Photoelectron spectroscopy of liquid water and aqueous solution:  
Electron effective attenuation lengths and emission-angle  
anisotropy

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Abstract

Photoelectron (PE) spectroscopy measurements from liquid water and from a 4m NaI aqueous solution are performed using a liquid microjet in combination with soft X-ray synchrotron radiation. From the oxygen 1s PE signal intensity from liquid water, measured as a function of photon energy (up to 1500 eV), we quantitatively determine relative electron inelastic effective attenuation lengths (EAL) for (photo)electron kinetic energies in the 70-900 eV range. In order to determine the absolute electron escape depths a calibration point is needed, which is not directly accessible by experiment. This information can instead be indirectly derived by comparing PE experiments and molecular dynamics (MD) simulations of an aqueous solution interface where density profiles of water, anions, and cations are distinctively different. We have chosen sodium iodide in water because iodide has a considerable propensity for the solution surface, whereas the sodium cation is repelled from the surface. By measuring the intensities of photoelectrons emitted from different orbitals of different symmetries from each aqueous ion we also evaluate whether gas-phase ionization cross-sections and asymmetry parameters can describe the photoemission from ions at and near the aqueous solution/vapor interface. We show that gas-phase data reproduce surprisingly well the experimental observations for hydrated ions as long as the photon energy is sufficiently far above the ionization threshold. Electrons detected at the higher photon energies originate predominantly from deeper layers, suggesting that bulk-solution electron elastic scattering is relatively weak.
1 Introduction

It is empirically well known that electrons emitted from condensed matter show an approximately exponential attenuation of the electron intensity as function of the depth from the surface, at which the electrons are created.\(^1\) The electron inelastic mean free path (IMFP) is defined as the length of the path an electron beam has traveled in a material after which the initial electron signal has decreased by 1/e (see Figure 1a). For most materials IMFPs show a qualitatively very similar dependence on electron kinetic energy (eKE), characterized by a minimum of about 5-10 Å in the 50-100 eV eKE range, with a steep increase towards the low energy side, and a steady but slower increase for higher eKEs: \(~20\) Å at 1000 eV and \(~30\) Å at 2000 eV\(^2\). In textbooks this behavior is sometimes referred to as the universal IMFP curve, or the master curve,\(^3\)\(^-\)\(^5\) presenting an average of measurements over many different materials. Material dependence is, however, significant and IMFP values vary by more than a factor of two. A concise update of the quantitative low-energy electron range, 50 eV to 2000 eV, relevant for typical X-ray photoelectron surface probing techniques in solid-state matter was given by Pianetta.\(^2\) Comprehensive IMFP data for routine solid state X-ray photo and Auger electron spectroscopy are available on the NIST database.\(^6\) The IMFP function for liquid water and aqueous solutions has not yet been determined experimentally, and it is the purpose of the present work to review this issue.

Knowledge of IMFP and electron stopping power for water is crucial for a diversity of application areas, e.g., optimizing individual patient dose planning in cancer radiotherapy, estimating radical formation in quantitative radiation chemistry, and controlling and limiting radiation damage due to secondary electrons in electron microscopy and X-ray microscopy. In the context of (photo- and Auger-) electron spectroscopy on liquid surfaces, knowledge of the IMFP curve for water is crucial for the experimental determination of solute density profiles at the aqueous solution interface. The exact knowledge of the interfacial element composition is for instance of large interest to the atmospheric community, in order to better understand the complex chemistry/photochemistry at the liquid-vapor interface of sea salt aerosols.\(^7\)\(^,\)\(^8\) With the above mentioned IMFP ranges (from a few to tens of molecular layers) photoelectron spectroscopy in conjunction with tunable X-ray radiation from a synchrotron source, allowing the photoelectron eKE to be varied over a wide energy range, is ideally suited to measure relative concentrations of solution components as a function of depth. Yet, such experimental data will remain qualitative as long as the IMFP(eKE) curve is unknown.
Considerable computational effort has been devoted to model electron inelastic scattering in water, based on the theory of dielectric response functions.\textsuperscript{9,10} Experimental determination of IMFP for water is yet a great challenge for researchers, and the present work presents a first attempt.

What makes the experimental determination of IMFP in liquid water so problematic? One reason is the difficulty to directly measure IMFP as this would require an exact understanding of elastic and inelastic scattering processes along the electron trajectory. Experiments can easier access the effective electron attenuation length (EAL), which is the (shortest) distance from a starting point $A$ to an arrival point $B$, at which the initial electron signal is reduced to $1/e$.\textsuperscript{11} As sketched in the left panel of Figure 1, the IMFP can be significantly larger than EAL if elastic scattering is efficient in the medium. But in the case of weak elastic scattering IMFP and EAL are almost identical, as depicted in the right panel of Figure 1. Obviously experimental distinction between inelastic and elastic scattering contributions to the total signal attenuation is currently impossible. Numerical values for EAL of up to 30% lower than IMFP have been reported from statistical path length simulation models.\textsuperscript{11} Clearly, for many practical purposes knowledge of EAL would be fully sufficient.

There are several methods to study electron attenuation lengths in solids. The most common is perhaps the overlayer technique, where a well-defined thin film of the material under investigation is deposited onto a crystalline substrate in ultrahigh vacuum.\textsuperscript{12} The thin-film/substrate system is then irradiated by UV/X-ray radiation and the attenuated signal of the photo/Auger electrons originating from the substrate, and traveling across the overlayer film, is monitored as a function of film thickness. This yields the EAL at the kinetic energy of the photo/Auger electrons originating from the substrate. Alternatively, EALs can be measured by electron backscattering with energy analysis of the reflected electrons. This is currently becoming the primary standard method for electron range measurements, because it works on plane surfaces of the bulk substance of interest, and does not require the manufacturing of well defined overlayer steps on an Ångström thickness scale. Its application to the aqueous phase has not yet been demonstrated. The overlayer approach for determination of EAL is clearly not applicable for highly volatile liquids, such as water, because aqueous-phase films of a given thickness would be impossible to make and to maintain under vacuum; it is not even clear how to define thickness under those conditions. Furthermore, simply the application of PE spectroscopy, i.e., the measurement of eKEs from photoelectrons emitted
from liquid water has only recently become possible by the liquid microjet-technique.\textsuperscript{13-16} Subsequent alternative methods use droplet trains or supported droplets.\textsuperscript{17}

In the present liquid-jet PE study we pursue the idea that the H$_2$O$_{aq}$ O1s photoemission intensity, measured as function of photon excitation energy, yields the EAL curve for liquid water and aqueous solution experimentally. Here, interpretation of the experimental data is quite complicated, and requires a thorough consideration of the processes leading to the emission of an electron. Our procedure is illustrated in Figure 2. Figure 2a shows the qualitative interfacial density profile of liquid water, exhibiting a monotonously increasing density of H$_2$O molecules with distance $z$ from the surface, eventually reaching the bulk density value. Figures 2b and 2c present the corresponding qualitative ‘ideal’ (2b) and ‘realistic’ (2d) PE signal emission and attenuation functions. The functions describe how many photoelectrons, originating at depth $z$, will reach the electron spectrometer; variations in the photoionization cross section as well as electron losses due to inelastic scattering are taken into account. The total PE signal is the emission and attenuation function multiplied by the density, and integrated over $z$. For Figure 2b we have assumed that the (unknown) exponential attenuation length factor can be altered without any change of the photoionization cross section. In a real PE experiment, however, variation of EAL inevitably requires variation of the excitation photon energy in order to adjust the KE of the photoelectrons. Short EAL is achieved by producing photoelectrons with kinetic energies approximately in the 50-200 eV range. This implies that photon energies are not too far above threshold, and ionization cross sections are relatively high, and consequently PE signals are strong despite the small probe volume. Signal intensity may be even higher than for the larger EALs – achieved through higher eKEs – because of the corresponding smaller photoionization cross sections. The two situations are contrasted in Figures 2c and 2e. Obviously, if the cross sections were known or could be reasonably well approximated, relative EAL values can be extracted. The measurements do not provide an absolute length scale of the EAL, though, and an independent calibration procedure is needed.

One way to calibrate the experimental relative EAL curve for water is through the comparison with PE data from an aqueous solution, one that is known, ideally from both MD calculations and from experiment to exhibit strong $z$-dependent ion density variations.\textsuperscript{18,19} NaI solution is an ideal choice for our purpose because the large and polarizable iodide anion can exist right at the surface, whereas the maximum of the sodium ion distribution lies about 4 Å
away from the solution surface. The situation is qualitatively depicted in Figure 3a. Figure 3b illustrates how the depth over which the signal in a PE spectroscopy experiment is actually sampled depends on the EAL (compare also with Figures 2b, d). For short enough EAL values the spatially separated density profiles of anions and cations should then be resolvable in a PE spectroscopy experiment, leading to non-stoichiometric anion-to-cation signal ratios (>1), with the exact values depending on EAL (which in turn depends on eKE); see Figure 3(c). Figure 3(c) assumes ideal PE emission, i.e., identical cross sections for ionizing the anion and cation with identical outgoing eKE. By comparing properly cross-section-corrected experimental intensity ratios – what we will call anion-to-cation PE ratios – as function of electron kinetic energy with a ‘theoretical PE experiment’ calculated from the MD simulated density profiles as function of EAL, absolute probing depths can be assigned for each eKE.

There is yet another hurdle to the experimental extraction of solute density profiles as a function of eKE, connected with the photoemission process itself. In addition to the total photoionization cross section it is important to understand how the angular distribution of outgoing photoelectrons depends on depth of their creation. One would expect elastic scattering (see Figure 1) of electrons originating in the bulk to reduce the angular anisotropy compared to the isolated ion. At the interface, although there is less scattering, one can no longer assume an isotropic distribution of hydration environments surrounding the ions. So, although one might have originally anticipated this problem to be removed if the measurements were to be performed at the magic angle, the loss of isotropy in the sample orientation means that the magic angle condition can no longer be assumed to hold. To our knowledge the issue of photoelectron angular distributions emerging from either a solute ion in the bulk or near the surface layer has not been previously considered, and even in rare-gas and water clusters these problems have only recently received attention. In the gas phase, the anisotropy of the electron angular distribution reflects the symmetry of the orbital from which the electrons were ejected. Here, we seek to shed some light on the issue by comparing the PE signals obtained from two different orbitals – of different symmetry – for each solute ion. If detection is made at an angle different from the magic angle, one can examine whether anisotropy parameters from gas-phase provide for a good description of the observed relative photoemission intensities from the aqueous ions. If so, the anion-to-cation PE ratios recovered from experiment – derived from ionizing the different orbitals – should be the same.
2 Methods

2.1 Experimental

The photoemission studies of liquid water and of 4m NaI aqueous solution were performed at the U41 PGM undulator beamline of BESSY (Berlin), using a 15 µm liquid jet with a velocity of 120 m/s (at 4°C). These conditions allow photoelectrons from the liquid phase to travel a sufficiently long distance (about 0.6 mm) without collisions with gas-phase water molecules to reach the electron analyzer. A schematic illustration of the experimental setup, depicting the liquid jet entering the experimental chamber is presented in Figure 4. Details of the technique and of the experimental setup have been described elsewhere.\textsuperscript{14-16} For the present experiments excitation is carried out with the synchrotron light polarization vector parallel to the flow of the liquid jet. The mean electron detection angle was about $\Theta_{\text{mean}} = 80^\circ$, i.e., nearly normal to the polarization vector. In order to realize this angle in the present experiments a 200 µm size entrance orifice to the electron spectrometer has been used, instead of 50 µm as in our previous liquid PE studies.\textsuperscript{15,16} In addition, the distance from the liquid jet to the spectrometer entrance was reduced to approximately 0.6 mm for matching the geometrical collimation of the entrance aperture to the large internal aperture angle of the spectrometer electron optics. The 15 µm liquid jet was positioned slightly off the central spectrometer axis. The present measurements are performed away from the magic angle, and aim at explicitly picking up angular effects at the liquid interface.

The small focal size (23x12µm$^2$) at the U41 PGM beamline, providing photon energies in the 180-1600 eV range, allows for good matching spatial overlap between the synchrotron-light beam and the liquid jet. At typical jet operation conditions the pressure in the interaction chamber is in the upper 10^{-5} mbar range. The total experimental resolution was better than 250 meV. Highly demineralized water was used to prepare the solutions, and sodium iodide salt was of highest purity commercially available (>99.9%, Sigma-Aldrich).

2.2 Molecular dynamics calculations

Molecular dynamics simulations of ~4m NaI aqueous solution were performed in the slab geometry. Polarizable potentials were employed both for water (POL3)\textsuperscript{24} and for the dissolved sodium and iodide ions.\textsuperscript{18,25} Simulations were run at 300 K for 2 ns after 1 ns of
equilibration with a 1 fs time step. Water OH bonds were constrained using the SHAKE algorithm.\textsuperscript{26} The induced electric field was converged in each step using a self-consistent procedure.

A slab of 864 water molecules was used to construct each system, adding 64 sodium cations and 64 iodide anions. Such a unit cell was placed into a $30 \times 30 \times 100 \, \text{Å}^3$ rectangular box, and periodic boundary conditions were applied to yield an infinite slab with two water/vapor interfaces. The smooth particle mesh Ewald method\textsuperscript{27} was used to calculate the long-range electrostatic energies and forces, and the van der Waals interactions and the real space part of the Ewald sum were truncated at 12 Å. The AMBER 7 program package was employed for the simulations.\textsuperscript{28}

3 Relation between electron attenuation lengths and PE signal intensity in a single-component system

In the following we discuss how PE signal intensity variations as function of electron kinetic energy for a single-component system can be used to extract relative EAL values. Once we are equipped with the necessary theoretical formalism, we attempt to derive the EAL(eKE) curve for pure water, based on O1s PE measurements.

Photoemission signals can be expressed as the integral over the density functions, $\rho_A(z)$, associated with each atomic or molecular species, exponentially attenuated with the effective attenuation length EAL for a given eKE, i.e., it is the Laplace transform of the density functions in the variable EAL\textsuperscript{-1}. Thereby it is implicitly assumed that the number of photons is constant (light absorption is negligible) within the sample volume contributing to the PE signal. Since the electron attenuation length, to a good approximation, is inversely proportional to the integrated particle density, from an emission depth z to 0 (at which all density functions have dropped to 0) the total recorded photoelectron signal $I$ from a species A, can be expressed as

$$I = \alpha F \sigma T \int_0^\infty \rho_A(z) \cdot \exp \left( -\frac{1}{\text{EAL}_{\text{jet}}} \int_0^z \frac{\rho_{\text{tot}}(y)}{\rho_0} \, dy \right) \, dz$$

(1)
where \( \rho_A(z) \) denotes the density profile of a species \( A \) in the illuminated liquid sample. \( \rho_{\text{tot}} \) is the sum of densities of all species, \( \rho_o \) is the total density of all components in the bulk, i.e., \( \rho_{\text{tot}}(\infty) = \rho_o \). \( \sigma \) is the differential photoionization cross-section which also depends on detection angle (see below), \( F \) is the total photon flux and \( \alpha \) is an experimental alignment factor, which is determined by the illuminated area of the sample and the entrance aperture solid angle of the electron analyzer. \( T \) is the transmission function of the electron analyzer. Note that the inner integral of Equation (1) describes the situation of a non-sharp surface, with the water density gradually increasing from zero to its bulk value. In the special case of a sharp interface, placed at \( z = 0 \), the expression in the parentheses of Equation (1) reduces to the more commonly known term \(-z/EAL\).³

Pure water consists of a single molecular species, yielding \( \rho_A(z) = \rho_{\text{tot}}(z) \). With the substitution \( \alpha' = \alpha \rho_o \), Equation (1) simplifies to

\[
I = \alpha' F \sigma T EAL
\]  

(2).

which can be used to determine the EAL because all other factors can be either measured or estimated. As the excitation energy is changed, in order to achieve variation of the electron KE and hence of EAL, we must account for the energy dependence of \( F \), \( \sigma \) and \( T \). \( F \) is monitored in the experiment by reading the current of a calibrated photodiode mounted inside the beamline. \( T \) is an inherent, well-characterized property of the electron analyzer. \( \alpha' \) is a remaining constant of proportionality that is independent of energy, and does not vary during the measurements reported here. The precision to which the EAL is determined in the experiment thus depends primarily on knowledge of the energy dependent cross sections \( \sigma \), which must be used for normalization.

4 Considerations of photodetachment/ionization cross sections and angular photoelectron distributions of negative and positive ions

Let us first consider the well-studied angular distributions of photoelectrons emitted from randomly oriented neutral gas-phase atoms and molecules.²⁹-³¹ In this case, the
probability of finding an electron at a given angle is given by the differential ionization cross section

$$\frac{d\sigma(h\nu)}{d\Omega}(\Theta) = \frac{\sigma(h\nu)}{4\pi} [1 + \beta(h\nu)P_2(\cos \Theta)]$$

(3).

Here, $\Theta$ is the electron emission angle with respect to the polarization vector of the linearly polarized (synchrotron) light, and $P_2$ is the Legendre polynomial of second order. $\beta$ principally reflects the orbital symmetry from which the electron is ejected but also depends on $\text{eKE}$. The solutions of Equation (3) are graphically displayed in Figure 5 for a set of $\beta$ values relevant for this work, and resulting curves are shown for a single quadrant only. Intersections of curves with the arrow mark the experimental mean detection angle of $\Theta_{\text{mean}} = 80^\circ$. $P_2(\cos \Theta_{\text{m}}) = 0$ defines the magic angle, $\Theta_{\text{m}} = 54.7^\circ$.

The analogous electron emission processes for gaseous ions also are described by Equation (3) but there is less experimental data because low achievable ion densities makes systematic studies over an appreciably large photon energy range (i.e., with synchrotron radiation) difficult. For anions in particular, only a few measurements, mostly using laser excitation below 10 eV and thus very near threshold, have, to our knowledge, been reported.\textsuperscript{23,32} The latter point is of considerable concern as the present work employs energies extending from tens to hundreds of electron volts above the ionization/detachment threshold. Moreover a theoretical description of the energy dependent $\sigma$ and $\beta$ for ionization of ions, and particularly the photodetachment from anions is often complicated by many-electron correlation effects, including intra-shell and inter-shell correlations, as well as rearrangement effects.\textsuperscript{33} These effects are difficult to calculate, and there exist only a few theoretical calculations on an advanced level. $\Gamma$ 4d photodetachment cross sections and $\beta$ parameters have been studied theoretically and experimentally, up to 150 eV photon energy, yet the agreement is quite poor (Figure 6 inset).\textsuperscript{34,35} For photon energies well above threshold, where these more subtle effects are expected to play a lesser role, the calculated cross sections of $\Gamma$ 4d and isoelectronic Xe 4d are almost identical, and the same holds for the anisotropy.\textsuperscript{34,35} Because of the lack of data over a wide enough energy range (hundreds of eV required for the current study) and for orbitals other than I 4d, we choose to use the calculated photoionization cross sections of neutral I\textsuperscript{36} and Na\textsuperscript{36} throughout as our starting point. Even though this is a somewhat arbitrary choice, Figure 6 shows that the theoretical cross sections and anisotropy
parameters of neutral I and Na are in fact very similar to Xe (isoelectronic to I) and Ne (isoelectronic to Na$^+$), respectively, when KEs are sufficiently far above threshold.

It is maybe reasonable to expect only small differences in the energy dependence of total ionization cross sections on immersing a given ion into aqueous solution. However, for treatment of angular distributions emerging from the condensed solution phase, the gas-phase data can only be taken as a zero-order model, as elastic scattering in the liquid phase would be expected to smear out the anisotropy of the electrons ejected several layers down into the bulk. For ions closer to the interface the angular distributions of the ejected electrons are even more difficult to predict because of possible effects from asymmetric solvation, and associated specific solvent-solute interactions,$^{23}$ leading to an inevitable breakdown of Equation (3). Regardless of these many uncertainties, our strategy for analyzing PE intensities can be considered the simplest approach. Here, we will test if Equation (3) together with the use of gas-phase cross sections as well as angular anisotropy parameters can consistently describe the observations from aqueous solution. We should point out that calculated atomic gas-phase cross sections were also used in previous PE spectroscopy depth-profiling studies from aqueous solutions.$^{37-39}$ Those measurements were performed at the magic angle, whereas the present experiments are performed at $\Theta_{\text{mean}} = 80^\circ$, i.e., near normal. Only then – since the signal intensity is now explicitly depending on the angular distribution – can we actually test whether Equation (3) is applicable.

5. Results

5.1 Photoelectron spectra

Figure 7 presents O1s PE spectra of liquid water measured at 638 eV. The O1s BE of liquid water is 538.1 eV, resulting in photoelectrons with 100 eV eKE.$^{40}$ Further O1s PE spectra were measured at additional photon energies, between 608 and 1438 eV (compare Table 1 for the photon energies used), which will be used to construct the IMFP curve over the 70-900 eV eKE range.

Figure 8 presents valence PE spectra from a 4m NaI aqueous solution, obtained at 200, 500 and 1000 eV photon energy, respectively. Multiple spectra of this kind were collected at a number of other photon energies covering the desired eKEs mentioned above. All photon
energies applied, and the resulting eKEs are summarized in Table 1. Spectral intensities in Figure 8 are normalized to the doublet peak signal, at 53.8/55.8 eV BEs, which arises from electron emission from I\textsubscript{aq} $^{4d}$. The peak at 35.4 eV BE is due to electron emission from Na\textsuperscript{+}$_{\text{aq}}$ 2p valence-level, and the lower binding-energy region, $< 35$ eV, contains contributions from the water valence orbitals, 2a$_1$, 1b$_2$, 3a$_1$, 1b$_2$.\textsuperscript{14} The small peak at 7.7/8.8 eV arises however from I\textsubscript{aq} $^{5p}$, and another solute contribution from the sodium cation, Na\textsuperscript{+}$_{\text{aq}}$ 2s, is observed at 68 eV BE. Iodide and sodium core-level PE spectra, I\textsubscript{aq} $^{3d}$ and Na\textsuperscript{+}$_{\text{aq}}$ 1s, are shown in Figures 9a and 9b, for 730 and 1177 eV photon energies. The respective BEs are 624.2/635.7 and 1076.9 eV, and the photoelectrons from the two ions have the same eKE of 100 eV.

### 5.2 Molecular dynamics simulations

The simulated density profiles of the iodide and sodium ions, and of water oxygen atoms are presented in Figure 10. To facilitate the comparison of the different profiles, densities are normalized such that the area under each curve is the same. As in previous studies of similar systems -- \textsuperscript{18,41} compare the qualitative Figure 3a -- we observe an appreciable surface propensity of iodide, followed by its sub-surface depletion and a sub-surface peak of sodium. Note that while the surface properties of the ions are well converged, the subsurface part of the density profiles are only semi-quantitative due to the finite width of the simulated slab.\textsuperscript{41}

In order to present the calculated density profiles in a form more suitable for comparison with the PE experiment we have simulated (Figure 11) the anion-to-cation PE ratios that would be recovered in an ideal experiment using the integral that appears in Equation (1) for each ion. For high enough EAL values the expected ratio for bulk solution of approximately unity is reached. For smaller values, the ratio increases because of the local surface enhancement of iodide.

### 6 Discussion

#### 6.1 Experimental Na$^+$/I$^-$ and I$^-$/water PE ratios from NaI aqueous solution
Applying Equation (1) for both ions, it can be seen that for identical outgoing eKE taking the ratio of the photoelectron signals eliminates $\alpha$ and $T$ and we can find the experimental anion-to-cation PE ratio after correcting for the respective photoionization cross sections and the measured photon flux. Thus, as illustrated in Figure 2, quantitative analysis of the PE signal intensities relies on knowing the variation of photoionization cross-sections with photon energy, which is troublesome as we have no direct information for aqueous ions. As discussed in section 4, we must start by assuming Equation (3) holds and by using the curves shown in Figure 5 for gas phase neutral atom ionization. Figure 12 presents the I/Na$^+$ PE ratios as function of eKE obtained in this way from the respective core and valence PE signals from NaI aqueous solution. Error bars in Figure 12 reflect the relative intensity variation in three different measurements, arising from the small variations in positioning the liquid jet with respect to the electron detector, rather than error in the cross sections applied. Notice that the region over which core- (circles in Figure 12) and valence-level (squares) data could be measured simultaneously is limited to eKE $\leq$ 300 eV because the cross sections to ionize the core levels at yet higher photon energies are too low as to yield sufficient electron signal. In addition, the photon flux at the U41 beamline drops by almost one order of magnitude near 1600 eV photon energy.

We can now assess the validity of our procedure to derive the PE ratios. For the larger probing depths, corresponding to eKE $\geq$ 600 eV, iodide-to-sodium PE ratios are almost constant, at a value of approximately 1. As this should indeed be the concentration ratio in the bulk solution, our use of gas-phase $\beta$ values seems to be justified, at least preliminarily. This is an interesting and important result. This could imply that elastic scattering is not that efficient and the angular anisotropy of emitted electrons is not greatly disturbed by escaping through several layers of water. It is interesting to see if a similar conclusion can be made, and in turn whether equation (3) is valid, for the situation where photoelectrons emerging primarily from the outermost layers, i.e., with eKEs near the EAL minimum. The PE ratios in Figure 12 for eKE <600 eV, which should correspond to probing the outermost surface region, exhibit a maximum near 175 eV, at a value of $\sim$1.35. This estimate is an average from the valence and the core measurements. We have obtained almost identical results for 8m NaI aqueous solution. The observed continuous increase of anion/cation ratios when going from predominantly bulk to surface probing qualitatively agrees with iodide’s larger surface propensity compared to the small and hard sodium cation (compare Figures 3a and 10). The occurrence of a maximum qualitatively mirrors the expected minimum in the electron escape
Why the ratio on the low energy site drops to unphysically low values < 1.0 is not clear, but we believe that this is a consequence of \( \sigma \) and \( \beta \) values being less accurately approximated in this near threshold region as was mentioned above.

Even though the high eKE (600-1000 eV) data points in Figure 12 suggest that the gas-phase differential cross sections seem applicable to solvated ions, the differences in the asymmetry parameters of \( \Gamma_{\text{aq}} \) 4d and \( \text{Na}^+_{\text{aq}} \) 2p in the considered energy range may be too small to be conclusive. As seen in Figure 6, the \( \beta \) values for I 4d vary very little around 1.25, whereas the values for Na 2p drop slightly from 1.2 to 1.0. The contrast in the emission patterns from these orbitals is thus low for >600eV eKE, and we cannot rule out the possibility that the behavior observed in Figure 12 arises instead from total angular isotropy (\( \beta = 0 \)) due to strong elastic scattering in the bulk. We therefore seek to compare emission from another pair of orbitals with more distinctly different angular emission patterns in the high eKE range. For this purpose we have measured the \( \Gamma_{\text{aq}} \) 3d and the O 1s water PE signals over a range of photon energies that yield identical eKEs (see Table 1). Since the oxygen orbital is of \( s \)-character the gas phase \( \beta \) parameter is constant at a value of 2, independent of eKE. The iodide-to-water PE ratios were evaluated in the same way as explained above, i.e., applying the differential cross sections for both I 3d and O 1s. There is unfortunately a similar paucity of information on photoionization cross sections of any of \( \text{H}_2\text{O}_{(\text{aq})} \)'s orbitals; values are not even known for gas-phase \( \text{H}_2\text{O}_{(\text{g})} \). For the analysis of the O1s PE intensities we thus also use the calculated cross sections of atomic oxygen from ref 36. Due to the localized and atomic-like character of the O 1s core orbital this should be a fairly good approximation, particularly for kinetic energies > 70 eV. In this case the final state wave function describing the outgoing photoelectron will be little affected by its surrounding, and can be approximated as a free travelling wave in the continuum.

The results for the iodide-to-water PE ratios, with all aforementioned corrections taken into account, are displayed in Figure 13. At eKEs \( \geq 800 \) eV, the \( \Gamma_{\text{aq}} \) 3d/O 1s PE ratio is nearly constant, almost approaching the macroscopic bulk concentration ratio – the dashed horizontal line corresponds to the macroscopic iodide-to-water concentration ratio of 4/55.5 in the 4m NaI aqueous solution. What if we had ignored the photoemission anisotropy and assumed an effective \( \beta \) parameter close to zero (due to substantial elastic scattering of photoelectrons emerging from the bulk solution)? We would deduce experimental ratios from the PE signals approximately four times larger than the expected bulk ratio. This is clearly
unphysical and provides additional justification for using gas phase $\sigma$ and $\beta$ values along with Equation (3) for describing electron angular distributions for bulk solvated ions. The smooth decrease of the iodide/water ratio towards lower eKEs is in qualitative agreement with Gibbs adsorption equation, predicting a net negative surface excess for inorganic salt solutions, such that the integrated ion concentration in the interface region is smaller than in the bulk. It is surprising though that at the lowest eKEs measured the I/water ratio continues to decrease, whereas one would expect a minimum near 60-100 eV eKE, mirroring the minimum in the EAL. We believe that this behavior is due to a similar reason leading to anion/cation signal ratios $< 1$ (Figure 12). That is approximated $\sigma$ and $\beta$ values within ~150 eV of threshold, where there is the biggest energy dependent variation, are likely to be not very accurate. On the other hand, we cannot rule out that Equation (3) is inappropriate in describing ionization from asymmetrically solvated ions in the outermost interfacial layer. But there is also the possibility that EAL for water is much shallower in the low eKE range than for most other materials. This idea is in fact supported by the O1s measurements from pure water described next.

6.2 Experimental electron attenuation lengths in liquid water

Having gathered all available ingredients we now derive the electron attenuation length values for liquid water and aqueous solutions in the range of 70-900 eV eKE. In the first step we consider the measured relative O1s intensities from liquid water as a function of electron kinetic energy, and the results are shown in Figure 14 (left axis). Here we have made the same assumptions for cross sections and angular distributions as in Figure 13. The data as presented in Figure 14 must be considered the best current experimental estimate of the shape of the electron EAL(eKE) curve for water – the absolute length scale has not yet to be determined. Towards higher eKEs the EAL curve exhibits the characteristic (smooth) increase found for most other materials. The minimum of the curve is however unusually wide, extending to 200 eV eKE. Moreover, for water the typical steep increase of EAL on the low-eKE side of the minimum is surprisingly shallow, and could be indicative of the specific nature of inelastic electron scattering processes in hydrogen-bonded water.

We can now estimate the absolute length scale of the EAL curve for water. As mentioned, the idea is to use the simulated ion interfacial density profile of NaI aqueous
solution as a ruler for the interface that is then projected onto water. Due to the linear proportionality between EAL and the PE signal intensity (Equation (2)) it takes a single calibration point to anchor the relative EAL length scale in Figure 14 to an absolute length scale. A good choice of calibration is the value of maximum I-to-Na<sup>+</sup> PE ratio, i.e., 1.35 (Figure 12), which is a direct consequence of the displacement between the iodide and the sodium ion density maxima, and corresponds to an eKE of 175±25 eV. Then, by comparison with the simulated ratios of Figure 11, a value of 1.35 is seen to correspond to an EAL of little less than 12 Å. Except for a missing geometrical correction factor of $\pi/2^1$, accounting for the curved liquid-jet surface, this is the correspondence between EAL(Å) and eKE, which determines the absolute length scale shown on the right-hand y-axis, A, of Figure 14. The length derived here is of course only accurate if our calibration point is correct. We have seen that our understanding of elastic scattering in solution, and solvation effects on the differential photoionization cross sections of ions near the solution interface is far from complete, which taken together does not allow for deriving a more precise value of the PE probing depth. Nonetheless it is instructive to compare the ion-density based length assignment of the electron EAL curve for water with the length scale using an independent calibration point – the closest we can get is using data reported for ice. We are not arguing that EALs for water and ice must be the same, but the comparison may still be instructive. Values of the electron mean (free) path for amorphous ice have been reported up to 100 eV eKE,<sup>43</sup> and EALs up to 68 eV.<sup>12</sup> If we make our calibration for 100 eV eKE, corresponding to EAL = 21.5 Å,<sup>43</sup> we obtain the length scale B of Figure 14, which almost exactly falls on top of A-axis. When using the 68 eV ice data from ref<sup>12</sup>, where EAL = 17 Å, the water EAL scale C is obtained, yielding approximately 10% shorter values. Taking these results together we feel that the true EAL for water seem indeed reasonably well reproduced in Figure 14. At the same time we are however somewhat surprised by the fact that the shortest EAL values for water are considerably larger than for most other materials.<sup>2,15</sup> This is surely related to oxygen being a weak scatterer (and hydrogen being negligible) but arguably, this may also be a consequence of water’s hydrogen bonding network facilitating electron passage. Density probably plays some role, and we notice that polymethylmethacrylat (PMMA), a hydrogen containing soft-matter compound with density $\sim 1.2$ g/cm$^3$, i.e., slightly higher density than for water, has a minimum EAL of approximately 8 Å as compared to 3 Å for aluminium, for example. We also like to mention that the results of Figure 14 contrast conclusions from previous surface-
sensitive PE studies from aqueous solutions, where shorter EALs were assumed, perhaps on the order of 5-10 Å.\textsuperscript{37,44} This controversy remains unresolved, though. A related puzzling issue is that much larger anion/cation PE-signal ratios than the ones found here for a NaI solution (1.35), were reported for KI, with I/\(K^+\) ion ratios >4,\textsuperscript{37} although the same calculated ionization cross section values were used for analysis. In the measurements of ref\textsuperscript{37} deliquesced samples supported on a cleaved salt crystal were used, and the PE spectra were collected at the magic angle. It can be easily seen from Figure 11 that a ratio of 4 would yield at least factor five smaller value for the shortest EAL.

It is perhaps interesting to speculate whether the high EAL derived in the current study arises because liquid water is in the weak elastic scattering limit (as described in Figure 1) as suggested by the evidence presented here that the anisotropy of photoelectrons emerging from the bulk is not washed out. It is therefore possible that for the standard materials characterized by surface science and used to construct the universal curve, even if they have comparable IMFP lengths, because there is more elastic scattering of the electrons, electron attenuation is more effective.

7. Conclusions

Despite the many uncertainties due to our incomplete understanding of the mechanism for electron scattering processes in liquid water and the photoemission anisotropy of the surface species, there is a reasonable agreement between the present first-time estimate of the effective attenuation length (up to 1000 eV electron kinetic energy) for liquid water derived here using the NaI ion profile as a ruler and that for ice. This suggests that the angular photoemission patterns of solvated ions in water can be fairly well approximated by the standard expression (and parameters) for the differential cross sections of randomly oriented atoms and molecules in the gas phase, which means that elastic scattering of photoelectrons is weak in the considered kinetic energy range. Our results specifically rule out complete loss of angle anisotropy of electrons emitted from deeper layers due to elastic scattering. The situation for the interface, which is inevitably connected with probing at smaller kinetic energy of the photoelectrons (and thus with photon energies closer to the ionization threshold) is not as clear. Interfacial orientation and polarization may play a role, but these effects are not understood. Yet, despite the several assumptions and crude approximations made in
interpreting the PE data, e.g., application of calculated cross sections of neutral atoms to hydrated ions, or employing a relatively small unit cell and simple empirical force field in the MD simulation, the analysis is self-consistent, and absolute EAL values for liquid water are in surprisingly good agreement with ice data. Future systematic angle resolved photoemission experiments from different aqueous solutions, which show qualitative variations in their surface structure, will help to determine both EAL and electron scattering for hydrated species more accurately.

Acknowledgments

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Figure and table captions

Figure 1
Illustration of the electron attenuation length (EAL) and inelastic mean free path (IMFP) in a medium. Left and right: many and few elastic scattering events, respectively. $I(A)$ is the electron intensity at starting point A, and $I(B)$ is the attenuated intensity at an arrival point B.

Figure 2
(a) Schematic illustration of the monotonously increasing water density profiles near the Gibbs dividing surface. (b) and (d) are PE emission and attenuation functions, i.e., the photoionization cross section multiplied by an exponentially decaying attenuation function, vs. probing depth. (b) depicts the ‘ideal’ (but unrealistic) situation, assuming that EAL can be changed without corresponding variation in the photoionization cross sections. (c) Illustration of how the PE spectra would vary qualitatively for the ideal case of (b). A more realistic situation is shown in (d) where changes in EAL, realized through variations in the excitation photon energy, is correlated with different cross sections which rescales the attenuation curve by a constant. Then, as shown in (e) stronger PE signals can be obtained even when probing shorter EALs, if the effect of cross section variations dominates.

Figure 3
(a) Schematic non-monotonous solute density profiles for the components of an aqueous salt solution with a large polarizable anion (such as iodide or bromide), as obtained from MD simulations. Negative (-) and positive (+) contributions to the net surface excess are indicated. The vertical dashed line is the position of the Gibbs dividing surface (defined such that the net surface excess of the solvent is zero). (b) The exponential curves illustrate the attenuation of the PE signal as function of the electron probing depth, for two different EALs. (c) The measured PE signal is the convolution of the sample density profile and the attenuation function. At short enough EAL (dashed PE peaks) differences in the density profiles of anions and cations can be resolved through relative PE signal intensities for the two ionic species. If EAL is too long, the interfacial density structures will make a minor contribution to the total signal, and PE intensities from the two ions are barely different. (Here we have assumed the ideal case of Figure 2, namely identical cross sections ionizing anion and cation.)
Figure 4
Schematic illustration of the experimental setup for photoemission studies, using a liquid microjet. The average electron emission angle is $\Theta_{\text{mean}} = 80^\circ$ (i.e., almost normal) with respect to the synchrotron light polarization vector. Photoelectrons pass through a narrow aperture skimmer, separating the main interaction chamber (at $\sim 10^{-5}$ mbar) from the differentially pumped hemispherical electron energy analyzer (at $\sim 10^{-9}$ mbar).

Figure 5
Graphical solutions of Equation (3), showing the differential photoionization cross section dependence on the $\beta$ parameter; results are presented for some selected $\beta$ values relevant for the present work. The straight lines mark the intersections at the mean detection angle, $\Theta_{\text{mean}} = 80^\circ$ (which is used in the present experiment) as well as the magic angle, at which the differential and total cross section are directly proportional.

Figure 6
Calculated partial photoionization atomic cross sections $\sigma$ (top) and anisotropy parameters $\beta$ (bottom) for I 4d, Xe 4d, I 3d, Xe 3d, Na 2p, Ne 2p, Na 1s, and Ne 1s, as a function of electron kinetic energy.36 The insets are adapted from ref 34, and compare $\sigma$ and $\beta$ values of I 4d obtained from different theoretical calculations. Top inset: curves 1, 2 and 3, 4 are from Hartree-Fock calculations and random phase approximation calculations with exchange (RPAE), respectively. The red squares are the I 4d $\sigma$ data from ref 36, and are the same ones shown in the main figure. The small dots are the I 4d experimental cross sections for CH$_3$I, from ref 35. Bottom inset: Calculated (solid line; using RPAE) $\beta$ parameter for photodetachment from I 4d; dots are the respective experimental I 4d data for CH$_3$I 35. Red squares are the I 4d $\beta$ values from the main figure.

Figure 7
O 1s photoelectron line from pure liquid water, recorded at a photon energy of 638 eV. The small shoulder at 539.9 eV arises from gas-phase water. To construct the EAL curve for water many such O 1s PE spectra were measured at different photon energies.

Figure 8
Set of $I_{aq}$ 4d and $Na^{+}_{aq}$ 2p PE spectra from a 4m NaI aqueous solution, measured at 200, 500 and 1000 eV photon energies. The $x$-axis presents electron binding energies; intensities of the three spectra are normalized to the height of the $I_{aq}$ 4d peak. The low binding energy region is dominated by the emission from the water valence orbitals. The small doublet peak at 7.7/8.8 eV BE, originates from $I_{aq}$ 5p$_{3/2,1/2}$. The two intense peaks at 35.4 eV and 53.8/55.5 eV binding energy arise from $Na^{+}_{aq}$ 2p and $I_{aq}$ 4d$_{5/2,3/2}$, respectively.

**Figure 9**
Core-level photoelectron spectra of the iodide and sodium ions in a 4m NaI aqueous solution. Left: $I_{aq}$ 3d spectrum. Right: and $Na^{+}_{aq}$ 1s spectrum. Photon energies were such that the photoelectrons from both ions had the same kinetic energy of 150 eV.

**Figure 10**
Density profiles of $Na^{+}$, $I$, and water oxygen from the center of the slab across the solution/vapor interface into the gas phase, as obtained from MD simulation.

**Figure 11**
Simulated anion-to-cation PE ratios as obtained from equation (1) using the MD density profiles of Figure 10, where different EALs of the photoelectrons were assumed. The dashed lines indicate values we refer to in the discussion of a calibration point.

**Figure 12**
Experimental anion-to-cation PE ratios as a function kinetic energy (corresponding to varying EAL) for a 4m NaI aqueous solution. Squares are ratios obtained from $I_{aq}$ 4d/$Na^{+}_{aq}$ 2p valence orbitals, and circles result from $I_{aq}$ 3d/$Na^{+}_{aq}$ 1s core-level measurements. The dashed line indicates the averaged maximum anion-to-cation PE ratio.

**Figure 13**
$I$/water PE ratios of a 4m NaI aqueous solution obtained from measurements of $I_{aq}$ 3d and O 1s, showing net ion depletion in the interfacial region, consistent with Gibbs adsorption equation. The dashed horizontal line at 4/55.5 corresponds to the macroscopic anion/water concentration proportions in a 4m solution.
Experimental EAL curve for water derived from O1s PE intensity measurements of pure liquid water (left y-axis). The (right-hand side) absolute length scale A was determined through experimental and simulated ion density profiles from NaI aqueous solution. B and C are the length scales obtained when using ice calibration points (see text for details).

Table 1
Applied photon energies, and resulting kinetic energies of the emitted photoelectrons from I$_{aq}$, Na$^+_aq$, and oxygen orbitals relevant here. $^a$ From ref $^{40}$. $^b$ From ref $^{45}$. $^c$ From this work.
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strong elastic scattering  weak elastic scattering

Figure 1
Figure 2
Figure 3
Figure 4
Figure 5
Figure 6
\[ h\nu = 638 \text{ eV} \]

Figure 7
$h\nu = 200$ eV

$h\nu = 500$ eV

$h\nu = 1000$ eV

Figure 8
$$h\nu = 730 \text{ eV}$$
$$h\nu = 1177 \text{ eV}$$

**Figure 9**
Figure 10
Figure 11
Figure 12
Figure 13
Figure 14
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Table 1