

Local Probing of Hydrogen Bonding Structures in Liquid Water

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The hydrogen bond (H-bond) in liquid water holds the key to its peculiar behavior, with implications for chemical, biological and geological processes. In liquid water, the dynamical motion of atoms at the picosecond time-scale 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 interactions: strong covalent O-H bonds within the water molecule, and relatively weak H-bonds between the molecules. In ice, each water molecule is tetrahedrally coordinated by four neighboring waters through H-bonds (2 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) studies have predicted that liquid water should contain a fraction of water molecules with broken H-bonds.

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 the *atomic* populations of the unoccupied states. Since we examined the excitation of O 1s electrons, the dipole selection directly allows the measure of the local atomic p contributions, most importantly to the levels derived from the antibonding O-H orbitals. The oxygen p-character of these orbitals is primarily affected by the local geometric arrangement and the H-bonding around the probed O-atom. In addition, the time-scale of inner-shell electronic excitations is faster than a femtosecond, which makes it feasible to use the O 1s excitations for studying the empty O-H antibonding orbitals centered around each different water unit

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. 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 spectra of liquid and gas phase water were obtained by examining the sample fluorescence. The spectrum of ice was collected at the MAX Lab, Sweden. We analyzed the experimental spectra with the help of theoretical calculations based on Density Functional Theory (DFT)¹. The molecular structures of liquid water used in the DFT calculations were generated by classical constant volume and energy (300K) Molecular Dynamic (MD) simulations² using flexible and polarizable potentials. For the DFT calculations of spectra, we have taken example structures (including the first and second hydration shells i.e. 26-30 water molecules) directly from the MD simulations.

Figure 1 shows O K-edge spectra of water in all different aggregation forms, gas, ice and liquid. The gas phase spectrum exhibits well-separated peaks corresponding to O 1s excitations into the antibonding O-H 4a₁ and 2b₁ molecular orbitals at low energies, and transitions into the Rydberg

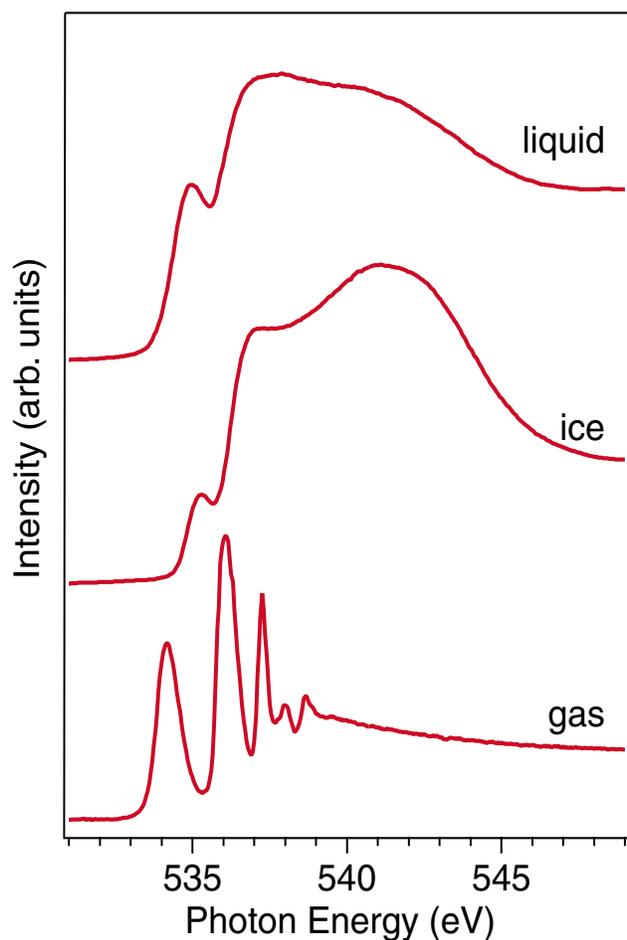


Figure 1. Experimental O K edge XAS spectra of water in gas phase, ice and liquid.

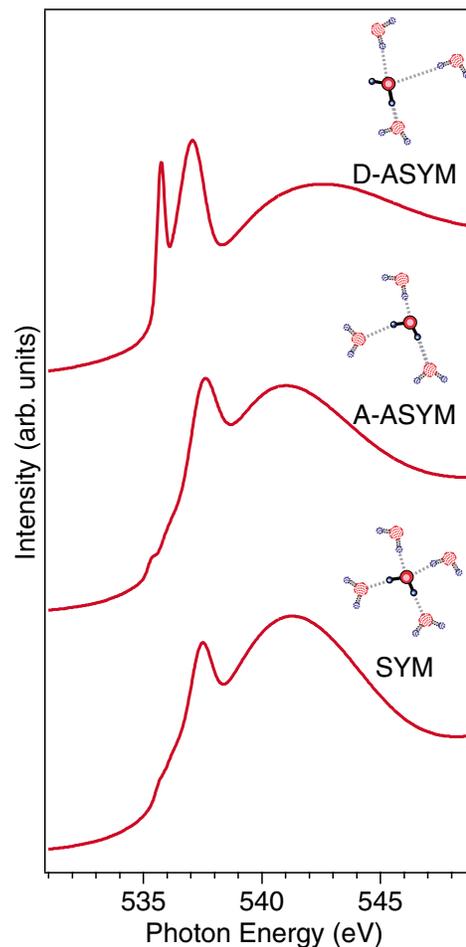


Figure 2. Calculated XAS spectra of three typical hydrogen bond structures in liquid water.

orbitals at high energies. In contrast, the spectrum of liquid water is relatively broad with a *pre-edge* feature at 535 eV. The spectrum of ice (I_h) also exhibits a pre-edge feature, but with a much smaller intensity. Our theoretical studies show that the spectral features of gas phase water and ice could be reproduced using their previously known structures. Liquid water does not have a well-defined structure and different MD parameterizations result in different distributions of the molecules. However, we find that only molecules with certain types of coordination contribute to the pre-edge feature, which indicates the possibility to estimate the distribution from the intensity of the pre-edge peak. The spectrum of ice shows a strong shift of the spectral distribution into the near continuum to form the conduction band; the molecular orbitals available for the excitations are now furthermore found to be strongly mixed. In particular the original $4a_1$ antibonding orbitals now exhibit mainly *s* character on the oxygen because of the tetrahedral symmetry of water molecules in ice, and hence these transitions are weak. In the gas phase the $1s \rightarrow 2b_1$ transition shows appreciable intensity, but in ice most of the oxygen 2*p* contribution to these orbitals has been pushed up into the continuum and can now be seen as the enhancement of the intensity just above the ionization edge.

Theoretical spectra of typical H-bond structures in liquid water is shown in Fig. 2. A symmetric species with 4 H-bonds (denoted SYM), locally similar to ice and broken H-bond configurations resulting in different asymmetric (ASYM) species, which result from the dynamical motion of

the water molecules. This will create a situation where one of the H-bonds becomes very short and the rest relatively long or even broken. 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). The simulated spectra of the SYM and A-ASYM species do not deviate significantly from ice (Fig. 2). However, the pre-edge features are shifted to higher energy for the A-ASYM species. In addition, the well-defined H-bonding interaction and long range order in ice when compared to liquid water cause the absorption edge of ice to be steeper. In contrast, the D-ASYM species show strong discrete pre-edge peaks. The energy position of their first peak coincides with that of the pre-edge peak seen in the experimental spectrum of liquid water. These theoretical results show that the species with a large asymmetry in H-bonding distance between the two hydrogen sites give rise to a unique local molecular orbital structure providing the increase of the pre-edge intensity. It should be noted that the computed *total* density of states for all of the situations above, i.e. ice, SYM, A-ASYM and D-ASYM are very similar. The variation in spectral features 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. In the D-ASYM species, on the other hand, one of the two hydrogen atoms is involved in a strong H-donor interaction with a corresponding A-ASYM species whereas the other one represents an essentially broken H-bond. This strong asymmetry on the two hydrogens 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 on the oxygen are much smaller since the lone-pairs do not have low-lying unoccupied orbitals with which to mix.

We conclude that the molecular orbital structure of liquid water is significantly different from that of crystalline ice and gas phase water. These experimental results together with the theoretical studies also provide direct evidence for the H-bonding environment, and its variation among different species of water molecules in liquid water. The intense, broad pre-edge feature in the NEXAFS spectra of liquid water shows that there are a significant number of water molecules with asymmetric H-bonds. Furthermore, this affects the electronic structure of the liquid: there are shifts of the molecular orbital composition and energy positions for different species, which can be related to a distribution of H-bond distances.

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