Compatibility of quantitative X-ray spectroscopy with continuous distribution models of water at ambient conditions

Johannes Niskanen[a,b], Mattis Fondell[a], Christoph J. Sahle[c], Sebastian Eckert[d,a], Raphael M. Jay[d,a], Keith Gilmore[c], Annette Pietzsch[a], Marcus Dantz[e], Xingye Lu[e], Daniel E. McNally[e], Thorsten Schmitt[e], Vinicius Vaz da Cruz[f,a], Victor Kimberg[f,g], Faris Gel'mukhanov[f,g], and Alexander Föhlisch[a,d,1]

[a]Helmholtz Zentrum Berlin für Materialien und Energie, Institute for Methods and Instrumentation for Synchrotron Radiation Research, Albert-Einstein-Str. 15, D-12489 Berlin, Germany; [b]University of Turku, Department of Physics and Astronomy, FI-20014 Turun yliopisto, Finland; [c]European Synchrotron Radiation Source,71 Avenue des Martyrs F-38000 Grenoble, France; [d]Universität Potsdam, Institut für Physik und Astronomie, Karl-Liebknecht-Strasse 24/25, D-14476 Potsdam-Golm, Germany; [e]Paul Scherrer Institut, Swiss Light Source, Photon Science Division, 5232 Villigen PSI, Switzerland; [f]Royal Institute of Technology, Theoretical chemistry and biology, Roslagstullsbacken 15, SE-10691 Stockholm, Sweden; [g]Institute of Nanotechnology, Spectroscopy and Quantum Chemistry, Siberian Federal University, 660041 Krasnoyarsk, Russia

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The phase diagram of water harbours controversial views on underlying structural properties of its constituting molecular moieties, its fluctuating hydrogen bonding network, as well as pair-correlation functions. In this work, long energy-range detection of the X-ray absorption allows us to unambiguously calibrate the spectra for water gas, liquid and ice by the experimental atomic ionization cross section. In liquid water we extract the mean value of 1.74 ± 2.1% donated and accepted hydrogen bonds per molecule pointing to a continuous distribution model. In addition, resonant inelastic X-ray scattering with unprecedented energy resolution also supports continuous distribution of molecular neighbourhoods within liquid water, as do X-ray emission spectra once the femtosecond scattering duration and proton dynamics in resonant X-ray–matter interaction are taken into account. Thus, X-ray spectra of liquid water in ambient conditions can be understood without a two-structure model, whereas the occurrence of nanoscale length correlations within the continuous distribution remains open.

Water | X-ray | Spectroscopy

Since the electronic structure of water molecules can support both 2- and 4-fold coordination in their molecular interaction, both a view of continuous distribution of molecular moities (homogeneous view) (1–7) and a view of oscillations between separate distinct phases (heterogeneous view) (8–12) of liquid water can be envisaged. The heterogeneous view foots strongly on the consideration that in the supercooled regime statistical response functions diverge at 228 K, introducing a liquid-liquid critical point, that would terminate the transition line between high-density and low-density liquid phases (13).

The possible heterogeneous picture with fluctuations between two classes applied in the supercooled regime have also been suggested to exist far up in temperatures (320 K) of the ambient regime (14). This suggestion contradicts the physical view that above a critical point the system is homogeneous and free from the need for multiphase classification (5, 15). However, even such a homogeneous or continuous distribution model does not exclude statistical variation: ambient and supercooled water have been found to naturally undergo density fluctuations in single-phase simulations (15). The two-phase model of liquid water has been repeatedly promoted by the interpretation of X-ray spectroscopic findings (16) (and references therein), but the spectra have also been interpreted on the basis of homogeneous water models (17–19).

X-ray absorption spectra

Soft X-ray Oxygen 1s X-ray absorption spectroscopy (XAS), electron energy loss spectroscopy (EELS), and equivalent information from hard X-ray Raman scattering (XRS) for the Oxygen 1s excitations has been utilized to characterize the various phases of water (11, 20–25). In these studies, integral or area-normalization within the measured spectral range between 530 eV and 550 eV has typically been employed, with the aim to fulfill the theoretical concept of the f-sum rule (26) present for an ideal – complete – spectral range with clearly discernible bound and continuum states. Combining simulations with area normalization, a significant signature of broken hydrogen bonds in liquid water has been postulated (11) based on the observation of increasing intensity in the $4a_1$ LUMO line (I in Fig. 1 (c)) along transitions from ice to liquid

Significance Statement

Water is the matrix of life and behaves anomalously in many of its properties. Since Wilhelm Conrad Röntgen, two distinct separate phases have been argued to coexist in ambient water, competing with the alternative view of the single-phase liquid, footing on X-ray scattering experiment and theory. We conducted a quantitative and high resolution X-ray spectroscopic multi-method investigation and analysis (X-ray absorption, X-ray emission, and resonant inelastic X-ray scattering). We find that all known X-ray spectroscopic observables can be fully and consistently described with continuous distribution models of near-tetrahedral liquid water at ambient conditions with 1.74 ± 2.1% H-bonds per molecule.

The RIXS experiment was done by JN, MF, SE, RMJ, AP, MD, XL, DMN, TS, and AF, and data handled by JN, SE, and AP. The XRS experiment was done by CJS and JN, and the data handled by CJS. The XES experiment was done by SE, RMF, JN, MF, AP and the data was handled by SE. The XES simulations were done by CJS and KG, and analysed by JN. The manuscript was written by JN, AF, FG, AP, VVDC, and VK. The research was planned by AF, JN, AP, and FG and directed by AF. All authors have been given the option to comment the manuscript.

Authors declare no competing interest

[1]To whom correspondence should be addressed. E-mail: alexander.foehlisch@helmholtz-berlin.de

water and finally gas phase. However, in the f-sum rule normalization, the decrease of intensity in the pre-edge region is exactly counterbalanced by an intensity gain in other regions within the normalization range, because the integrated spectral intensity is forced to a fixed value. Therefore, employing area-normalization within the range of 530 eV and 550 eV to fulfil the f-sum rule induces a trade-off in spectral intensity within the experimentally accessed energy range. Moreover, this trade-off is limited to the normalization range, which is unjustified as such spectra do not meet each other at the end of the integration interval (see SI Appendix, Fig. S1).

In Fig. 1(a),(b) and (c) we present the phase diagram of water in relation to Oxygen 1s XAS spectra obtained from saturation-free hard X-ray Raman spectroscopy for ice and liquid, and electron-energy-loss spectroscopy for gas from Ref. 20 (raw data after subtraction of constant background), where we follow the idea presented in Refs. 25, 27 and replace the f-sum rule normalization with f-density ($\mathrm{d}f(E)/\mathrm{d}E$) normalization at the high-energy end (see also SI Appendix, Fig. S2). Panels (b) and (c) represent scans of gas, liquid and ice. The use of f-density normalization is based on the reasoning that at the sudden limit (a fast photoelectron) the photoionization cross section is an atomic property, independent of sample composition and varying bonding situations. Thus f-density links XAS state populations of different materials and molecules via fundamental core–continuum transition properties in the most reliable way when the spectra reach the asymptotic regime.

Most notably, the intensity variation of the LUMO $4a_1$ pre-edge feature in region I of Fig. 1(b) under f-density normalization yields a quantitative measure of donated hydrogen bonds per molecule for the liquid, ice and gas phase of water. With 0 donated bonds for gas and 2 donated bonds for ice and a linear dependence between the structural parameter average and line intensity, we derive from the f-density normalized pre-peak intensities (SI Appendix, Table S1) of liquid water an average of 1.74 ± 2.1% donated hydrogen bonds per molecule (for discussion about the error estimate and linear interpolation used, see SI Appendix). One should notice that correlation between the area of the pre-edge peak σ and the number of donated H-bonds used here is based on our work (28) and it resembles the relation of the relative intensity of pre-edge peak and bond order between the donor H and the acceptor O atoms (see Fig.1 in Ref.(29)). The result obtained in this manner is significantly closer to the 2 donated bonds of ice than the previously derived 1.1 (see Ref. 11 and SI Appendix) bonds per molecule. With the interpolation method used here, for the spectra normalized in area up to 550 eV the value 1.67 is obtained. We conclude that breaking of H-bonds between ice and liquid water occurs to a lesser degree than concluded in Ref. 11.

Quantitative line-intensity–structural-parameter correlation based on a first principles liquid simulation (28) can now be considered (Fig. 1(d)). For the pre-edge LUMO $4a_1$ (region I), intensity is anticorrelated to donated (D) and accepted (A) hydrogen bonds, but correlated to the sum angular deviation from tetrahedrality (Δ_a) as well as furthest-nearest difference (Δ_d) of the closest four neighbouring O sites.

For the post edge region III, we observe in f-density normalization a strong rise of spectral intensity going from liquid water towards ice structures, and no contributions in gas (Fig.

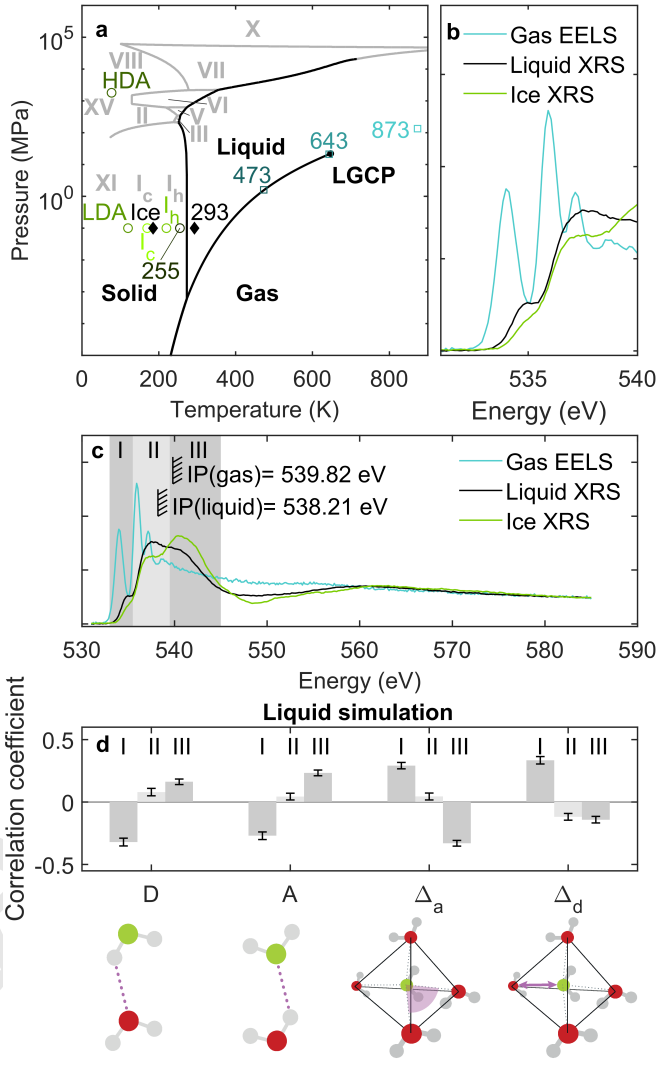

Fig. 1. (a) Schematic phase diagram of water in relation to Oxygen 1s X-ray absorption spectra obtained from saturation-free hard X-ray Raman spectroscopy. (b,c) We replace the f-sum rule normalization with f-density ($\mathrm{d}f(E)/\mathrm{d}E$) normalization at mean ionization cross section between 580 eV and 585 eV for gas, liquid and ice. Region I: LUMO $4a_1$ pre-edge feature. Region II: overlaping LUMO+1 $2b_2$ and continuum features. Region III: Continuum region, with shape resonance (hv_{in} ∼542 eV) from second shell O–O continuum scattering resonance. (d) Line-intensity–structural-parameter correlation coefficients based on first principles liquid simulation (28) for regions I-III (lesser correlations in SI Appendix, Fig. S4): donated (D) and accepted (A) hydrogen bonds, sum angular deviation from tetrahedrality (Δ_a) and furthest-nearest difference (Δ_d) for the closest four neighboring O sites.

1(c)). Since the post edge of condensed water resides in the continuum (O1s binding energy in liquid BE_{O1s}=538.21 eV (30)), its interpetation must not foot on bound state arguments, but can only be attributed to continuum scattering resonances (shape resonances) reflecting structural order (24). The shape resonances provide direct information about bond length or radius of a coordination shell (see Refs. 31 and 32). For a shape resonance at hv_{in} ∼542 eV the poles of the electronic wave function in continuum with E_{kin}=hv_{in}-BE_{O1s}= 542 eV - 538.21 eV ∼ 4 eV show characteristic lengthscales of 3.1 Å and 4.6 Å, respectively (see Supplementary Information). This makes the shape resonance region sensitive to the

first and the second solvation shell radii (33), and the corresponding potential barrier height, values of which (from digitization) are presented in SI Appendix, Table S2. The interpretation of the post-edge (III) as a shape resonance has been proposed to originate from the nearest neighbours (34). We attribute the post-edge (III) intensity behaviour to be caused by a shape resonance that is due to both first and second solvation shells. This conclusion is supported by matching the solvation shells and their radial-distribution-function (RDF) peak heights as a measure of the mean barrier height. This continuum scattering resonance in liquid and ices is responsible for the artificial suppression of the pre-edge when area normalization from 530 eV to 550 eV is used.

The complete break-down of the hydrogen-bond network of water in the gas phase is reflected in a rising pre-edge (I) (Fig.1 (b) and (c)), whereas the post-edge (III) disappears due to loss of solvation-shell order needed for the shape resonance. In the language of quantitative line-intensity–structural-parameter correlation coefficients based on first principles liquid simulation (28) in Fig. 1(d) this is expressed as dominant anti-correlation between the shape-resonance intensity in region (III) with the sum angular deviation from tetrahedrality (Δ_a) and correlation with donated (D) and accepted (A) hydrogen bonds.

Resonant inelastic X-ray scattering spectra

Next we turn to liquid water by studying O K-edge resonant inelastic X-ray scattering (RIXS) (Fig. 2). We focus on the bound excitations to $4a_1$ LUMO (region I), to states at the main edge, and core ionization continuum through the scattering resonance. In this work the spectra were recorded with unprecedented resolving power (>10000) by using the SAXES spectrometer (35) at the ADRESS beamline (36) on the Swiss Light Source at Paul Scherrer Institut. Finally we present X-ray emission spectra (XES) taken at numerous incident energies approaching the sudden core ionization, measured with instrument of more modest resolution (for complete XES spectra, see SI Appendix, Fig. S3).

Comparing the RIXS spectra of electronic loss features (Fig. 2 panel b) taken at 545 eV to those excited to the shape resonance at ∼540 to 542 eV (region III) a noticeable shift of +0.20 eV is observed, due to different coupling and screening of a fast photoelectron, and a slow resonantly trapped photoelectron. Trivially, for both continuum excitations, photoionization leads to no vibrational excitations in the quasielastic region (Fig. 2 panel (c)), as the ionized system can not return to the neutral ground state. We note that XES spectra with differing energy calibrations have been reported (37, 38); we calibrated with respect to data from Ref. 37.

As seen in Fig. 2 panel (c), excitation into the electronic bound state $4a_1$ LUMO of liquid water yields strong vibrational excitations next to the elastic line. These excitations represent the projection of the core-hole-state-propagated wavepacket back onto the molecular ground state potential energy surface (39–41). For the main edge the experimental vibrational progression in liquid water shows significant shortening over the gas phase, a sign of suppression to exhibit the symmetric stretch mode in the liquid environment.

In Fig. 3 we show side by side the experimental vibrational losses via the electronic bound state $4a_1$ LUMO for gas phase water (Fig. 3 (a)) and for liquid water (Fig. 3 (d)). The ground state potential energy surface as a function of O–H distance extracted from experimental RIXS for the gas phase, using a Morse-potential-cut approach as has been used in Ref. 41, are shown for gas (Fig. 3 (c)). The vibrational progressions for both gas and liquid water show only a single dominant O–H stretch mode. In the gas phase this mode persists as a distinct peak up to very high vibrational quantum numbers. In the liquid phase, however, broadening towards higher vibrational quantum numbers sets in, which is caused by a statistical distribution of the liquid local environments. No indication for two energetically shifted, distinct O–H stretch frequencies indicative of a two-phase model can be detected.

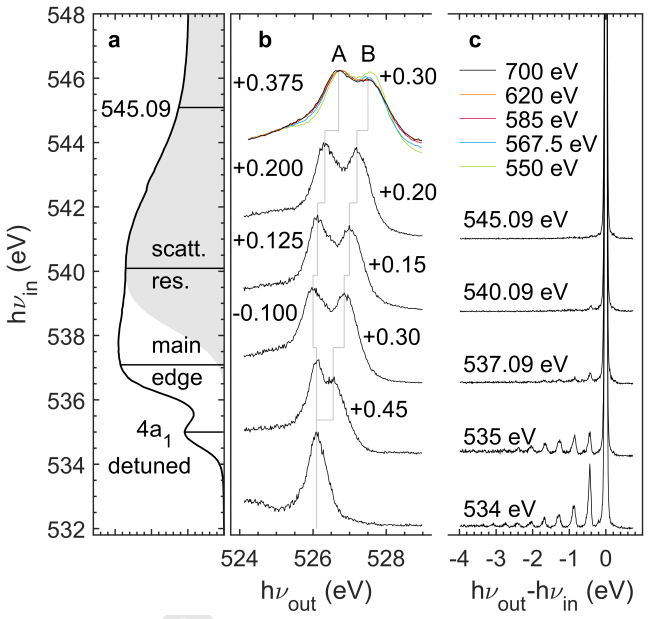

Fig. 2. Liquid water at ambient conditions: (a) Oxygen 1s X-ray absorption in direct relation to O1s resonant inelastic X-ray scattering with sub-natural-line-width spectral resolution of 50 meV. (b) $1b_1$ HOMO electronic losses at various incident-photon energies normalized to respective maximum value. (c) vibrational losses normalized to main elastic peak height mapping the ground state potential energy surface along selected coordinates. Shaded area is the contribution of photoionization continuum with an ionization threshold built up from step functions of each of the manifold of the molecular species in liquid water.

X-ray emission spectra

Finally let us turn to the RIXS electronic losses in Fig. 2 (b), where the $1b_1$ emission line in the water O K-edge XES appears as a double peak in condensed phases (16). This splitting (A,B in Figure 2 (b)) has been promoted as a fingerprint of two distinct structural motifs within the liquid phase (42), which is opposed by arguments of nuclear dynamics causing this effect (18, 19, 43). In the latter view it is important to realize that the splitting at ionization may have different origin compared to those of different resonant states due to different core-hole-state potential energy landscapes, and therefore possibly different dynamics.

The XES spectrum taken at 550 eV and above in Fig. 2 (b) (for full spectra see SI Appendix, Fig. S3) manifests the photon energy dependence in the continuum, which indicates the ionized electron still to be coupled to the decay. Matching the behaviour of the XAS spectra in Fig. 1 (c), at 585 eV

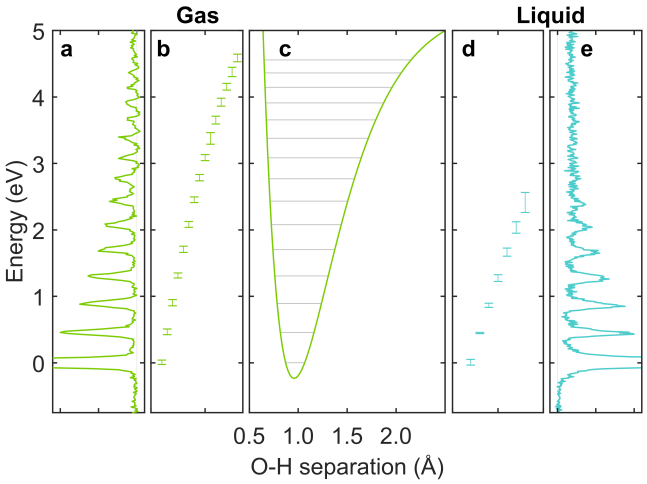

Fig. 3. Ground state vibrational levels along the O–H coordinate of molecular moities present in gas phase (a,b) and liquid water at ambient conditions (d,e) extracted from the vibrational progressions of O1s sub-natural linewidth RIXS excited at the $4a_1$ LUMO X-ray absorption resonances, respectively. Broadening of vibrational progression in the liquid phase from continuous distribution of molecular configurations (d). No broadening in the single H_2O molecule configuration in the gas phase (b) and the single potential energy surface along the O-H coordinate extracted from the Morse potential (c).

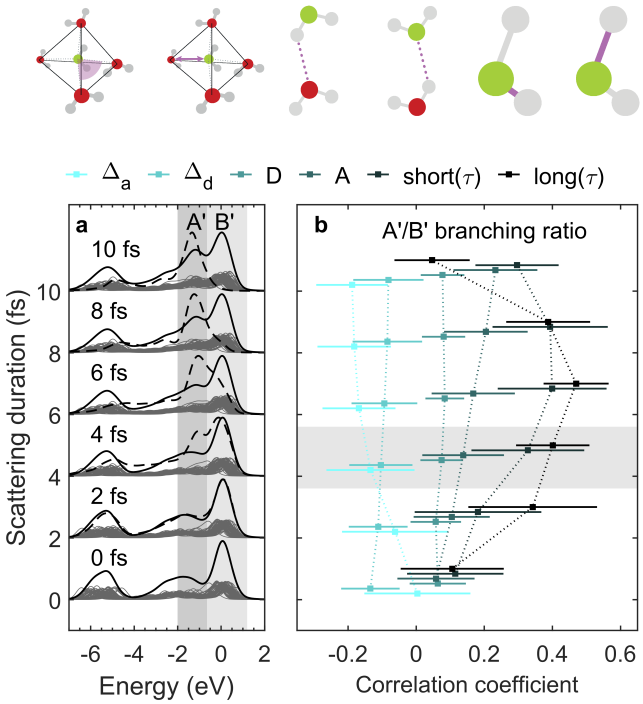

Fig. 4. Formation of a split-peak in the $1b_1$ HOMO electronic losses from ultrafast molecular relaxation during the femtosecond natural-lifetime of the O1s core ionized intermediate state of RIXS in the sudden limit (X-ray emission, XES). (a) MD simulation of O1s RIXS under sudden limit as a function of scattering duration τ = 0, 2, 4, 6, 8, 10 fs (individual decay-time averaged spectra scaled x0.2). The instantaneous average is shown as dashed line. (b) Correlation coefficients between the split-peak branching ratio (A'/B') from core hole dynamics (time-averaged integrated XES spectra) and structural parameters at the site of ionization. The error bars represent 1000-fold bootstrap re-sampling. Weak correlation of split-peak intensity sum branching ratio (A'/B') to angular deviation from tetrahedrality (Δ_a), to the furthest-nearest difference (Δ_d) for the closest four neighboring O sites, and to donated (D) and accepted (A) hydrogen bonds (the parameters are calculated at the moment of ionization). Stronger correlation to the elongation of the short O-H bond during the scattering process (short(τ)). Strongest correlation to the elongation of the long O–H bond during the scattering process (long(τ)).

and above convergence of the XES spectral shape is observed, with a resulting spectrum that significantly resembles that recorded for ice recorded using an X-ray tube (44) (Figure 1 in the reference) than at lower energies. This finding alone questions the use of the split peak components as indicators of two liquid phases, as this would imply solid ice at liquid nitrogen temperature to have these phases.

Our Bethe-Salpeter equation XES simulations (average 1.88 accepted and donated hydrogen bonds per molecule) account for core-hole dynamics of different durations (Fig. 4(a)). They show that the formation of the lower-energy split component requires core-ionized-state dynamics in the long and the short O–H bonds to take place between ionization and X-ray emission. This dynamical interpretation also explains why slower-moving deuterated samples show a reduced peak A (19, 38, 45–48). For resonant excitations and ionization, the the quantitative details of the split peak may be different, as the potential energy surfaces governing the dynamics, in principle, may differ from each other. Still the dynamic view is consistent with spectra obtained at detuned $4a_1$ resonance, where the electronic loss feature appears as a single line that develops into a double peak when tuned to the $4a_1$ and above. This is understood as an indication of longer effective scattering duration.

The split-peak has a weak dependence to underlying structure seen in the branching ratio A/B, similarly to what we have established for the chain length dependence in liquid alcohols (49). We performed (Fig. 4) a full statistical analysis linking the the A'/B' branching ratio to the continuum RIXS simulation for liquid water. We reveal how A'/B' increases by increased hydrogen bonding (donated D, accepted A) and decreases by increased deviations from tetrahedrality (Δ_a angular, Δ_d distances) of the environment (Fig. 4 (b)). These findings are in full agreement to experiments presented here and earlier: the lower-energy component (A in Figure 2) of the split peak in water is reduced in higher temperatures of the liquid (19, 45) and increased upon freezing (19, 44). The occurance of the split-peak of water XES itself is a dynamical effect, equivalent to i.e. alcohols, where the branching ratio picks up some weak but notable statistical trend to structural parameters, as shown in our simulations.

Conclusions

When putting the information from the three spectroscopies X-ray absorption, resonant inelastic X-ray scattering (RIXS) and non resonant X-ray emission together we can proceed to conclusions. Analysis of the X-ray absorption across the phase diagram of water using f-density normalization reveals for liquid water 1.74 donated hydrogen bonds per molecule, being closer to the 2 donated hydrogen bonds in 4-fold coordinated tetrahedral ice than previously derived from short range spectral normalization. In this quantitative normalization the occurance of a continuum scattering or shape resonance representing the structural order of the Oxygen-Oxygen next neighbour coordination shells in the liquid and ice is established. This shape resonance is absent in gas and supercritical phases,

since the number of hydrogen bonds is reduced.

Consequence of this quantitative understanding is that resonant inelastic X-ray scattering via the H_2O LUMO $4a_1$ state is sensitive to all bonding arrangements that might be present in liquid water. Potential-energy-surface mapping with sub-natural line width RIXS on gas phase and liquid water finds no indication of two distinct molecular potentials. A split peak in RIXS vibrational progression would be a potential (but not conclusive) indication of two structural motifs. This kind of behavior is not observed at spectral bandwidth of 50 meV. Instead we observe gradual broadening in a continuous way, which strongly supports the continuum model description of liquid water.

In non-resonant X-ray emission spectroscopy the branching of the HOMO $1b_1$ state into a split peak has been promoted as a signature of two structural motives in liquid water. The experimental finding, that in the sudden limit (at high incident energy) the photoelectron decouples from decay yielding an ice-like emission spectrum, rules out the use of this emission spectrum as an evidence for two structural motives in the liquid. This reasoning roots on similarity of the emission spectra and the fact that ice does not have two liquid phases. Additional support is given by a liquid 64-water simulation with periodic boundary conditions including both structural variation and core-hole-state dynamics on equal footing, being in line with numerous previous simulations. In particular, split peak branching ratio relationships show that dynamics play a key role in the formation of the $1b_1$ double peak, with a very weak dependence on the starting structure.

Thus, the findings of X-ray spectroscopic tools are in full agreement with the continuous distribution model of liquid water structure equally reported in the vast number of non-X-ray based investigations of water.

Supporting Information (SI). Available as a separate file.

Materials and Methods

The hard X-ray Raman experiment for liquid water and ice was performed using the X-ray Raman scattering spectroscopy instrument (50) at the beamline ID20 of ESRF. The momentum transfer used for detection was $q = 2.6 \pm 0.6$ Å^{-1}. The scans for the ice sample were performed from below and from above to confirm that radiation damage does not introduce an error in the data (see SI Appendix, Fig. S2). For the experiment, the liquid water sample was filled into a custom-made flow cell (51), and the ice sample was prepared *in situ* in a 2 mm quartz capillary continuously cooled by using a cryostream (Oxford cryosystems) at approximately at -88 °C. For both samples, milli-Q water was used. The raw data was handled as described in (52). The intensity integral values in the data are presented in SI Appendix, Table S1. There are also problems in using f-sum rule due to varying completeness of the set of accessible final states (53), here seen as mismatch between gas phase and condensed phases. The XAS of Fig. 3 was recorded using the flat-jet transmission NEXAFS setup (54) at BESSY-II. The ionization step of Fig. 2 is taken from gaussian-shaped-assumed O1s photoline (30) with width from Ref. 55.

The RIXS experiment was performed with the SAXES spectrometer (35) at the ADRESS beamline (36) on the Swiss Light Source at Paul Scherrer Institut. The RIXS process proceeds via a core-hole state, thus rendering the technique element specific and local. Core excitation with subsequent decay into the electronic ground state can furthermore lead to population of purely vibrational final states. The energy spacing of the obtained vibrational progression allows extraction of the local ground state potential energy surface (39, 56) The propagation in the core excited state potential takes the wave packet violently away from the ground state equilibrium position. Decay of this wavepacket then allows population of ground-state vibrational eigenstates; in particular is it possible to easily reach the high eigenstates that are not accessible by Raman or IR spectroscopy. This enables reconstruction of the potential energy surface far away from the equilibrium geometry. The dynamics of the core-excited wave packet is state dependent, which allows for different modes of the system to be probed by selection of the excited state (57).

We utilized a flow-cell separating the sample from the vacuum by a Si_3N_4 window of 150 nm thickness with a ∼10 nm Au coating. The energy calibration was based on O_2 spectrum (39). Due to breakdown of the windows in irradiation, the cell was moved between the spectra. To avoid errors from this procedure, these individual scans were shifted to the same energy by using a fit to the elastic line before joining them. The data in the electronic loss region is presented with larger energy binning for improved statistics.

The XES experiment for photon energies 550 eV and above was performed at the beamline U49-2/PGM-1 in BESSY-II by using the setup described in Ref. (58). The XES data was calibrated by using the spectrum at 550.1 eV reported in Ref. (37).

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