these gas-phase measurements also allow for a comparison of shape resonances of a given atom/ion (iodine) in the gas phase vs. aqueous solution.

The gas-phase spectra presented here were obtained at the U125/2-SGM beamline at BESSY II. The alkali-halide salt was evaporated from a metal crucible heated at temperatures between 400-600 °C. Electrons were detected with a Scienta SES-2002 hemispherical analyzer mounted at the magic angle [43] with respect to the polarization axis of the synchrotron light. For monitoring the photofragments (charge-to-mass ratio) a time-of-flight ion spectrometer was used.

Gas-phase CsX photoemission, $\mathbf{X} = \mathbf{F}$, Cl, Br, I. Similar to aqueous solutions (see section 4.2.2), photoemission spectra of a gas-phase salt series (CsX) were measured. The spectra from free Cs atoms and Cs halide salts obtained for 100 eV photons are displayed in Fig. 4.33. The halogen ion derived features (at about 10 eV binding energy) are assigned to $\mathbf{F}^{-}(2p)$, $\mathbf{Cl}^{-}(3p)$, $\mathbf{Br}^{-}(4p)$, $\mathbf{I}^{-}(5p)$ emission. Peaks correspond to the *p* shell spectra of the isoelectronic rare gases, but they are noticeably broader due to the highly dissociative nature of these ionized molecular states [106]. The strong intensity of the $\mathbf{I}^{-}(4d)$ emission is due to a shape-resonance enhancement (see section 4.2.4).

The Cs(5*p*) feature, in the case of atomic Cs, reveals a richer structure than the simple ²P doublet as one would expect for p^6 ionization. This results from the strong interaction in the final state, involving the configurations $5p^57s$, $5p^56s$ and $5p^55d$ [107]. The Cs⁺(4*d*) emission is entirely core like and therefore exhibits two features, $4d_{3/2}$ and $4d_{5/2}$. The splitting has a constant value of 2.3 eV for all investigated species.

The only experimental data available for the free Cs⁺ ions is the 5*p* ionization energy of 23.14 eV [108]. Based on a simple model, Benson *et al.* [103] calculated a value of 23.13 eV for Cs⁺(5*p*), which is in good agreement with the experimental finding. Applying the same model for the 4*d* level a value of 88.55 eV was obtained.



Figure 4.33: Photoemission spectra of Cs and Cs halides (CsF, CsCl, CsBr, CsI) in the gas phase obtained for 100 eV photon energy. These high-resolution spectra of the gasphase molecules were obtained using a separate apparatus equipped with a Scienta electron analyzer [56]; see text.

CATION	aq Cs^+	Cs^{0}	Cs_{gas}^+	$(CsF)_{gas}$	$(CsCl)_{gas}$	$(CsBr)_{gas}$	$(CsI)_{gas}$
$Cs(4d_{5/2})$	80.6	82.74	$88.55^{\rm b}$	81.96	82.71	82.86	83.01
$\mathrm{Cs}(4d_{3/2})$	82.9	85.01		84.31	85.01	85.16	85.28
$\operatorname{Cs}(5p)$		17.23 ^a	23.14 ^b	16.76	17.41	18.13	18.45

Table 4.10: Cs(4d) and Cs(5p) electron binding energies measured for various gas-phase Cs halides as inferred from Fig. 4.33. Cs(4d) gas-phase values are reported in the literature ^a [56], ^b [103]. The measured value for aqueous Cs^+ is also shown.

It is noted that the binding energy of the Cs(5p) and (4d) states slightly increases with decreasing electronegativity of the halogen anion, but the values are very close to those of the free atomic Cs^0 (see Table 4.10). This might imply that in the gas phase the positive charge of the Cs^+ is being compensated by the halogen ion in such a way that the influence on the electron binding energy is almost nonexistent. The same behavior was previously reported for ionization of the metal cation in alkali halides molecules [103].

Gas vs. liquid photoemission spectra: Cs, $(CsI)_{gas}$, $(CsI)_{aq}$. Auger energies. Photoemission spectra of atomic Cs (top), gas-phase CsI (center) and aqueous solution CsI (bottom) obtained for 100 eV photons are shown in Fig. 4.34. The energy scale is with respect to the vacuum level; notice that all spectra align at the $1b_{1g}$ water gas-phase emission feature indicated by the dashed line. The assignment of the Cs spectrum follows the one given in [107]; electron binding energies are in complete agreement.

The important information inferred from Fig. 4.34, as it concerns the binding energies, is that the Cs(4d) photoemission lines from aqueous CsI shifts by ca. 2.5 eV towards lower binding energy as compared to the gas-phase values. On the other hand, the values for atomic Cs and gas-phase CsI are almost identical (see Fig. 4.33).

Another aspect of the gas phase-liquid comparison is the Auger emission. For both ions, Cs^+ and I^- , this process was assigned to a 4d - 5p5p transition. The main observation from Fig. 4.34 is that Auger energies are lower in the gas phase as compared to the corresponding liquid-phase values. The effect is more pronounced for Cs, ca. 5 eV; however, the direct comparison is hampered by the broadening of the liquid photoemission features.



Figure 4.34: Photoemission spectra of atomic Cs (top), gas-phase CsI (center), and aqueous solution CsI (bottom) obtained for $100 \,\text{eV}$ photon energy. The high-resolution gas-phase spectra were obtained using a separate apparatus equipped with a Scienta electron analyzer [56]; see text.



Figure 4.35: Photoemission spectra of gas-phase CsI (top), NaI (center), and aqueous solution NaI (bottom) obtained for 100 eV photon energy. These high-resolution gas-phase spectra were obtained using a separate apparatus equipped with a Scienta electron analyzer [56]; see text.

Gas vs. liquid photoemission spectra: $(CsI)_{gas}$, $(NaI)_{gas}$, $(NaI)_{aq}$. Fig. 4.35 displays the photoemission spectra of gas-phase CsI, NaI, and aqueous NaI, obtained for 100 eV photon energy. The relevant binding energies are summarized in Table 4.11. The doublet character of the I⁻(4d) feature for NaI (center spectrum) results from dimer contributions; about 25% of the vapor is known to contain dimers [56]. An interesting result of this comparison is that the I⁻(4d) electron binding energy of aqueous I⁻(4d) and of the XI gas-phase molecule is almost identical. However, probably more important is the question how these energies relate to the I⁻(4d) gas-phase value. As mentioned, no reliable value has been reported in the literature, which leaves open how the alkali atom affects the I⁻(4d) electron binding energy. At the end of section 4.2.5, the origin of the different direction of gas-liquid electron binding energy shifts for anions vs. cations will be discussed.

ANION	aq I^-	I^0	I^{gas}	$(NaI)_{gas}$	$(CsI)_{gas}$
$I(4d_{5/2})$	53.8	57.83 ^a	57.41*	54.10	53.40
$I(4d_{3/2})$	55.5	$59.73^{\rm a}$		55.84	55.10

Table 4.11: I(4d) electron binding energies measured for gas-phase CsI, NaI, and aqueous NaI as inferred from Fig. 4.35. $I^{0}(4d)$ value is found in the literature ^a [98]. The value marked with * is calculated [94].

4.2.4 Iodide 4d Shape Resonance: Effect of Molecular Environment

It has been known for some time that the photoabsorption cross section of atoms with a closed 4d subshell, namely Xe, Cs, and Ba, are dominated by a resonance positioned above the 4d threshold [94]. Experiments and theory show that I and I⁻ exhibit the same behavior, i.e. a pronounced resonance. The maximum of the resonance has been calculated to be positioned at almost the same energy in I⁻, I, and I²⁺, near 96 eV [94]. The present experiment provides the possibility to measure this resonance also for *solvated* I⁻.

Generally, the analysis of such resonances accounts for the competition between continuum transitions $4d \rightarrow \epsilon f$ and discrete $4d \rightarrow 4f$ transitions [109]. A decisive part in this competition is played by the 4f electrons, which move in an effective double-well potential given by the sum of a Coulombic term and an angular momentum dependent term. Depending on the shape of the effective potential (for $l \geq 2$ a potential barrier is formed), the continuum wave function can exhibit a resonance behavior called *shape resonance* [110]. For low kinetic energies, the continuum function can hardly penetrate the potential barrier. However, for sufficiently high kinetic energies (amounting to the height of the barrier) the continuum function has a large amplitude in the region of the 4d orbital, which results in a strong enhancement of the photoionization cross section. Due to the potential barrier the maximum of the resonance lies several eV above the ionization threshold, resulting in a *delayed onset*. For higher kinetic energies, the wave function starts to oscillate in the atomic region, and due to resulting positive and negative portions of the radial dipole matrix element, the cross section decreases [111].

In order to map the resonance behavior of the $I^-(4d)$, photoemission spectra of 2 m NaI aqueous solution were measured for several photon energies, covering a range of 70-135 eV. The $I^-(4d)$ photoemission intensity as a function of photon energy is displayed in Fig. 4.36



Figure 4.36: Partial relative cross section for aqueous $I^{-}(4d)$, and total relative cross section for gas-phase NaI [56], I₂ [112], I and I⁺ [95]. Arrows mark the photoionization threshold.

(top); prior to the analysis, all the spectra were normalized to the photon flux. Since the present experimental setup did not permit measuring photoemission spectra at the magic angle (see 4.1.3), our data had to be corrected for changes of the anisotropy parameters β_i (compare also discussion on page 59). Again, with the β_i not known for the solution, one can only use the gas phase values. For the present analysis β_i values for I(4d) in molecular CH₃I were used [113]. These values turned out to be consistent with an atomic-like nature of the I atom in the molecule; the measured anisotropy parameter of the I(4d) subshell is presented in Fig. 4.37 [113]. In Fig. 4.36 the corrected relative cross section for aqueous I⁻(4d) is displayed along with the total relative cross section for gas-phase NaI [56] and for



Figure 4.37: Angular-distribution asymmetry parameter of the I(4d) subshell in CH₃I [113].

gas-phase I₂ [112], I, and I⁺ [95], respectively. The indicated error bars also account for the different ionization threshold of CH_3I and aqueous NaI.

Arrows mark the photoionization threshold of the respective species. The main observation from Fig. 4.36 is that the energy spacing between the 4d threshold and the resonance maximum is rather similar for I₂, I, and I⁺, but it gets larger for gas-phase NaI and even larger for aqueous NaI. The resonance behavior of the wave function depends on the shape of the 4d atomic potential; thus a change in the potential, by a different environment for instance, might cause a change of the resonance. The data actually suggest an increase of the potential barrier height, which would result in a larger *delayed onset*. It has to be emphasized that the present analysis of the I⁻(4d) shape resonance for aqueous solution may considerably suffer from an inappropriate choice of the gas phase β_i . Certainly, measuring solution β_i would be highly desirable in order to correctly interpret the data.

4.2.5 Estimation of Electron Binding Energies of Aqueous Ions: Born Solvation Model

Interpretation of photoemission data. The present experiment is concerned with relating measured peak positions in a liquid photoemission experiment to electron binding energies of the aqueous species. As in aqueous salt solutions *ions* are solvated, one needs to correlate the free energy of solvation to the change of the ionization energy of the respective ion. The situation is different as compared to photoemission from pure water, considered in 4.1.2, where no solvation shell exists prior to the photoemission process, and furthermore any re-orientation of the water structure (in terms of nuclear position) about the ionized species is negligible on the time scale of the photoemission process. In the previous section (4.2.2) it was shown that hydrated alkali cations exhibit solvation energy shifts towards lower binding energies, while for anions the shift is towards higher binding energies. These shifts are relative to the respective gas-phase ions, i.e. alkali X⁺ and halide Y⁻, respectively. They are usually referred to as the liquid-phase binding-energy shift [25], which can be derived from the Gibbs free energy of solvation, based on the Born equation [12]:

$$\Delta G^{Born} = -\frac{Z^2 e^2}{8\pi\epsilon_0 R} (1 - \frac{1}{\epsilon_{st}}) \,. \tag{4.5}$$

As outlined above in the liquid water section (4.1.2), in this model the ion is considered as a sphere with a point charge in its center and the solvent as a dielectric continuum with static (relative) permittivity ϵ_{st} ; Z, e, R and ϵ_0 denote the charge of the ion, the unit charge, the ion radius and the vacuum permittivity, respectively (compare also section 2.3).

Equation 4.5 generally overestimates the magnitude of the experimental solvation free energy, which has lead to numerous modifications of the expression as has been discussed in detail [15,24,88]. The main shortcoming of this continuum model arises from the fact that the Born equation is valid for distances $r \gg R$ only. For distances r comparable to R the strength of interaction of a water molecule with the ion exceeds that of its interaction with any other single water molecule and consequently the preferred orientation of the water molecules need to be accounted for [114]. A model that appears to better meet the requirements, by accounting for the interaction with immobilized water molecules within the first hydration shell, has been proposed by Y. Marcus [13]. This model explicitly accounts for different interactions by not only allowing for contributions to the free energy from inside the ion radius but also from the first hydration layer with the thickness depending on the electrostatic field of the ion Ze/r. Specifically, the model involves (i) the cavity in which the ion is located in the water, (ii) a completely immobilized first hydration shell, and (iii) surroundings. For the latter region the Born term is applied using the permittivity of bulk water ($\epsilon_{st} = 81.1$ [16]), while $\epsilon = 1$ is assumed for the first hydration shell (dielectric saturation due to strong orientation of the water molecules). The ion radius related with region (i) can be defined as $R_{ion} = d_{ion-water} - R_{water}$, where $d_{ion-water}$ is the shortest distance between the ion and the oxygen atoms of the water molecules in their first hydration shell (as derived from the first minimum of the pair-correlation function $g_{ij}(r)^{9}$) [88]. R_{water} is an appropriate distance that characterizes the radius of a water molecule; the average of reported values is $R_{water} =$ 0.142 nm [88]. Various simplified, rather empirical expressions for R_{ion} have been proposed as well, which in fact turn out to be quite useful for discussing the experimental binding energies for aqueous ions obtained in this study. The concept followed here to calculate ΔG^{Born} is based on modelling the solvent molecular effects in the immediate vicinity of the charged solute using an effective ion radius, R_{eff} . It thus accounts, yet in a much simpler way, also for different interactions of water very near the ion and far away. R_{eff} was found to be well approximated by $R_{ion}^{crystal}$ and the solvation radius R_{gmax} according to [15]:

$$R_{eff} = \frac{R_{ion}^{crystal} + R_{gmax}}{2} , \qquad (4.6)$$

where $R_{ion}^{crystal}$ is the crystal ionic radius, and $R_{gmax} = d_{ion-water}$ (see above). Values for $R_{ion}^{crystal}$ and $d_{ion-water}$ used with equation 4.6 are presented in Table 4.12 (from Ref. [88]).

One now needs to relate the Gibbs free energy ΔG^{Born} , equation 4.5, to the measured electron binding energies of solvated ions. I.e., one likes to interpret the photoemission experiment, which involves ionization of solvated ions giving rise to a change of the ion's charge state $(q \rightarrow q \pm 1)$, in terms of the change of the solvation free energy for the initial and final state solvate. Then, for aqueous cations and anions, the relevant processes can be expressed by:

$$X_{aq}^{+} + h\nu \to X_{aq}^{2+} + e^{-}(vac),$$
 (4.7)

$$Y_{aq}^{-} + h\nu \to Y_{aq}^{0} + e^{-}(vac)$$
 (4.8)

Since the photoemission process is much faster than the time scale required to reorganize the initial solvation shell, the detected photoelectron carries only the information of the original configuration (the reorientation of the solvent molecules in terms of nuclear positions

⁹The distance r of the first peak in the dependence of $g_{ij}(r)$ on r gives the shortest interatomic (internuclear) distance d_{ij} between two particles i and j.

ATOM		$E_g(\mathbf{X}^+)$	$E_{aq}(\mathbf{X}^+)$	$E_{aq}^{Born}(\mathbf{X}^+)$	$R_{ion}^{crystal}$	R_{gmax}	R_{eff}
Х		[eV]	[eV]	[eV]	[Å]	[Å]	[Å]
Li	2s				$0.74^{\rm c}$	2.08 ^c	1.41
	1s	$75.64^{\rm \ a}$	60.4 ± 0.07	60.50			
	3s						
Na	2p	$47.28^{\rm a}$	35.4 ± 0.04	34.65	$1.02^{\rm c}$	$2.36^{\rm c}$	1.69
	2s	$80.07^{\rm a}$	68.0 ± 0.15	67.44			
	4s						
K	3p	$31.62^{\rm a}$	22.2 ± 0.06	21.41	$1.38^{\rm c}$	$2.80^{\rm c}$	2.09
	3s	$47.81^{\rm a}$					
	6s						
	5p	$23.14^{\rm \ b}$		14.32			
Cs	5s				$1.70^{ m c}$	$3.14^{\rm c}$	2.42
	$4d_{5/2}$	$88.55^{\rm b}$	80.6 ± 0.03	79.73			
	$4d_{3/2}$		82.9 ± 0.04				

Table 4.12: Comparison between measured (E_{aq}) and calculated (E_{aq}^{Born}) electron binding energies using the Born continuum model. Gas-phase values are also included (^a [102], ^b [103]). $R_{ion}^{crystal}$ (^c [88]) is the crystal ionic radius, R_{gmax} (^c [88]) is the shortest ion-oxygen atom distance and R_{eff} is the effective radius as defined in equation 4.6.

can be neglected due to the fast time scale [25]). In other words the energy required for reactions 4.7 and 4.8 is the *vertical ionization* energy, which can be determined by photoemission. The calculated electron binding energies, E_{aq}^{Born} , presented in the Table 4.12 were obtained using equation 4.5 in

$$E_{aq}^{Born} = E_g + \Delta G \,, \tag{4.9}$$

with

$$\Delta G = \Delta G_f^{Born} - \Delta G_i^{Born} \,. \tag{4.10}$$

 ΔG_i^{Born} and ΔG_f^{Born} are the solvation energies for the respective initial and final state of a given anion or cation in solution. Hence, determination of E_{aq}^{Born} requires to calculate the net energy change associated with the water solvation-shell rearrangement that follows the ionization of an ion¹⁰. Within this simple continuum consideration, the solvation en-

 $^{^{10}}$ Of course, no reorientation occurs on the time scale of photoemission process. One thus calculates ΔG

ATOM		$E_g(\mathbf{Y}^-)$	$E_{aq}(\mathbf{Y}^{-})$	$E_{aq}^{Born}(\mathbf{Y}^{-})$	$R_{ion}^{crystal}$	R_{gmax}	R_{eff}
Y		[eV]	[eV]	[eV]	[Å]	[Å]	[Å]
Cl	3p	3.61 ^a	9.6 ± 0.07	6.46	1.81 ^b	3.19^{b}	2.50
	3s						
	4p	3.36 ^a	8.8 ± 0.06	6.02			
Br	4s				$1.96^{\rm b}$	3.37^{b}	2.67
	$3d_{5/2}$		73.2 ± 0.07				
	$3d_{3/2}$		74.3 ± 0.09				
	5p	3.06 ^a	7.7 ± 0.20	5.49			
			8.8 ± 0.20				
Ι	5s	15.10^{*}		17.53	$2.20^{\rm b}$	$3.65^{\rm b}$	2.93
	$4d_{5/2}$	57.41^{*}	53.8 ± 0.03	59.84^{*}			
	$4d_{3/2}$		55.5 ± 0.03				

Table 4.13: Comparison between measured (E_{aq}) and calculated (E_{aq}^{Born}) electron binding energies using the Born continuum model. Gas-phase values are also included $(^{a} [8])$. $R_{ion}^{crystal}$ $(^{b} [88])$ is the crystal ionic radius, R_{gmax} $(^{b} [88])$ is the shortest ion-oxygen atom distance and R_{eff} is the effective radius as defined in equation 4.6. The asterisk for iodide indicates that experimental values are not available, and theoretical values were used instead [94].

ergy around a neutral atom is assumed to be negligible. A cartoon depicting the different situations is presented in Fig. 4.38.

Since the present liquid photoemission experiment accesses vertical electron binding energies of aqueous ions (no reorientation of the water molecules on the time scale of the photoemission process) the relevant reactions for determining ΔG^{Born} are equations 4.7 and 4.8. Specifically, from equation 4.10 one obtains:

$$\Delta G^{Born}(cation) = \Delta G^{Born}(X_{aq}^{2+}) - \Delta G^{Born}(X_{aq}^{+}), \qquad (4.11)$$

$$\Delta G^{Born}(anion) = \Delta G^{Born}(Y^0_{aq}) - \Delta G^{Born}(Y^-_{aq})$$
(4.12)

for cations and anions, respectively.

With equations 4.11 and 4.12 the observed larger binding-energy shift towards lower

for solvating the initial ion of charge q and the product ion (after photoemission) of charge (q-1). Notice that one may also use thermodynamically measured values (if available) of the solvation energy for cations and anions as discussed in Ref. [24].



Figure 4.38: Schematic depicting the polarization effects for ion solvation relevant for the photoemission process. The ovals containing arrows represent oriented and polarized water molecules. The energy level diagrams (right side) illustrate the liquid-phase binding energy shifts in terms of the solvation free energy (ΔG) relative to the respective gaseous ion. E_g and E_{aq} are the electron binding energies of the gas-phase species and the hydrated species, respectively. The different direction of gas-liquid shifts for solvated anions vs. cations can be directly inferred from the lengths of the arrows labeled E_{aq} relative to E_g . The cartoons also indicate that shifts are larger for the case of cations.

values and the smaller shift in the opposite direction for cations and anions, respectively, can be directly explained. From equation 4.11 and equation 4.5, i.e. for the case of cations one obtains:

$$\Delta G^{Born}(cation) = -\frac{3e^2}{8\pi\epsilon_0 R_{eff}} (1 - \frac{1}{\epsilon_{st}}).$$
(4.13)

For anions, using equation 4.12 and equation 4.5 one obtains:

$$\Delta G^{Born}(anion) = \frac{e^2}{8\pi\epsilon_0 R_{eff}} (1 - \frac{1}{\epsilon_{st}}). \qquad (4.14)$$

Notice that equations 4.13 and 4.14 differ by a factor of -3. Consequently, for anions the net energy difference between the final and initial state in the liquid is on the order of $\Delta G^{Born}(anion)$ larger than in the gas phase, while for cations the total energy difference between the final and initial state is smaller by about $3 \cdot \Delta G^{Born}(anion)$ as compared to the gas phase. Hence, the anion peaks in the photoemission spectra of solution are expected to appear at increased binding energy, whereas the cation peaks occur at lower binding energy with the shift being larger in the latter case.

As presented in Tables 4.12 and 4.13, calculated and experimental electron binding energies, E_{aq}^{Born} and E_{aq} , respectively, agree within about 1 eV for cations. For anions the values differ by about 2-6 eV. The reason for better reproducing the former values is assumed to partly result from the fact that the total gas-liquid shift is larger in that case. Then, any other contributions to the peak shift such as polarization screening (see 4.1.2) would be rather negligible as they are small. This is not true for the case of anions, where this competitiveness is of a larger concern.

It is noteworthy to mention that classical continuum dielectric models have also been proven useful for modelling ion solvation in large (water) clusters (e.g. [115]); these systems are of great significance to the understanding of the solvation phenomena in bulk solutions. For I⁻(H₂O)_n clusters experimental electron binding energies were in fact shown to fit an analogous model where the anion is solvated at the surface of the solvent cluster [116]. Photoelectron spectra of I⁻(H₂O)_n, $n \leq 60$, are shown in Fig. 4.39, which was adapted from Ref. [115]. The strong initial changes of electron binding energies up to six water molecules, followed by reduced changes for subsequent addition of a water molecule, indicates the formation of the first solvation shell with a coordination number of six. In 4.2.6 the relevance of these data for the interpretation of the present results will be discussed in the context of I⁻ and Na⁺ solvation at near saturation concentration. Cluster studies of solvated alkali atoms, e.g. Cs(H₂O)_n [117] and Na(H₂O)_n [118], indicate that for the alkali atom surrounded by



Figure 4.39: Photoemission spectra of $I^-(H_2O)_n$ clusters [115]. The excitation photon energy was 7.1 eV.

more than four water molecules the ionization potential does not depend on the metal atom but on the solvent species. In the latter work the sodium atom was proposed to spontaneously ionize with the emitted electron getting solvated (compare 5.2.1). As opposed to the anionic solvation these cation results are difficult to be compared with the present photoemission data in which case electron binding energies of the solvated cation have been directly accessed (ca. 81 and 35 eV for $Cs^+(4d)$ and $Na^+(2p)$, respectively; see Table 4.8).

In this section it has been shown that the Born continuum model can quite accurately describe certain trends in the energetics of ion solvation. Yet, it is not an exact theory as it does not consider any microscopic details of the solvation shell structure. It may therefore surprise that the model works so well. There is no doubt, however, that the specific molecular interactions between water molecules and ions of different charge and size must hold the key to the very different solvation behavior of the different ions. Particularly this immediate (contact) interaction is barely included in the Born description, and even worse, the Born model is strictly applicable only for distances considerably larger than the ion radius (see section 2.3).

In the following I will touch upon some of the aspects that seem importantly related to the microscopic solvation process. Notice that there is little input from theory yet. An interesting question is how one can understand the different gas-liquid shifts (just discussed above) for solvated anions vs. cations in a microscopic picture. This must have got to do with specifically distinct interactions of a water molecule with the two types of ions. An obvious difference is role of the H-bonding. Differences also exist for ion/atom solvation in small water clusters as mentioned above. For cationic solvation the O-H groups will point away from the ion (then the oxygen atom points to the ion; compare Fig. 2.5) in order to form $O-H \cdots O$ hydrogen bonds with bulk water molecules at the solvation shell boundary. Notice that this is less destructive to the bulk water structure [2]. For anions, the water molecules are bound by directional $O-H \cdot \cdot \cdot Y^-$ hydrogen bonds. For $Y^- = Cl^-$, Br^- , I^- , the $O-H \cdots Y^-$ hydrogen bond is in fact observed to be weaker than the $O-H \cdots O$ hydrogen bond between two water molecules, and is observed to become weaker within the halogenic series [2]. This may well have an effect on the effective dipole moment associated with stabilizing the solvation shell. Moreover, partial charge transfer between solvent molecules and the solute ion will be different for the two solvation situations. At present, the issue is far from being understood, but it may be worthwhile discussing some of the observations for gas-phase alkali halides (presented in 4.2.3) in that context. In Table 4.10 the Cs electron binding energy (in gas-phase $Cs^{\delta+}Y^{\delta-}$) can be seen to decrease within the halogenic series. Even though these results await theoretical analysis in terms of charge transfer and its dependence on the halide counter anion, it seems that alkali halide systems may be useful to also understanding some of the electronic interactions in ion solvation by water. The interesting result from Table 4.10 is that the measured electron binding energy for aqueous $Cs^+(4d)$, which is ca. 82 eV, is quite similar to the $Cs^+(4d)$ energies in gas-phase CsY, being 83.5 eV (averaged over different co-ions and peak splitting). To what extend this result may, however, answer the above question is not clear at present. As pointed out above (section 4.2.3; Table 4.11) also the $I^{-}(4d)$ electron binding energy is found to be very similar for aqueous $I^{-}(4d)$ and for the XI gas-phase molecule, but a precise value for the $I^{-}(4d)$ gasphase energy is missing. Hence, the effect of the alkali atom on the $I^{-}(4d)$ binding energy remains unclear. For the same reason it remains an open question to what extend studies of gas-phase alkali halides may provide information to better understand ion solvation by

water.

4.2.6 High-Concentration Aqueous NaI Solutions

Using 100 eV photon energy, which corresponds to the shape resonance maximum of aqueous iodide (Fig. 4.36), it is possible to detect the $I^-(4d)$ photoemission signal for a concentration as low as 0.1 m (e.g. in aqueous NaI). This allows the investigation of solution properties from moderately low to saturation concentration. A particularly interesting aspect concerns the atmospheric reactivity of aqueous sea-salt microparticles for which a relative chloride ion surface excess was proposed by theory [119]. One then would like to better understand the interaction between solvate complexes. It seems feasible that for sufficiently high density of solvate complexes the latter may attract each other, and, for a given case, the simple solvation shell might be no longer energetically favorable. In fact, the assumption of perfectly separated ions by the polar solvent molecules (Debye-Hückel model for electrolytes [90]) has been known to fail for high salt concentrations [119, 120]. Several mechanisms have been suggested, including ion association (ion pairing) with various forms of solvation shell sharing [87, 121]. Clearly, investigating such processes by the surface-sensitive photoemission may provide useful information on structural details of the solvation complexes.

Near saturation limit. Figs. 4.40 and 4.41 display photoemission spectra of aqueous NaI solutions for the low and the high salt concentration range, respectively, obtained for 100 eV photons. Fig. 4.40 covers the 0.1 to 1.0 m range, and Fig. 4.41 shows spectra for 0.5 to 12.0 m NaI concentration. The highest concentration investigated here corresponds to nearly saturation. With a solubility of $184 \,\mathrm{g/cm^3}$, saturation occurs at about $13 \,\mathrm{m}$ concentration. Since experimental handling of such high concentrations in terms of crystallization rate and potential changes (compare section 4.3) is difficult, the highest concentration investigated here was 12.0 m. The spectra in Figs. 4.40 and 4.41 are vertically displaced relative to each other, and normalized with respect to the synchrotron flux. The spectral assignments was adapted from the preceding paragraphs. Great care was taken to maintain constant experimental conditions for obtaining all spectra in each figure, as this is important for accessing absolute signal attenuation/increase for varying salt concentration. In order to follow the emission intensities of both ions as a function of concentration, the corresponding peak integrals (based on Gaussian peak fitting) of the $I^{-}(4d)$ and the Na⁺(2p) features have been evaluated. The result is presented in Fig. 4.42. The main figure shows the photoemission intensities for both anions and cations over the full concentration range, and the inset presents



Figure 4.40: Photoemission spectra of NaI aqueous solution obtained for different salt concentrations as labeled. Intensities were normalized to the synchrotron photon flux. The excitation photon energy was $100 \,\text{eV}$.

data for the lower concentrations only. Obviously, the data show no evidence for any differential surface effect for anions vs. cations; intensities for both ions behave identically. Hence, no anion surface excess can be inferred from the data (see below). However, the present study clearly shows that for concentrations larger than 2 m NaI the ion signals increase no longer linearly (Fig. 4.42). In order to also quantify the water signal attenuation in Fig. 4.43 the dependence of the water photoemission intensity as a function of the salt concentration is presented. The decrease of the water signal can be qualitatively explained by water molecules being replaced by salt ions.

From the ion signal plot as a function of the concentration (Fig. 4.42), and being aware of the surface sensitivity of the present photoemission study, one concludes that for sufficiently large salt concentration, ion densities must be lower at the surface than in the bulk solution. Such a *depletion* may simply reflect that for near-saturation a larger number of ions can be stabilized by solvation shells in the bulk, as compared to the surface. High concentrations of ions may only exist in the bulk as all inter-complex dipoles average out, while unbalanced dipoles in the case of a surface are energetically unfavorable. Compare also the discussion of



Figure 4.41: Photoemission spectra of NaI aqueous solution obtained for different salt concentrations as labeled. Intensities were normalized to the synchrotron photon flux. The excitation photon energy was 100 eV. The inset displays the spectra of lowest and highest salt concentration on top of each other, but scaled to have identical intensities. From this comparison constant electron binding energies of both $I^-(4d)$ and $Na^+(2p)$ as a function of salt concentration are inferred.

the iodide signal for the surface-active tetrabutylammoniumiodide (But_4NI) in section 4.3.

Peak positions of both Na⁺ and I⁻ features are found to be constant for all concentrations studied. This has been indicated in the inset of Fig. 4.41 for 0.5 and 12 m NaI concentration. Fig. 4.44 displays I⁻(4d) electron binding energies, as obtained by careful Gaussian peak fitting (compare Fig. 4.30), as a function of the NaI concentration. Statistical errors are indicated; systematic errors are not accounted for. From Fig. 4.44 it is concluded that binding energy shifts are no larger than ca. 30 meV, and also no obvious trend as to the direction of a peak shift can be inferred. The fact that the electron binding energy not even changes for near-saturation concentration may surprise. In section 4.3.1 two principle sources for peak shifts will be discussed in detail. One results from the decreasing coordination



Figure 4.42: Increase of the $I^-(4d)$ and $Na^+(2p)$ photoemission signal as a function of the NaI concentration (based on peak fitting and integration of spectra in Figs. 4.40 and 4.41). The inset presents data for low concentrations. The sub-linear increase for concentrations larger than 2 m is attributed to surface depletion of bulk ions, i.e. relatively lower ion density as compared to the bulk solution.

(solvation) number (smaller shell as there are fewer water molecules available), and the other is associated with surface dipoles due to an electric double layer. The latter effect would cause the I^-/Na^+ ion intensity ratio to change, which is not the case here. Hence, the present results are in disagreement with previous theoretical results [89] according to which the large anion, favors an asymmetric location in the solvation cage (which would give rise to an anion surface excess).

It is interesting to note that for the 12 m concentration, the ratio of water molecules to salt molecules (about 5:1) implies that the solvation structure must be different than in the Debye-Hückel limit, where each ion is individually solvated. This raises the question whether or not this experiment is sensitive to solvation structural changes (e.g. ion pairing and the related propensity for surface anion excess). It certainly should be, unless the effect is compensated by other contributions. At this point a comparison with respective cluster studies would seem interesting as these systems may be considered valuable models



Figure 4.43: Decrease of the $1b_1$ liquid water photoemission signal as a function of NaI concentration.

providing microscopic details of the ion-solvent and solvent-solvent interaction. Studies of larger clusters, here we are concerned with halide anions solvated in water clusters, containing tens of solvent molecules or even more, may elucidate the evolution of solvation layers in confined environments, and their convergence to bulk properties [115] (compare to section 4.2.5). The particular interest here is in the experimental electron binding energy obtained for $I^-(H_2O)_n$ and the related dependence on n. It has to be pointed out, however, that for clusters *surface* solvation has been proposed to be energetically favorable (see page 103). Notice that the comparison with cluster studies may provide information on the distance over which the water feels the ion.¹¹

As opposed to clusters, in macroscopic systems surface solvation might be prevented. If surface anions, solvated by incomplete shells, would exist one would have expected to at least observe a change of the electron binding energy. In fact the absence of surface solvation for bulk NaI aqueous solution would be consistent with the existence of the depletion layer in which full-shell solvation is maintained by keeping ions away from the very liquid/vacuum

¹¹The situation may be more complicated as in the cluster studies particularly ion-ion interactions are absent.



Figure 4.44: Experimental $I^-(4d_{5/2})$ electron binding energies as a function of the NaI concentration. Data result from fitting the spectra shown in Fig. 4.41. No statistically significant binding energy shifts can be inferred.

boundary. It is interesting to note that cluster studies yield identical electron binding energies (7.7 eV) for $n \simeq 100$ (extrapolated from Ref. [115], see Fig. 4.39) as obtained for the bulk solution. Whether this information is useful for the interpretation of the present data is difficult to judge. It should be pointed out that fundamental differences exist between liquid phase and cluster solvation. In the latter case three extra solvation contributions have to be considered: (i) the formation of a spherical cavity in the solvent continuum, (ii) the introduction into this cavity of an ion-solvent molecule cluster performed in vacuum, and (iii) the rearrangement of the solvent molecule in the vicinity of the cluster [10].

4.3 Surface Segregation

A special property of hydrogen bonding (H-bonding) in water is the *hydrophobicity* which causes non-polar molecules such as hydrocarbon chains to associate with each other in an aqueous environment. Here, water 'squeezes' non-polar molecules together, and as a consequence the dissociated hydrophobic ions will be non-uniformly distributed in the solvent. Often, considerable surface accumulation occurs, which is referred to as *surface activity*.

The focus of this section is on the surface-active tetrabutylammoniumiodide $(C_4H_9)_4NI$ (But₄NI) dissolved in water. The But₄N⁺ cation is one of the most efficient and intensively investigated phase-transfer catalysts¹² [122] by numerous methods. But₄NI in formamide is known to form a surface layer of about 1 nm thickness which roughly corresponds to the diameter of the But₄N⁺ ion [123, 124].

Given the high surface sensitivity of photoemission, the method would seem predestinated to investigate the nature of such a surface-active system. Specifically, one should be able to identify surface idea and particularly the existence of an electric double layer (see below) by spectral changes of the photoemission spectra. This would include both peak shifts and relative signal variations. Detailed analysis of the spectra might even allow to infer information on the microscopic structure of the segregation layer. The only photoemission study of $But_4N^+I^-$ aqueous solution was performed by Watanabe [125]. He used a rotating target and monochromatized light from a hydrogen lamp, the experiment was, however, limited to photoionization threshold (see also section 4.2). $But_4N^+I^-$ dissociates in water and the large hydrophobic But_4N^+ cations segregate at the surface. For electrostatic reasons surface But_4N^+ ions are always accompanied by their counter ion, iodide [123, 124]. The surface activity of the But₄NI was shown to correlate with a decrease of surface tension, as this minimizes the energy of the system [126]. Angle-resolved X-ray spectroscopy (ARXPS) revealed no relative ion surface excess, i.e. no differential segregation between the cations But_4N^+ and anions I⁻ within the depth resolution of few Å [127]. The existence of iodide in the topmost layer, giving rise to an electric *double layer*, was confirmed by metastable induced electron spectroscopy (MIES) [128]. These previous spectroscopic techniques were

¹²Phase transfer catalysis is a concept that relates to chemical reactions where the reactants are in two separate phases. In such cases, the rates and yields are very often limited by the slow transport of reactants from one phase to another. Phase transfer catalysts were found to be useful in transporting the reactants, thus increasing yields and rates, and facilitating reactions which are otherwise not feasible or very difficult to carry out.

exclusively performed for organic solvents, often formamide, as such an organic solvent can be easier handled under high-vacuum conditions. Hydrophobic effects are expected, however, to be more pronounced for water.

Other investigations of $\operatorname{But}_4 \operatorname{N}^+ \operatorname{I}^-$ dissolved in water, e.g. measurements of osmotic and activity coefficients, have shown that the surface activity increases for increasing alkyl chain length [126]. Furthermore, $\operatorname{But}_4\operatorname{NI}$ surface segregation strongly depends on the counter ion; it decreases in the order $\operatorname{I}^- > \operatorname{Br}^- > \operatorname{Cl}^-$ [126]. This behavior was explained in terms of the so called *solvent structure-enforced ion pairing* [123, 129]. The model assumes that the total disturbance of the water structure, by both the anions and the cations, is minimized if, e.g. $\operatorname{But}_4\operatorname{N}^+$ and I^- are put in the same cavity of the disturbed water structure. Then, for a smaller radius, i.e. for a better dissolvable ion, the tendency for ion pairing is reduced. Notice that this pairing mechanism would also allow for a higher surface concentration as compared to the case of unpaired ions due to the more compact solvate complex structure [123].

Here, photoemission spectra from $\operatorname{But}_4\operatorname{NI}$ aqueous solution as a function of the salt concentration are reported. Particular focus is on the identification of the completed segregated surface layer by following the relative intensity changes of the photoemission signal of the iodide anion as a function of the salt concentration. Furthermore, another question is whether changes of the hydration shell structure (solvent coordination), particularly for surface vs. deeper ions, may be identified by different electron binding energies. Finally, results on the exchange of iodide located within the segregation layer with bulk solution bromide are presented. The experiments were performed in order to elaborate on the effect of the anion size, specifically on the reluctance of the large I⁻ anion to exchange with the smaller Br⁻ anion. Photoemission spectra are presented for But₄NI dissolved in aqueous XBr solutions, X = Na, K, Cs. The effect of the counter cation will be addressed as well.
4.3.1 Identification of the Completed Tetrabutylammoniumiodide (But₄NI) Monolayer on the Water Surface

Photoemission spectra of pure water, 2 m NaI, and $0.025 \text{ m But}_4\text{NI}$ aqueous solutions obtained for 100 eV photon energy are displayed in Fig. 4.45. The spectra are vertically displaced with respect to each other, and relative intensities are properly matched. Scaling was



Figure 4.45: Photoemission spectra of pure water, 1 m NaI, and $0.02 \text{ m But}_4\text{NI}$ aqueous solutions, respectively. For normalization procedure see text. $I^-(4d)$ intensities are almost identical even though the concentrations differ by a factor of 80. This is a direct evidence for $But_4\text{NI}$ surface segregation.

done with reference to Fig. 4.46 (see below) in order to account for the relative photoemission signal attenuation of the water $1b_1$ (liquid) emission by the overlayer. The energy axis refers to electron binding energies with respect to $1b_{1g}$, as described above (section 4.1.1). In the photoemission spectra from aqueous But₄NI and NaI solutions (top and center spectra in Fig. 4.45) one can recognize the underlying H₂O molecular orbital features, $2a_1$, $1b_2$, $3a_1$, $1b_1$ (see 4.1.1). The features from the Na⁺ and I⁻ emission are labeled according to the previous spectra. Although the concentrations are completely different, the I⁻(4d) peak is found to be of almost identical intensity for both solution spectra. This directly points to substantial But₄N⁺I⁻ surface segregation, assuming that anions and cations segregate pair-wise (see below). With the I⁻(4d) iodide signal ratio I⁻(But₄NI)/I⁻(NaI) being 0.9, as inferred from Fig. 4.45, and an iodide concentration ratio of 1/80, one obtains an effective segregation factor of about 70 for the given concentrations. It is useful to now estimate the fraction of iodide ions residing at the surface vs. the number of ions inside the bulk solution volume as this would be a more meaningful quantity (relative segregation). For a given salt (But₄NI) concentration this fraction may be obtained by comparing the total volume of ions in the solution, and the volume available at the surface. Certainly the result depends on the particular geometry. For 0.02 m But₄NI solution, one obtains a relative surface segregation factor of > 100.¹³

Further information on surface structural details may be obtained from the evolution of the photoemission signal as a function of the But_4NI concentration. Selected spectra of different concentrations, 0.005, 0.015, 0.025, 0.030, 0.040 m But₄NI in water are displayed in Fig. 4.46 together with a reference water spectrum. The intensities in the figure are normalized with respect to the ring current, hence relative intensity changes directly correlate with true relative variations of the emission signal. For the purpose of displaying the evolution of emission *intensities*, the But_4NI solution spectra in Fig. 4.46 have all been energy-shifted in order to align at the liquid water $1b_1$ feature (at 11.16 eV binding energy, see section 4.1.2). The amount and the origin of these differential peak shifts will be addressed below. The main result from Fig. 4.46 is that the $I^{-}(4d)$ signal steadily increases up to about 0.02 m But_4NI concentration, which corresponds to 33.3% of maximum solubility, and levels off for larger concentrations. The water signal, on the other hand, is attenuated as the overlayer grows. For a more quantitative analysis the iodide signal increase as a function of the But_4NI concentration is displayed in Fig. 4.47a. Each data point represents the integral of the $I^{-}(4d)$ emission feature assuming Gaussians on a constant background. Indicated errors are statistical errors. Two regimes of different slopes may be clearly identified, and the break near $0.02 \text{ m But}_4 \text{NI}$ concentration might be attributed to the completion of the salt monolayer on top of the water surface. A similar behavior is known for adsorbate systems, if growth proceeds layer-by-layer as, for instance, C_{60} /Ni [130]. This is the first time that the layer completion on a solution surface was probed by photoemission. In adsorbate/crystal

¹³Consider an outer shell volume V_{surf} of the liquid (thickness 1 nm, which is the diameter of But₄N⁺ cation). With r the jet radius, l the jet length, and R the ion radius, $V_{surf} = 4\pi R l(r-R)$. The total volume of the jet is $V_{jet} = \pi r^2 l$ and thus the ratio $V_{jet}/V_{surf} = 4R/r$. For R = 5 Å and $r = 3 \,\mu$ m, one obtains a ratio of volume sites vs. surface sites of 1.5×10^3 . For $0.02 \,\mathrm{m}$ But₄NI concentration, the effective number ratio of volume vs. surface ions is ca. 10, which is an enormous effect yielding a segregation factor > 100.



Figure 4.46: Photoemission spectra of But_4NI aqueous solution obtained for different salt concentrations, as labeled. Intensities are normalized to the synchrotron photon flux. The excitation photon energy was $100 \, eV$. For the purpose of comparing relative intensities small spectral shifts have been compensated for (see text).

systems one typically observes several linear, equally spaced segments in the uptake, where each break correlates with the completion of a different layer. Only *one* break is observed in the present experiment since only *one single* monolayer can be formed by the surfactant. This, in a simple picture, reflects the low salt solubility and the fact that once the layer is saturated no additional But_4N^+ can be stabilized at the surface. Moreover, the mere existence of a break in the uptake in Fig. 4.47a confirms that the salt concentration must change significantly just below the overlayer. The almost constant signal for concentrations above $0.02 \text{ m But}_4\text{NI}$ is another corroboration of rather insignificant ion enrichment (second layer) next to the *dipole layer*. In fact, any slight signal increase may be identified with the filling of the still remaining surface sites.

Identifying 0.02 m concentration with the surface monolayer coverage in the present jet experiment would imply that at the point where the synchrotron light intersects the jet (1 mm after the nozzle, which corresponds to 10^{-5} s travel time) a sufficiently large number of bulk solution molecules had diffused to the surface. From Fick's law of diffusion the mean



Figure 4.47: (Top) Increase of the $I^-(4d)$ photoemission signal as a function of the But₄NI concentration (based on peak fitting and integration of spectra in Fig. 4.46). The straight line (no fit) at lower concentrations suggests the successive completion of the surface segregation layer. The break off near 0.02 m concentration characterizes the onset of electron emission through the completed segregation layer. The inset presents a fit to the data using $(1 - e^{-ax})$ where a is a fit parameter. Notice that the fit poorly reproduces the signal intensities in the saturation regime as it does not account for the varying information depth. (Bottom) Analogue analysis and plot for the liquid-water signal (2a₁) decrease.

distance L over which an ion travels through a liquid medium can be expressed as [46]:

$$L = \sqrt{4Dt} \,, \tag{4.15}$$

where D is the diffusion constant and t is the time. For $D = 0.52 \times 10^{-5} \text{ cm}^2/\text{s}$ and $t = 10^{-5} \text{ s}$ one obtains a diffusion length of ca. 140 nm, which corresponds to about 450 monolayers of water. Hence, only molecules within a 140 nm thick outer shell are able to diffuse to the surface. Clearly, diffusion from deeper locations would be possible if the experiment was performed at a distance farther than 1 mm downstream from the nozzle. For the present experimental conditions one can estimate that indeed at a concentration of about 0.02 m But₄NI sufficient salt molecules exist in the outer layer of the jet. Hence, the travelling time of the jet and the diffusion constant just match in a way to allow for the formation of a full But₄NI surface monolayer.¹⁴ One may consider this result to also support the interpretation of the data in Fig. 4.47a in terms of linear segments, but still, this is not fully conclusive. For that reason the inset in Fig. 4.47a presents a fit, which models the formation of the segregation layer up to saturation. Here the build up is assumed to be proportional to $(1 - e^{-ax})$, where a is a fit parameter representing the concentration with respect to the saturation concentration. Even though the experimental data can be fit reasonably well, the simple model cannot account for any effect of the photoelectron information depth, which inherently leads to relative signal attenuation. In fact the linear segments fit the data better, particularly in the saturation regime.

Qualitatively similar information can be inferred by analyzing the attenuation of the water signal for increasing But₄NI coverage. The corresponding plot is presented in Fig. 4.47b for the $2a_1$ water orbital. As before, data points represent integrals based on Gaussian peak fitting on a constant background. Also the water attenuation behavior can be interpreted to reflect the completion of the segregation surface layer near 0.02 m concentration. This is suggested by the straight lines (no fit). Notice that the values in the case of water are not as accurate as for the iodide signal presented in the top figure. Clearly the latter signal is the more reliable probe in the present experiments due to the intense I⁻(4d) doublet peak on a smooth background.

¹⁴Consider an outer shell volume V of the liquid jet (thickness 140 nm) which contains $N = cN_A V$ molecules. The volume of these N molecules is $V_{molec} = \frac{4\pi R^3}{3}N$. Equating V_{molec} with the surface volume (volume of one surface monolayer), $V_{surf} = 4\pi R l(r - R)$, one calculates the concentration being $c = 3r/\pi N_A R^2 L(2r - L)$. With the Avogadro number $N_A = 6.02 \times 10^{23} \text{mol}^{-1}$, the ion radius R = 0.5 nm, the jet radius $r = 3 \,\mu$ m, and the diffusion length L = 140 nm one obtains a concentration of 0.023 mol/kg.

The water signal attenuation is related to the solute layer thickness d and the electron mean free path λ_e by the following expression [40]:

$$I_{ad} = I_0 \exp(-\frac{d}{\lambda_e}).$$
(4.16)

Here I_0 and I_{ad} denote the photoemission intensity of the uncovered (pure) water and the salt-covered water, respectively. Hence, assuming $\lambda_e = 3 - 4 \text{ nm}$ for 90 eV electrons¹⁵ (see Fig. 3.4) equation 4.16 may be used to cross-check the segregation layer thickness. According to Fig. 4.47b, at 0.02 m But₄NI concentration, the water signal is being reduced by about 32 % with respect to its intensity for pure water. Then equation 4.16 yields d = 1.2 nm which is close to the expected value of 1.0 nm [123].

Regarding the iodide intensities it is interesting to compare the data for NaI (Fig. 4.42) and for But_4NI (Fig. 4.47) aqueous solutions. Since the concentrations used for these two situations were very different, Fig. 4.48 presents the $I^{-}(4d)$ intensities for both experiments vs. the logarithm of the concentration. Relative intensities were inferred from the previous spectra, and the $I^{-}(4d)$ intensity for the saturated But₄NI solution has been set to unity. For the highest NaI concentration, 12 m, the iodide signal is about a factor of 4 larger than for the But₄NI solution at saturation coverage, which at a first glance may be a surprise. The main reason for this intensity ratio is the size of the corresponding ions. As depicted in the simple cartoon in Fig. 4.48, at the surface, assuming close packing and neglecting solvation shells, the ratio of But_4NI surface sites vs. NaI surface sites is about 1:2.3. This corresponds to the ratio of the respective ion radii, 5 Å vs. 2.2 Å [10,88]. Radii in the cartoons (Fig. 4.48) are drawn to scale. Notice that the point at which the $I^{-}(4d)$ signal from NaI solution gets near 2.5 times the intensity of $I^{-}(4d)$ from saturated But₄NI just corresponds to the concentration at which the $I^{-}(4d)$ begins deviating from the linear increase (Fig. 4.48). This might well corroborate the earlier interpretation of maximum accommodation of solvated ions near the surface. The signal increase beyond a factor of 2.5 must be attributed to the emission contributions from deeper layers. As depicted in the cartoons of Fig. 4.48 contributions from deeper layers in the But₄NI case are negligible because of the low concentration of But_4N^+ and I^- ions everywhere in the bulk. Notice that the electron mean free path is, however, larger than the segregation layer thickness. Hence, in the case of NaI solution, where the ions are homogeneously dispersed throughout the bulk solution, $I^{-}(4d)$ photoelectrons can also

¹⁵Notice that this time (compare page 60 for water) the thickness of one monolayer corresponds to ca. 1 nm, which is the size of the But₄N⁺ ion. In Ref. [123] λ_e was found to be ca. 2.5 nm, which is somewhat smaller than the value assumed here.



Figure 4.48: Comparison of the relative $I^-(4d)$ emission intensity obtained for But₄NI and NaI aqueous solutions as a function of the respective salt concentrations. The concentration is presented on a logarithmic scale since very different concentrations are required to obtain either identical photoemission signal intensity or saturation concentration (compare Figs. 4.42 and 4.47). Notice, that about the 80 times higher NaI salt concentration corresponds to the But₄NI maximum signal (for saturation coverage). The cartoons illustrate the different structural character of the near surface region of the two solutions. For But₄NI, near saturation, the large anion-cation 'pairs' form the segregation layer while the bulk concentration is comparably low. I.e., within the range of detection, the maximum electron mean free path λ_e (as indicated), signal contribution from any deeper layers is negligible. In contrary, for NaI solutions the ions are almost homogeneously dispersed, and photoemission signal from deeper layers will considerably contribute to the total signal, which is about 4 times larger (for saturation) as compared to But₄NI. Large, medium and small circles represent But₄N⁺, I^- and Na⁺ ions. The ion radii are 5 Å, 2.2 Å and 1 Å for But₄N⁺, I^- and Na⁺, respectively. In this simple cartoon no solvation shells were taken into account.

contribute from larger distances. In fact assuming a layer thickness d = 4.4 Å (which is the I⁻ diameter), and using equation 4.16 one calculates that the measured total I⁻(4d) signal is effectively generated by photoelectrons originating from within the first 3-4 layers.¹⁶ This

¹⁶From Fig. 4.48 maximum signal for the But₄N⁺ monolayer is 1. For the I^- ion being two times smaller, the corresponding signal would be $I_0 = 2$. Accounting for contributions originating from deeper layers, the



Figure 4.49: Full-range photoemission spectra, including the cutoff region, from aqueous But_4NI obtained for different concentrations (selection from Fig. 4.46). Spectra are displayed as measured, i.e. the indicated peak shifts correspond to true apparent binding energy differences (see text). Notice that all spectra are characterized by the identical cutoff (compare Fig. 4.50). The initial shift of the liquid main features to nominally higher binding energies (for the lowest concentration) is considered an experimental artifact. The successive energy shifts to lower binding energy for higher concentrations is largely assigned to a change of the solution work function due to an increasing molecular surface dipole density.

is a reasonable value for $50 \,\mathrm{eV}$ electrons (see Fig. 3.4).

The other important result obtained from the segregated But₄NI is the spectral energy shift shown in Fig. 4.49. The figure displays a selection of photoemission spectra (from Fig. 4.46) as measured, i.e. without any energy offset, but including the low kinetic energy cutoff region. One observes that all distinct liquid features of a given spectrum are *uniformly* shifted for different concentrations as indicated by vertical lines. The $1b_{1g}$ water gas-phase peak also shifts, however, by a smaller amount. Rigid shifts can be attributed to work function changes, $\Delta \Phi_{dipole}$, associated with the molecular surface dipoles within the electric double layer. In the present experiment, however, additional effects have to be accounted

maximum signal can be expressed by the following sum: $I = I_0 + I_0 exp(-\frac{2d}{\lambda}) + I_0 exp(-\frac{3d}{\lambda})$. Then, for d = 4.4 Å and a mean free path $\lambda \simeq 30$ Å, one obtains I = 4.7, which is somewhat larger than the actual value of 3.8 in Fig. 4.48.

Concentration	Measured peak positions [eV]			
[mol/kg]	$1b_1$ (liq)	$I^-(4d)$	$I^{-}(5p)$ [125]	$I^{-}(4d) - 1b_1$ (liq)
0	11.28(4)			
0.005	11.67(5)	54.25(3)	6.60	42.58(8)
0.015	11.06(5)	53.72(3)	6.30	42.66(8)
0.025	10.88(4)	53.41(3)	6.20	42.53(7)
0.030	10.83(4)	53.37(3)	6.24	42.54(7)
0.040	10.78(4)	53.28(3)	6.20	42.53(7)

Table 4.14: Experimental peak positions (apparent electron binding energies), with respect to the water $1b_{1g}$ orbital (12.6 eV), for But₄NI aqueous solutions as a function of the salt concentration. The right column is the energy difference between the $I^-(4d)$ and the $1b_1$ (liquid) peak position. This value is almost constant, which rules out any true electron binding energy shifts (for instance due to relative dehydration).

for since liquid and gas-phase features shifts are not identical. These extra potentials are artifacts caused by salt adsorption on the surface of the analyzer skimmer. Distinguishing the effect quantitatively from the actual surface potential shift is difficult and further experiments need to be performed. Here this artifact will not be considered in further detail. Notice that also the large energy shift towards nominally higher binding energies with respect to the liquid water features, for the lowest But_4NI concentration, is considered an artifact. A rough estimation of the surface dipole contribution to the shift may be obtained by considering the peak shifts with respect to the water $1b_{1g}$ gas-phase binding energy. In paragraph 4.1.1 this energy was shown to be a well-defined external reference, which may be not necessarily true in the presence of extra potentials. Table 4.14 presents apparent binding energy shifts of the water $1b_1$ (liquid), $I^-(4d)$, and $I^-(5p)$ [125] orbitals inferred by fixing the respective water $1b_{1g}$ gas-phase feature at 12.6 eV. The table also includes the energy spacing between I⁻(4d) and $1b_1$ (liquid) peaks. The fact that this spacing (or any other between liquid features) is independent of the concentration implies that no differential binding energy changes occur for the liquid features. This conclusion contradicts a previous report [125], which attributes the observed spectral shifts to dehydration effects of surface iodide, but entirely neglects surface dipole effects. Obviously this discrepancy arises from the fact that the study in Ref. [125] reports mere threshold energies, and is lacking a well-defined reference energy, evidently leading to a misinterpretation of the data.

This aspect will be considered in further detail by discussing the spectral cutoff, which



Figure 4.50: a) Schematic energy level diagram illustrating the origin of the observed (rigid) spectral energy shifts for the But₄NI solution. In the absence of surface dipoles (pure water; Fig. 4.44 left) the measured electron kinetic energy, E_{kin} , is given by $E_{kin} = h\nu - BE - \Phi$, where $h\nu$ is the excitation photon energy, BE is the electron binding energy, and Φ denotes the work function. The presence of surface dipoles (direction as shown in Fig. 4.44b; right) causes a decrease of the work function, $\Delta \Phi_{dipole}$, which for level alignment with respect to the vacuum level, leads to a larger maximum kinetic energy measured in the photoemission spectra. This is accompanied by a larger width of the entire spectrum (as experimentally observed; see Fig. 4.49). Full and open circles denote electrons and holes, respectively. b) Cartoon of the location and the orientation of the But₄N⁺I⁻ molecular surface dipole.

is inherently related to the sample work function. Apparently, for the liquid jet the orbital energies are pinned to the vacuum level. (Only) in this case a change of the liquid-sample work function would result in an increase/decrease of the measured maximum kinetic energy of the photoelectrons, which is accompanied by a decrease/increase of the width of the photoemission spectrum by $\Delta E = h\nu - \Delta \Phi_{\text{dipole}}$. Notice that for alignment at the Fermi



Figure 4.51: Experimental $I^-(4d)$ and $1b_1$ (liquid) relative peak shifts, with respect to the water $1b_{1g}$ orbital (12.6 eV) observed for But₄NI aqueous solutions of different concentrations. The decrease of the energy shifts is assumed to largely reflect work function changes of the solution due to an increasing number of surface dipoles. Almost identical shifts are observed for different liquid features implying negligible differential electron binding energy effects.

energy (as is typically the case for adsorbate systems) any work function change would result in a shift of the cutoff energy (which is not the case here). The present spectra (Fig. 4.49) exhibit identical cutoff energies; only the width and hence the maximum kinetic energy of the photoelectrons varies. This situation is sketched in the energy level diagram in Fig. 4.50, where $h\nu$ denotes the excitation photon energy and Φ is the work function (or ionization potential) of the liquid. A decrease of the work function, i.e. negative $\Delta \Phi_{dipole}$, is associated with a dipole layer with negative charge in the liquid substrate and positive charge on the surface. Hence, an emitted electron is being accelerated within this dipole field, leading to a larger kinetic energy. The orientation of the dipole would be consistent with the hydrophobic But₄N⁺ cation located at the very surface and the anions being accommodated within a second layer (together forming the electric double layer). This is the commonly assumed structure of the But₄N⁺I⁻ segregation layer [123, 124].

I conclude with a comment on the evolution of spectral shifts (due to work function changes) as a function of the salt concentration and by also estimating the expected work function changes based on But₄NI surface dipole density. From the graphical presentation of the energy shifts shown in Fig. 4.51 (as derived from Table 4.14) it can be seen that the work function strongly decreases from 0.005 to 0.025 m But₄NI concentration. This behavior is consistent with an increasing surface dipole density, and there seems to be no obvious indication for dipole orientation changes until the monolayer is completed. For higher concentrations additional dipole-dipole interactions associated with denser surface packing may be responsible for the slight peak shifts observed for > 0.025 m concentration. With the total number of surface But₄N⁺ being ca. 1.3×10^{14} cm⁻² [123] and the dipole moment of But₄NI being m = 13 D¹⁷ using [61]:

$$\Delta \Phi_{\rm dipole} = \frac{enm}{\epsilon_r \epsilon_0} \,, \tag{4.17}$$

one obtains a work function change of about 1 eV and 5 eV for 0.005 and 0.025 m But₄NI, respectively. In equation 4.17, m denotes the dipole moment ¹⁸, and n is the surface density of segregated dipoles. ϵ_r has been assumed unity in order to account for the liquid/vacuum interface, see footnote page 50. The poor agreement with the experimental values is probably not only due to the crude value for the But₄NI dipole moment. Further experiments are required to determine the energy shifts more accurately.

In summary, the observed spectral rigid shifts indicate the importance of work function changes $\Delta \Phi_{dipole}$ rather than dehydration effects in But₄NI aqueous solutions. Quantifying $\Delta \Phi_{dipole}$ in the present experiment was complicated due to the presence of extra potentials. In order to assess surface dipoles more quantitatively, further experiments are required to better understand the origin of the energy shifts of the photoemission spectra.

¹⁷Determined from density functional formalism (m = 13.2 D) and semi-empirical (AM1) calculations (11.8 D) for the isolated molecule, i.e. not accounting for solvation [131].

¹⁸The dipole is assumed perpendicular to the surface, hence the normal component $m_{\perp} = m$.

4.3.2 Effect of the Alkyl Chain Length: But₄NI vs. Prop₄NI

In the following the effect of a smaller chain length on the surface segregation will be considered. For that reason photoemission experiments were also performed for tetrapropylammoniumiodide, $Prop_4NI$, which has one carbon atom less per chain as compared to But_4NI . The photoemission spectra obtained for several concentrations, using 100 eV photon energy, are displayed in Fig. 4.52. Intensities are normalized to the ring current, and spectral peak positions appear as measured. Rigid shifts of the entire spectrum are observed; they are smaller as compared to the But_4NI case (Fig. 4.49), but they are assumed to be of the same origin. A quantitative analysis of these shifts will not be given since the interpretation of the data would rely on similar considerations mentioned for But_4NI aqueous solutions. For comparison only the evolution of the iodide $I^-(4d)$ photoemission intensity as a function of the Prop₄NI concentration is shown in Fig. 4.53.



Figure 4.52: Photoemission spectra of $Prop_4NI$ aqueous solutions obtained for different salt concentrations, as labeled. Intensities are normalized to the synchrotron photon flux. The excitation photon energy was 100 eV.

The behavior considerably differs from that observed for But_4NI . In Fig. 4.53 no sudden saturation is found, hence $Prop_4N^+$ ions are not as spatially confined at the surface as But_4N^+ . This reflects the reduced surface activity of the molecule having the shorter chains,



Figure 4.53: $I^-(4d)$ signal increase as a function of the Prop₄NI concentration (based on peak fitting and integration of spectra in Fig. 4.52).

which in turn allows the ions to more evenly spread into the bulk liquid. This also implies a reduced surface density, and thus the (net) surface dipole is smaller than for the But_4NI case, which explains the above mentioned smaller energy shifts.

4.3.3 Anion Exchange at Surface

In addition to studying the But₄NI concentration dependence, the effect of co-ions on the segregation layer was investigated. The main objective was to investigate to what extent the large surface I⁻ anion would exchange with the smaller Br⁻ anion. Specifically, photoemission spectra were measured for $0.02 \text{ m But}_4\text{NI}$ aqueous solution dissolved in 1.0 m XBr (X = Na, K, Cs) aqueous solution. The former concentration just warrants a complete overlayer, as described in the previous section, while the latter concentration was chosen as it provides reasonably intense solute photoemission signal of these non surface-active alkali-halide salts. Results are shown in Figs. 4.54, 4.55, and 4.56 for 100 eV photons. In each figure the top and the center panels display the spectra for $0.02 \text{ m But}_4\text{NI}$ in both aqueous solution and in 1.0 m XBr solution, respectively. The bottom panels present the spectrum of the respective 1.0 m



Figure 4.54: Photoemission spectra of 1 m NaBr (bottom), $0.02 \text{ m But}_4\text{NI} @ 1 \text{ m NaBr}$ (center) and $0.02 \text{ m But}_4\text{NI}$ (top) aqueous solutions. Excitation energy was 100 eV. For the mixed solution the $I^-(4d)$ signal can be seen to decrease while the $Br^-(3d)$ signal increases relative to the NaBr solution.

XBr substrate solution. Intensities were normalized to the photon flux. Each set of data has been acquired within two subsequent ring fillings (injections) as alignment variations during the experiment must be avoided if one attempts to determine differences in absolute signal intensity.

Photoemission peaks are labeled according to the spectra presented in section 4.2.2. The larger intensity of the water features in the bottom spectra of each figure is due to the larger absolute emission from water in the absence of a salt overlayer (compare Figs. 4.46 and 4.47b). For the same reason is the alkali-cation intensity lower for the mixed solution.

The most noticeable result from Figs. 4.54, 4.55, and 4.56 is the decrease of the I⁻(4d) signal which is accompanied by an increase of the bromide co-anion signal, Br⁻(3d). Numbers in the figure indicate the absolute intensity increases and decreases with respect to the monosalt solutions. The effect is seen to weakly, but not systematically, depend on the size of the co-cation. Such intensity variations must be due to an anion exchange, as illustrated in the cartoon on Fig. 4.58. The replacement of surface iodide by bulk bromide may surprise since But₄NI is known to be more surface-active than But₄NBr [123, 126]. Considering, however,



Figure 4.55: Photoemission spectra of 1 m KBr (bottom), $0.02 \text{ m But}_4\text{NI} @ 1 \text{ m KBr}$ (center) and $0.02 \text{ m But}_4\text{NI}$ (top) aqueous solutions. Excitation energy was 100 eV. For the mixed solution the $I^-(4d)$ signal can be seen to decrease while the $Br^-(3d)$ signal increases relative to the KBr solution.

the large bromide ion excess (1.0 m XBr vs. $0.02 \text{ m But}_4\text{NI}$), the results show in fact a strong reluctance of the larger iodide ion for bulk-bromide exchange. I.e., the ca. 60% effect observed here simply reflects the probability of a relatively low number of bromine ions to diffuse to the surface. Since the present experiment barely detects But_4N^+ , one cannot rule out salt *concentration* changes at the surface of the mixed solution, which would contrast the simple replacement of an iodide anion near its But_4N^+ cation by a bromide anion. On the other hand, the surface activity for But_4NI is larger than for But_4NBr [123, 126]. Thus an increase of the But_4N^+ surface concentration would seem unlikely.

The comparison of data for different X in XBr shows that the exchange does depend on the counter cation. For instance in $But_4NI/CsBr$ solution, the relative iodide signal decrease and the bromide increase are by the same amount, 70 %. In $But_4NI/NaBr$ and But_4NI/KBr , the corresponding ratio is 1:1.7 and 1:1.3, respectively, suggesting some additional mechanism to be effective. The attenuation of the co-cation signal is by about 40-60% for NaBr and CsBr *substrate* solutions. The smaller value for KBr, 15%, correlates with a larger error of this number due to the small signal.



Figure 4.56: Photoemission spectra of 1 m CsBr (bottom), $0.02 \text{ m But}_4\text{NI} @ 1 \text{ m CsBr}$ (center) and $0.02 \text{ m But}_4\text{NI}$ (top) aqueous solutions. Excitation energy was 100 eV. For the mixed solution the $I^-(4d)$ signal can be seen to decrease while the $Br^-(3d)$ signal increases relative to the CsBr solution.

The reason for these latter observations is unclear, and I like to conclude with the following quote: "Qualitatively, the tendency of an anion to segregate towards the surface will be a competition between the solvation forces and the ion pairing tendency at the surface. It is not obvious which of these factors will be dominant in a given case" [122]. A detailed discussion of structural details in terms of different coexisting ion pair situations is presented in Ref. [122]. The classical treatment of electron-solution interfaces, where the electric double layer is considered as being composed of a closely bound inner and outer Helmholtz layer as well as the diffuse Gouy-Chapman layer, can be found in Refs. [10, 16, 46].

Finally, Fig. 4.57 presents the result on the ion exchange for the less hydrophobic $Prop_4NI$ in 1.0 m NaBr aqueous solution. Due to the higher solubility of $Prop_4NI$ and its lower surface activity, 0.14 m $Prop_4NI$ solution could be used (as compared to 0.02m But_4NI). The percentage of surface iodide that exchange with bulk bromide is reduced to about 30% instead of ca. 60% in the case of But_4NI . This again is consistent with the segregation layer being dispersed into the bulk solution. The smaller concentration gradient also reduces any need for diffusion to the surface.



Figure 4.57: Photoemission spectra of 1 m NaBr (bottom), 0.14 m Prop₄NI @ 1 m NaBr (center) and 0.14 m Prop₄NI (top) aqueous solutions. Excitation energy was 100 eV. For the mixed solution the $I^{-}(4d)$ signal can be seen to decrease while the Br⁻(3d) signal increases relative to the NaBr solution.

In conclusion, the present results show that photoelectron spectroscopy can be used to study the exchange of surface iodide by bulk excess bromide ions. As expected this is not a favorable process as But_4NY surface segregation is increased for the larger counter anion. Furthermore, the strong alkali ion emission intensity from bulk solvation is a confirmation that the probing depth in the present experiments clearly exceeds one monolayer of But_4N^+ . This is important information regarding the interpretation of ion signal as a function of salt concentration discussed in sections 4.2.6 and 4.3.1.



Figure 4.58: Cartoon depicting the exchange of the I^- anion, paired with the surface But_4N^+ cations, with Br^- anions in the bulk solution. Circles represent ion radii to scale: $5 \text{ Å } (But_4N^+)$, $2.2 \text{ Å } (I^-)$, $1.96 \text{ Å } (Br^-)$, and $0.96 \text{ Å } (Na^+)$ [10].