Structure and dynamics in liquid water from x-ray absorption spectroscopy

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Abstract. Oxygen K-edge x-ray absorption spectra of water are discussed. The spectra of gas-phase water, liquid water and ice illustrate the sensitivity of oxygen K-edge x-ray absorption spectroscopy to hydrogen bonding in water. Transmission mode spectra of amorphous and crystalline ice are compared to x-ray Raman spectra of ice. The good agreement consolidates the experimental spectrum of crystalline ice and represents an incentive for theoretical calculations of the oxygen K-edge absorption spectrum of crystalline ice. Time-resolved infrared-pump and x-ray absorption probe results are finally discussed in the light of this structural interpretation.

1. Introduction
Ordinary yet unique, liquid water is probably the most important and least understood substance. A fluctuating network of hydrogen bonds connecting the constantly mobile molecules determines both structure and anomalous properties of water. The hydrogen bonds are strong enough to link the water molecules but they are also weak enough to constantly break and reform on an ultrafast time scale of 1 picosecond (10^{-12} s). It is therefore straightforward to claim that understanding the fast making and breaking of these bonds and the involved molecular rearrangements is a prerequisite for understanding structure and properties of water.

Ever since the first x-ray scattering [1-5] and infrared (IR) [6] studies of liquid water, methods based on x-ray and IR radiation have been important probes for the time-average equilibrium structure of liquid water. However, hydrogen bond configurations cannot be determined uniquely with x-ray diffraction data [7, 8] and the structure-frequency correlation used in IR studies is less strict than often assumed [9].

X-ray spectroscopy has emerged as a new tool for the investigation of liquid water [10-23]. The near edge features in the Oxygen (O) K-edge x-ray absorption spectra (O K-edge NEXAFS or XANES) are discussed as to what can be learned about the local structure of liquid water in terms of time- and ensemble-averaged hydrogen-bond configurations with relative orientation and distances of neighboring water molecules [10, 18-27]. In contrast, the extended range of the O K-edge absorption spectrum (O K-edge EXAFS) can be used to infer complementary information on the nearest neighbor O-O radial distributions [28, 29]. We note that with this, is has recently been possible for the first time to determine the O-O radial distributions in liquid water and ice with the same method under identical experimental conditions [30].
Investigations of the hydrogen-bond dynamics in water have so far been largely dominated by ultrafast mid-IR spectroscopy [31-35]. The main vibrational probe is the O-H stretching vibration at 3400 cm\(^{-1}\). Its eigenfrequency is particularly sensitive to structural changes of the hydrogen-bond network. Pump-probe and photon echo spectroscopy have been extensively used to study intra- and intermolecular energy relaxation and transfer as well as spectral diffusion to study the dynamics and underlying coupling mechanisms of the rapidly fluctuating network.

A combination of both, ultrafast IR and ultrafast x-ray spectroscopies, promises to reveal fundamentally new insight into the structure of liquid water. This has come into reach with the recent advent of short-pulse x-ray sources and the related development of methods and instrumentation for ultrafast x-ray science [36-52]. Our first results on the picosecond (ps) dynamics in liquid water with time-resolved IR-pump and x-ray absorption-probe spectroscopy [53, 54] were confirmed recently with the same technique [55] as will be reviewed here.

2. Results and discussion

[The graph in the document is not described in the text, but it is included in the image.]

The O K-edge x-ray absorption spectra of gas-phase water, liquid water, and ice in figure 1 clearly demonstrate that hydrogen bonding in water can be effectively probed with x-ray absorption spectroscopy. The spectra illustrate the correlation of the near edge features in the x-ray absorption spectrum with hydrogen bonding environment in water. The gas-phase and ice spectra can be used as
well-known model or reference systems. More details can be inferred by comparison to spectra of further experimental model systems or to calculated spectra [10].

The amorphous ice sample [figure 1 (c)] was prepared by condensing deionized water in ultrahigh vacuum onto a Si3N4 membrane that was cooled to liquid Nitrogen temperature. The crystalline ice I_h sample [abbreviated simply by “crystalline ice” hereafter, figure 1(d)] was made from the amorphous sample by slowly heating it to about 150 K [14, 56]. Crystallization was observed to be complete after approximately 30 min. Both ice samples were approximately 200 nm thick. For details about the liquid water sample refer to [54]. Note that transmission mode was shown to be an effective way of measuring the O K-edge absorption spectrum of water [57].

The gas-phase spectrum [figure 1(a)] is dominated by absorption to the lowest unoccupied molecular orbitals of the free molecule (2b_2 and 4a_1 symmetry). In contrast, in the liquid water [figure 1 (b)] and ice spectra [figure 1 (c), (d)] the unoccupied molecular orbitals of neighboring molecules overlap and form conduction bands and absorption to this unoccupied density of states dominates the spectra of water molecules in the condensed phases [58].

It is useful to distinguish three regions in the condensed-phase spectra since, as a first approximation, absorption intensity is simply redistributed between these regions when going from the liquid to ice [10-12, 14, 59]: a pre-edge region centered at 535 eV, a main-edge region at 537 eV and a post-edge region at 541 eV. The spectra in figure 1 (c) and (d) clearly show that intensities in the pre- and main-edge regions (in the post-edge region) increase (decrease) when going from the disordered but saturated hydrogen-bond environment in amorphous ice to the liquid with broken hydrogen bonds. The overall absorption intensity remains approximately constant but intensity is shuffled from the post to the pre and main edges when hydrogen bonds are broken.

Detailed analyses showed that varying the contribution of two structurally different configurations can explain these spectral changes [10, 12, 60]: An increase of absorption in the pre- and main-edges and with a decreasing absorption in the post-edge is consistent with the increase of the relative amount of locally asymmetric configurations and the concomitant decrease of the relative amount of locally symmetric configurations. The symmetry refers here to hydrogen bonding on the donor side (hydrogen side) of the water molecules: The asymmetric species are characterized by one well-defined hydrogen bond on the donor side and one weak or broken donor hydrogen bond while in symmetric configurations both donor hydrogen bonds are strong or intact. This approach could also used to explain the changes in the O K-edge x-ray absorption spectra upon steady-state heating and cooling of liquid water [26] and the differences between liquid H2O and D2O [60]. It has also been used to interpret the steady-state temperature changes in the x-ray emission spectrum of liquid water [22].

More subtle changes can be detected in the spectra of figure 1 (c) and (d) when going from amorphous to crystalline ice. The differences between amorphous and crystalline ice as shown in figure 1 are not yet understood. In particular, to our knowledge, no calculated spectra exist that would explain these spectral differences. The question hence arises how well-known ice as a model or reference system is. This is particularly important since the pre-edge feature in the ice and liquid water spectra can be used to determine the number of broken hydrogen bonds in liquid water. In addition, doubts could arise about how well one knows whether the ice sample really is amorphous or crystalline and, hence, how reliable relative intensities in the ice spectrum as a reference really are [61].

In this respect, we compare in figure 2 the ice spectra obtained in transmission mode from figure 1 with crystalline ice spectra taken with x-ray Raman scattering [61, 59]. X-ray Raman scattering is a bulk sensitive technique as is uses hard x-ray radiation of several keV photons and, under certain circumstances, the Raman scattering intensity is proportional to the x-ray absorption cross section at the respective edges of the elements in the sample [62, 63, 61, 29, 64].

For more direct comparison and in order to account for the difference in energy resolutions, the transmission mode spectra were convoluted with Gaussian profiles with a FWHM corresponding to the energy resolution of the respective x-ray Raman experiment. The convoluted amorphous ice transmission spectra disagree with the crystalline ice Raman spectra [figures 2 (a) and (b)].
The agreement of the convoluted crystalline ice transmission spectra with the Raman spectra [figures 2 (c) and (d)] and in particular the very good agreement with the high resolution Raman spectrum [figures 2 (d)] however clearly shows that the spectrum of crystalline ice as shown in figures 1 and 2 (and most probably the transmission spectrum of amorphous ice as well) is reliable. Note that the transmission and Raman spectra were obtained on very different samples grown under different environments and according to different procedures. In addition, the transmission samples were only 200 nm thick while in the Raman scattering experiments the ice was probed to a depth of several 100 μm. Still, they both represent bulk measurements of ice compared to surface sensitive electron yield techniques [16, 56]. This agreement should be an incentive for further theoretical calculations with the aim to reproduce all features in the crystalline ice spectrum and to consolidate ice as a model or reference system for liquid water.

Independent of debates or uncertainties about the interpretation of the liquid water and ice spectra it is clear that the breaking of hydrogen bonds in water is reflected in an increase of absorption in the pre-edge region of the O K-edge absorption spectrum. This was used in the time-resolved IR-pump and x-ray absorption-probe experiment as described in the following. We used femtosecond (fs) IR pulses centered at 3400 cm⁻¹ (wavelength approximately 3 μm) as generated with an optical parametric amplifier (OPA) fed with an 800 nm fs Ti:Sapphire laser to pump a liquid water sample by exciting the O-H stretching vibration of a certain fraction of the water molecules. The laser was synchronized to the electron storage ring BESSYII. Together with gated detection of the transmitted x-ray pulses this
allowed for time-resolved detection of the x-ray transmission with variable time delay between pump and probe pulses. The overall time resolution amounted to 80 ps and is limited by the duration of the x-ray pulses at BESSYII. Details can be found in [53, 54].

A steady-state O K-edge x-ray transmission spectrum of liquid water and changes of the transmission at two different photon energies close to the pre-edge energy of 535 eV are shown as a function of delay time in figure 3.

![Figure 3. (a) O K-edge transmission spectrum. (b) Change of transmission $\Delta T/T_0$ with $\Delta T = (T - T_0)$ (T and $T_0$: transmission before and after excitation) as a function of pump-probe delay time at the photon energies of 534.6 (solid circles and solid line) and 534.8 eV (open circles and dashed line). Measured data are shown as circles and fits using a Gaussian (FWHM = 80 ps) broadened step function are shown as solid lines. All data are taken from [54].](image)

The time-resolved data in figure 3 (b) clearly depict a decrease of the transmitted intensity within our time resolution (see fitted line). It decreases by up to 3.2 % and stays constant up to the longest measured delay of 280 ps. This effect, confirmed recently by Huse et al. [55], can be understood in a straightforward manner [53, 54]. The fs excitation of the $\nu = 1$ state of the O-H stretching vibration decays with a time constant of 200 fs [33-35] via the O–H bending mode and the excess energy is transferred into low-frequency intermolecular vibrations of the hydrogen bond network [34]. The sample is hence fully equilibrated and macroscopically heated on a timescale of a few ps with a larger
fraction of hydrogen bonds broken. We deduce from experimental parameters such as the pump pulse
power (2.3 μJ) and the sample thickness that we induce a temperature jump of close to 20 K [54]. The
observed pre-edge transmission decrease (pre-edge absorption increase) is the result of this transient
heating and clearly indicates in accordance with the above discussion that the number of molecules in
locally asymmetric configurations with one weak/broken hydrogen bond increases within our time
resolution. The data in figure 3 (b) also show that the amount of transmission decrease (absorption
increase) is smaller when approaching the pre-edge energy of 535 eV. We find a maximum change at
534.6 eV.

The calculated absorption spectra in figure 4 depict the changes expected over the whole O K-edge
absorption spectrum when breaking hydrogen bonds such as during an ultrafast temperature jump.
Starting with two arbitrarily chosen but representative configurations in liquid water with different
spectra one sees that when breaking hydrogen bonds in both cases the pre- and main-edge absorption
increases while the post-edge absorption decreases.

![Figure 4](image)

**Figure 4.** (a) Schematic depiction of possible structural changes in local
configurations associated with breaking hydrogen bonds in liquid water. Red (white)
spheres denote oxygen (hydrogen) atoms. Dotted lines represent hydrogen bonds. (b)
Calculated O K-edge absorption spectra corresponding to the respective
configurations (spectral changes in (b) are denoted by arrows and correspond to the
configurational changes above the respective spectra in (a)). Spectra are taken from
[10] (see Fig. 3A a, c and h in [10] for details about the configurations).

In order to test this we recorded a transient x-ray transmission spectrum at a delay time of 280 ps.
This spectrum is depicted in figure 5. It clearly depicts the expected reshuffling of intensity within the
spectrum: Absorption increases in both the pre and main edges while it decreases in the post edge. We note, however, that 1) the maximum change in the pre-edge region is not in the pre-edge maximum in agreement with the data in figure 3 (b) and 2) the changes in the pre and main edges are different by about a factor of 2. These observations are in disagreement with the measured changes in the x-ray absorption spectrum upon steady-state heating of liquid water [53, 54]. For steady-state heating, the absorption changes at or very close to the pre-edge energy and pre- and main-edges change by the same amount. This was confirmed as well in [55].

![Figure 5](image)

**Figure 5.** Transient O K-edge absorption spectrum at a pump-probe delay time of 280 ps (open circles: data, solid line: smoothed curve). $\Delta T/T_0$ is the transmission change with $\Delta T = (T - T_0)$ ($T$ and $T_0$: transmission before and after excitation). The spectrum is taken from [53]. The transmission change is smaller than the one reported in figure 4 due to a smaller effective temperature jump [54].

The data in figure 5 demonstrate that transient spectra can be used for more than for merely detecting the breaking of hydrogen bonds. A detailed analysis of the spectral changes is under way and, again, compared to model systems and calculated spectra will reveal unprecedented structural details upon ultrafast temperature jumps in liquid water. Huse et al. observed that the transient spectrum resembles the changes observed upon steady-state heating after several nanoseconds and claimed that the difference between transient and steady-state heating is due to a pressure jump accompanying the temperature jump.

3. Summary and conclusions

X-ray absorption spectra at the O K-edge of gas-phase water, liquid water and different forms of ice illustrate the sensitivity of the technique to hydrogen bonding in water. The ice spectra as measured with transmission mode are compared in detail with O K-edge spectra of ice from x-ray Raman scattering. The very good agreement represents a consolidation of the experimental O K-edge x-ray absorption spectrum of crystalline ice and should stimulate theoretical calculations of this spectrum. Time-resolved measurements with IR pumping of the O-H stretching vibration and x-ray absorption probing at the O K edge with a time resolution of 80 ps are reviewed. Spectral changes are
qualitatively as expected from an ultrafast temperature jump as induced by IR excitation. Quantitative
difference compared to steady-state heating and forthcoming measurements with fs time resolution are
expected to reveal unprecedented insight into the structure and dynamics of liquid water.

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