Photoelectron Spectroscopy of Liquid Water with Tunable Extreme-Ultraviolet Radiation: Effects of Electron Scattering

Conaill F. Perry, Inga Jordan, Pengju Zhang, Aaron von Conta, Fernanda B. Nunes, and Hans Jakob Wörner*

Cite This: J. Phys. Chem. Lett. 2021, 12, 2990−2996

ACCESS

ABSTRACT: We report the first systematic photoelectron measurements of the three outer-valence bands of liquid water as a function of the ionizing photon energy in the near-threshold region. We use extreme-ultraviolet (XUV) radiation tunable between ∼17.1 and 35.6 eV, obtained through monochromatization of a high-harmonic source. We show that the absolute values of the apparent vertical ionization energies and their respective peak widths show a decreasing trend of their magnitudes with increasing photon energy close to the ionization threshold. We find that the observed effects do not only depend on the electron kinetic energy but are also different for the various outer-valence bands. These observations are consistent with, but not fully explained by, the effects of inelastic electron scattering.

Photoelectron spectroscopy of liquids is a promising technique that offers considerable potential for a deeper understanding of the electronic structure of liquids and solutions. WATER is arguably the most important liquid, owing to its significance to all living organisms. Therefore, photoelectron spectra of liquid water have been studied in considerable detail. Time-resolved photoelectron spectroscopy of aqueous solutions on picosecond to femtosecond time scales is a very active area of research that is providing new insights into the dynamics of solvated species. With the development of attosecond time-resolved photoelectron spectroscopy, the perspective of performing time-resolved measurements on the electronic time scale in liquid water and aqueous solutions has emerged. Such measurements, which have very recently been reported for the first time, offer experimental access to electronic dynamics in solution, i.e. in the real conditions under which most chemical reactions and biological transformations take place. Expanding attosecond science to the liquid phase therefore has the potential of creating fundamentally new knowledge about the elementary processes underlying chemistry and biology.

Most photoelectron measurements of liquid water have been performed at high photon energies, ranging from 60 eV to 1000 eV, with the recent exceptions of refs 10, 24, and 25 (29.5 and 27.9 eV respectively). Many of these studies have focused on the determination of the ionization energies of the valence bands of liquid water, i.e. the outer-valence (1b1, 3a1, 1b2) and inner-valence (2a1) bands. Remarkably, the reported ionization energies differed for all valence bands, e.g. ranging from 11.16(4) eV to 11.31(4) eV to 11.67(15) eV in the case of the outermost 1b1 valence band. Part of this discrepancy has been attributed to the streaming potential and the vacuum-level offset. In a recent publication, which was the first to explicitly take both effects into account, we have proposed that the latter can simultaneously be compensated for by applying a bias potential, a method that has also been used in this study.

In this letter, we report a detailed analysis of the photoelectron spectra of liquid water with a tunable extreme-ultraviolet (XUV) source. Specifically, we chose to work with harmonic orders 11 to 23 of an 800 nm driving field, corresponding to photon energies from ∼17.1 to 35.6 eV. Our detailed analysis of these spectra reveals that the apparent vertical ionization energies (AVIEs) of the outer-valence bands of water decrease in absolute value with increasing photon energy, showing evidence of convergence toward an asymptotic value for kinetic energies above ∼12 eV. This trend is, a priori, consistent with the expected contributions from inelastic scattering that reduce the kinetic energy of the outgoing electron. Such effects were also observed in previous experimental works with respect to the peak position and

Received: November 17, 2020
Accepted: March 5, 2021
Published: March 18, 2021

https://doi.org/10.1021/acs.jpclett.0c03424
shape of the solvated electron ionized from a liquid-water jet.\textsuperscript{24,25} Inelastic scattering increases the magnitude of the AVIE compared to the true vertical ionization energy. The previous works have investigated the range of kinetic energies from 0 to 3 eV\textsuperscript{24} and 23 to 26 eV,\textsuperscript{25} showing a significant impact of inelastic scattering on the AVIE in the low-energy range and no measurable effect in the high-energy range. The influence of inelastic scattering has been confirmed in the classical-trajectory Monte-Carlo simulations of Luckhaus et al.\textsuperscript{30} This work, however, used scattering cross sections that were indistinguishable from those of amorphous ice\textsuperscript{31} and extracted a remarkably non-Gaussian distribution of the solvated-electron band, at odds with more recent work using higher photon energies\textsuperscript{25} or UV photon energies on water clusters.\textsuperscript{32} Several publications have since suggested artifacts to be responsible for the suggested non-Gaussian band shape of the solvated electron.\textsuperscript{25,32−34} One possible explanation for the failure of the Monte-Carlo simulations is the classical treatment of electron propagation at very low energies. At a typical kinetic energy of 2 eV, the de-Broglie wavelength of the electron amounts to 8.7 Å, which is much longer than both the nearest O−O distances, 2.75 Å, and the physical elastic mean-free paths.\textsuperscript{35} The limited accuracy of classical Monte Carlo calculations in this regime has been documented previously.\textsuperscript{36}

The tunable XUV radiation employed in this study is provided by a time-preserving monochromator of high-harmonic radiation described in a previous publication.\textsuperscript{37} High-harmonic generation (HHG) is driven by laser pulses of 1.5 mJ energy, 35 fs pulse duration, centered at 800 nm with a repetition rate of 5 kHz. The laser pulses are focused (f/30) into a semi-infinite gas cell filled with argon at a pressure of 20 mbar. The diverging radiation is recollimated by means of a first toroidal mirror, subsequently energy dispersed by a plane grating in conical-diffraction geometry and refocused onto a 200-μm-wide slit that selects the desired harmonic order. The plane of the selection slit is imaged into the interaction region of a previously described 1-m-long magnetic-bottle photoelectron spectrometer equipped with a liquid microjet.\textsuperscript{21} The photoelectron spectrometer and the exact photon energies that depend on the details of the experimental settings were calibrated by recording photoelectron spectra of gas-phase argon and krypton measured using a leak valve in tandem with the liquid jet, the design of which is described in a previous publication.\textsuperscript{11} The resolution of the spectrometer amounts to 0.14−0.34 eV over the investigated kinetic-energy range.\textsuperscript{21} The spectral widths of the individual XUV harmonics are 0.30−0.35 eV. All measurements reported in this letter were performed on a 0.05 mol/L solution of NaCl in high-purity water (Milli-Q, 18.2 MΩ cm) that was delivered through a 25 μm inner-diameter quartz capillary into high vacuum. The nozzle holder and mounting system (PEEK) were coated with graphite and grounded. The nozzle itself was capped by Cu

Figure 1. Photoelectron spectra of gas-phase water molecules evaporating from the liquid microjet (left) and total photoelectron signal including both liquid- and gas-phase contributions (right). The labels refer to the orbitals of isolated water molecules.
tape, covered with a layer of Sn solder to prevent the buildup of charge on the insulating quartz, and grounded. The bias voltage applied to the jet was determined from peak-position and peak-width measurements of gas-phase water photoelectron spectra described in more detail previously. The photon flux is attenuated such that we record a maximum of 20 electrons per shot to avoid charging and space-charge effects.

We have recorded measurements with count rates up to 30 electrons per shot that have shown negligible change or shift in the spectral widths and positions reported in this work. The measured photoelectron spectra of gas-phase water and the combined spectra of liquid- and gas-phase water are shown in the left and right columns of Figure 1, respectively. These spectra were analyzed on the basis of a principal-component analysis.

Figure 2. Schematic illustration of the convolution procedure. Ionization energies and relative amplitudes reported in the literature are indicated as stick spectra. The literature data were convoluted with a Gaussian in order to obtain an illustrative reference spectrum (left panels). (Top) Gas-phase water (ionization energies from ref 39, relative intensities from ref 38); (bottom) liquid water (ionization energies from ref 9, relative intensities from ref 5). Both literature spectra were broadened by the same instrument-response function shown in the middle panel.

Figure 3. Individual outer-valence-band contributions to the overall extracted liquid spectrum at each harmonic order used. The black curve indicates the liquid-phase spectrum. The blue, red, and green curves show the individual contributions of the 1b1, 3a1, and 1b2 bands, respectively. The dashed red and dotted red curves represent the 3a1(H) and 3a1(L) contributions to the 3a1 band, respectively.
The principal components were created by a convolution of literature data, with the instrument-response function, that incorporates the spectral bandwidth of the XUV pulses and the line-shape function of the photoelectron spectrometer, as illustrated in Figure 2. The ionization energies and spectral widths describing the photoelectron bands reported in the literature\textsuperscript{5,9,38,39} were used to construct an initial guess of the photoelectron spectra on the binding-energy axis. The instrument-response function was represented by the convolution of a Gaussian distribution with the product of the Heaviside function\textsuperscript{\textsuperscript{τ}} and an exponential decay, commonly referred to as the “exponentially modified Gaussian distribution”\textsuperscript{3}

$$f(x; \tau, x_0) = A \exp\left(-\frac{1}{2} \frac{(x-x_0)^2}{\omega^2}\right) \cdot \left(\mathcal{H}(x-x_0) \exp\left(- \frac{x-x_0}{\tau}\right)\right)$$

(1)

Here, $x_0$ is related to the position of the peak maximum, $\tau$ to the exponential tail of the peak, and $\omega$ is the width parameter of the Gaussian component. $A$ represents the amplitude. The Gaussian broadening associated with the bandwidth of the XUV radiation is included in $\omega$. The choice of the exponentially modified Gaussian function is based on the permanent-magnet magnetic-bottle collection principle,\textsuperscript{40} i.e. electrons emitted at large polar angles relative to the polarization of the ionizing radiation have a smaller velocity component along the time-of-flight axis and are collected less efficiently, therefore forming an exponential tail of the photoelectron band toward longer times of flight.

The instrument-response function is positioned on the photon-energy axis according to the high-harmonic photon energy, which was independently calibrated as described above. The convolution procedure (Figure 2) was applied to the photoelectron signal of each final electronic state of the cation (gas phase) or band (liquid phase) separately. The response function used for the convolution is determined individually for each data set at each harmonic order. Time-of-flight spectra were not Jacobi-corrected after conversion to the energy domain, because a comparison of relative intensities of the gas-phase signal with measured photoionization cross sections\textsuperscript{41} revealed that the Jacobian was almost exactly compensated by the energy-dependent collection efficiency for kinetic energies above $\sim3$ eV. The resulting photoelectron spectrum is obtained by resampling the convoluted spectrum on the kinetic-energy axis.

The reference spectra convoluted with the spectrometer-response function (eq 1) were fitted to the experimental data using their positions and widths as fit parameters. The pure gas-phase spectra were analyzed first, followed by the analysis of the liquid-phase spectra, whereby the fitted pure gas-phase spectrum was reused, only allowing for an overall adjustment of its amplitude. The maxima and the full widths at half-maximum (fwhm) of each photoelectron band (gas and liquid) obtained in this way were then determined numerically and averaged over all measured spectra to yield the final results and corresponding error intervals. These parameters are reported

Figure 4. (a–c) Energy-dependent AVIEs (maxima of the fitted photoelectron bands) of the liquid-water valence bands determined using XUV radiation in the range between 17.1 and 35.6 eV. Panel a additionally shows the 1b\textsubscript{1} binding energy as determined from the local maximum of the liquid-phase spectra ("peak"). (d–f) Binding energies for the gas-phase valence bands extracted from the liquid+gas spectra. The purple diamond represents the reported literature value measured at 21.2 eV photon energy,\textsuperscript{40} and the red triangle represents the value obtained from a Gaussian fit of the convoluted literature spectrum. (g–j) Full width at half-maximum of the orbital contributions to the liquid signal at each harmonic order used. The number of measurements taken into account were $N = 10, 8, 10, 10, 15, 8$ for H11–H23. Error bars represent the standard deviation of these measurements.

\[ \text{https://doi.org/10.1021/acs.jpclett.0c03424} \]
in Figure 4 and are discussed below. Photoelectron spectra of condensed-matter targets are usually characterized by the presence of a background consisting of secondary electrons, as well as photoelectrons that have lost a sufficient amount of kinetic energy through inelastic scattering. This contribution, represented by the red curves in Figure 1 was also modeled by an exponentially modified Gaussian. We note that the neglected Jacobi correction leads to an underrepresentation of this background signal below ~3 eV, but we have verified that the results reported below are insensitive to this.

Figure 3 shows the isolated liquid-phase contribution to the photoelectron spectra (blue-shaded areas in Figure 3) and its decomposition into the individual outer-valence band contributions. Here, the gas-phase and background contributions have been left out to provide a clearer depiction of the liquid-phase spectra. The 3a1 band of liquid water has an interesting structure when compared to the other two outer-valence bands. It has been reported previously that the 3a1 band is comprised of two contributions, one originating from a hydrogen-bond-donor moiety and the other from a hydrogen-bond-acceptor moiety. Within our principal-component fits, we describe the 3a1 band as a sum of two Gaussian contributions, each with individual peak positions, widths, and amplitudes.

Overall, we find a substantial change of the spectral shape from H11 (17.1 eV) over H13 (20.2 eV) to H15 (23.3 eV) but less change thereafter. At lower photon (and thus kinetic) energy, the widths and peak positions of the bands are broadened and shifted compared to the results obtained at higher energies. This observation is consistent with the findings in refs 24 and 25 concerning the solvated-electron band shape. The photoelectron spectra measured with H19 to H23 are very similar in terms of peak positions and widths. These observations are quantified in Figure 4, which shows the photoelectron band maxima (panels a–c) and full widths at half-maximum (panels g–i) of the individual bands contributing to the liquid-phase spectra. The shape of the liquid spectrum taken at the higher photon energies (H19 upward) is consistent with previously reported spectra, whereas those recorded at lower photon energies are broadened and shifted.

Figure 4 shows the detailed results of the fitting procedure. Panels a–c show the AVIEs of the three outer-valence bands of liquid water, panels d–f, the AVIEs of gas-phase water, and panels g–i, the fwhm of both liquid- and gas-phase photoelectron bands. The AVIEs of gas-phase water do not significantly vary with the photon energy, supporting the validity of the Condon approximation. The measured ionization energies moreover agree well with those previously reported (see, e.g., refs 38, 39, and 42). The corresponding vertical ionization energies are indicated as violet diamonds, and the result of a Gaussian fit to the photoelectron spectra from ref 38 as a red triangle. The latter agrees with our results, demonstrating the consistency of the gas-phase results, as well as the successful compensation of the effects of streaming potential and vacuum-level offsets.

In contrast to the gas phase, the AVIEs of the 1b1 and 1b2 liquid-phase bands depend on the photon energy, a behavior that was not observed in previous measurements realized at much higher photon energies (e.g., 60–100, 516–532, 600, 550–1000 eV, etc.). In our measurements, we find that the AVIEs of 1b1 and 1b2 increase (by 0.5 and 0.3 eV, respectively) over the range of the three lowest photon energies in each case. This variation is commensurate with the energy loss due to inelastic scattering.

Additional evidence for the influence of inelastic scattering can be found in the evolution of the widths of the liquid-phase photoelectron bands (panels g–i). The width of the 1b1 band decreases from ~2.3 eV at the lowest energy to below 2 eV for kinetic energies higher than 11.8 eV. The width of each of the two contributions to the 3a1 band also decreases monotonically over kinetic energies of 5.5 to 11.7 eV, varying little thereafter. Finally, the width of the 1b2 band decreases by more than 1 eV from 5.3 to 8.6 eV, remaining essentially constant toward higher kinetic energies. The observed decrease of the width, paired with the increase of the AVIEs are both consistent with the effect of inelastic scattering. The only deviation from this overall trend is the lack of a clear trend in the AVIEs of the 3a1 band. This result can be attributed to the fact that the 3a1 band of liquid water has the strongest spectral overlap with other contributions.

The effect of inelastic scattering should (significantly) depend on the origin of the photoelectrons, i.e. the nature of the ionized valence band of liquid water. The weaker photon-energy dependence observed in the positions and widths of the 3a1 and 1b2 bands, compared to the 1b1 band of liquid water could thus suggest that inelastic scattering is not the only relevant factor. Additional contributions might originate from a breakdown of the Condon approximation in the near-threshold photoionization of liquid water.

Before concluding, it is worth pointing out that our corrected (1b1) binding energy of liquid water (11.67(15) eV), as determined from the local maximum of the liquid-phase photoelectron spectra (black line in Figure 4a) and averaging over harmonic orders 15–21 (or 23.3–32.6 eV), lies closer to that of ice than the earlier values for liquid water (dashed lines in Figure 4a). Measurements on ice that were referenced to the vacuum level indeed agreed on a 1b1 binding energy of 11.8 eV (ref 43 and references therein), whereas more recent measurements were referenced to the Fermi level (ref 44 and references therein). Our binding energy of liquid water is moreover not inconsistent with the ionization energies of large water clusters, which amount to 11.5–11.6 eV. First, their structure is known to be more similar to ice (varying from amorphous to crystalline with increasing cluster size) than to liquid water. Second, owing to the shallow probing depths of ~2 nm at the kinetic energies of interest, the variation of the binding energy with cluster size can be expected to be reduced once the cluster radius is equal to the probing depth, i.e. beyond cluster sizes of ~1000. Finally, we note that, contrary to the recent results of Nishitani et al., our calibration of the photoelectron spectrometer has been verified to be independent of the applied bias potential.

We have investigated the photoelectron spectra of liquid water with tunable XUV radiation at energies close to the valence ionization thresholds. We have found that the apparent ionization energies of all three outer-valence bands depend on the photon energy. This observation is partially attributed to the energy dependence of inelastic scattering in liquid water, but the observed trends were found to depend on the nature of the ionized valence band. These results provide new insights...
into the photoelectron spectroscopy of liquids, particularly relevant to measurements at low photon energies. More specifically, they establish the quantitative understanding of these spectra required to interpret attosecond time-resolved measurements of liquid water in more depth. These results also demonstrate a systematic approach to the determination of the effects of inelastic scattering in other liquids and will serve as a benchmark for modeling low-energy scattering of electrons in liquid water. They also suggest a possible influence of non-Condon effects in low-energy photoionization of liquid samples, which can be expected to apply to other liquids and solutions, as well.

### ACKNOWLEDGMENTS

The authors thank Andreas Schneider and Mario Seiler for technical support and Uwe Bovensiepen for helpful discussions. This work was supported by the European Research Council (project no. 772797-ATTOLIQ) and the Swiss National Science Foundation through the NCCR-MUST and project no. 200021_172946 and ETH Career Seed Grant No SEED-12 19-1/1-004952-000.

### REFERENCES

(1) Siegbahn, H.; Siegbahn, K. ESCA applied to liquids. *J. Electron Spectrosc. Relat. Phenom.* 1973, 2, 319–325.

(2) Siegbahn, H. Electron spectroscopy for chemical analysis of liquids and solutions. *J. Phys. Chem.* 1985, 89, 897–909.

(3) Faubel, M.; Steiner, B.; Toennies, J. P. Photoelectron spectroscopy of liquid water, some alcohols, and pure nonane in free micro jets. *J. Chem. Phys.* 1997, 106, 9013–9031.

(4) Winter, B.; Faubel, M. Photoemission from liquid aqueous solutions. *Chem. Rev.* 2006, 106, 1176–1211.

(5) Winter, B.; Weber, R.; Wildra, W.; Dittmar, M.; Faubel, M.; Hertel, I. V. Full valence band photoemission from liquid water using EUV synchrotron radiation. *J. Phys. Chem. A* 2004, 108, 2625–2632.

(6) Winter, B.; Aziz, E. F.; Hergenhahn, U.; Faubel, M.; Hertel, I. V. Hydrogen bonds in liquid water studied by photoelectron spectroscopy. *J. Chem. Phys.* 2007, 126, 124504.

(7) Nishizawa, K.; Kurahashi, N.; Sekiguchi, K.; Mizuno, T.; Ogi, Y.; Horio, T.; Oura, M.; Kosugi, N.; Suzuki, T. High-resolution soft-X-ray photoelectron spectroscopy of liquid water. *Phys. Chem. Chem. Phys.* 2011, 13, 413–417.

(8) Thürmer, S.; Siegel, R.; Faubel, M.; Eberhardt, W.; Hemminger, J. C.; Bradforth, S. E.; Winter, B. Photoelectron angular distributions from liquid water: Effects of electron scattering. *Phys. Rev. Lett.* 2013, 111, 173005.

(9) Kurahashi, N.; Karashima, S.; Takahashi, Y.; Horio, T.; Abe, A.; Suzuki, Y. I.; Ogi, Y.; Oura, M.; Suzuki, T. Photoelectron spectroscopy of aqueous solutions: Streaming potentials of NaX (X = Cl, Br, and I) solutions and electron binding energies of liquid water and X. *J. Chem. Phys.* 2014, 140, 174506.

(10) Nishitani, J.; West, C. W.; Suzuki, T. Angle-resolved photoemission spectroscopy of liquid water at 29.5 eV. *Struct. Dyn.* 2017, 4, 044014.

(11) Perry, C. F.; Zhang, P.; Nunes, F. B.; Jordan, I.; von Conta, A.; Wörner, H. J. Ionization energy of liquid water revisited. *J. Phys. Chem. Lett.* 2020, 11, 1789–1794.

(12) Buchner, F.; Lübcke, A.; Heine, N.; Schultz, T. Time-resolved photoelectron spectroscopy of liquids. *Rev. Sci. Instrum.* 2010, 81, 113107.

(13) Suzuki, Y. I.; Shen, H.; Takahashi, N.; Sekiguchi, K.; Mizuno, T.; Suzuki, T. Isotope effect on ultrafast charge-transfer-to-solvent reaction from I to water in aqueous NaI solution. *Chemical Science* 2011, 2, 1094–1102.

(14) Buchner, F.; Ritz, H. H.; Lühl, J.; Lübcke, A. Time-resolved photoelectron spectroscopy of adenine and adenosine in aqueous solution. *Phys. Chem. Chem. Phys.* 2013, 15, 11402–11408.

(15) Elkins, M. H.; Williams, H. L.; Shreve, T. A.; Neumark, D. M. Relaxation mechanism of the hydrated electron. *Science* 2013, 342, 1496.

(16) Buchner, F.; Nakayama, A.; Yamazaki, S.; Ritz, H. H.; Lübcke, A. Excited-state relaxation of hydrated thymine and thymidine measured by liquid-jet photoelectron spectroscopy: Experiment and simulation. *J. Am. Chem. Soc.* 2015, 137, 2921–2938.

(17) Ojeda, J.; Arrell, C. A.; Longetti, I.; Chergui, M.; Helling, J. Charge-transfer and impulsive electronic-to-vibrational energy conversion in ferricyanide: Ultrafast photoelectron and transient infrared studies. *Phys. Chem. Chem. Phys.* 2017, 19, 17052–17062.

(18) Engel, N.; Bokarev, S. I.; Bogulevsky, A.; Raheem, A. A.; Al-Obaidi, R.; Möhle, T.; Gréll, G.; Siefermann, K. R.; Abel, B.; Aziz, S. G.; et al. Light-induced relaxation dynamics of the ferricyanide ion revisited by ultrafast XUV photoelectron spectroscopy. *Phys. Chem. Chem. Phys.* 2017, 19, 14248–14255.

(19) Paul, P. M.; Toma, E. S.; Breger, P.; Mullot, G.; Augé, F.; Balco, P.; Müller, H. G.; Agostini, P. Observation of a train of attosecond pulses from high harmonic generation. *Science* 2001, 292, 1689–1692.

(20) Drescher, M.; Hentschel, M.; Kienberger, R.; Uiberacker, M.; Yakovlev, V.; Scrinzi, A.; Westerwalbesloh, T.; Kleineberg, U.; Heinmann, U.; Krausz, F. Time-resolved atomic inner-shell spectroscopy. *Nature* 2002, 419, 803–807.

(21) Jordan, I.; Huppert, M.; Brown, M. A.; Van Bokhoven, J. A.; Wörner, H. J. Photoelectron spectrometer for attosecond spectroscopy of liquids and gases. *Rev. Sci. Instrum.* 2015, 86, 123905.

(22) Jordan, I.; Huppert, M.; Rattenbacher, D.; Peper, M.; Jelovina, D.; Perry, C.; von Conta, A.; Schild, A.; Wörner, H. J. Attosecond spectroscopy of liquid water. *Science* 2020, 369, 974–979.

(23) Wörner, H. J.; Schild, A.; Jelovina, D.; Jordan, I.; Perry, C.; Luu, T. T.; Yin, Z. Attosecond dynamics in liquids. In *Ultrafast electronic and structural dynamics*; Ueda, K., Ed.; Springer Nature, 2020.

(24) Yamamoto, Y.; Karashima, S.; Adam, S.; Suzuki, T. Wavelength dependence of UV photoemission from solvated electrons in bulk water, methanol, and ethanol. *J. Phys. Chem. A* 2016, 120, 1153–1159.

(25) Nishitani, J.; Yamamoto, Y.; West, C. W.; Karashima, S.; Suzuki, T. Binding energy of solvated electrons and retrieval of true
UV photoelectron spectra of liquids. Science Advances 2019, 5, No. eaaw6896.

(26) Holstein, W. L.; Hayes, L. J.; Robinson, E. M.; Laurence, G. S.; Buntine, M. A. Aspects of electrokinetic charging in liquid microjets. J. Phys. Chem. B 1999, 103, 3035–3042.

(27) Preissler, N.; Buchner, F.; Schultz, T.; Lübcke, A. Electrokinetic charging and evidence for charge evaporation in liquid microjets of aqueous salt solution. J. Phys. Chem. B 2013, 117, 2422–2428.

(28) Tissot, H.; Gallet, J. J.; Bournel, F.; Olivier, G.; Silly, M. G.; Sirotti, F.; Boucly, A.; Rochet, F. The electronic structure of saturated NaCl and NaI solutions in contact with a gold substrate. Top. Catal. 2016, 59, 605–620.

(29) Olivier, G.; Goel, A.; Kleibert, A.; Cvetko, D.; Brown, M. A. Quantitative ionization energies and work functions of aqueous solutions. Phys. Chem. Chem. Phys. 2016, 18, 29506–29515.

(30) Luckhaus, D.; Yamamoto, Y.-i.; Suzuki, T.; Signorell, R. Genuine binding energy of the hydrated electron. Science Advances 2017, 3, e1603224.

(31) Michaud, M.; Wen, A.; Sanche, L. Cross sections for low-energy (1–100 eV) electron elastic and inelastic scattering in amorphous ice. Radiat. Res. 2003, 159, 3–22.

(32) Svoboda, V.; Michiels, R.; LaForge, A. C.; Med, J.; Stienkemeier, F.; Slavíček, P.; Wörner, H. J. Real-time observation of water radiolysis and hydrated electron formation induced by extreme-ultraviolet pulses. Science Advances 2020, 6, No. eaaz0385.

(33) Bartels, D. M. Is the hydrated electron vertical detachment genuinely bimodal? J. Phys. Chem. Lett. 2019, 10, 4910–4913.

(34) Herbert, J. M. Structure of the aqueous electron. Phys. Chem. Chem. Phys. 2019, 21, 20538–20565.

(35) Schödl, A.; Peper, M.; Perry, C.; Rattenbacher, D.; Wörner, H. J. Alternative approach for the determination of mean free paths of electron scattering in liquid water based on experimental data. J. Phys. Chem. Lett. 2020, 11, 1128–1134.

(36) Liljequist, D. A study of errors in trajectory simulation with relevance for 0.2–50 eV electrons in liquid water. Radiat. Phys. Chem. 2008, 77, 835–853.

(37) Von Conta, A.; Huppert, M.; Wörner, H. J. A table-top monochromator for tunable femtosecond XUV pulses generated in a semi-infinite gas cell: Experiment and simulations. Rev. Sci. Instrum. 2016, 87, 073102.

(38) Kimura, K. Handbook of HeI photoelectron spectra of fundamental organic molecules: ionization energies, ab initio assignments, and valence electron structure for 200 molecules; 1981.

(39) Reutt, J. E.; Wang, L. S.; Lee, Y. T.; Shirley, D. A. Molecular beam photoelectron spectroscopy and femtosecond intramolecular dynamics of H2O and D2O. J. Chem. Phys. 1986, 85, 6928–6939.

(40) Krüt, P.; Read, F. H. Magnetic field paralleliser for 2π electron-spectrometer and electron-image magnifier. J. Phys. E: Sci. Instrum. 1983, 16, 313–324.

(41) Banna, M. S.; McQuaide, B. H.; Malutzki, R.; Schmidt, V. The photoelectron spectrum of water in the 30–140 eV photon energy range. J. Chem. Phys. 1986, 84, 4739–4744.

(42) Lauzin, C.; Jacovella, U.; Merkt, F. Threshold ionization spectroscopy of H2O, HDO and D2O and low-lying vibrational levels of HDO and D2O. Mol. Phys. 2015, 113, 3918–3924.

(43) Campbell, M.; Liesegang, J.; Riley, J.; Jenkin, J. G. Ultraviolet photoelectron spectroscopy of the valence bands of solid NH3, H2O, CO2, SO2 and N2O4. J. Phys. C: Solid State Phys. 1982, 15, 2549.

(44) Henderson, M. A. The interaction of water with solid surfaces: fundamental aspects revisited. Surf. Sci. Rep. 2002, 46, 1–308.

(45) Barth, S.; Oncák, M.; Ulrich, V.; Mucke, M.; Lischke, T.; Slavíček, P.; Hergenhahn, U. Valence ionization of water clusters: From isolated molecules to bulk. J. Phys. Chem. A 2009, 113, 13519–13527.

(46) Pradzynski, C. C.; Forck, R. M.; Zeuch, T.; Slavíček, P.; Buck, U. A fully size-resolved perspective on the crystallization of water clusters. Science 2012, 337, 1529–1532.

(47) Suzuki, Y.-I.; Nishizawa, K.; Kurahashi, N.; Suzuki, T. Effective attenuation length of an electron in liquid water between 10 and 600 eV. Phys. Rev. E 2014, 90, 010302.

(48) Nishitani, J.; Karashima, S.; West, C. W.; Suzuki, T. Surface potential of liquid microjet investigated using extreme ultraviolet photoelectron spectroscopy. J. Chem. Phys. 2020, 152, 144503.