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LETTER TO THE EDITOR

Spectroscopic probing of local hydrogen-bonding structures in liquid water

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Abstract

We have studied the electronic structure of liquid water using x-ray absorption spectroscopy at the oxygen K edge. Since the x-ray absorption process takes less than a femtosecond, it allows probing of the molecular orbital structure of frozen, local geometries of water molecules at a timescale that has not previously been accessible. Our results indicate that the electronic structure of liquid water is significantly different from that of the solid and gaseous forms, resulting in a pronounced pre-edge feature below the main absorption edge in the spectrum. Theoretical calculations of these spectra suggest that this feature originates from specific configurations of water, for which the H-bond is broken on the H-donating site of the water molecule. This study provides a fingerprint for identifying broken donating H-bonds in the liquid and shows that an unsaturated H-bonding environment exists for a dominating fraction of the water molecules.

(Some figures in this article are in colour only in the electronic version)

The hydrogen bond (H-bond) in liquid water holds the key to its peculiar behaviour, with implications for chemical, biological, and geological processes. In liquid water, the dynamical motion of the atoms at the picosecond timescale causes the H-bonds to break and reform, resulting in a statistical distribution of different coordinations for the water molecules. Water molecules in liquid and solid phases exhibit two types of O–H interaction: strong covalent O–H-bonds within the water molecule, and relatively weak H-bonds between the molecules.

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In ice, each water molecule is coordinated by four neighbouring waters through H-bonds (two H-bonds to the oxygen atom, and one to each hydrogen). Although liquid water primarily exhibits the same coordination environment, experimental (vibrational spectroscopy, neutron and x-ray diffraction) and theoretical (molecular dynamics (MD)) studies have indicated that liquid water contains a fraction of water molecules with broken H-bonds [1–7]. Recent time-resolved vibrational spectroscopic studies of liquid water have shown two distinct molecular species: strongly (with four H-bonds), and weakly H-bonded structures (with one or two broken H-bonds) [1, 2]. Except for the strongly H-bonded structure, specific information on the number of H-bonds and local coordination structure could not be obtained from these studies. Similarly, the radial distribution functions of the O–O, O–H, and H–H distances in liquid water, measured with x-ray and neutron diffraction [3, 4, 8], do not provide information on the local, directional structure of the H-bond environment. MD simulations have been considered to be the only possible means to visualize the H-bonding network in liquid water. The results of these simulations depend both on the chosen interaction potentials, classical [9] or *ab initio* [10], and whether quantum effects are incorporated in the dynamics [5, 11]. We need a method that locally, around individual water molecules, can identify the nature of different H-bonding configurations. Chemical bonding has in general a large effect on the valence electronic structure and we can anticipate that different H-bonding configurations can show a variation in the local water molecular orbital structure. In the present report we demonstrate how these differences in the local water electronic structure can be measured and how they are related to different H-bonding configurations.

X-ray absorption spectroscopy (XAS) is a probe of the empty electronic states, and the localized nature of the core hole, in combination with the dipole selection rule, makes it possible to probe unoccupied states in an atom-specific way [12]. Since we examine the excitation of O 1s electrons, the dipole selection directly allows the measurement of the local atomic p contributions, most importantly to the levels in water derived from the antibonding O–H molecular orbitals. The oxygen p character of these orbitals is primarily affected by the local geometric arrangement, i.e. the H-bonding around the probed O atom. In addition, the timescale of inner-shell electronic excitations is much shorter than a femtosecond, which makes it feasible to use the O 1s excitations for studying the empty O–H antibonding states centred around different water units in frozen-in instantaneous structures.

We obtained the O K-edge XAS spectra of water in liquid and gaseous forms using the soft x-ray endstation for environmental research (SXEER) and beamline 8.0 at the Advanced Light Source, Berkeley, USA, using an energy resolution of 0.1 eV. The sample assembly in the SXEER is kept in He atmosphere at a pressure of 760 Torr, and is separated from the high vacuum of the beamline by a Si₃N₄ window. The XAS spectra of liquid- and gas-phase water were obtained by examining the sample fluorescence using a GaAs photodiode. For measurements on liquid water, the sample was obtained by water flowing over a metal plate with the surface of the water film near normal to the incident beam and the fluorescent light detected at an emission angle of 3°–5° with respect to the water surface to minimize saturation effects. The ice sample was prepared at MAX-Lab, Sweden, by epitaxial growth on Pt(111), and the XAS spectrum measured using partial-electron-yield detection.

We interpreted the experimental spectra with the help of theoretical calculations based on density functional theory (DFT) [13]. The techniques used have been shown to give a very reliable description of XAS spectra for molecules and complex systems [13]. In order to generate some realistic model structures for the spectrum calculations we used classical constant-volume-and-energy (300 K) MD simulations [14]. For the DFT calculations of spectra, we have taken example structures (including the first and second hydration shells, i.e. 29–33 water molecules) from the MD simulations.

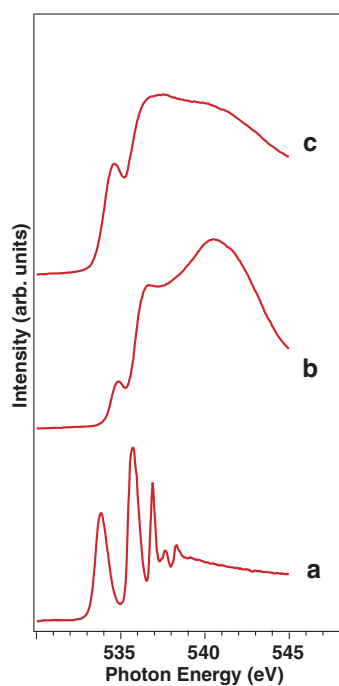


Figure 1. Experimental XAS spectra of water in (a) gas phase, (b) ice, and (c) liquid.

Figure 1 shows O K-edge spectra of water in its three forms of aggregation indicating that the electronic transitions in the condensed forms are significantly different from those in the gas phase. The gas-phase spectrum exhibits well-separated peaks corresponding to O 1s excitations into the antibonding O–H $4a_1$ and $2b_1$ molecular orbitals at low energies (534 and 536 eV), and transitions into the Rydberg orbitals at high energies [12, 16]. As water converts from the gas phase into ice, the spectrum broadens and shows a weak pre-edge feature at 535 eV. The latter we assign as being dominated by contributions from the surface region of ice [17]. Compared with that of ice, the spectrum of liquid water is different, with a very strong pre-edge peak (535 eV), a slight enhancement at the bottom of the conduction band (537 eV), and a much less pronounced structure in the continuum (542 eV). There has recently been another attempt to measure the difference in XAS spectra of liquid water and ice using core-to-valence electron x-ray inelastic scattering—however, without high enough resolution to resolve the essential pre-edge peak [20].

From DFT calculations of many different structures as generated in the MD simulations, we learned that it is mainly the local structure within the first coordination shell that makes a difference in the spectral profile. Thus although bond distances and coordination vary continuously, we can summarize the findings into three qualitatively different H-bond structures; see figure 2. There is a symmetric species with four H-bonds (denoted as SYM) with a tetrahedral coordination similar to that in ice. The other two structures correspond to broken H-bond configurations resulting in different asymmetric (ASYM) species. From a local viewpoint we distinguish two types of asymmetric species: asymmetry in the length of the two H-bonds *accepted* by the water molecule (A-ASYM) or asymmetry of the two H-bonds *donated* by the water molecule (D-ASYM). We can expect the asymmetric configurations in the liquid water—as compared to symmetric species and to the symmetric coordination in ice—to cause

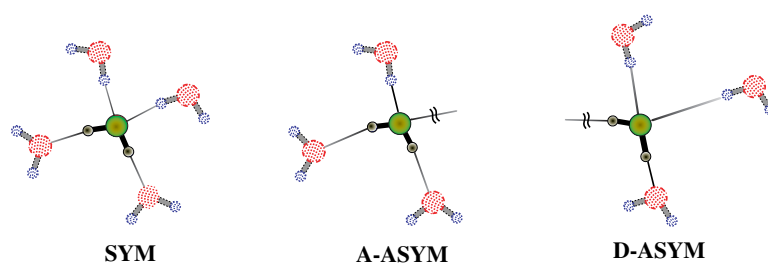


Figure 2. Typical local structures of hydrogen bonding in liquid water corresponding to fully coordinated and symmetric H-bonded species (SYM), and broken asymmetric H-bond networks on either the oxygen site (A-ASYM) or hydrogen site (D-ASYM). The second hydration shell was included in the calculations but is not shown in the figure.

significant changes in the molecular orbital structure affecting the XAS spectrum. However, the question is: which ASYM species contributes to the large pre-edge intensity?

Figure 3 shows a collection of simulated spectra for the three different H-bond structures as indicated in figure 2 and for bulk ice. For easy comparison, the experimental spectra of water and ice are displayed above each set of simulated spectra. The calculated ice spectrum shows an overall agreement with the experimental spectrum with two main features corresponding to the adaptation of the oxygen 2p orbitals to the near-tetrahedral environment in the ice at 537.5 eV and to the development of the ice conduction band centred at 541 eV. There is a discrepancy with respect to the pre-edge intensity and to a too small splitting of the two main bands that we attribute to the surface contribution in the experimental spectrum [17]. For each of the main three different H-bond configurations we show a comparison of the experimental spectrum with a collection of computed spectra, which shows the spectral variations that result from differences in H-bond distances and angles due to the thermal motion. We can directly see that the spectral contributions from the different SYM and A-ASYM species do not deviate significantly from ice, with a main broad feature around 541 eV. In contrast, the D-ASYM species show a strong discrete pre-edge peak and a strong feature at the bottom of the conduction band. The strong increase of the pre-edge intensity thus comes specifically from species with a large asymmetry in the H-bonding distance between the two hydrogen sites. The large asymmetry makes the protons strongly nonequivalent and causes the molecular orbitals to localize along the two internal bond directions. This gives rise to the pre-edge feature, corresponding to the free OH group, and another feature at higher energy due to the other, strongly interacting OH group. The variation in spectral features between the different species (SYM, A-ASYM, D-ASYM) is primarily due to a change in molecular orbital composition. The more symmetric H-bond environment in ice and SYM water reduces the oxygen p character in the mainly a_1 -derived orbitals. The strong asymmetry between the two hydrogens in the D-ASYM species, on the other hand, leads to a significant orbital mixing of a_1 - and b_1 -derived orbitals, with the latter providing pure oxygen p character. When the asymmetry is on the oxygen atom (A-ASYM species) the orbital changes are much smaller since the lone pairs do not have low-lying unoccupied orbitals with which to mix; the out-of-plane polarizability of water is much smaller than the in-plane polarizability.

The intense, broad pre-edge feature in the XAS spectra of liquid water shows that there are a large number of water molecules with asymmetric donating H-bonds. Since all other configurations give a spectral profile qualitatively similar to the ice spectrum, we can estimate the amount of D-ASYM-related species using a simple subtraction procedure based on the experimental spectra. With the aim of removing the ice feature at 542 eV in the liquid

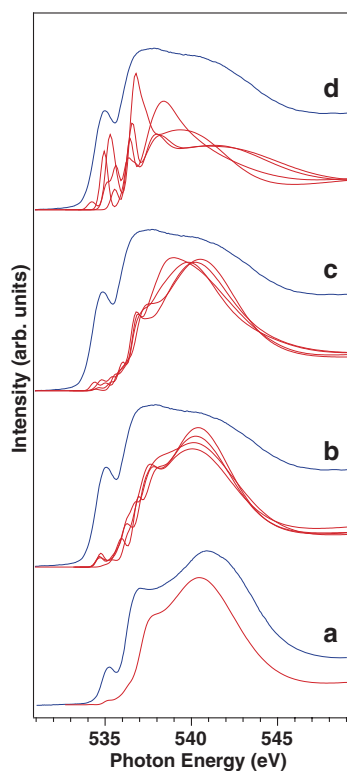


Figure 3. Calculated x-ray absorption spectra of (a) ice and of the three typical hydrogen-bond structures (b) SYM, (c) A-ASYM, and (d) D-ASYM in liquid water as shown in figure 2. For each of the liquid species, four spectra corresponding to typical variations in distances and angles are shown. The experimental spectra of water or ice are shown above each set of simulated spectra.

spectrum, without introducing any strong negative features in the difference spectrum, we find limits of 20–40% for how much of the ice spectrum can be subtracted from that of the liquid. Since the experimental ice spectrum can be used to represent contributions both from SYM and A-ASYM species, the remaining 60–80% can then be assigned to distorted, mainly D-ASYM, species. Since the number of broken H-bonds on donor and acceptor sites should be equal, we can expect the same amount of species that also have a broken acceptor H-bond. We can then estimate the average number of broken H-bonds per molecule as 1.2–1.6. Since this value is above 1, a number of molecules will have both a broken donor and acceptor H-bond. Computed spectra of such D-ASYM species do not significantly deviate from the D-ASYM spectra shown in figure 3. Furthermore, molecules with two broken donor bonds give a contribution to the spectrum that in the pre-edge region is very similar to that of the gas phase; this is not observed with any significant intensity in the experimental water spectrum. We can thus make a first crude estimate of the average number of H-bonds as 2.4–2.8. This number is much lower compared with previous MD simulations that often give a value around 3.5 [6, 8]. It is interesting to note that the number of nearest-neighbour water molecules within a radius of 3.5 Å is in the range 3–5 molecules for all the D-ASYM species shown in figure 3. This is in accordance with the average value of 4.5 molecules in the first coordination shell determined from an integration of the radial distribution function to the first minimum at 3.5 Å [3, 4, 8].

In many ways the D-ASYM species can be connected to other observations unique to liquid water. There is an important librational motion where the hydrogen atom that is involved in the donating H-bond in a D-ASYM species is exchanged through breaking and recreating the bond using the other hydrogen. In a water trimer cluster this motion has recently been observed to allow for rapid switching between the bonded hydrogens in the first excited state [20]. These motions are thermally excited in the liquid phase and can be related to the fast relaxation times below 0.1 ps, derived from simulations of liquid water [6]. The D-ASYM species and librational motions can also be related to the fast orientational relaxation process seen in pump-probe femtosecond IR spectroscopy [1, 2]. The measured spectral intensities reported in the present work indicate that there is a substantially larger fraction of these D-ASYM species than expected from earlier simulations. Quantum simulations of the dynamics, however, show that there is a tendency to underestimate the number of broken H-bonded species using classical methods [5].

Thus, we have a tool to study the existence of asymmetric H-bonds in water and related aqueous systems through their effects on the local electronic structure. Most importantly, we have demonstrated direct effects on the electronic structure of water from the local coordination and have shown that XAS, in combination with theoretical structure and spectrum simulations, provides a probe for examining different types of H-bonding species. This can be expected to be applied in the future to a large range of aqueous solutions and interfaces and to provide new insight into the effects on the local electronic and coordination structure of water.

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- [17] The ice spectrum was measured using electron detection, which is inherently surface sensitive. We have a contribution of 10–20% from the topmost layer. It has previously been shown that a strong pre-edge is seen in the XA spectrum of ice using detection of desorbing hydrogen ions; see
Rosenburg R A *et al* 1983 *Phys. Rev. B* **28** 3026
Coulman D *et al* 1990 *Chem. Phys.* **93** 58
Mase K *et al* 1998 *J. Chem. Phys.* **108** 6550
This feature was interpreted as originating from the surface region where hydrogen ions can be easily ejected into vacuum after excitation into the OH antibonding $4a_1$ orbital. Using grazing electron emission in Auger-yield mode, the pre-edge intensity is enhanced in the spectrum, which supports the previous interpretation.
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