

Probing the Electronic Structure of Bulk Water at the Molecular Lengthscale with Angle-Resolved Photoelectron Spectroscopy

Samer Gozem^{a,†}, Robert Seidel^{b,c,†}, Uwe Hergenhahn^{d,e,g}, Evgeny Lugovoy^{e,f},
Bernd Winter^g, Anna I. Krylov^{h,i,*}, Stephen E. Bradforth^{h,*}

^a Department of Chemistry, Georgia State University, Atlanta, GA 30303, USA

^b Helmholtz-Zentrum Berlin für Materialien und Energie,

Albert-Einstein-Straße 15, 12489 Berlin, Germany

^c Humboldt-Universität zu Berlin, Department of Chemistry,

Brook-Taylor-Strasse 2, D-12489 Berlin, Germany,

^d Max-Planck-Institut für Plasmaphysik, Wendelsteinstr. 1, 17491 Greifswald, Germany

^e Leibniz-Institute of Surface Modification (IOM), Chemistry Department,

Permoserstr. 15, 04318 Leipzig, Germany

^f University of Leipzig, Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry,

Linnéstr. 3, 04318 Leipzig, Germany

^g Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

^h Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

ⁱ The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22671 Hamburg, Germany

[†] Contributed equally

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Abstract

We report a combined experimental and theoretical study of bulk water photoionization. Angular distributions of photoelectrons produced by ionizing the valence band of neat water using X-ray radiation (250-750 eV) show a limited ($<30\%$) decrease in the β anisotropy parameter compared to the gas phase, indicating that the electronic structure of the individual water molecules can be probed. By theoretical modeling using high-level electronic structure methods, we show that in a high-energy regime photoionization of bulk can be described as an incoherent superposition of individual molecules, in contrast to a low-energy regime where photoionization probes delocalized entangled states of molecular aggregates. The two regimes—low energy versus high energy—are defined as limiting cases where the de Broglie wavelength of the photoelectron is either larger or smaller than the intermolecular distance between water molecules, respectively.

Understanding how a solvent affects the electronic properties of solutes is of paramount importance for chemistry. Particularly important are the local solvent structure around solvated molecules and the changes in the shapes and energies of solute’s orbitals induced by the interactions with the solvent. Understanding the local structure of water is crucial in the context of solution chemistry, water in confined environments (e.g., biological water), or water on interfaces (e.g., metal surfaces, or electrodes).

Photoelectron spectroscopy (PES) is a powerful tool for probing electronic structure.¹ The kinetic energies of ejected electrons contain the information about their energy levels within the molecules (molecular orbitals), whereas the photoelectron angular distribution (PAD) encodes the information about the shape of the orbital from which they originate.^{2,3} Although X-ray and ultraviolet PES (XPS⁴ and UPS,^{5,6} respectively) were originally developed for gas-phase molecules in high or ultra-high vacuum,⁷ the liquid-microjet technique⁸ and ambient-pressure instruments⁹ have extended PES to the liquid phase, giving rise to an increasing number of XPS and UPS studies of solutions and liquids.¹⁰

Aqueous-phase XPS and UPS experiments can be used to probe how water molecules interact with solutes and with each other. If a solute’s intrinsic electronic structure is only weakly perturbed by the solvent, one would expect the PAD of the solute to resemble that of the gas-phase species and the difference between the two could then be attributed to the

solvent-induced perturbation of the molecular orbitals of the solute and elastic scattering of photoelectrons.^{11,12} In other words, if the solute maintains its chemical identity, as imprinted in the respective molecular orbitals, then the PAD of solvated species should maintain the gas-phase attributes, even if new features or energetic shifts emerge due to hydrogen-bonding or electrostatic interactions. However, what about a neat substance like liquid water? The bulk is likely to have a delocalized valence electronic structure, akin to excitonic bands in molecular solids.¹³ Indeed, electronic-structure calculations of water clusters^{14–16} have shown the delocalization of the valence states over many water molecules, except for valence states that have an ionization energy at the band edge (i.e., at low or high ionization energy). Of course, the extent of delocalization depends on how ordered the system is as well as the shape and energy of the molecular orbital. For example, valence bands in highly ordered solids show perfect band structure while compact core orbitals remain localized. Should one then expect the PAD of bulk water to be entirely different from the PAD of water vapor due to delocalization? Or would water in bulk maintain some semblance of its individual electronic character? To which extent does thermally induced disorder affect delocalization? For example, in a perfect water crystal at 0 K, degenerate atomic orbitals might form a perfect delocalized band, but local disorder in liquid water would induce localization, meaning that localization is a function of disorder.

In this work, we attempt to answer these questions by measuring the PAD of the valence states of neat water using high-energy electromagnetic radiation (ranging over several hundreds of electron-volts) and computing the anisotropy parameter β from first principles. Although several studies have interrogated these questions by measuring PADs of neat or doped water clusters and microjets,^{11,12,17–21} a complete picture is still elusive. The main challenge stems from many competing effects, such as intrinsic changes in the electronic structure, elastic and inelastic scattering, and surface versus bulk sensitivity that might affect the experimental observables and that are difficult to disentangle theoretically.^{22,23} Moreover, the signatures of these phenomena and the magnitude of the relevant cross sections are system- and energy-dependent. For example, it is not obvious whether changes in the PAD of bulk water compared to the gas phase are due to intrinsic changes in the electronic structure of water molecules (i.e., due to delocalization or changes in orbital shape due to rehybridization and loss of symmetry)

or due to scattering.^{12,17–19,21,23,24} The work by Thürmer *et al.*¹⁷ helps to disentangle these two effects by measuring the PAD for ionization of the $1s_O$ core orbital of water. Because this core orbital should not be significantly perturbed by the other water molecules and should, therefore, retain its shape, any difference between the measured PAD in a microjet and the ideal PAD of $\beta=2$ (at high energies) for an isolated water molecule²⁵ (obtained as a theoretical or an experimental gas-phase PAD) can be attributed to scattering. Thürmer *et al.* have shown¹⁷ that the anisotropy parameter is reduced by about 20% at photoelectron kinetic energies above 100 eV, reaching the asymptotic value of $\beta \sim 1.6$. The reduction of β was found to be more pronounced at low energies, in agreement with shorter electron attenuation lengths of slow photoelectrons.¹² We note that surface sensitivity of the experiments may affect the interpretation of this result in terms of elastic and inelastic mean free paths.²⁴

These results by Thürmer *et al.* also agree with the observations of Ahmed and co-workers^{26,27} who studied PADs from the $1s$ core orbitals in a variety of nanoparticles. They found that while the β anisotropy parameter is substantially reduced at low kinetic energies, the elastic mean free path increases considerably at high electron energies, resulting in $\beta \approx 2$ expected for ionization of $1s$ orbitals in the absence of scattering.

The results of these earlier studies^{12,17} provide an important stepping stone for the present work: It is reasonable to expect that the extent of scattering should be the same for the ionization of the valence bands of water with a similar electron kinetic energy as for the $1s_O$ core orbital, so any further reduction in the magnitude of β for the valence orbitals beyond that seen for $1s_O$ can be ascribed to the changes of the molecular orbitals upon solvation.

Recently, Signorell and coworkers have investigated valence PADs in water clusters and microjets,^{11,19,21} with the goal to disentangle different phenomena affecting PADs and to determine the convergence of the anisotropy to the bulk limit. They observed that β at low energy rapidly decreases with the cluster size and concluded that essentially bulk-like electronic structure is attained in clusters of 5-6 water molecules. Consistent with extrapolation of their cluster results and modeling of scattering, their bulk measurements yielded a significantly reduced β .^{19,21} The crucial difference between the present paper and the work of Signorell and co-workers is the energy range — the latter study has employed low-energy radiation giving rise to photoelectrons much below 100 eV. As discussed in this Letter, this difference leads to

strikingly different results.

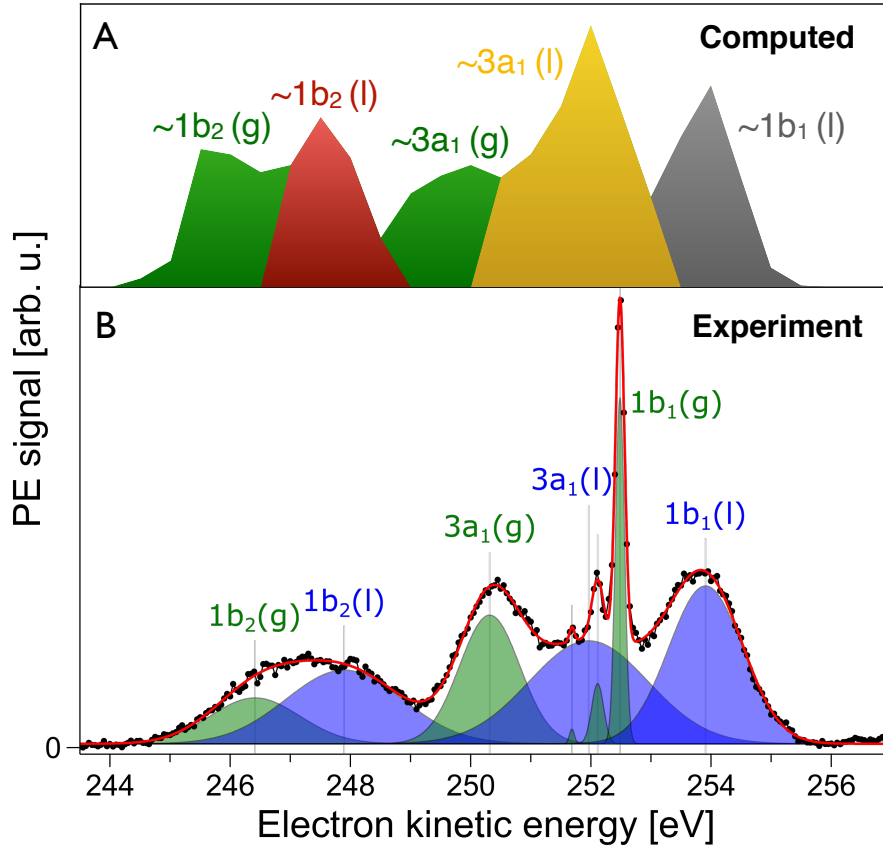


Figure 1: Photoelectron spectrum of liquid water. Top: Theoretical PES computed with EOM-IP-CCSD using pentamer clusters extracted from equilibrium MD simulations of liquid water. The $1b_1$ band (grey) is defined as any state falling in the 9.5-12.5 eV ionization energy range, the $3a_1$ band (yellow) is defined as any state falling in the 12-15 eV range, and the $1b_2$ band (red) is defined as any state falling in the 16.5-18.5 eV range. Bottom: Deconvolution fit of the experimental PES (symbols) obtained at $h\nu=265$ eV and $\theta=0$. The fit gives peaks corresponding to ionization from the $1b_1$, $3a_1$, and $1b_2$ orbitals of water for gas phase (green peaks) and liquid (blue peaks).

Fig. 1B shows total valence PES of neat water using a microjet at a photon energy of 265 eV. Fig. S1 in the SI shows an example of the spectrum as a function of θ , which represents the angle between the polarization axis of the incoming light and the orientation of the electron analyzer. Experimental details of our setups, including the SOL³PES and the LiquidPES station used for the PES measurements at the UE52-SGM beamline at the BESSY II synchrotron radiation facility in Berlin as well as the High Harmonic Generation (HHG) setup at the University of Leipzig, can be found in the SI.

The spectral bands (Fig. 1, and Figs. S1 and S2 in the SI) can be assigned to the ionization from the three highest energy molecular orbitals of isolated (gas-phase) water molecules and of liquid water. The analysis of the PADs confirms that, as in the core-ionization study,¹⁷ the standard equation (Eq. (S1) in the SI) derived for randomly oriented molecules is valid and that the PAD is determined entirely by the dipole anisotropy parameter β . β values associated with each peak are extracted from fitting the gas-phase features in our spectra. Those β values corresponding to the gas-phase peaks are shown in Fig. 2 along with the wealth of β values from the literature that have electron kinetic energies up to ~ 100 eV.^{28,29} Our HHG result at low photon energy, shown by green dot in Fig. 2 agrees well with the previous measurements. These HHG β values refine the earlier published values by Faubel *et al.*,³⁰ which were measured in the same HHG lab in Leipzig but lacked a complete set of polarization angles and a proper error analysis. A summary of the experimental data from this work is given in Tables S1, S2, and S3 in the SI.

The PAD of the valence photoelectrons in gas-phase water^{28,29} can be explained by the shapes of the respective molecular orbitals. The $1b_2$, $3a_1$, and $1b_1$ orbitals of water have predominantly p -like character: the $1b_1$ orbital is a pure p -like lone pair orbital whereas $1b_2$ and $3a_1$ are slightly bent (σ_{OH}). Consequently, for all 3 transitions we expect predominantly an s -wave ($\beta=0$) at low electron kinetic energies and significant contributions of the d -wave ($\beta > 1$) at higher energies. This is exactly what is observed here and in the previous experiments,^{28,29} as well as in the calculations using correlated Dyson orbitals and simple photoelectron description (similar trends were reported in an earlier study using density functional theory²⁵). Thus, PADs of gas-phase water clearly show the atomic provenance of the molecular orbitals, while reporting on the variable extent of their hybridization in a molecular environment (e.g., out of the three orbitals, the shape of the $1b_2$ orbital is most deformed, leading to the largest deviations of β from those expected from a pure p -orbital).

The theoretical β s in Fig. 2 were computed using correlated Dyson orbitals, which encode the information about electronic structure before and after the ionization, with the ejected photoelectron wave function treated either as a free particle (plane wave) or as a particle perturbed by the Coulomb potential due to +1 point charge representing the water cation (Coulomb wave).^{31,32} The theoretical framework is described in detail in Refs. 31,33 and in

the SI. The difference between the two computational models (using plane waves or Coulomb waves) is reduced above kinetic energies of ~ 100 eV, indicating that the two models converge to the same result for high-energy photoelectrons. While neither the plane nor Coulomb wave calculation quantitatively reproduce the experimental data (at high kinetic energies, the theory overestimates β s for the $1b_1$ state and appears to be out of phase with the experiment for the $1b_2$ state), the plane wave model reproduces several features of the experimental data, including the sharp rise in β at low kinetic energies and the small oscillations of β around values of 1-1.5 at high kinetic energies. This indicates that the simple single-expansion model employed here captures the variations of the angular distribution of the different ionized states of water using the corresponding Dyson orbitals, which describe deformation of atomic orbitals within a molecular environment. We employ plane waves in the rest of the calculations in this work.

How should we modify this simple picture for a water dimer, larger clusters, and eventually bulk? The measurements by Signorell and co-workers^{19,21} on water valence bands suggest that anisotropies in the bulk are quickly washed out, giving rise to strongly reduced β , whereas, as we show later, our PADs show a persistent anisotropy consistent with a p -like character of the respective Dyson orbitals. To understand these seemingly contradictory findings for bulk water PADs, we start by discussing the theoretical framework for treating photoionization in molecular aggregates (dimers, trimers, etc). Conceptually, should we think about photoionization of the dimer as a sum of two incoherent waves coming from each monomer or a single wave corresponding to ionization of an entangled dimer state? The answer to this question determines whether the theoretical model should entail two independent calculations based on localized Dyson orbitals of the monomers or a single-center expansion and a delocalized Dyson orbital of the dimer.

The difference between the two frameworks is illustrated in Fig. 3, which shows β computed for the state derived from the $1b_1$ monomer states of two non-interacting water molecules. For symmetry-identical monomers, the dimer states are two degenerate states corresponding to in-phase and out-of-phase linear combinations of monomer states. The PAD computed using these delocalized states and a single-center expansion placed in the centroid of the Dyson orbital (that is, in between the two fragments) gives $\beta \sim 0.5$ (red curve in Fig. 3). However, in the case of exactly degenerate states, any linear combination can be used, so instead of the

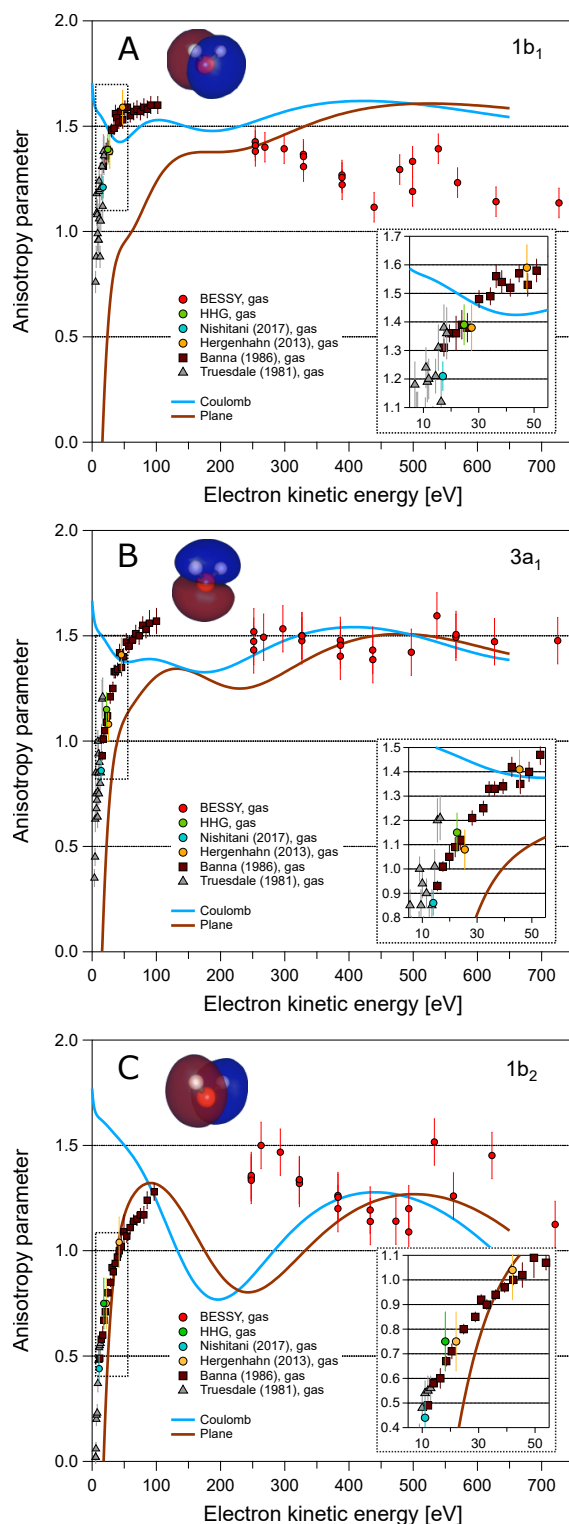


Figure 2: Experimental (symbols) and computed (solid lines) β values for ionization of the $1b_1$ (panel A), $3a_1$ (panel B), and $1b_2$ (panel C) orbitals of vapor-phase water over a range of 700 eV. Experimental data are from Truesdale *et al.*²⁸ (grey triangles), Banna *et al.*²⁹ (brown squares), Nishitani *et al.*²⁰ (cyan circles), Hergenhahn and co-workers¹⁸ (yellow circles), and this work (HHG data in green; BESSY data in red). Computed anisotropies are shown as solid lines using a plane wave (brown) and Coulomb wave (blue) description of the photoelectron. The corresponding EOM-IP-CCSD Dyson orbitals are shown for each transition.

delocalized states one can consider two localized Dyson orbitals as another possible solution. The respective PADs (grey curves in Fig. 3) are monomer-like, giving rise to $\beta \sim 1$. For the two infinitely separated waters, the latter description must be the correct one, but at short distances one may expect the delocalized picture to be more appropriate. Fig. S7 in the SI shows how the anisotropy changes upon an increasing delocalization of the orbitals in a more realistic (geometry-optimized) model water dimer. It is clear that once the delocalization develops, anisotropy is reduced drastically (however, it does not vanish, because the delocalized molecular orbital of the dimer still has symmetry). The key question is then which model applies better to photoionization of bulk water. Are molecules in the liquid far enough apart to justify a monomer-based treatment of photoionization or should one use delocalized orbitals?

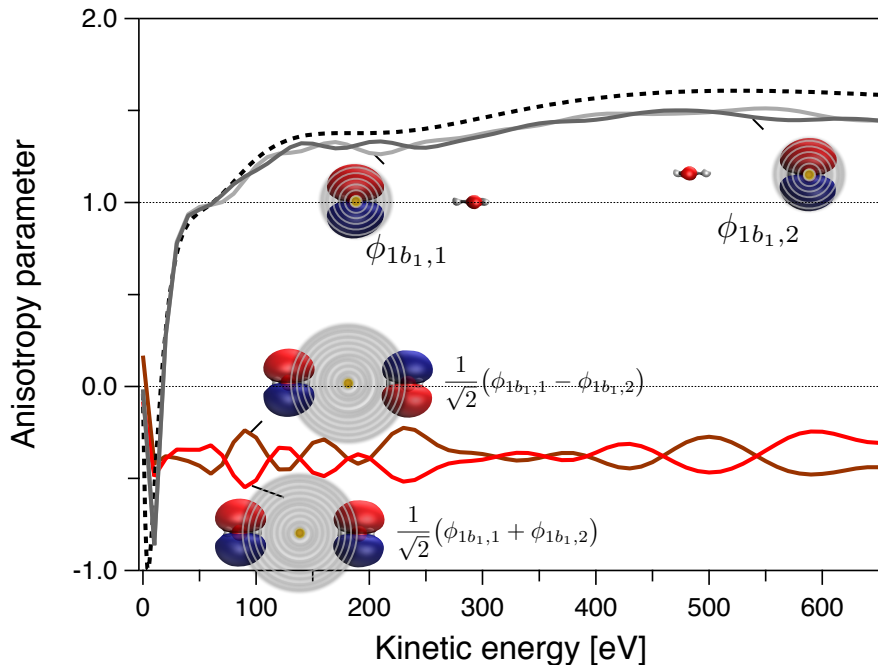


Figure 3: Anisotropies of two non-interacting water molecules computed using localized monomer states (grey) and delocalized dimer states (red). Yellow dots indicate the center of the expansion for the free electron state, which are placed at the centroids of the corresponding Dyson orbitals. The black dashed line shows anisotropies for the $1b_1$ ionized state of the monomer. See text for details.

This exact question has been posed and discussed by Sanov and co-workers³⁴ using photodetachment from dissociating I_2^- , which the authors described as a “molecular interferometer”. They have shown that at large I-I distances, the PAD corresponds to the atomic-like signal

(detachment from a p -orbital), whereas at short distances the PAD reflects a delocalized π^* molecular orbital (which has the same symmetry as a d -orbital placed at the middle of the I-I bond). The latter situation can also be described as the interference of the two coherent waves, one coming from each atom. The transition between the two regimes depends on the photoelectron energy, which determines de Broglie wavelength (λ) of the photoelectron: if the distance between the two centers (R) is larger than λ , then one can treat the photodetachment as two independent non-interfering waves, whereas for $\lambda \sim R$ the two waves interfere and the photodetachment signal reveals an entangled state. Alternatively, one can think about the energy gap between the delocalized states versus the energy of the ionizing pulse – if the energy gap is small relative to the photon bandwidth, then the states can be treated as degenerate.

Below we discuss the implications of these two distinct regimes in photoionization experiments of bulk water. To simulate the photoionization of bulk water, we consider a model system, a water pentamer cut out from the equilibrium molecular dynamics (MD) simulation of liquid water. To account for thermal motions, we average the results over 100 random snapshots. Our choice of the pentamer is based on the conclusions of a recent PES study of water clusters¹⁹ that suggested that water clusters with five or more waters capture the effect of one solvation shell and, therefore, are a reasonable first-order approximation of bulk water. To model the photoelectron spectra, we compute the EOM-IP-CCSD ionization energies and Dyson orbitals for all valence states for each of the 100 pentamer structures. The computed valence photoelectron spectrum is shown in Fig. 1A. For comparison, Fig. 1B shows a measured valence photoelectron spectrum obtained at 265 eV photon energy and $\theta=0$. The features in the experimental spectrum are broken into the contributions from the liquid and gas-phase water molecules and clearly show distinct bands corresponding to the three valence molecular orbitals of water in each phase. The computed spectrum is obtained as a histogram of the frequency of occurrence of different ionization energies. The computed spectrum also shows the features of both liquid- and gas-phase peaks. Three of the peaks have similar energies and shapes as the experimental spectra of bulk water, and are shown in grey ($1b_1$), yellow ($3a_1$), and red ($1b_2$). Additional peaks (marked by green) in the computed spectrum have energies and shapes that are more similar to the experimental spectra for gas-phase water. These peaks originate from the orbitals localized on surface water molecules that do not strongly interact

with the others and, therefore, resemble gas phase water more than bulk water. Overall, Fig. 1A illustrates inhomogeneous broadening of 2-4 eV of individual bands, leading to their partial overlap. A good agreement between the theoretical and experimental spectra provides further support of our computational protocol and justification of using the pentamer model.

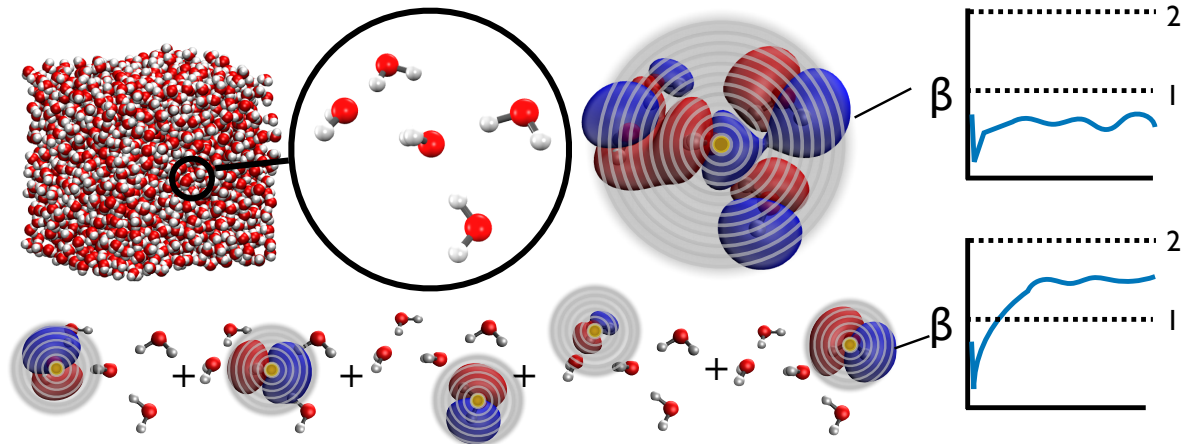


Figure 4: Schematic representation of two protocols for PAD’s calculations. Top left: 100 pentamer geometries were extracted from a molecular dynamics simulation of liquid water. Top center: Representation of the single-center expansion approach, with the center (shown by yellow dot) placed at the centroid of the delocalized Dyson orbital. This approach yields a more isotropic PAD, as illustrated at top right drawing. Bottom: Representation of the multi-center approach in which the total PAD is given by the sum of the PADs contributed by each water (yellow dots mark the centroids of the localized Dyson orbitals). These calculations yield anisotropic PADs consistent with *p*-like character of the Dyson orbitals, as illustrated by the drawing on the right.

To simulate the PAD of bulk water, we computed β ’s for each pentamer structure using two different approaches illustrated in Fig. 4. In the first approach, we used delocalized Dyson orbitals and a single-center plane-wave expansion (Fig. 4, top); in this approach, orbital deformation, interference, and scattering within the first solvation shell (i.e., ejected electron scattering between each water and its immediate neighbors) is accounted for. In the second approach, we split the Dyson orbital into the fragments contributions, each localized on a single water molecule. We compute the differential cross section for each of the fragment orbitals in the pentamer using a plane-wave expansion centered on the respective fragment’s orbital, and then sum up the contributions of the five water molecules to the total PAD (Fig. 4, bottom); in this approach only orbital deformation is included while scattering and interference

with neighboring water molecules is neglected. A related multi-center approach was employed by Manson and co-workers to model photoionization for molecules fixed in space³⁵ and for scattering from molecules.³⁶

Fig. 5 shows the computed and experimental β values as a function of kinetic energy for the liquid peaks in the photoelectron spectrum. Also shown are the HHG data from this work (35.6 eV photons) and the data by Nishitani *et al.*²⁰ (29.5 eV photons) for the three valence states of liquid water. The experimental β values are derived by fitting the peak areas for the individual water valence bands (see Fig. 1B, and Tables S1, S2, and S3 in the SI) as a function of the angle between the electron analyzer and the polarization direction. The data shown include four independent runs with 19 different photon energies from the synchrotron and a lower photon energy dataset recorded with HHG radiation. The error bars reflect the fluctuations of the liquid jet position, the fitting errors, and the deviations from the ideal polarization provided by the UE52-SGM-1 beamline. Due to a large peak-overlap and fit constraints, the error bars for the $3a_1$ and $1b_2$ orbitals are larger than for the $1b_1$ orbital. More details about the data acquisition, data analysis, fitting routine and the error bar determination can be found in the SI.

The experimental β curves reveal considerable similarity between the bulk (Fig. 5) and gas phase (Fig. 2). At high kinetic energies (i.e., above 250 eV), β for bulk ionization ranges around 1-1.25, to be compared with the 1.25-1.5 range for the gas-phase ionization. In both cases, the largest β values are observed for the $3a_1$ band.

The theoretical β values computed using a single delocalized Dyson orbital (dashed line) are strikingly different from those computed by using fragment orbitals and multi-center expansion (solid lines). The multi-center approach gives β values that are in much better agreement with the experiment for electron kinetic energies above 40 eV, while the single-center expansion model is qualitatively incorrect. The blue line in Fig. 5 shows the total β from all valence states of the 100 pentamer snapshots. To obtain β values corresponding to the $1b_1$, $3a_1$, and $1b_2$ liquid bands theoretically, we select states that fall in the grey, yellow, and red bands of Fig. 1A, respectively. Although the agreement is not quantitative, the computed β values are in the same range as the experimental ones.

To better understand the discrepancies associated with the theoretical model, it is instruc-

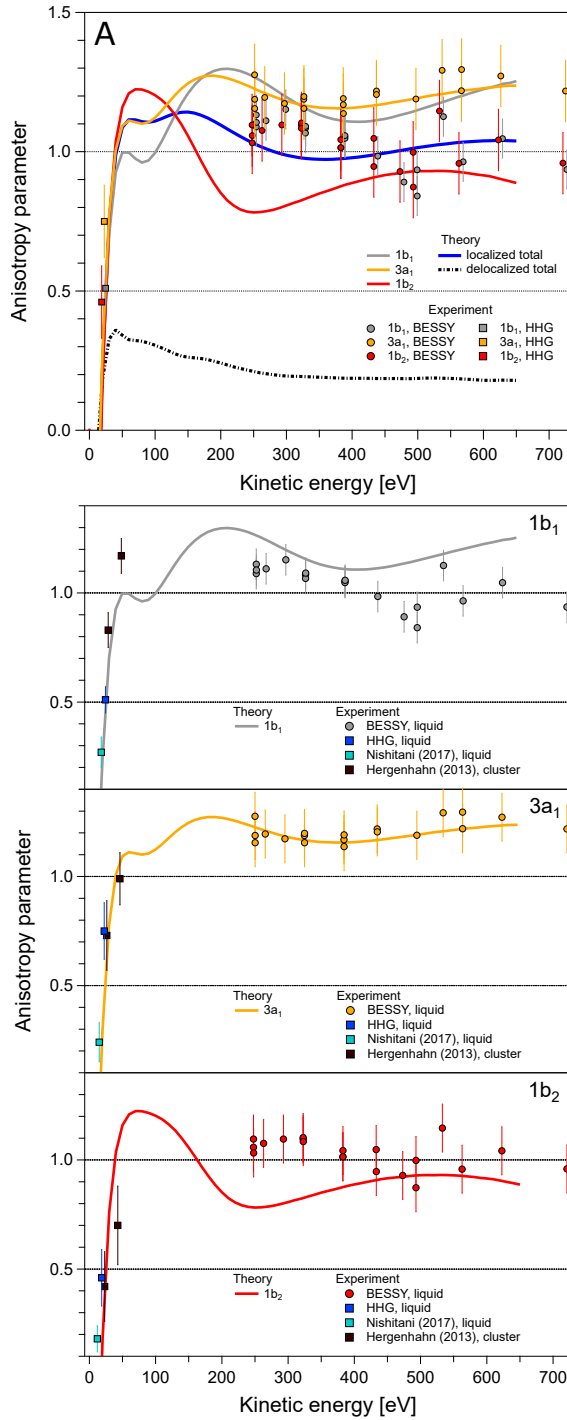


Figure 5: Experimental (symbols) and computed (lines) β values as a function of energy for valence ionization of liquid water. Grey, yellow, and red denote the values for the $1b_1$, $3a_1$, and $1b_2$ bands. In the top panel, the solid blue line shows β computed by summing the contributions of all valence states of individual waters to the pentamer's PAD. The black dashed line shows the result of using a single plane-wave expansion placed at the centroid of the pentamer Dyson orbital. In the three following panels, theoretical β values are assigned based on the energy of the binding energies (see Fig. 1; the experimental fitting procedure is described in the SI). Experimental data are from Nishitani *et al.*²⁰ (liquid microjet, cyan squares), Hergenhausen and co-workers¹⁸ (water cluster, black squares), and this work (HHG indicated by dark blue squares, BESSY data with circles, color coded depending on the orbital).

tive to compare the differences between the theory and experiment for each band for gas-phase water ionization. In this case, the main limitation of the theoretical treatment is an approximate treatment of the free-electron state. In the plane-wave treatment, the perturbation of the continuum state by the molecular ionic core is entirely neglected, whereas in the Coulomb-wave treatment it is approximated by a centro-symmetric Coulomb potential. As Fig. 2 shows, the resulting discrepancies at high energies are the smallest for the $3a_1$ state (the theoretical curves are within the experimental error bars). For the $1b_1$ state, theory overestimates β and for the $1b_2$ state it underestimates it. We also note that for the latter, both theory and experiment show oscillatory behavior, but the phase of the oscillation does not match. The observed discrepancies for the gas-phase ionization (Fig. 2) provide a numeric measure of the theoretical errors due to approximate treatment of the continuum state. These errors apparently propagate into the bulk ionization calculations (Fig. 5): the discrepancy between the theoretical (multi-center model) and experimental β are smallest for the $3a_1$ state, while for the $1b_1$ and $1b_2$ states we observe the same trend (theory overestimates β for the former and underestimates it for the latter). This systematic behavior and a similar magnitude of the differences suggests that our simple theoretical treatment captures the main differences between gas-phase and bulk photoionization correctly.

To understand the implications of the results shown in Fig. 5, let us revisit the analysis of the two limiting regimes of dimer photoionization (Fig. 3). A qualitatively incorrect β obtained for delocalized Dyson orbitals indicates that in the present experimental regime bulk water ionization can be described as incoherent superposition of the photoionization of individual water molecules rather than photoionization of delocalized entangled states. We can understand this in the context of Sanov and co-worker’s molecular interferometer,³⁴ where the short-time evolution of time-resolved photoelectron images from the dissociating I_2^- are discussed in terms of the interference between the two waves coming from the individual atoms. This interference can be described as ionization of an entangled state spanning both iodine atoms at short I_2^- bond length. However, at longer times (i.e., at large separations between the atoms) the variation in β ceases and it approaches the asymptotic value corresponding to the PAD of I^- . The distance at which the atoms become independent is related to the energy of the ionizing radiation, which in turn determines the energy of photoelectrons. In Sanov’s study the distance

at which the iodine atoms are no longer coherently ionized (or, said in another way, at which the photoelectrons no longer interfere) was found to be 35 \AA , which was in excellent agreement with the de Broglie wavelength of the ejected photoelectrons (0.12 eV).

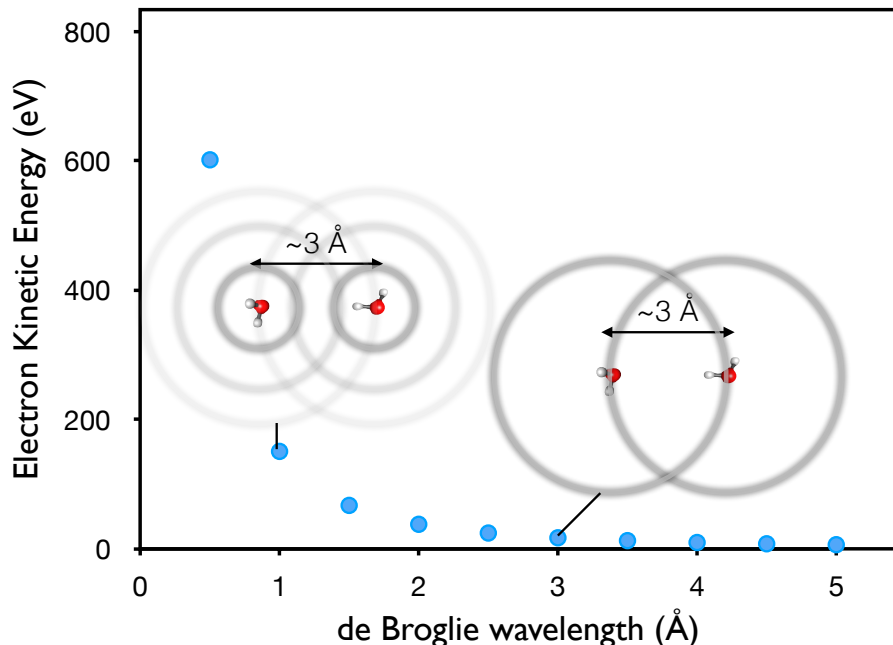


Figure 6: De Broglie relation between the energy of an electron and its wavelength. The distance between two waters in the optimized dimer is $\sim 3 \text{ \AA}$, which corresponds to electron kinetic energy of $\sim 17 \text{ eV}$. At such energies or below, an ejected photoelectron is likely to undergo interference with the electrons coming off the nearby waters and loses its anisotropy. At higher energies (e.g., at 150 eV , where the electron wavelength is 1 \AA) interference is not significant enough to reduce the photoelectron’s anisotropy.

In bulk water, the typical distance between the centers of two water molecules is on the order of 3 \AA . This corresponds to an electron kinetic energy of $\sim 17 \text{ eV}$ (see Fig. 6). At this energy or lower, the photoionization would likely probe a coherent delocalized state of water (or, using alternative language, reflect interference between the photoelectrons ejected from the individual fragments). This is consistent with the recent measurements at low kinetic energies by Signorell and co-workers²¹ that show a significant reduction in the β of valence bands from large water clusters. Therefore, at low energies, the single-center expansion of the photoelectron wave function is justified (note that this model also implicitly includes elastic scattering within the first solvation shell). In contrast, at high energies (e.g., above 150 eV where the photoelectron wavelength is 1 \AA), it is more appropriate to describe photoionization

using localized orbitals. The observed persistent anisotropy of photoelectrons confirms that water’s valence orbitals retain their identity, although they are slightly distorted (polarized and hybridized) by their environment. This implies that PES and photoelectron imaging can probe the local electronic structure of a molecule even in a solvent, as long as the ejected photoelectron has a de Broglie wavelength smaller than the proximity of nearby solvent molecules.

Our results are relevant in the context of the analysis by Sanche and co-workers,²³ who categorize contributions to scattering in the bulk into two types. The first type of scattering is due to intermolecular interactions that affect the electronic properties of the bound states in individual water molecules. These interactions are captured in our localized cluster model. The second contribution is from the ejected electron interacting with neighboring molecules when the de Broglie wavelength of the ejected electron is comparable to the separation between the bulk water molecules. This effect, which is described by the delocalized model, is expected to be less significant at high electron kinetic energies due to the small de Broglie wavelength of the electron.

To quantitatively analyze the reduction of anisotropies in bulk relative to the gas phase, we consider the reduced β defined as:

$$\beta_{red} \equiv 1 - \frac{\beta_l}{\beta_g}, \quad (1)$$

where β_l and β_g denote liquid and gas-phase anisotropies. If the anisotropy in the liquid phase is the same as in the gas phase, then $\beta_{red} = 0$. Conversely, $\beta_{red} \approx 1$ signifies a complete loss of anisotropy in liquid. The water $1s_O$ core-level study¹⁷ showed that β_{red} decreases as a function of photoelectron kinetic energy and at high kinetic energies (above 200 eV), $\beta_{red} \approx 0.2$. Ahmed and coworkers²⁶ observed a similar trend in β for the $1s_C$ ionization in squalene nanoparticles (at their highest kinetic energy of ~ 40 eV, $\beta \approx 1$, corresponding to $\beta_{red} \approx 0.5$). Interestingly, they observed larger values of β for the $1s_B$ ionization of dry boric acid nanoparticles, approaching 2 at energies above 50 eV.

The reduction of the anisotropy for core ionization at high energies has been attributed by Thürmer *et al.* entirely to elastic scattering, because the shape of the compact $1s_O$ orbital is not perturbed by the interactions with neighboring waters.¹⁷ Our calculations of the anisotropy for $1s_O$ ionization of water pentamers (Fig. S10) yield $\beta = 2$ at electron kinetic energies above 20 eV, thus providing computational support to this conjecture.

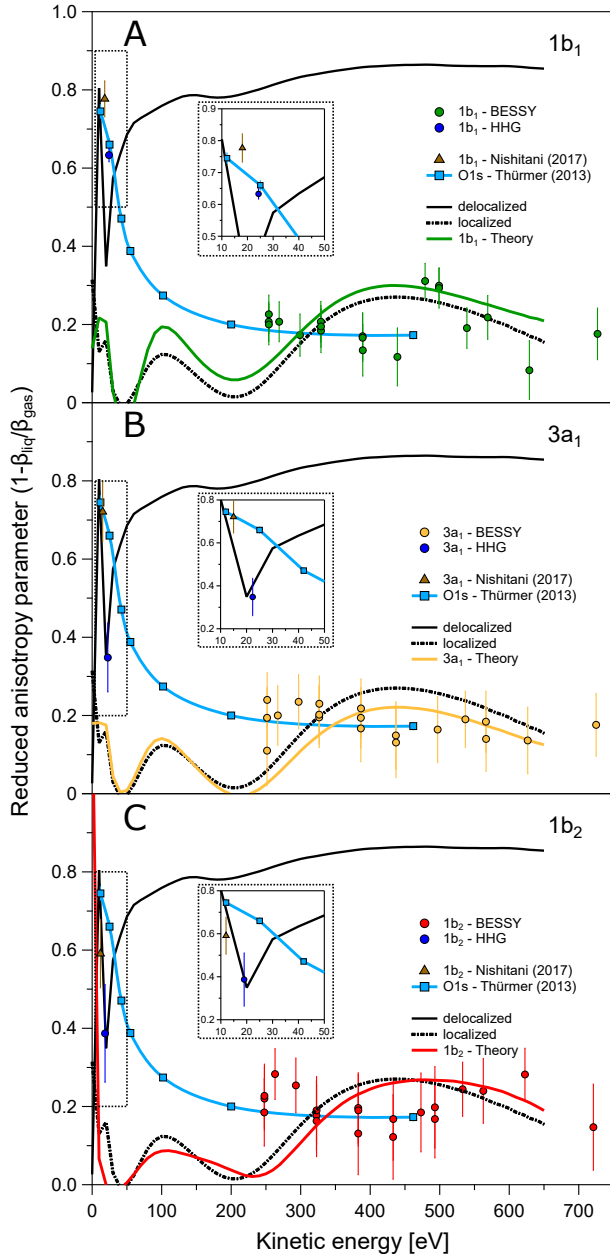


Figure 7: Experimental (symbols) and theoretical (lines) reduced β values for the $1b_1$ (panel A), $3a_1$ (panel B), and $1b_2$ (panel C) bands of water. The blue squares and solid blue line correspond to the reduction in anisotropy due to scattering extracted from the water $1s_O$ core-ionization study.¹⁷ The insets show HHG data points (35.6 eV photons, dark blue squares) and data by Nishitani *et al.*²⁰ (29.5 eV photons, brown triangles). Solid and dashed black lines show the combined results for all valence photoelectrons computed using delocalized (single-center) and localized (multi-center) approaches, respectively.

Fig. 7 shows the experimental and theoretical β_{red} values for core and valence ionization. As in the core-level study,¹⁷ we observe a systematic reduction of β in liquid for valence photoionization. Surprisingly, within the experimental error bars, $\beta_{red} \approx 0.2$ at high energies for both the $1s_O$ and valence orbitals (compare the β values for the data from BESSY in this work with the light-blue curve derived from Thürmer *et al.*). This is surprising because it might be expected that the valence orbitals would undergo a further reduction in β upon solvation compared to the core $1s_O$ orbital due to delocalization or distortion of the orbital shape. In fact, the binding energies of the valence bands in liquid are significantly broadened and shifted to lower binding energies, by around 1.5 eV, due to solvation (with small variations depending on the orbital shape).³⁷ However, the similar β_{red} for the $1s_O$ and valence orbitals suggests either that the reduction in β for valence orbitals is due to scattering and therefore that the shape of the valence orbitals of water is not perturbed by the interactions with the neighboring waters, or that the effect of elastic scattering is smaller for valence ionization than for the core ionization.

The comparison between the theoretical and experimental β_{red} curves supports the latter argument. We observe that for high kinetic energies (>250 eV), the agreement between theory (localized model) and experiment is good for all three bands. We note that in β_{red} , the systematic discrepancies between theory and experiment (i.e., the overestimation of β for $1b_1$ and underestimation of β for $1b_2$ in both the gas and the liquid calculations compared to experiment) largely cancel out, giving rise to the better agreement between all three bands. Because the localized theoretical model does not account for the reduction due to scattering, the results of the calculations suggest that the reduction in β of the valence orbitals are largely due to the perturbation of the orbital shape and not to scattering.

As expected, the results for the single-center expansion show almost a complete loss of anisotropy ($\beta_{red} \approx 0.8$ at high energies). While this treatment is inappropriate for the high kinetic energy regime, at lower energies it correctly captures the interference effects and also accounts for scattering within the first solvation shell. We note that for the lower energy data points from Nishitani *et al.*²⁰ and for the HHG data points, the delocalized model is in excellent agreement with the experiment for all three bands, suggesting that the scattering beyond the first solvation shell is not important. At the same time, the experimental HHG β_{red}

for ionization from the $3a_1$ and $1b_2$ bands differs markedly from β_{red} from the core-level study (light blue curve), implying that even at below 50 eV the effect of elastic scattering for valence photoelectrons is less significant than for the core photoelectrons.

The comparison between our experimental PADs for valence and core-level photoionization at high and low-energy regimes, along with the comparison between the theoretical and experimental β_{red} , suggest that the effect of elastic scattering on the photoelectron anisotropy is less pronounced for valence photoelectrons than for $1s_O$ photoelectrons. Given the limitations of the present theoretical treatment and the available experimental data, we can only speculate about possible reasons for this puzzling observation. One possibility is that the extent of scattering depends on the angular momentum of the photoelectron, i.e., p -waves may have a greater probability of scattering than d -waves. While there is no obvious reason to expect that scattering cross section should depend on the angular momentum of the photoelectron, simple geometric considerations suggest that different angular momenta can affect the probing depth and relative contributions of the surface relative to bulk. For example, a p_z -wave emanating from a molecule at a given distance z from the microjet surface would travel a $\sqrt{2}$ shorter path to the surface than a d_{xz} -wave. Consequently, it is plausible that the probing depth is shorter (by around 30 %) for valence photoionization than for $1s$ core photoionization (the exact value would depend on the polarization of light relative to the surface). If this is the case, the contribution of surface waters relative to bulk would increase, thus reducing the effect of elastic scattering for ionization from valence orbitals. We note that the data for selected atomic solids quoted in Ref. 22 suggests that elastic scattering becomes less significant for higher angular momentum (for example, transport mean free path, which is inversely proportional to the elastic mean free path, is 30 % smaller for $4p$ than for $4s$ ionization of Au). Similarly, Zhang *et al.* have also found that, in rare-gas clusters, the reduction of β from the gas phase to the cluster due to scattering depends on the orbital shape with scattering for Ar $3s$ ionization being larger than Ar $2p$ at equal kinetic energies.^{18,38} This is in line with the hypothesis above as well.

In order to unambiguously explain the observed trends, more sophisticated theoretical treatment is needed, which should include modeling of scattering, as done, for example in Refs. 11,24, as well as electronic effects, as done in the present work. On the experimental side, more data at intermediate photoelectron energies would help to clarify these issues. To better assess

possible effects due to the surface waters and back-scattering of the photoelectrons emanating from gas-phase molecules, experiments with different geometries of the jet (e.g., flat jets) are desirable. Such experiments are currently under way.

In conclusion, we presented a combined experimental and theoretical study of valence photoionization of liquid water using X-ray radiation. The results show that using sufficiently high energy enables probing the electronic structure of individual water molecules within the bulk. The decrease in anisotropy values in bulk relative to gas-phase water, which can be attributed to the deformation of valence orbitals due to rehybridization and loss of symmetry, is remarkably small. The comparison with core-photoionization study suggests that the effect of scattering is smaller for valence photoionization than for core. Although unexpected, these results provide an important contribution towards developing a comprehensive picture of photoionization in the condensed phase and highlight the need for developing a unifying theoretical framework seamlessly connecting low- and high-energy regimes.

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Supporting information available: Experimental details, computational details, and additional comparisons of gas-phase versus liquid anisotropies. This information is available free of charge via the Internet at <http://pubs.acs.org>.

Conflicts of interest: A.I.K. is the President and a part-owner of Q-Chem, Inc.

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Probing the Electronic Structure of Bulk Water at the Molecular Lengthscale with Angle-Resolved Photoelectron Spectroscopy:

Supplemental Information

Samer Gozem^{a,†}, Robert Seidel^{b,c,†}, Uwe Hergenhahn^{d,e}, Evgeny Lugovoy^{e,f},
Bernd Winter^g, Anna I. Krylov^{h,i,*}, Stephen E. Bradforth^{h,*}

^a Department of Chemistry, Georgia State University, Atlanta, GA 30303, USA

^b Helmholtz-Zentrum Berlin für Materialien und Energie,
Albert-Einstein-Straße 15, 12489 Berlin, Germany

^c Humboldt-Universität zu Berlin, Department of Chemistry,
Brook-Taylor-Strasse 2, D-12489 Berlin, Germany,

^d Max-Planck-Institut für Plasmaphysik, Wendelsteinstr. 1, 17491 Greifswald, Germany

^e Leibniz-Institute of Surface Modification (IOM), Chemistry Department,
Permoserstr. 15, 04318 Leipzig, Germany

^f University of Leipzig, Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry,
Linnéstr. 3, 04318 Leipzig, Germany

^g Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

^h Department of Chemistry, University of Southern California, Los Angeles, CA 90089, USA

ⁱ The Hamburg Centre for Ultrafast Imaging, Luruper Chaussee 149, 22671 Hamburg, Germany

[†] Contributed equally

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I. EXPERIMENTAL DETAILS

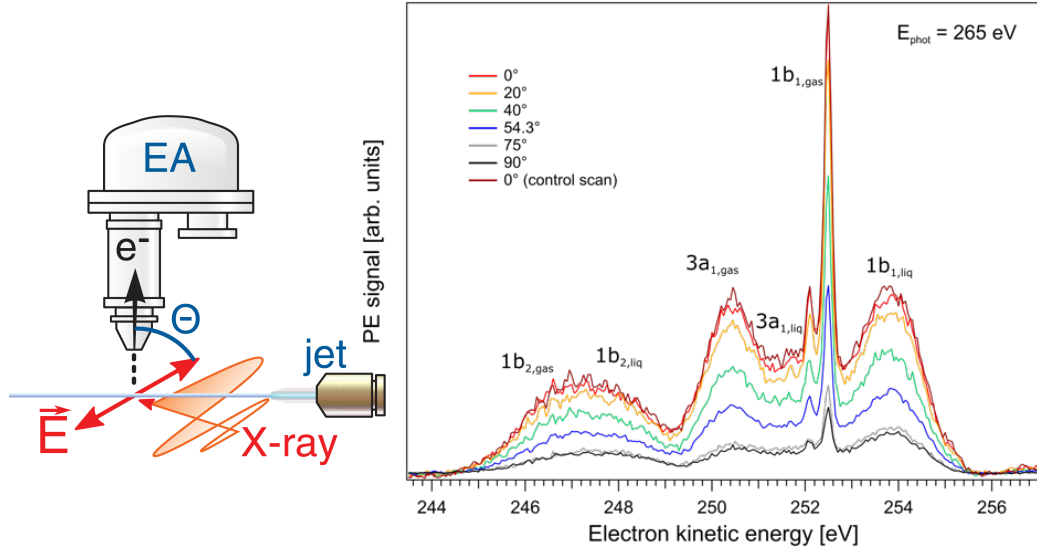


FIG. S1: Photoelectron spectroscopy of liquid water using the microjet technique. Left: Schematic representation of the experimental setup. Water from a liquid microjet is ionized with linearly polarized radiation. The polarization is varied along θ with respect to the orientation of the hemispherical electron analyzer (EA). Reproduced with permission from reference [1]. Right: Photoelectron spectra obtained with 265 eV ionizing radiation at different values of θ . β anisotropy values are derived by fitting the PADs using the cross sections obtained at different values of θ .

A. Photoelectron angular distribution

Photoionization with photon energies below 1 keV is well described within the electric dipole approximation for the photon field[2]. For an unoriented sample, the angular distribution function of the photoelectrons is most easily presented in the laboratory frame. Its general form depends on the polarization state of the ionizing radiation, which can be represented by the Stokes parameters S_{1-3} (Ref. 3). For a non-chiral target in a polar coordinate system with z being the propagation direction of the radiation, x along the horizontal, and θ, ϕ denoting the emission direction, we have[4]:

$$I(S, \theta, \phi) = 1 - \frac{\beta}{2} \left[P_2(\cos \theta) - \frac{3}{2} (S_1 \cos 2\phi + S_2 \sin 2\phi) \sin^2 \theta \right]. \quad (\text{S1})$$

Here, S_1 refers to the degree of polarization along the horizontal or vertical axis and S_2 refers to linear polarization with a 45° (135°) degree tilt; P_2 denotes the second Legendre polynomial. β is the angular distribution parameter (or anisotropy parameter), which contains the details of the interaction between photon field, initial state and outgoing electron. Here and below I is normalized to 4π when integrated over the unit sphere. To be interpreted as a differential cross section, the functions should be multiplied by $\sigma/4\pi$, with σ denoting the total photoionization cross section for a particular band. Note that the degree of circular polarization S_3 has no influence on the angular distribution.

It is often more convenient to write this equation in a slightly different form,

$$I(S, \theta, \phi) = 1 - \frac{\beta}{2} \left[P_2(\cos \theta) - \frac{3}{2} p \cos 2(\phi - \lambda) \sin^2 \theta \right], \quad (\text{S2})$$

with p denoting the degree of linear polarization along the major axis of the polarization ellipse and λ denoting the tilt of the ellipse to the horizontal:

$$p \equiv (S_1^2 + S_2^2)^{1/2}, \quad (\text{S3})$$

$$\lambda \equiv \arctan(S_2/S_1)/2. \quad (\text{S4})$$

In most experiments, the angular distribution is measured in the dipole plane, i.e., perpen-

pendicular to the propagation direction of the photon beam. Eq. (S2) then simplifies to

$$I(S, \pi/2, \phi) = 1 + \frac{\beta}{4} [1 + 3p \cos 2(\phi - \lambda)]. \quad (\text{S5})$$

In this work, we used this form of the angular distribution to analyze the data. For perfect linear polarization ($p = 1, \lambda = 0$), this is equivalent to the better known

$$I(\phi) = 1 + \beta P_2(\cos \phi). \quad (\text{S6})$$

For ionization by linearly polarized radiation, the electron emission pattern typically shows a propensity for emission along the dipole axis, measured by a positive value of the angular distribution parameter β . The exact value of β , however, depends on the details of the initial state and the ionization process. Determining β from $I(\phi)$ involves a comparison of measurements under at least two different emission angles.

B. Measured β parameters for the valence photoelectrons from microjet experiments

Tables S1-S3 summarize the measured anisotropies and the respective error bars for each water band. β values at kinetic energies above 248 eV were measured at the synchrotron radiation facility BESSY II with the LIQUIDPES and SOL³PES setups. Data points at low kinetic energy (18 eV - 1b₂, 22 eV - 3a₁, and 24 eV - 1b₁) were derived from High-Harmonic Generation experiments at the IOM Leipzig. The details for the data analysis in each experiment are given in sections E and H.

TABLE S1: Measured β parameters of the 1b₁ band.

E_{kin} , eV	β , gas	β , liquid	β_{red}
24	1.390(60)	0.510(60)	0.633(17)
254	1.426(70)	1.132(70)	0.207(50)
254	1.408(70)	1.089(70)	0.226(49)
254	1.381(70)	1.105(70)	0.200(52)
269	1.400(70)	1.111(70)	0.207(51)
299	1.393(70)	1.152(70)	0.173(54)
329	1.366(70)	1.084(70)	0.207(52)
329	1.308(70)	1.067(70)	0.184(56)
329	1.356(70)	1.091(70)	0.195(53)
389	1.268(70)	1.053(70)	0.170(60)
389	1.256(70)	1.048(70)	0.166(61)
389	1.222(70)	1.058(70)	0.134(66)
439	1.115(70)	0.984(70)	0.117(74)
479	1.294(70)	0.891(70)	0.311(45)
499	1.333(70)	0.935(70)	0.299(45)
499	1.190(70)	0.841(70)	0.293(51)
539	1.393(70)	1.126(70)	0.191(52)
569	1.232(70)	0.964(70)	0.218(56)
629	1.142(70)	1.047(70)	0.083(76)
727	1.136(70)	0.936(70)	0.176(66)

TABLE S2: Measured β parameters of the $3a_1$ band.

E_{kin} , eV	β , gas	β , liquid	β_{red}
22	1.150(130)	0.750(130)	0.348(88)
251	1.433(110)	1.276(110)	0.110(91)
251	1.473(110)	1.188(110)	0.194(77)
251	1.519(110)	1.155(110)	0.240(69)
267	1.493(110)	1.195(110)	0.200(76)
297	1.533(110)	1.173(110)	0.235(69)
327	1.476(110)	1.188(110)	0.195(77)
327	1.501(110)	1.198(110)	0.202(75)
327	1.499(110)	1.155(110)	0.230(71)
387	1.403(110)	1.169(110)	0.167(85)
387	1.478(110)	1.191(110)	0.194(77)
387	1.455(110)	1.137(110)	0.218(75)
437	1.432(110)	1.218(110)	0.149(86)
437	1.387(110)	1.205(110)	0.131(91)
497	1.422(110)	1.189(110)	0.164(84)
537	1.595(110)	1.292(110)	0.190(72)
567	1.493(110)	1.219(110)	0.184(78)
567	1.506(110)	1.295(110)	0.140(83)
627	1.472(110)	1.272(110)	0.136(85)
725	1.477(110)	1.218(110)	0.176(80)

TABLE S3: Measured β parameters of the $1b_2$ band.

E_{kin} , eV	β , gas	β , liquid	β_{red}
18	0.750(130)	0.460(130)	0.387(125)
248	1.346(110)	1.096(110)	0.185(86)
248	1.357(110)	1.058(110)	0.220(80)
248	1.334(110)	1.032(110)	0.227(81)
263	1.500(110)	1.076(110)	0.283(65)
293	1.468(110)	1.096(110)	0.254(70)
323	1.333(110)	1.096(110)	0.177(88)
323	1.319(110)	1.103(110)	0.163(91)
323	1.338(110)	1.084(110)	0.190(86)
383	1.262(110)	1.014(110)	0.196(90)
383	1.200(110)	1.043(110)	0.131(105)
383	1.254(110)	1.015(110)	0.190(91)
433	1.193(110)	1.048(110)	0.122(108)
433	1.139(110)	0.947(110)	0.168(105)
473	1.140(110)	0.929(110)	0.185(101)
493	1.200(110)	0.998(110)	0.168(99)
493	1.089(110)	0.873(110)	0.198(104)
533	1.516(110)	1.146(110)	0.244(69)
563	1.260(110)	0.958(110)	0.240(83)
623	1.452(110)	1.042(110)	0.282(67)
721	1.125(110)	0.959(110)	0.147(110)

C. Synchrotron radiation

Data for kinetic energies of the photoelectron above ≈ 250 eV were recorded using synchrotron radiation. Experiments were carried out with the LIQUIDPES and with the SOL³PES setups[5] at the UE52/SGM-1 beamline of the BESSY II electron storage ring at Helmholtz-Zentrum Berlin. The relative angle between the analyzer and the polarization axis was varied by rotating the axis of linear polarization of the synchrotron radiation produced in an Apple II undulator[6, 7]. Its design enables generation of linearly polarized radiation with a direction of the polarization vector which is arbitrary within a 90° sector. By virtue of this setup, angular distribution measurements can be carried out without mechanically rotating the electron analyzer. Polarization properties of the so-produced radiation were measured for a single photon energy ($h\nu = 851$ eV)[8]. We observed a systematic decrease of the degree of linear polarization p from 1.0 for horizontal polarization to ≈ 0.965 for vertical polarization, as well as a systematic deviation of the measured direction of the polarization vector from its nominal value, which amounted to $\approx -2^\circ$ for directions between 30° to 80° with the horizontal. We assume that in our experiment the deviations from the ideal polarization are of a similar magnitude.

D. Data acquisition, synchrotron radiation data

We collected synchrotron radiation data in four different beamtimes. In all cases, a liquid jet of water was produced by methods described earlier[9]. Briefly, a liquid water filament with a diameter of $25\ \mu\text{m}$ from a fused silica nozzle was injected into our vacuum chamber. The jet temperature prior injection was held at 10°C by a recirculating chiller (Julabo F12-ED) and the jet velocity was about $40\ \text{m/s}$. A $50\ \text{mM}$ admixture of NaCl was used to prevent sample charging. The energy resolution of the UE52-SGM beamline was better than $70\ \text{meV}$ at $265\ \text{eV}$ photon energy and better than $450\ \text{meV}$ at $1000\ \text{eV}$ photon energy. The exit slit of the beamline was set to a rather large value of $120\ \mu\text{m}$, which lead to a large focal point of similar size, allowing to measure the liquid phase and the surrounding gas sheet of the liquid jet simultaneously. For our experiments, a hemispherical analyzer pointing vertically downward on a horizontal liquid jet was used. While most measurements used the LIQUIDPES setup[9, 10], they were complemented by some data points taken with

the more recent SOL³PES setup[5]. The energy resolution of our hemispherical analyzers was better than 200 meV (SPECS/Leybold, LIQUIDPES) at 20 eV pass energy used, and better than 100 meV (HIP-2 R4000, SOL³PES) at 100 eV pass energy used. No systematic differences between results from the two setups were found, therefore, to reduce clutter, we do not distinguish them in the figures displaying our results in the main text. For a fixed energy, the spectra were recorded starting at vertical linear polarization (0° relative angle between the analyzer and polarization axis), and then going to larger relative angles. The spectra at different angles were recorded over different acquisition times to approximately compensate for the loss of intensity caused by the general shape of the angular distribution function. At the end of the angle series for each energy, a spectrum at 0° relative angle was repeated to check the stability of the liquid jet and the acquisition conditions.

E. Data analysis, synchrotron radiation data

Data were normalized to variation of the current in the storage ring (those were minor, as we recorded most of our data in a continuous injection mode, 'top-up'-operation) and to acquisition time. A Shirley-type background[11–13] was then removed from the spectra. As an initial check of data integrity, the total intensity recorded under each angle was fitted to the angular distribution expression, Eq. (S5). While this leads to a β -parameter the value of which has no particular meaning, excessive deviations of the individual data points from the parameterization are indicative of some problem with the underlying data, *e.g.*, fluctuations of the gas-liquid ratio. Two sets of data (fixed photon energy, multiple angles) were discarded on such grounds. For the remaining, a least squares fit was used to partition the spectrum into contributions from the valence orbitals of water, each with a gas-phase and a liquid-phase component. Typical results are shown in Fig. S2. The water valence band (corresponding to the highest three orbitals, $1b_1$, $3a_1$, and $1b_2$) was fitted by 7 Gaussians, representing the gas-phase and liquid-phase contributions of each orbital. In order to arrive at well-defined results, the following constraints were used for the fit parameters: For the $1b_2(g)$, $1b_2(l)$, $3a_1(g)$, and $1b_1(l)$ values of the peak width (FWHM) were taken from Ref. 14. Additionally, the difference in binding energy between the gas-phase components was set to values from the same work (while their overall position was allowed to vary). Fig. S2 shows that the two components of the $1b_1$ are spectroscopically fairly separated from the

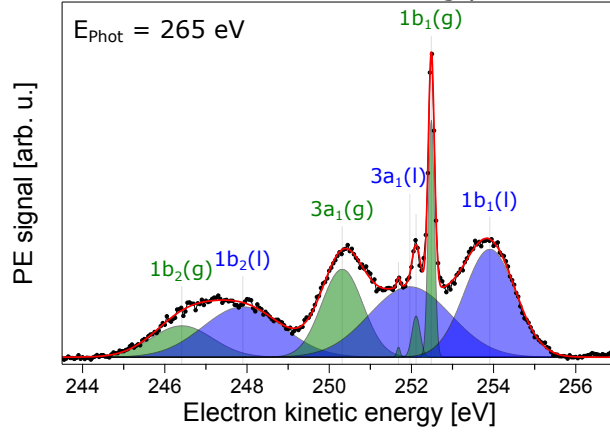


FIG. S2: Decomposition of a measured photoelectron spectrum into gas-phase and liquid contributions pertaining to the three outer valence orbitals. Measured data are shown by symbols, and the result of the fit by a solid line. Labels (g) and (l) denote gas-phase and liquid components.

rest of the spectrum. Therefore, the intensities retrieved for this orbital could, in principle, be determined without peak fitting. In contrast, for the $3a_1$ and $1b_2$ orbitals, the peak areas sensitively depend on details of the fit model.

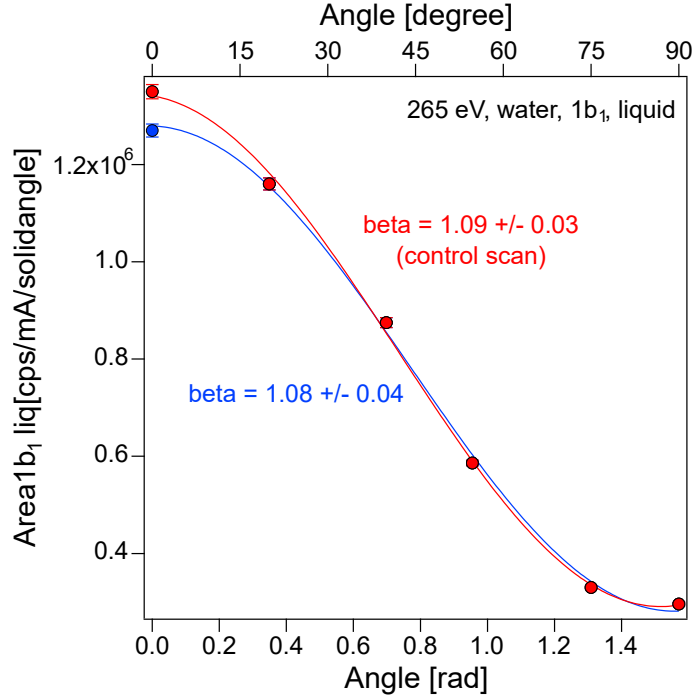


FIG. S3: Area of the first peak in the water valence band as a function of angle between analyzer and polarization direction (symbols). Parameters of the angular distribution function (solid lines) were then determined to best represent the data. As a check of stability of the apparatus, angular distribution fits were carried out taking either the first (blue color) or second measurement at 0° (red color) relative angle. Data points shown in the main text are an average of both values.

For each band, the resulting intensities as a function of relative angle between polarization and spectrometer were fitted to Eq. (S5), using σ , β and λ as free parameters (Fig. S3).

Error bars of the β parameter were determined as follows: the observed deviation between the repeated measurements at 0° was interpreted as the impact of uncontrolled fluctuations, *e.g.*, of the liquid jet position, on the experiment. From that a typical relative error of peak area was determined, and was applied to the area under *each* angle. The propagated error of β determined by that exercise is 0.04. We double this error for the orbitals whose peak area depends on details of the fit model ($3a_1$ and $1b_2$). Finally, we linearly add a systematic error of 0.03 to account for deviations from the ideal polarization (as this is an undulator parameter, it might be different for each energy).

F. Higher Harmonic Generation

A data point at low kinetic energy was recorded using a laboratory source for Vacuum-Ultraviolet radiation based on Higher Harmonic Generation (HHG) of a short pulse optical laser, using the setup described in Ref. [15]. Briefly, optical radiation from a commercial short-pulse optical laser running at a wavelength of 796 nm is guided into a gas cell filled with Ar for harmonics production. Most experiments used the 23rd harmonics, thus leading to a photon energy of 35.6 eV. In this setup, the direction of polarization was rotated by changing the polarization of the driving laser using a half-wave plate. As the utmost time resolution was not of importance in this experiment, a single higher harmonic was selected by a toroidal grating. A Pt coated 600 l/mm grating with a blaze angle of 1.5° (Yobin Ivon) was used in first diffraction order. Depolarization by reflection on the grating can in principle occur because of different reflectivities for *s*- and *p*-polarized radiation. These effects were estimated using the established simulation program REFLEC[16]. For the conditions encountered in our experiment, tolerable depolarization effects to $\approx p = 0.96$ and angle deviations of $-3^\circ < \lambda < 3^\circ$ from the nominal value were found in the simulation. We summarize these effects in the error bar.

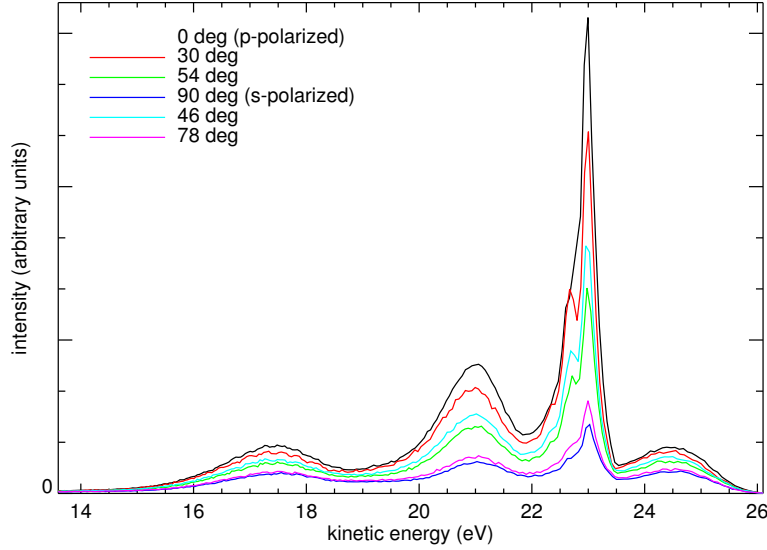


FIG. S4: Electron spectra of a liquid water jet excited by VUV radiation produced in an HHG process. A single harmonic with a photon energy of ≈ 35.6 eV was selected by a diffractive grating. Spectra were normalized to acquisition time and HHG intensity, and are displayed as normalized intensity/energy interval.

G. Data acquisition, HHG data

The method for producing the liquid jet, and its properties, were very similar to the ones delineated above[15]. Full sets of measurements (six angles each) were repeated on different days, normalized for HHG intensity, and eventually averaged over (‘data 1’). These data were generated using the 23rd harmonic of an 800 nm fundamental, corresponding to a 35.6 eV photon energy. This is the data used in plots in the main manuscript. As an additional cross check, a single set of measurements was carried out at a later stage (and after the set-up has moved into a different laboratory) (‘data 2’). These data were generated using the 25th harmonic of a 796 nm fundamental, corresponding to a 38.9 eV photon energy. A substantial gas-phase contribution is present in all measurements, as the VUV focus is much larger than the liquid jet. Electrons were recorded in a linear time-of-flight analyzer under 90° angle both to the liquid jet (pointing downward in this set-up) and the propagation direction of the radiation. Spectra were converted from time to an energy axis using an empirical relation fitted to gas-phase calibration points. The set of spectra recorded thus is shown in Fig. S4.

H. Data analysis, HHG data

We analyzed the angular distribution of the total intensity for the spectra shown in Fig. S4 and for the second set of spectra recorded as a cross-check. Apparent intensity fluctuation showed up in the second data set, attributed to fluctuations of the pump laser. Therefore, this data set is of lower quality, but its analysis is, nevertheless, carried out. On the same occasion, we also recorded a reference data set for molecular water.

Compared to the high kinetic energy spectrum shown in the main text, some differences are apparent in Fig. S4: the gas-phase contribution is more apparent, the HOMO has a relatively lower cross section and in the region between the $3a_1$ and $1b_2$ bands the spectrum is less structured.

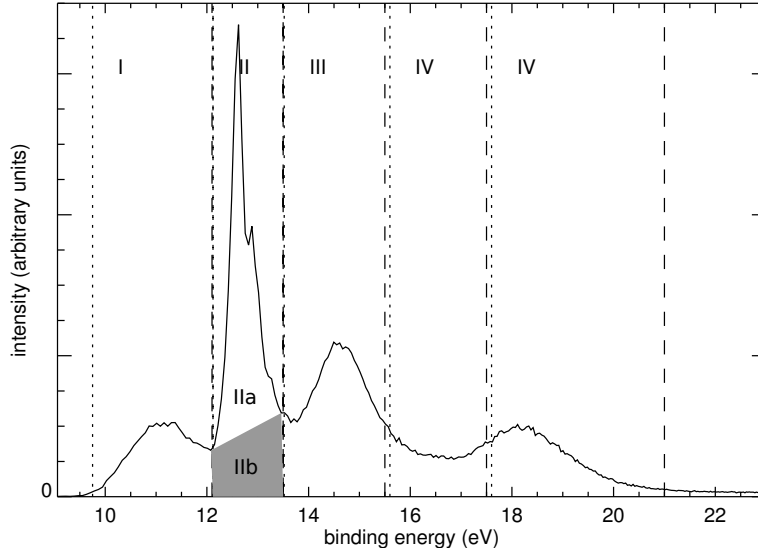


FIG. S5: Regions used to analyze the angular distribution of the water valence spectrum at low kinetic energies.

We carried out the first analysis of angular distribution effects in the spectrum without resorting to least squares fitting. For our gas-phase reference data set, we obtained the values well within the error bar of an earlier study[17]. Next, we separated the gas+liquid spectra in different regions of interest (‘roi’), akin to the analysis in Ref. 18 (Fig. S5). The results for β of the different regions are shown in Table S4. We also compare our results for the liquid-jet data to published data for water clusters (size $\langle N \rangle = 58(5)$), recorded with a similar photon energy of 40 eV.

Generally, the results for our liquid-jet experiment are similar to the measurements for

TABLE S4: β parameter for different regions of the valence photoelectron spectrum of liquid water in our HHG experiment and of water clusters[18] recorded with synchrotron radiation of 40 eV photon energy. For liquid water, β was determined either from a fit of intensities at all angles, or from taking into account the spectra at 0° and 90° only. See text for details.

Region	Assignment	cluster ^a	liq liq (0,90) data 1	liq liq (0,90) data 2
I	$1b_1$ (cluster)	0.79(10)	0.50 0.53	0.58 0.55
II ^b	$1b_1$ (mol), $1b_1$, $3a_1$ (cl)	1.21(6)	1.17 1.19	1.06 1.06
IIa	$1b_1$ (mol.)	1.46(8)	1.53 1.61	1.92 2.29
IIb	$1b_1$ (cl.), $3a_1$ (cl.)	0.83(12)	0.80 0.77	0.74 0.61
III	$3a_1$ (mol.), $3a_1$ (cl.)	0.86(10)	0.95 0.97	0.85 0.85
IV	$1b_2$ (mol.), $1b_2$ (cl.)	0.54(10)		
	$1b_2$ (liq.)		0.62 0.63	0.58 0.56
	$1b_2$ (mol.)		0.61 0.63	0.56 0.55
derived				
	$3a_1$ (cl., liq.)	0.73(16)	0.75 0.78	0.73 0.74
	$1b_2$ (cl., liq.)	0.42(16)	0.46 0.49	0.49 0.48

^a Results labeled ‘cluster’ are from Ref. 18.

^b Results in row ‘II’ refer to the sum of rows ‘IIa’ and ‘IIb’.

clusters for all regions of the spectrum, except for the HOMO peak which has significantly lower anisotropy in the liquid case. At least for dataset 1, the results do not vary much if only spectra und 0° and 90° are analyzed, confirming our assumption about a small importance of depolarization effects due to reflection at the grating. Regions IIa and IIb refer to a partitioning of region II into the sharp $1b_1$ gas-phase component and a linear background underlying it, which is assigned to liquid photoemission. For regions III and IV, being a blend of the molecular and liquid $3a_1$ and $1b_2$ orbitals, a β -parameter applying solely to the liquid component can be calculated from the liquid to gas phase intensity ratio and the β -values for the $3a_1$ and $1b_2$ molecular components, measured in separate experiments. Molecular β -values of 1.16 for $3a_1$ and 0.77 for $1b_2$ from our own experiments (see above), in good agreement with literature[17], were used. The liquid to gas-phase ratio was determined from areas of the respective $1b_1$ components measured at an emission angle of 54° , and attributing area I and 50 % of IIb to the liquid $1b_1$. By this procedure, we obtained the values reported in the lowest two columns of Table S4 (labeled ‘derived’).

The results again compare favorably to the values for clusters derived in the same manner. To complement this analysis, we also attempted to derive β -values from a least squares fit. Positions and widths of the gas-phase components were taken from a fit to our reference spectrum, and were only allowed to vary in intensity. To accommodate the more diffuse

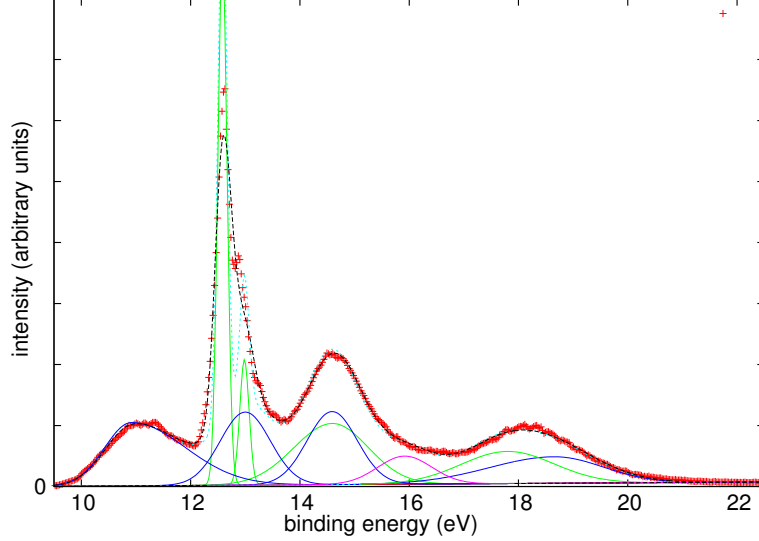


FIG. S6: Decomposition of a photoelectron spectrum measured in the HHG set-up at $h\nu = 35.6$ eV into gas-phase and liquid contributions pertaining to the three outer valence orbitals. Measured data are shown by symbols, and the result of the fit by a broken line. Blue and green color distinguishes peaks assigned to liquid- and gas-phase components, respectively. An auxiliary component, the assignment of which is unclear, is shown in purple color (see text for details). The spectrum measured at the magic angle (54.7°) is shown.

TABLE S5: β -parameter of different regions of the valence photoelectron spectrum of liquid water in our HHG experiment, comparison of fit and roi-analysis. Roi results are repeated from Table S4. Gas-phase values for dataset 2 are given in brackets, as the fit was forced to converge to these via constraints applied to the peak areas under the respective angles (and are taken from Ref. [17]). See text for details.

peak	fit (data 1)	fit (data 2)	roi (data 1)	roi (data 2)
$1b_1(\text{gas})$	1.39	(1.37)	1.53	1.92
$3a_1(\text{gas})$	1.15	(1.16)		
$1b_2(\text{gas})$	0.75	(0.77)		
$1b_1(\text{liq})$	0.51	0.57	0.50	0.58
$3a_1(\text{liq})$	0.88	0.69	0.75	0.73
$1b_2(\text{liq})$	0.49	0.33	0.46	0.49
aux(liq)	0.63	0.84		

nature of the spectra compared to the ones at higher energies we slightly modified the fit model: The liquid $3a_1$ peak was modeled as a doublet with components of equal widths and intensity[14], and we introduced an additional peak (of low intensity) in-between the $3a_1$ and $1b_2$ contributions, which could be assigned to either one of those orbitals. A number of other constraints was applied to the fit parameters of the liquid phase components in order to arrive at well-defined results.

Only spectra at 0° , 54.7° , and 90° were subjected to a least squares fit. Angular anisotropies derived eventually are collected in Table S5, and are compared to the roi-analysis. Deviations are visible, and lead to a slightly higher error bar of the β results for low kinetic energy, compared to the high energy data. As the final result (Tables S1-S3), we quote the values from the roi analysis with the error bars sufficiently large to encompass also the results from areas determination based on peak fitting.

II. COMPUTATIONAL DETAILS AND ADDITIONAL DATA

A. Theoretical framework for calculations of anisotropies

All electronic structure calculations were carried out using *Q-Chem* [19]. Angular distributions were computed with *ezDyson* [20].

We computed PADs and β parameters using the approach described in Ref. [21]. PADs and β values are directly related to the differential cross sections. Within certain approximations (see Refs. [20, 22, 23]), the differential cross section can be expressed in terms of a dipole moment element between a Dyson orbital and the photoelectron wave function:

$$\frac{d\sigma}{d\Omega_k} = \frac{4\pi^2 k E}{c} |D_k^{IF}(\theta, \phi)|^2, \quad (S7)$$

$$D_k^{IF} = \mathbf{u} \langle \Psi_I^N | \mathbf{r} | \Psi_F^{N-1} \Psi_k^{el} \rangle, \quad (S8)$$

where k is the magnitude of the photoelectron wave vector \mathbf{k} , E is the energy of the ionizing radiation, and c is the speed of light. D_k^{IF} is the photoelectron dipole matrix element. The Dyson orbital, ϕ^d , contains all the necessary information about the molecular system (i.e., before and after it is ionized), while the photoelectron wave function Ψ_k^{el} describes the ejected photoelectron. Ψ_k^{el} may be treated as a simple plane or Coulomb wave function.

Because the plane and Coulomb waves yield similar anisotropies and β profiles at high energies (see main text for comparison), we used plane waves throughout most of this work:

$$\Psi_k^{el} = \frac{1}{(2\pi)^{3/2}} e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (S9)$$

The $(2\pi)^{-3/2}$ factor is the “continuum normalization” typically used for plane waves [24]. Plane waves can be written as a sum of spherical waves (this is known as the plane-wave expansion) [25]:

$$e^{i\mathbf{k} \cdot \mathbf{r}} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^l i^l R_l(kr) Y_{lm}(\mathbf{r}) Y_{lm}(\mathbf{k}). \quad (S10)$$

Using the partial wave expansion of Eq. (S10) in the calculation of the photoelectron dipole matrix element allows one to analyze the wave function of the ejected photoelectron in terms of angular momentum quantum numbers. The partial wave expansion also facilitates the derivation of an exact analytical expressions for averaging over molecular orientations (see

Refs. [26] and [20]). However, since it is an infinite expansion over all angular momentum quantum numbers l , in practice it must be truncated after several terms. Such a truncation is justified by the selection rules in atoms or symmetric molecules, or at low photoelectron kinetic energies where high angular momentum contributions are small. However, at high energies the partial wave expansion would have to include many terms. Instead, here we use an approach that does not rely on the partial wave expansion:

$$|D_k^{IF}|_{par}^2 = \frac{1}{(2\pi)^3} \langle \phi_L^d | \mathbf{r}_u | e^{i\mathbf{z} \cdot \mathbf{r}} \rangle \langle e^{-i\mathbf{z} \cdot \mathbf{r}} | \mathbf{r}_u | \phi_R^d \rangle, \quad (\text{S11})$$

$$|D_k^{IF}|_{perp}^2 = \frac{1}{(2\pi)^3} \left(\frac{1}{2} \langle \phi_L^d | \mathbf{r}_u | e^{i\mathbf{x} \cdot \mathbf{r}} \rangle \langle e^{-i\mathbf{x} \cdot \mathbf{r}} | \mathbf{r}_u | \phi_R^d \rangle + \frac{1}{2} \langle \phi_L^d | \mathbf{r}_u | e^{i\mathbf{y} \cdot \mathbf{r}} \rangle \langle e^{-i\mathbf{y} \cdot \mathbf{r}} | \mathbf{r}_u | \phi_R^d \rangle \right). \quad (\text{S12})$$

Eq. (S11) and (S12) give parallel and perpendicular cross sections, respectively, which can be used to compute the β values and the total cross sections using the following expressions:

$$\beta = \frac{2(\sigma_{par} - \sigma_{perp})}{\sigma_{par} + 2\sigma_{perp}}. \quad (\text{S13})$$

$$\sigma = \frac{4\pi}{3} (\sigma_{par} + 2\sigma_{perp}). \quad (\text{S14})$$

The averaging is done numerically. Specifically, σ_{par} and σ_{perp} are calculated at 150 different orientations. The orientations are generated by rotating the molecule to align along vectors pointing towards 150 equidistant points on the surface of a sphere, precomputed with the program REPULSION [27]. This numerical approach is implemented in *ezDyson* (version v4.0 and higher) [20].

B. Details of calculations for monomer, dimer, and pentamer

The β values of the monomer were obtained on structures optimized with ω B97X-D/aug-cc-pVTZ [28]. Dyson orbitals and ionization energies were computed with EOM-IP-CCSD/aug-cc-pVTZ [29–31].

To verify that the optimized monomer is a good model for gas phase water and that β is not sensitive to the geometry of the monomer, we performed an *ab initio* molecular dynamics (AIMD) simulation of water and computed β for 100 different geometries. Specifically, we

randomly sampled a set of 100 initial geometries and velocities from a Maxwell-Boltzmann distribution, propagated each trajectory for 100 fs (with a time-step of 1 fs) at the ω B97X-D/cc-pVTZ level of theory, and used the final structure of the 100 fs dynamic to compute the Dyson orbital and corresponding β . The results of these calculations are discussed in Section II.D. of this supporting document.

We carried out dimer calculations in two different ways. In the first calculation, a monomer was optimized and then a symmetric dimer was produced by generating a copy of the monomer and translating it along the x axis. This results in a symmetric dimer structure where the water oxygen atoms are exactly 6 Å apart. In the absence of interaction between the two water molecules, their degenerate orbitals can be expressed as any (normalized) linear combination of the two valence states of the monomers. The results of these calculations are shown in Fig. 3 of the main manuscript.

In the second calculation, we used dimer's structure optimized with ω B97X-D/aug-cc-pVTZ. The distance between the water molecules in this dimer was then varied and the β was computed as a function of the distance. Fig. S7 shows the results of the two calculations.

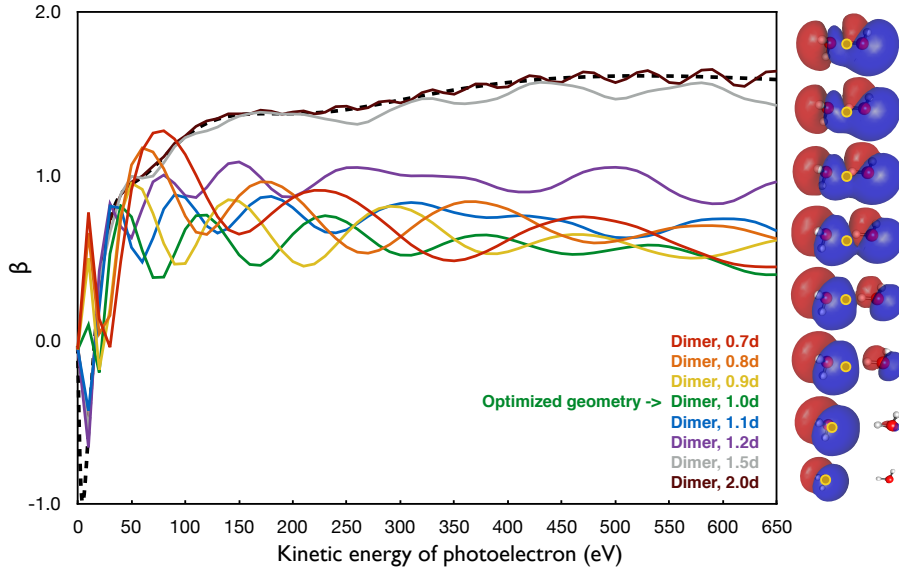


FIG. S7: Computed β values for a water dimer as a function of the distance between the two water molecules. The values for the optimized dimer is shown in green. At long distances, the behavior of the dimer β approaches that of the monomer (shown as a dashed line for reference). The Dyson orbital for the dimer at different distances are shown on the right (starting from 70% of the optimal geometry at the top to 200% of the optimal geometry at the bottom). The centroids of the Dyson orbital (used here as the center of expansion of the plane wave) are shown by yellow circles.

The pentamer geometries were obtained from molecular dynamics simulations of liq-

liquid water with *Tinker* [32] using the TIP3P force field [33] in a periodic boundary box of $40\text{\AA} \times 40\text{\AA} \times 40\text{\AA}$. The system was equilibrated for 1 ns and followed by a production run of 500 ps, where a snapshot was taken every 5 ps, yielding 100 snapshots. From each snapshot, a pentamer was extracted by selecting a random water molecule far from the edge of the box and its four nearest neighbors. This procedure ensures that the pentamer snapshots are uncorrelated. For each snapshot, ionization energies and Dyson orbitals were computed for the 15 valence states with EOM-IP-CCSD/aug-cc-pVDZ. The simulated photoelectron spectrum in Fig. 1A of the main manuscript is derived from the computed EOM-IP-CCSD ionization energies using an area plot showing the count of ionization energies within a certain range (we used a 0.5 eV bin size). More specifically, the figure is a histogram representing kinetic energies for electrons ionized from valence orbitals of 100 pentamer snapshots at 265 eV. The plot shows features of both liquid- and gas-phase peaks, and so is colored accordingly with the grey peak representing $1b_1(l)$, yellow representing a combination of $3a_1(l)$ and $1b_1(g)$, green representing $3a_1(g)$ and $1b_2(g)$, and red representing $1b_2(l)$. Notably, the simulated spectrum still shows the five main features, even if the area plot is plotted with different bin sizes (see Fig. S8).

We computed differential cross sections using a plane wave model of the photoelectron. As explained above, the cross sections were computed without using a plane wave expansion and using numerical averaging. Fig. S9 shows the β values for all valence orbitals of all 100 pentamer geometries.

C. Photoionization of the $1s_O$ core orbitals

To test the main assumption that scattering is responsible for reducing the β for the $1s_O$ core orbital in liquid [1, 34], we carried out calculations of the core-level Dyson orbitals of a water monomer and a randomly selected water pentamer. We used the core-valence separation variant of EOM-IP-CCSD, fc-CVS-EOM-IP-CCSD [35], and the aug-cc-pVTZ basis set. In the pentamer calculation, it was not necessary to enforce multi-core expansion since the five core $1s_O$ orbitals were all localized. The results are shown in Fig. S10. As expected, owing to the localized nature of the $1s_O$, it has nearly perfect s character, leading to $\beta=2$ at energies above 30 eV, although we note a small reduction of β at low energies (<20 eV).

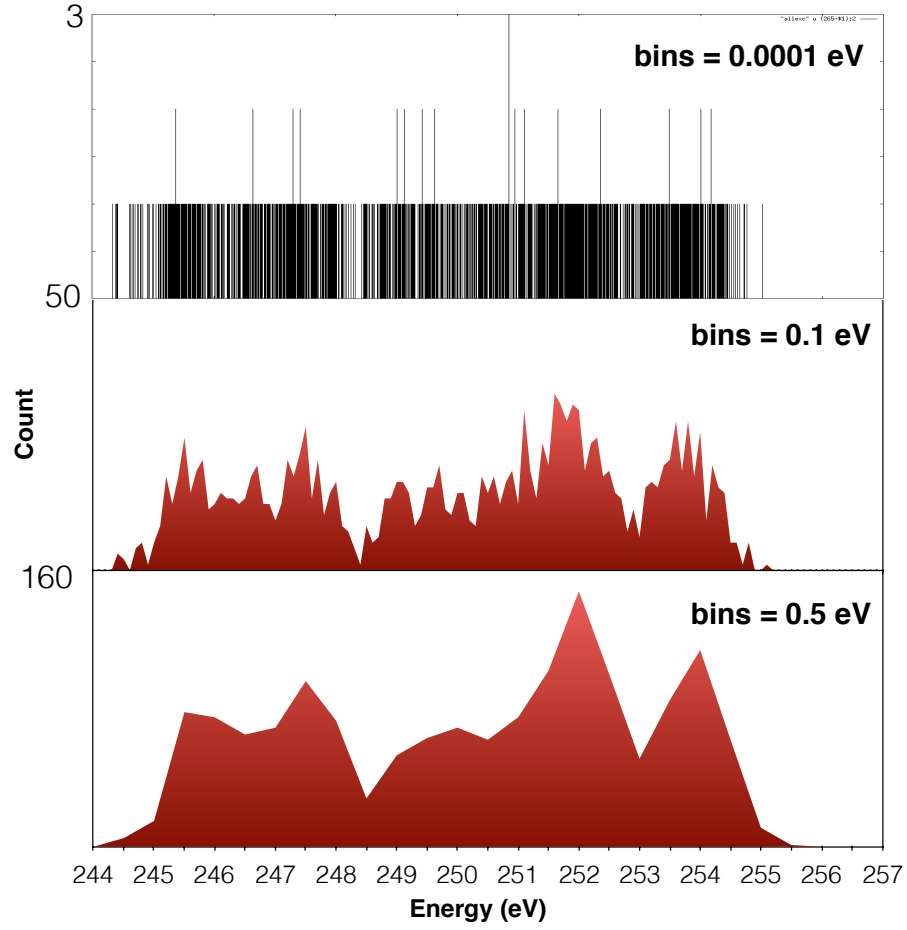


FIG. S8: Area plot of electronic kinetic energies from computed EOM-IP-CCSD ionization energies of all valence orbitals of 100 pentamer snapshots, assuming 265 eV photon energy. Three different bin sizes are shown. All three plots plot roughly indicate that there are five main peaks where EOM-IP energies are more concentrated.

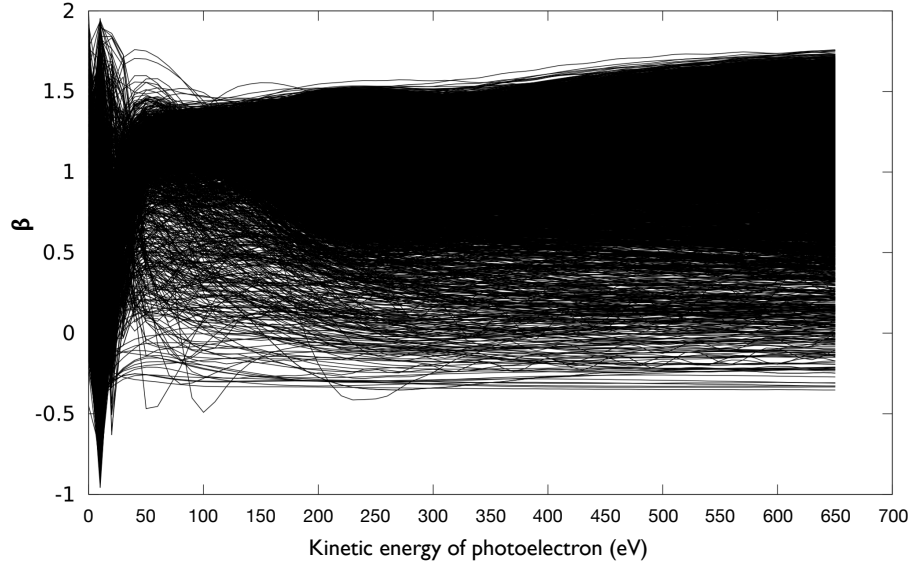


FIG. S9: Computed β values as a function of energy for individual water molecules in 100 pentamer geometries. Results are shown for all valence orbitals.

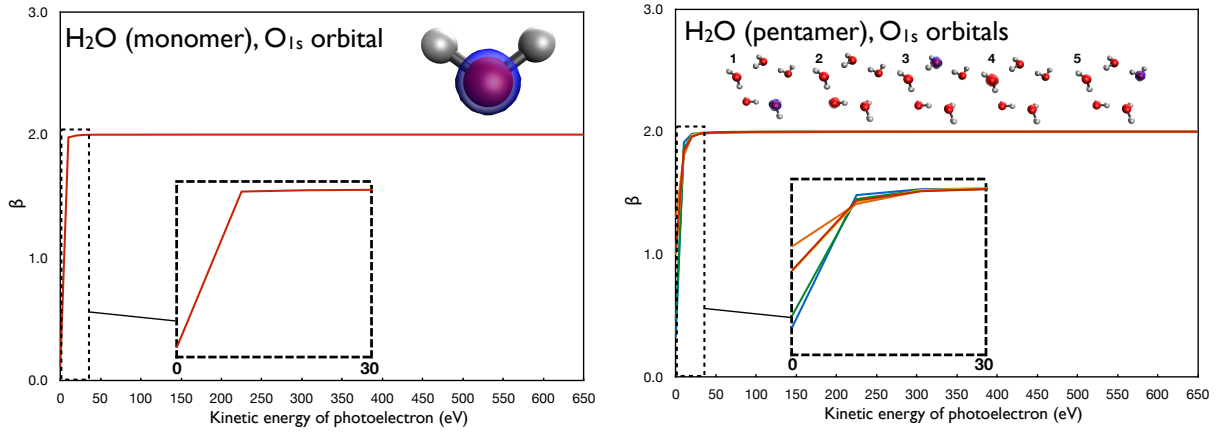


FIG. S10: Computed β values for the core $1s$ orbital as a function of energy for water molecule (left) and a water pentamer (right).

D. Effect of monomer's vibrations on β

As anticipated in Section II.A. above, we performed AIMD on a water monomer to compute the average β for an ensemble of water snapshots. We find that dynamics have no effect on the β in the case of the $1b_1$ orbital, but cause a slight reduction in the β value for $3a_1$ and $1b_2$.

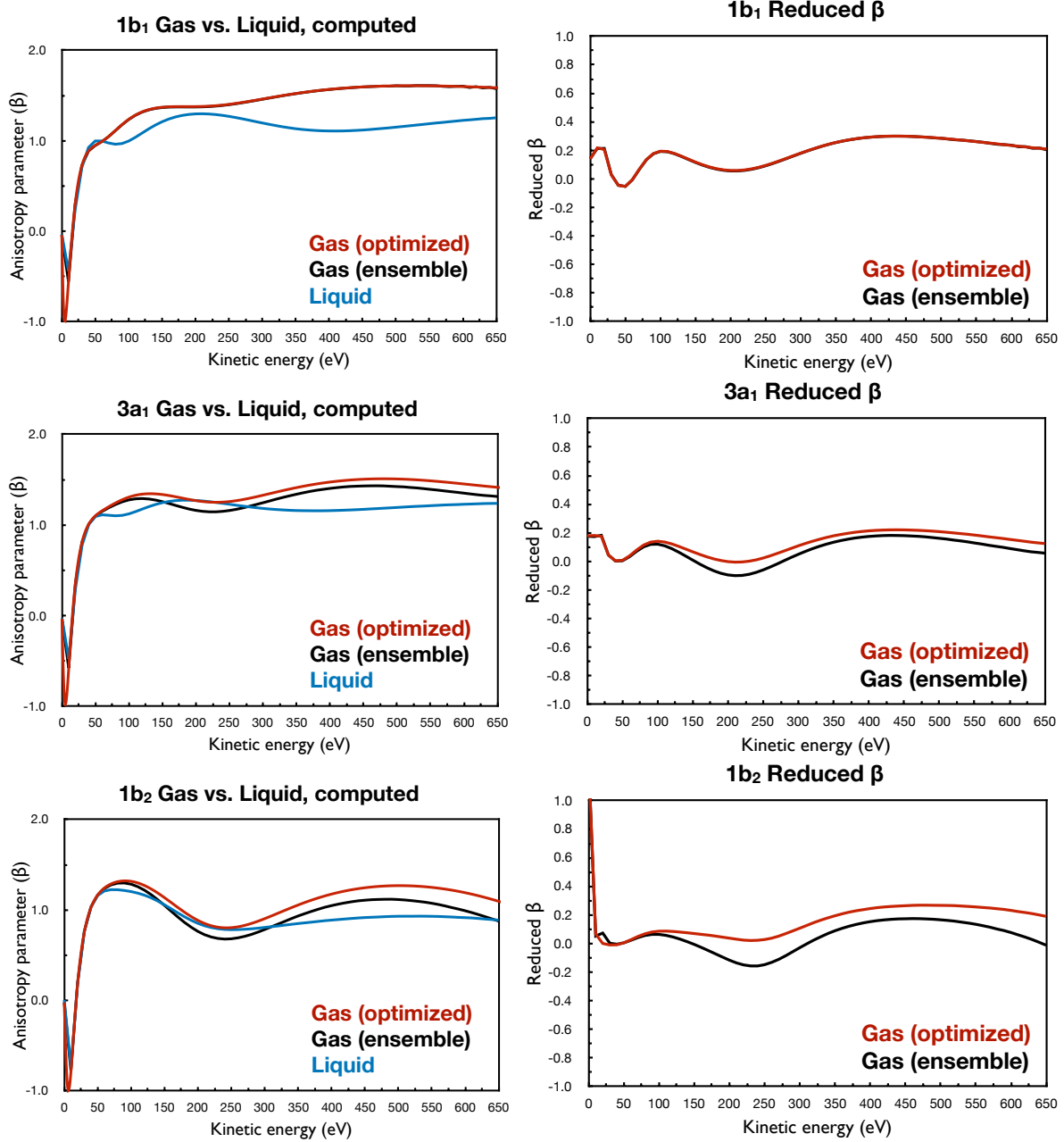


FIG. S11: Left: Theoretical values for liquid and gas-phase anisotropies. Gas-phase calculations are shown both for a single optimized monomer and an average over 100 geometries from AIMD calculations. Right: The corresponding theoretical β_{red} .

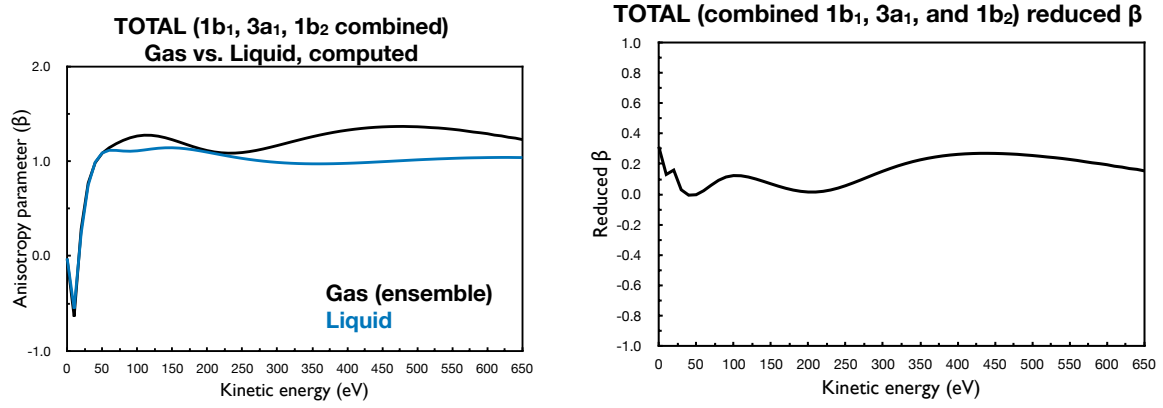


FIG. S12: Left: Theoretical values for liquid and gas-phase anisotropies, combined for the $1b_1$, $3a_1$, and $1b_2$ bands. Gas-phase data is averaged over 100 geometries from AIMD calculations. Right: The corresponding theoretical β_{red} .

III. GAS-PHASE VERSUS LIQUID ANISOTROPIES: THEORY AND EXPERIMENT

To directly analyze the reduction of anisotropies in liquid relative to the gas-phase, we introduce the reduced β defined as:

$$\beta_{red} \equiv 1 - \frac{\beta_l}{\beta_g}, \quad (\text{S15})$$

where β_l and β_g denote liquid and gas-phase anisotropies. If the anisotropy in the liquid phase is the same as in the gas phase, then $\beta_{red} = 0$. Conversely, $\beta_{red} \approx 1$ signifies a complete loss of anisotropy in liquid. The results are collected in Fig. 7 of the main manuscript; here we provide an alternative representation.

Left panels of Fig. S13 show measured anisotropies (see Section I for the detailed explanation of the data analysis) for liquid and gas-phase water. Fig. S14 shows the theoretical values of the anisotropies and β_{red} for the isolated water molecule and for water pentamers. In the case of the pentamer, the approximate assignment of the ionized states to specific bands (e.g., $1b_1$, $3a_1$, $1b_2$) is carried out using energy criteria, as explained above.

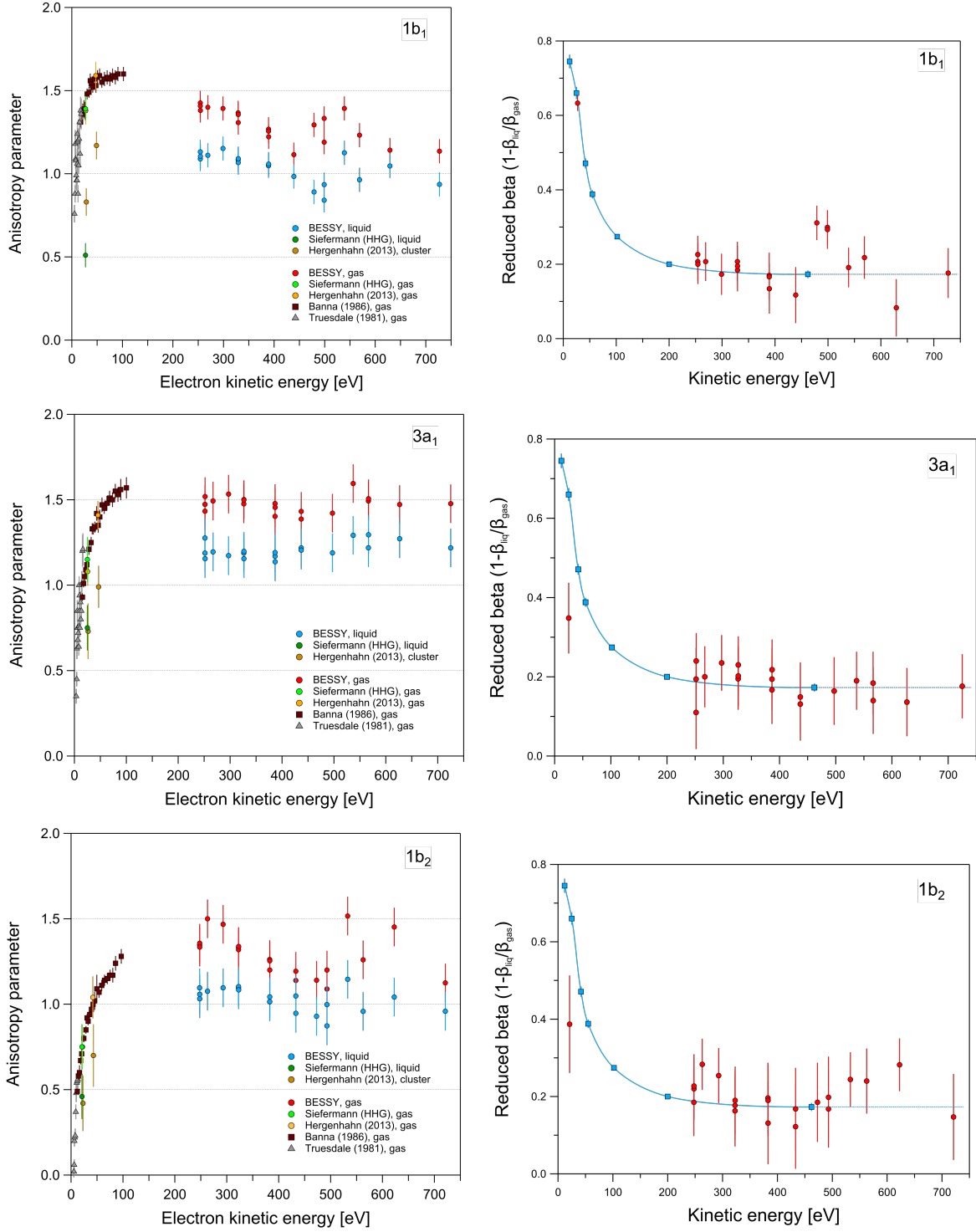


FIG. S13: Left: Liquid and gas-phase experimentally determined anisotropies. Right: the corresponding β_{red} . The solid blue line on the right shows β_{red} for $1sO$.

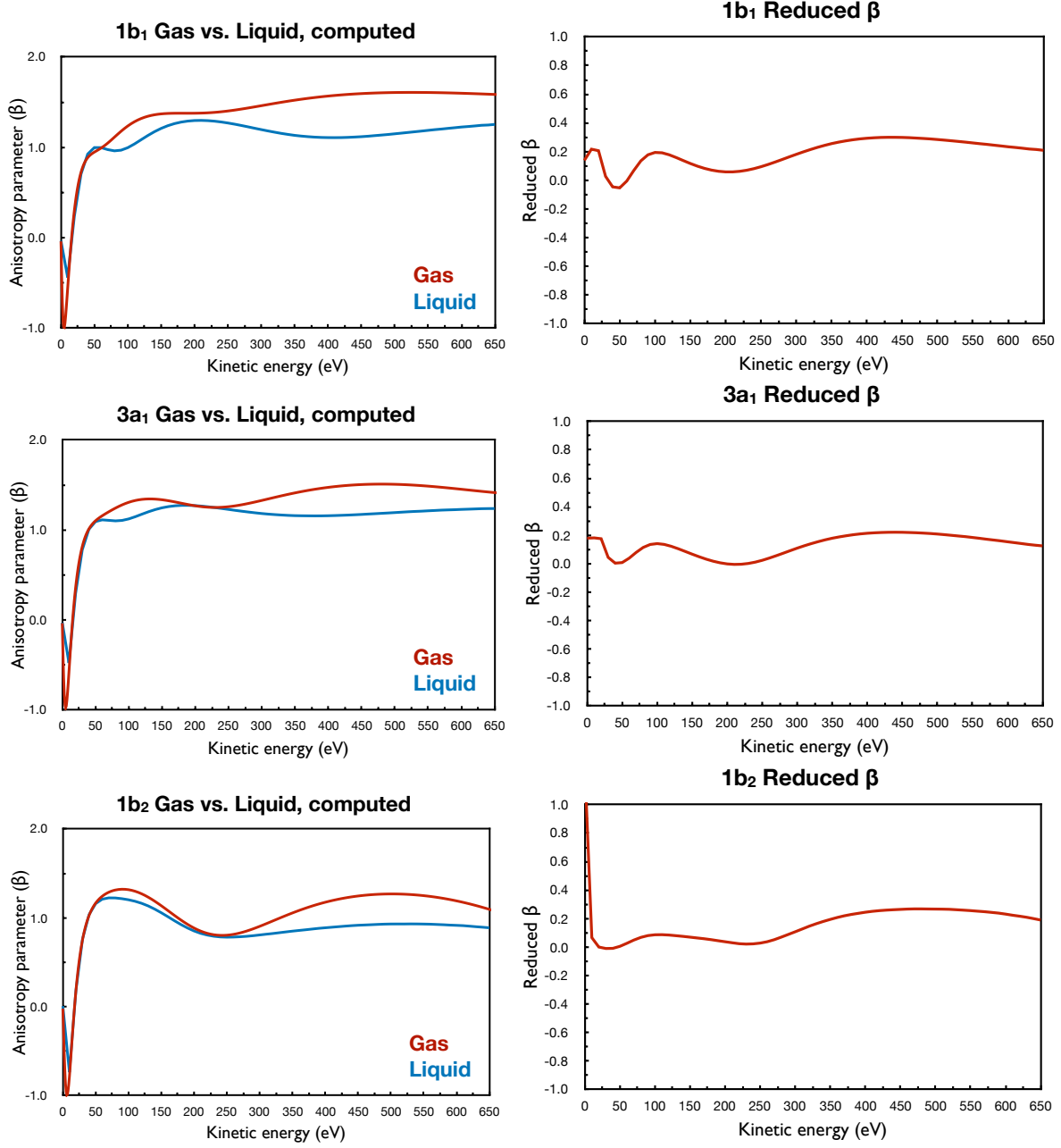


FIG. S14: Left: Theoretical values for liquid and gas-phase anisotropies. Right: Theoretical β_{red} .

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