

## X-ray Raman spectroscopy at the oxygen *K* edge of water and ice: Implications on local structure models

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The oxygen *K* edge of water and ice has been recorded with a resolution of 1 eV using x-ray Raman spectroscopy at 10 keV. The improved resolution allows for a clear observation of the strong pre-edge intensity in the liquid water spectrum. This is an independent experimental confirmation of this feature, which was recently detected by high-resolution soft-x-ray absorption spectroscopy and identified as a fingerprint of strongly asymmetric local configurations of the water molecules. The pre-edge peak as observed here with the truly bulk-sensitive x-ray Raman technique demonstrates that these configurations dominate the bulk of the liquid. Comparison with the *K* edge of ice gives an experimental limit on the fraction of fully coordinated waters in the liquid.

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Despite its simple elemental composition water has a complicated local structure, which has puzzled scientists since more than a century (Ref. 1, and references therein). X-ray absorption spectroscopy (XAS) and in particular the investigation of the near edge region as a probe of empty electronic states yields unique element-specific information that can be connected to the local structure and chemistry.<sup>2</sup> It thus appears to be an ideal technique to study water. Nevertheless, conventional XAS studies of the oxygen *K* edge of bulk water at ambient conditions have proven extremely difficult, and first results have been reported only very recently.<sup>3</sup> The reasons are manifold. First, at an attenuation length of x rays above the O *K* edge of less than one micron, transmission experiments are very difficult.<sup>4</sup> Second, fluorescence-detected XAS can suffer from spectral distortions mainly due to the large O concentration (saturation effects),<sup>5,6</sup> but also due to changes in the fluorescence yield above the edge.<sup>7</sup> Third, the ion/electron yield detection is surface sensitive ( $\sim$ nm) and can only be performed in vacuum. It is therefore unsuited for bulk studies at ambient pressure. Inner shell electron energy loss spectroscopy suffers from similar restrictions.

The strong pre-edge observed with XAS in Ref. 3 was interpreted as due to a predominance of local structures in the liquid with only one donating hydrogen bond. A remaining uncertainty from the study in Ref. 3, however, is the short penetration depth in XAS. A bulk-sensitive ( $\sim$ mm) hard-x-ray probe can avoid these difficulties and x-ray Raman scattering (XRS) is such a technique, still yielding XAS information.<sup>8,9</sup> In an XRS experiment the incident photon is inelastically scattered, and a small fraction of its energy is transferred to the sample. Besides vibrational (10–500 meV) and valence-band excitations (1–10 eV) the high energy of hard-x-ray photons permits electronic excitations of core levels in the sample (100–1000 eV). Therefore, absorption spectra with edge energies lying in the soft-x-ray regime can be measured effectively using hard x rays.<sup>10–20</sup>

Its inherent bulk sensitivity and good penetration makes XRS especially valuable for the investigation of liquids, concentrated complex systems, and samples under ambient and extreme conditions. The main difficulty of XRS lies in its weak cross section, but due to powerful new synchrotron sources and improvements in x-ray instrumentation, this problem is more and more under control. In a recent XRS study the XAS spectrum of liquid water has been recorded with a resolution of 2 eV,<sup>18</sup> and a very recent review shows that high quality XRS spectra can now be obtained in a matter of minutes to hours for second row elements.<sup>21</sup>

In this study we report O *K*-edge spectra of liquid water and ice using XRS with an energy resolution of  $\sim$ 1 eV. The spectra are compared with the conventional XAS data obtained by Myneni *et al.*<sup>3</sup> and with the 2-eV resolution XRS results obtained by Bowron *et al.*<sup>18</sup> The results shed light on the water puzzle and demonstrate the power of XRS as a bulk sensitive probe of local structure and chemistry.

The transition probability for XRS can be related to the same matrix element that determines x-ray absorption.<sup>8</sup> For  $qr \ll 1$ , where  $q$  is the momentum transfer and  $r$  the mean orbital radius, the dipole approximation is valid and the Raman scattering intensity is proportional to the dipole x-ray absorption matrix element.<sup>8</sup> In the present study, we used an array of analyzers to capture a larger solid angle. The corresponding  $q$  range of  $0.36 < qr < 0.57$  is well within the dipole limit. This is confirmed below by a detailed comparison of XRS and XAS spectra.

The experiments were performed at the Advanced Photon Source undulator beamline 18ID using a Si(400) double crystal monochromator and focusing mode. Raman scattering was analyzed with a high-resolution multicrystal analyzer.<sup>22</sup> The instrument employs eight Si(660) analyzer crystals on intersecting Rowland circles operated close to backscattering at a Bragg angle  $\theta_B = 87^\circ$ , and an energy of 9699 eV. The Raman spectrum is swept by scanning the beamline monochromator energy at a fixed analyzer setting,

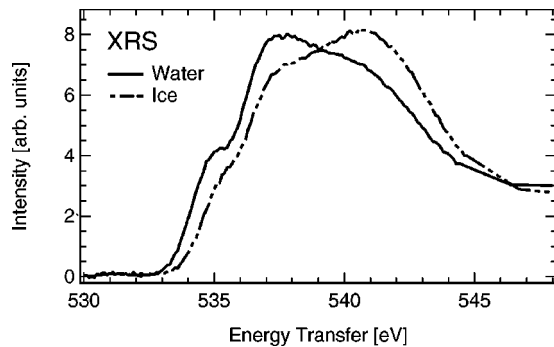


FIG. 1. X-ray Raman spectra of the oxygen  $K$  edge of liquid water (solid line) and ice (dashed line) displayed as a function of the energy transfer.

and the overall energy resolution (convolution of beamline and analyzer resolution) was found to be  $\sim 1$  eV (full width at half maximum, FWHM) by measuring the elastic scattering peak. The scattered intensity was measured with a lead shielded  $LN_2$  cooled Ge detector. The incident photon flux ( $I_0$ ) was recorded with a  $N_2$  filled ion chamber, and the spectra were normalized by dividing the detector signal through  $I_0$ .<sup>23</sup> The Raman spectrum was furthermore corrected for background from Compton scattering, by subtracting an extrapolated function fitted to the region well below the absorption edge. Different functions such as exponential and hyperbolic were tested, all giving essentially the same result for the corrected spectrum in the near edge region. To avoid any possible radiation damage purified water was flowed through a tube and the ice sample assumed to be ice  $I_h$  was scanned between individual spectra.<sup>24</sup>

Figure 1 shows the O  $K$ -edge spectra as measured by XRS for liquid water and ice. The spectra are displayed as a function of the energy transfer obtained by subtracting the fixed spectrometer energy (9699 eV) from the scanned incident photon energy. The spectra show remarkable details, the most important one being a pre-edge feature at 535 eV in the liquid water spectrum. Besides this, the main absorption edge (537 eV) and a broad continuum structure (541 eV) can be discerned. The intensity of these three spectral features is clearly different when comparing water in its different condensed phases. The pre-edge and main edge are much more intense in the liquid water spectrum, while the continuum feature is strongly enhanced in the ice spectrum. This shows that O  $K$ -edge spectra as measured by XRS can effectively visualize changes in the hydrogen-bonding (H bonding) environment of bulk water.

Chemical bonding has a large effect on the valence electronic structure. Different H-bonding configurations in water can therefore show a variation in the local orbital structure of the molecules. With Fig. 1 we demonstrate how these changes can be monitored by probing the empty electronic states with truly bulk-sensitive x-ray absorption as measured by XRS. Bowron *et al.* outlined this in their XRS investigation of water,<sup>18</sup> but the limited resolution and statistics in their experiment restricted a detailed discussion of the near edge region of the O  $K$ -edge spectra. Figure 1 shows that the changes in the electronic structure of the water molecules

can be effectively measured with XRS by improving the experimental conditions. The observation of the pre-edge feature at 535 eV in the liquid bulk water spectrum is a crucial observation since it allows for a structural interpretation of the spectra.

This pre-edge feature has recently been observed with high-resolution XAS and it has been interpreted with the aid of density-functional theory (DFT) calculations.<sup>3</sup> It originates from specific asymmetric configurations of the water molecules, for which the H bond is strongly distorted or broken on the H-donating site of the molecule. Due to the localization of the core hole in both XAS and XRS it is possible to probe H-bonding structures locally around individual water molecules and the O  $K$ -edge spectra are mainly determined by the structural arrangement within the first coordination shell of the probed water molecule.<sup>25</sup> The pre-edge in the O  $K$ -edge spectrum of liquid water is therefore indicating that a large fraction of the molecules in liquid water exhibit strongly distorted or broken H bonds.<sup>3</sup>

The 10-keV XRS data probing a depth in the mm range<sup>26</sup> represent an independent experimental confirmation of this strong pre-edge peak and thus clearly corroborate the structural interpretation of bulk water. As a consequence of the pre-edge intensity detected here by XRS in the liquid water spectrum the large amount of distorted/broken H bonds in liquid bulk water can be confirmed ruling out any residual surface effects possibly influencing the spectra as measured with XAS. The XRS ice spectrum in contrast is similar to the calculated spectra of symmetric configurations with four intact H bonds.<sup>3</sup> Based on an analysis of the relative intensities of the main edge and of the continuum structure in the liquid water spectrum compared to the ice spectrum in Fig. 1, we can therefore give a conservative upper limit of 30% for the amount of symmetrically four H-bonded species in liquid bulk water at room temperature. As a consequence we can deduce a minimum of 70% for the amount of molecules with a strongly distorted or broken H bond on the H-donating site. This means that at least 1.4 H bonds per molecule are strongly distorted or broken in liquid bulk water at room temperature.<sup>27</sup> A more precise determination of these numbers requires the knowledge of the crystal structure of the ice sample not available in this study. Nevertheless, it is crucial for the determination of these numbers that the XRS spectra do not suffer from spectral distortions such as saturation effects. This is demonstrated in the following with the aid of Fig. 2.

With Fig. 2 we compare in detail the O  $K$ -edge spectra of liquid water and ice obtained by XRS and XAS. The top of Fig. 2 depicts the ice spectra by XRS as a function of the energy transfer and by XAS as a function of the incident photon energy. For easier comparison the XAS spectrum has been convoluted with a Gaussian function (1 eV FWHM) in order to account for the different energy resolutions ( $\sim 0.1$  eV in the XAS measurement). All features detected by XAS are clearly reproduced with XRS. Discrepancies can be observed in the intensities of the pre and main edges: they are enhanced in the XRS measurement. A possible explanation for this is based on the different sample preparation techniques. For the XAS measurement a carefully grown, long-

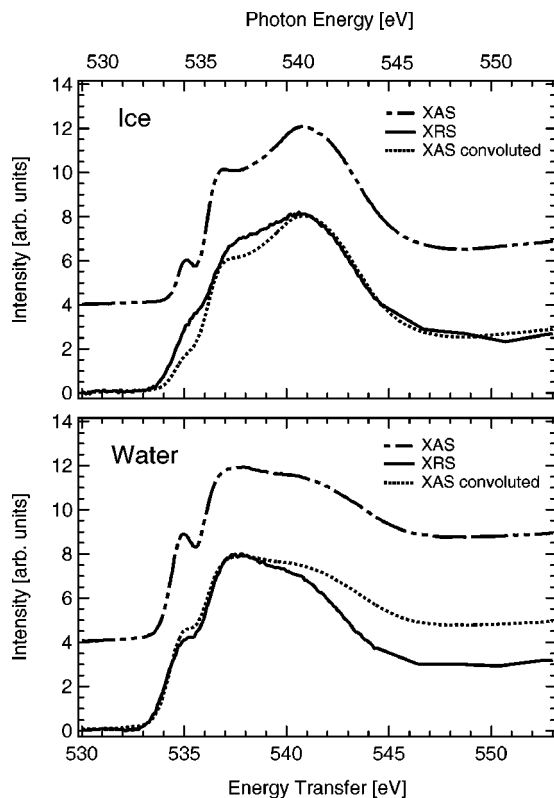


FIG. 2. O  $K$ -edge absorption spectra of polycrystalline ice (Ref. 24) from x-ray Raman scattering (solid line, taken from Fig. 1) compared to the Auger yield XAS spectrum of a single crystal ice (dashed line) at the top (dotted line: spectrum obtained by convoluting the XAS spectrum with a 1-eV Gaussian) and the same for water at the bottom. The XAS spectra are taken from Ref. 3.

range ordered, single crystal overlayer of ice ( $I_h$ ) on a clean Pt(111) surface was prepared under UHV conditions.<sup>28</sup> The XRS measurement was done on polycrystalline ice.<sup>24</sup> We assume that the pre and main edge intensities in the XRS measurement are enhanced due to numerous grain boundaries in the sample where we expect the H bonds to be distorted/broken. Recent XAS studies on disordered vs ordered ice support this speculation.<sup>28</sup>

Figure 2 shows at the bottom the O  $K$ -edge XRS and XAS spectra of liquid water (again the XAS spectrum was convoluted with a 1-eV Gaussian). The three essential spectral features discussed above can be found in both spectra. The most prominent difference between the spectra is the enhanced intensity above 540 eV in the XAS measurement (the spectra have been matched in intensity in the main edge). We can trace the differences back to a saturation of the fluorescence yield XAS measurement. Saturation effects can influence bulk sensitive soft-x-ray absorption as measured by fluorescence detection.<sup>5,6</sup> Although special care had been taken to minimize saturation effects in the XAS measurement,<sup>3</sup> the XRS data reveal some remaining influence. A careful analysis aiming to correct for saturation in the XAS measurement shows that the maximum of the main absorption edge is suppressed (correspondingly intensities at higher energies seem enhanced) due to saturation as compared to the “true”

absorption cross section. As a consequence the intensities of the continuum structure at 541 eV and of the pre-edge are enhanced compared to the XRS spectrum when matching the intensities of the main edges. The comparable intensities of the ice spectra above 540 eV at the top of Fig. 2 clearly show the negligible influence of saturation in the electron yield XAS measurement. Saturation can be excluded for the XRS measurement, underlining its importance when relating structural information and the relative intensities of spectral features in a quantitative analysis of bulk-sensitive x-ray absorption spectra. In addition, the absence of saturation for XRS considerably simplifies the liquid sample preparation.

Finally, we examined whether the Raman spectra could be affected by non-dipole contributions. Bowron *et al.* measured the water and ice XRS spectra in the strict dipole limit [ $qr=0.15$  (Their published value is  $qr=0.29$  with  $r$  referring to the O  $1s$  mean diameter, whereas we and, e.g., Suzuki<sup>9</sup> use the mean radius.)].<sup>18</sup> Except for the observation of the pre-edge in the present work, due to the better energy resolution, the spectral shape from the two experiments is very close. In addition, the pre-edge region of the XRS spectrum is very similar to the XAS spectrum, which only has dipole contributions, if saturation effects in the soft-x-ray measurement are accounted for. We can therefore exclude any significant influence of nondipole contributions to the O  $K$ -edge XRS spectrum of water and ice as measured here.

Our investigation clearly demonstrates the important role of O  $K$ -edge XRS as a powerful tool for the investigation of the bulk structure of liquid water. An essential pre-edge peak in the O  $K$ -edge absorption spectrum, a fingerprint of strongly distorted or broken H bonds, has been observed with a truly bulk-sensitive method with a probing depth in the mm range. We can give a stringent lower limit for the number of strongly distorted or broken H bonds in liquid bulk water at room temperature of 1.4 per molecule. Taking into account resolution and saturation effects we show the close similarity of the near-edge region of the O  $K$ -edge spectra as obtained by x-ray Raman and conventional soft-x-ray absorption spectroscopy. The bulk sensitivity of the XRS method has important consequences for the investigation of water and liquid samples in general. Experimental simplifications have been briefly discussed and other aspects can be anticipated: using XRS to determine the structure of water under extreme conditions such as high temperature and high pressure up to the supercritical regime will yield unique information. In addition, monitoring the absorption edges of different light elements lying in the soft-x-ray energy region (such as the O and C  $K$  edges), we believe that x-ray Raman spectroscopy provides a unique tool for the investigation of chemical reactions at high temperature and high pressure.

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- <sup>23</sup>The incident beam intensity was on the order of  $3 \times 10^{12}$  photons/s in a 0.1-mm vertical by 0.2-mm horizontal focus. Individual scans took 30 min with 10 sec per step. For the liquid water spectrum 15 scans were added.
- <sup>24</sup>Water was flowed at 23 °C through a 5-mm diameter plastic tube with a 50- $\mu$ m thick kapton window at a rate of 750 ml per hour at an angle of 45° toward the beam direction. This corresponds to less than 30 msec of exposure per irradiated volume element. The ice sample was obtained by dipping a water sample into liquid nitrogen. In order to minimize radiation damage scans were taken at 10 K in a He flow-through cryostat. To address the issue of possible radiation damage further, two back-to-back 30-min scans were performed at one position before the sample was moved to a fresh spot. Seven sets of such scans were taken, and the first and second sets were added respectively. A small change could be observed between the two sweeps, indicating the onset of radiation damage. Therefore only the ice spectrum obtained in the first sweep is used in our data analysis.
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- <sup>26</sup>The penetration depth of photons with energies between 9700 and 10600 eV in water amounts to 1.8–2.3 mm (as calculated with the Berkeley Lab CXRO program [[www-cxro.lbl.gov/optical\\_constants/](http://www-cxro.lbl.gov/optical_constants/)]; also see B. L. Henke, E. M. Gullikson, and J. C. Davis, *At. Data Nucl. Data Tables* **54**, 181 (1993)]. This applies to the incident and detected fluorescence photons and characterizes the path length in the absorbing medium corresponding to a 1/e intensity decrease.
- <sup>27</sup>A distorted/broken H bond on the H-donating site immediately entails the distortion/disruption of a H bond on the H-accepting site of the neighboring molecule. Therefore the number of distorted/broken H bonds per molecule (e.g., 1.4) is simply twice the fraction of molecules with a distorted/broken H bond on the H donating site (0.7). Consequently, we estimate that at least 40% of the molecules have a distorted/disrupted H bond on both the H-donating and accepting site. Calculated spectra show that the O K-edge absorption spectrum is not sensitive to H-bond distortion on the H-accepting site (Ref. 3), which is consistent with this finding.
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