Local Structure of Amorphous Ice as Revealed by O K-Edge EXAFS


The oxygen K-edge extended X-ray absorption fine structure (EXAFS) spectrum of an ice film prepared by deposition of water vapor on a substrate at 100 K was measured in the surface-sensitive Auger yield mode. Five distinct peaks are revealed in the Fourier transform spectrum of the EXAFS data. The peaks are attributed to O–H bonds (with overlapping contributions from intramolecular covalent and intermolecular hydrogen bonds) as well as to intermolecular O–O scattering paths in the distance range of 1–7 Å. The pattern of the longer O–O distances resembles that of a high-pressure crystalline modification of ice (ice II).

Introduction

The structures of liquid water and different phases of ice have attracted noticeable attention over the last century (for recent reviews, see refs. [1–5] and references therein). Experimental techniques such as X-ray,[6–9] neutron,[10–16] and electron[17,18] scattering have been extensively used for the exploration of the structural details of water-based systems. For ordered crystalline polymorphs of ice, the space symmetry group, unit cell parameters, and the atomic positions of O and H in the unit cell,[19–23] have been characterized by single crystal or powder diffraction techniques.[1] However, for phases without a long-range translational order, such as liquid water or low- (LDA), high- (HDA), and very high-density amorphous (VHDA) ice,[14–16] information at this level of precision is unattainable. Scattering techniques are capable of reconstructing radially averaged atomic distribution functions around an arbitrarily selected central atom. These functions give the probability of finding a neighboring atom in the distance range from R to R + dR from the central atom. The total radial distribution function (RDF), that is, a weighted sum of atomic positions of O and H in the unit cell.[19–23] To date, at least thirteen crystalline modifications of ice, which are stable or metastable in certain ranges of the p,T phase diagram, have been characterized by single crystal or powder diffraction techniques.[1] However, for phases without a long-range translational order, such as liquid water or low- (LDA), high- (HDA), and very high-density amorphous (VHDA) ice,[14–16] information at this level of precision is unattainable. Scattering techniques are capable of reconstructing radially averaged atomic distribution functions around an arbitrarily selected central atom. These functions give the probability of finding a neighboring atom in the distance range from R to R + dR from the central atom. The total radial distribution function (RDF), that is, a weighted sum of O–O, O–H, and H–H partial contributions, is produced by the Fourier transformation of the experimentally measured scattering curve.[5,1] The separation of the total curve into partial pair correlation functions (also referred to as atom–atom pair correlation functions) can be done unambiguously (i.e., mathematically correct, without further input) by a combined analysis of three independent, experimentally measured total RDFs with different weighting coefficients for the pair contributions; these are given by X-ray, neutron, and electron scattering[24] or, in the case of neutron scattering, by isotope-substituted water with a variable D2O content.[14–16] X-ray scattering by the hydrogen atom is roughly eight times weaker than that by the oxygen atom. Therefore, the total X-ray scattering is dominated by O–O contributions.[5,1] In contrast, neutron scattering patterns for D2O are dominated by D–D and D–O contributions. (Due to a lower incoherent scattering background and to a higher contrast between D and O atoms as compared to H and O, D2O is more frequently studied by neutron scattering).[8,13,18] In the case of electrons, the scattering intensities of O and H are comparable.[17] Theoretical simulations are often used in combination with experimental scattering techniques.[2,14–16,25] Important information, supplementary to that obtained from scattering, can be obtained using EXAFS (extended X-ray absorption fine structure) spectroscopy. EXAFS is an established technique for the characterization of the local structure of materials using hard X-rays produced by synchrotron sources.[26,27] In the soft X-ray regime, required for EXAFS on light atoms such as oxygen,[28,29] the application of this technique is hampered by two major factors:

- The extended oscillations of the X-ray absorption coefficients above the absorption edges of light atoms are weak, and their fast decay prevents the collection of data in the wide spectral range required for an accurate analysis.

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Heavy elements have many closely spaced absorption edges, which lead to an appearance of spurious peaks in the wide energy range of interest (ca. 500–1000 eV for O K-edge).

In contrast to RDF analyses of neutron and X-ray scattering, which are ideally suited for amorphous samples, EXAFS allows direct comparisons between phases with different degrees of the long-range order. Local structure studies of water in liquid or gaseous state are also feasible without major modifications of the instrumentation. Moreover, the local surrounding of oxygen atoms is selectively probed by EXAFS; this gives rise to a pseudo-RDF with only two out of three partial pair contributions: O–H and O–O (with the latter dominating). Various detection schemes developed for soft X-ray spectroscopy (e.g., transmission, fluorescence yield, electron yield, and ion yield) allow the variation of the probing depth from bulk sensitivity (transmission or fluorescence yield) through intermediate surface sensitivity (total, partial, or Auger electron yields) to extreme surface sensitivity (ion yield). Finally, EXAFS can be easily combined with other soft X-ray spectroscopic techniques, such as near-edge X-ray absorption fine structure (NEXAFS) or resonant inelastic X-ray scattering (RIXS), since they require similar instrumentation. The latter two methods give valuable information on the hydrogen bonding from the perspective of electronic rather than geometric structure. Evident disadvantages of EXAFS are its limitation to short-range order around the atom being probed (a few coordination spheres) and a limited accuracy in the determination of the structural parameters, especially coordination numbers.

Only few experiments on the local structure around the oxygen atoms in water-based systems by means of O K-edge EXAFS have been conducted to date. In ref. [35], the EXAFS spectrum of amorphous ice, condensed at 90 K in vacuum, was measured using total electron yield (TEY). The photoelectron scattering phase shift for the closest intermolecular O–O contact was extracted from the experimental data and compared to theoretical predictions; a good agreement was shown. In ref. [36], the EXAFS spectrum of liquid water was measured in the transmission mode using a thin wet cell with two silicon nitride windows. The Fourier transformation of the experimental spectrum revealed a strong O–O peak at 2.6 Å (not corrected for the scattering phase shift) and a peak at 1 Å, attributed to the intramolecular O–H contact. These results were reanalyzed in ref. [37], where the initial interpretation of the two features was confirmed by ab initio FEFF simulations. Moreover, an EXAFS spectrum of water vapor, measured in the total ion yield (TIY) mode, clearly demonstrated that the photoelectron backscattering by the H atoms makes a substantial contribution to the EXAFS spectrum. This result allows the structural parameters of the O–H bonds to be extracted. Finally, in a recent publication, EXAFS spectra of ultrasonic liquid water microjets, measured in the total electron and ion yield modes, were compared. A difference in the O–O closest intermolecular distances, namely, 2.85 Å (bulk sensitive TEY) and 3.00 Å (surface sensitive TIY), was interpreted by the authors as a manifestation of a surface relaxation.

Herein, we report a detailed analysis of high-quality EXAFS spectra of ice condensed at 100 K in vacuum, measured in the Auger electron yield acquisition mode, to obtain information about the structural properties of thin amorphous ice films, in particular, on the O–H and O–O distances in its near-surface region.

Results and Discussion

The raw O K-edge EXAFS spectrum of an ice film is depicted in Figure 1. The inset shows a NEXAFS spectrum, which is in good agreement with the spectra of ice reported earlier. Note that the second distinct maximum of the raw EXAFS spectrum at approximately 562 eV is symmetric. As reported in refs. [40] and [41], the shape of this feature can be used to monitor the amorphous ice—cubic ice phase transition, which occurs at about 150 K. As a result of the transition, a smooth symmetric peak, characteristic of the amorphous phase, is replaced by a split multipeak structure of cubic ice. Since we observe no splitting (see Figure 1), our film is considered to be amorphous, as expected from the preparation conditions (vacuum deposition at 100 K).

The normalized EXAFS curve obtained by subtraction of the smooth, atomiclike background (dotted line in Figure 1) from the raw X-ray absorption spectrum is shown in Figure 2. A $k^2$-weighting scheme was applied for further numerical data analysis to compensate for the fast decay of the EXAFS oscillations. We point out that, even in the high photoelectron wavenumber part of the spectrum (up to $k = 11 $ Å$^{-1}$), EXAFS oscillations dominate over the noise level, which justifies the weighting scheme selection. Since the low-$k$ part of the curve does not contain direct structural information (it is primarily formed by multiple scattering of the photoelectron by the closest neighbors), the lower limit for the Fourier transformation was set at $k = 2.5 $ Å$^{-1}$.

![Figure 1. Raw O K-edge X-ray absorption spectrum of an amorphous ice film measured in the Auger electron yield (AEY) acquisition mode and smooth atomiclike background used to extract EXAFS oscillations. The inset shows a higher-resolution scan of the near-edge region.](image-url)
The Fourier transform (FT) of the normalized EXAFS curve, \(k^3 \chi(k)\), in the \(k\) range: 2.5±11 Å\(^{-1}\), is shown in Figure 3. Several peaks, marked 1 to 5, are clearly distinguishable in the FT. We attribute peak 1 to O–H bonds (from both covalent and hydrogen-bridging bonds), peak 2 to the closest intermolecular O–O distances, and peaks 3–5 to longer O–O separations. Note that the peak positions in the FT do not coincide with real interatomic distances, since they are shifted to lower values due to a nonzero scattering phase shift. This shift amounts to approximately –0.35 Å for the O–O pair (central atom–backscatterer), in accordance with the FEFF ab initio calculations. In the discussion below, phase shift-corrected (real) interatomic distances, rather than positions of maxima in the FT spectrum, are always referred to.

The FT region of 0.4±3.0 Å (with the two predominant maxima 1 and 2) was back Fourier transformed and fitted. The simplest model with three contributions, [ O–H \((N=2, \ R \approx 1.00 \ \text{Å})\), O–H \((N=2, \ R \approx 1.75 \ \text{Å})\), and O–O \((N=4, \ R \approx 2.75 \ \text{Å})\] which is consistent with the so-called Pauling’s rule\(^{[43]}\) and correctly describes the closest environment of oxygen atoms in most of the known crystalline and amorphous ice modifications, does not give a good fit to the experimental data. In particular, to reproduce the shape of peak 1, three O–H scattering paths have to be included. The following constraints were applied in the fitting procedure to reduce the number of independent parameters: Equal Debye–Waller parameters were used for the three O–H scattering paths and the total O–H coordination number was fixed as four. The coordination number of the O–O scattering path was also fixed at four. The best-fit values of the structural parameters, as well as some other parameters of the fitting procedure, are summarized in Table 1. The best-fit curve in \(R\) space, shown in Figure 3 as a dotted line, reproduces the experimental FT reasonably well. The most significant discrepancies relate to the shape of peak 1.

Figure 4 compares Fourier filtered EXAFS oscillations, which correspond to the FT peaks 1 and 2 (solid line), with the fitting results (dotted line) in the \(k\) space. Contributions from individual scattering paths used in the fitting procedure are also shown. Note that the O–H(1) and O–H(3) oscillatory contributions, which are assigned to covalent and H-bridge bonds, respectively, have prominently different periods. In general, the intensities of the O–H contributions are substantially smaller than those of the O–O\(_1\) scattering path. Nevertheless, they are

![Figure 2. Oscillatory part of the EXAFS signal obtained by a subtraction of the atomic-like background from the raw spectrum.](image)

![Figure 3. Fourier transform of the EXAFS spectrum (---) and best-fit curve for peaks 1 and 2 (--.-).](image)

![Figure 4. Back-Fourier-transformed oscillations corresponding to FT peaks 1 and 2 (---), best-fit curve (--.-), and individual single-scattering contributions used in the fitting.](image)

<table>
<thead>
<tr>
<th>Path</th>
<th>(R) [Å]</th>
<th>(N)</th>
<th>(\sigma^2) ([10^{-3}\ \text{Å}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>O–H(_1)</td>
<td>1.01(2)</td>
<td>0.6(3)</td>
<td>0.2(1)</td>
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<tr>
<td>O–H(_2)</td>
<td>1.41(2)</td>
<td>1.6(3)</td>
<td>0.2(1)</td>
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<tr>
<td>O–H(_3)</td>
<td>1.89(2)</td>
<td>1.8(3)</td>
<td>0.2(1)</td>
</tr>
<tr>
<td>O–O(_1)</td>
<td>2.73(2)</td>
<td>4.0</td>
<td>6.1(9)</td>
</tr>
</tbody>
</table>

Interatomic distances (\(R\)), effective coordination numbers (\(N\)), and Debye–Waller parameters (\(\sigma^2\)). Fitting ranges: \(k=2.5–11 \ \text{Å}^{-1}\), \(R=0.4–3.0 \ \text{Å}\). Fit quality index\(^{[29]}\) \(R_I=0.05\). Values in brackets are estimated standard deviations of the corresponding best-fit values.

![Table 1. Best-fit values of the structural parameters of the amorphous ice film according to O K-edge EXAFS.](image)
non-negligible. These fits are very stable to variations in parameters of the data processing such as background removal ($R_{\text{back}}$ values between 0.15 and 0.7 Å were tested in the Autobk program\cite{46}, weighting schemes ($k^2$ weighting with $n = 1–4$ were tested), and spectrum truncation ($k_{\text{max}}$ was varied from 7 to 11 Å$^{-1}$).

The reason why more than two O–H peaks (namely, covalent and H-bridge bonds) are observed in the FT is still not clear. It has to be mentioned that EXAFS has been applied to determine the local environment of light second-row elements only in a limited number of cases (see Introduction) and thus it has not been thoroughly explored in terms of methodology. Indeed, interatomic distances significantly shorter than 2 Å represent a serious challenge for a correct background removal in experimental spectra as well as for theoretical simulations. In particular, it has been found\cite{45–47} that the low-$R$ part of EXAFS FTs often exhibits peaks due to photoelectron scattering within the electron shells of the central atom (these features are known as atomic XAFS, or atomic x-ray absorption fine structure = AXAFS). Commonly, the AXAFS features are much weaker than and well-separated from the peaks due to backscattering by neighboring atoms. In our case, O–H bonds occur at very short distances $\approx 1.0$ Å, and the backscattering amplitude of an H atom is quite small. Therefore, the respective backscattering peaks can easily overlap and, as a consequence, be noticeably distorted by AXAFS features of the oxygen atom. The electrostatic potential around the oxygen atoms in water and ice deviates strongly from spherical symmetry.\cite{48} Partly, this is due to a specific orientation of the lone-pair valence electrons of the oxygen involved in the formation of H bonds. In high-precision single-crystal X-ray diffraction measurements, the lone pairs of oxygen are revealed as distinct peaks of the electron density distribution function, with heights comparable to those of the hydrogen atoms.\cite{49,50}

The FT peaks 3–5 (see Figure 3) can be simulated as O⋯O single scattering paths at distances of 3.61 ($N = 1$), 5.36 ($N = 2$), and 6.57 Å ($N = 4$). The effective coordination numbers shown in brackets were obtained by fitting with the Debye–Waller parameters fixed at the best-fit value for the O–O(1) scattering path (see Table 1). This set of longer O–O distances corresponds neither to the two most common crystalline modifications of ice (also referred to as ice I), that is, hexagonal (I$_h$) and cubic (I$_c$) ice, nor to low-density amorphous ice, whose local structure was suggested to be quite similar to ice I$^{19}$4 The experimental FT spectrum is compared to the simulated FT spectra for hexagonal ice\cite{19} and cubic ice\cite{20} in Figure 5 (only O–O single- and multiple-scattering contributions have been taken into account in these simulations). As is clearly seen, no O–O distances in the range 3–4 Å are present in the two simulated FT spectra, but a very strong peak at approximately 4.50 Å is apparent (see below). In the experimental FT, there is a prominent peak at 3.6 Å (labeled 3) and no distinct maximum around 4.5 Å. A similar peak in the O–O pair correlation function at 3.3–3.7 Å was reported for liquid water\cite{6,15,51} amorphous ice prepared by slow deposition at very low temperatures (10 K),\cite{36} high-density amorphous ice\cite{21,14} and very high-density amorphous ice.\cite{14} Furthermore, O–O intermolecular distances around 3.6 Å were also found in some high-density crystalline phases of ice such as ice II,\cite{21} ice III,\cite{22} and ice IX (the latter is essentially a proton-ordered low-temperature modification of ice III),\cite{23} which are prepared at elevated pressures.

The main building block of the crystal structure of ice \cite{19,20} is a (H$_2$O)$_6$ hexagon with a “chair” conformation as shown in Figure 6a. The hexagons are fused to form an open three-dimension framework in such a way that each oxygen atom of the water molecule is tetrahedrally surrounded by four oxygen neighbors. The closest intermolecular O–O distance is around 2.75 Å, whereas the next one, which corresponds to a chain O–O–O, with the tetrahedral angle (ca. 109.5°) at the central oxygen atom, is approximately 4.50 Å. Distances shorter than 4.50 Å clearly indicate a distortion of the tetrahedral angles at oxygen atoms. Indeed, in the crystal structure of ice II\cite{19} the hexagons are substantially distorted due to a wide distribution of the O–O–O angles (as shown in Figure 6b). This type of distortion results in a much higher density of ice II (1.17 g cm$^{-3}$) than ice I (0.92 g cm$^{-3}$).\cite{15} Furthermore, as previously suggested,\cite{16} similar distortions play a key role in the structure of liquid water, which has an intermediate density (1.00 g cm$^{-3}$), and also in that of high-density amorphous modifications of ice (HDA and VHDA).\cite{36}

![Figure 5. Comparison of the experimental Fourier transform (Exp) with simulations for different crystalline ice phases: I$_h$: hexagonal ice \cite{17} I$_c$: cubic ice \cite{18} and I$_l$: ice \cite{20} (only oxygen atoms are used in the simulations).](image1)

![Figure 6. Fragments of the crystalline structures of ice \cite{17} (a) and of ice \cite{20} (b).](image2)
tron diffraction study.\(^{[21]}\) The similarity between the simulated curve and the experimental FT for the thin amorphous-ice film is remarkable. Not only peak 3, which is a "fingerprint" of the distortions of the tetrahedral angles, but also the longer-distances-peaks, 4 and 5, are correctly reproduced by the model curve of ice II with respect to both the positions of the features and their relative intensities. This means that the local environment around the oxygen atoms in the thin film of amorphous ice is, probably, similar to that in the high-density crystalline modification of ice (ice II).

To rationalize this observation, it has to be taken into account that the experimental setup used in the current study is surface sensitive. The probing depth provided by the Auger electron detection is 20–40 Å, which is comparable to the probing depths of low-energy electron diffraction (LEED) or photoelectron diffraction (PD) measured by means of angular-resolved X-ray photoelectron spectroscopy (ARXPS). Meanwhile, most of the structural information on amorphous ice has been obtained using bulk-sensitive neutron- and X-ray scattering. In particular, the formation of high-density amorphous ice by a very slow vacuum deposition at extremely low temperatures (<30 K), suggested on the basis of X-ray\(^{[20]}\) scattering, was not confirmed in a dedicated neutron scattering experiment\(^{[52]}\) and was thus attributed to different effective probing depths of the two techniques.

There are several mechanisms, which can be responsible for distortions of a surface structure with relation to the bulk, such as, for instance, the surface premelting. As it has been shown by H. Dosch et al. using the grazing-incidence X-ray diffraction,\(^{[31]}\) the near-surface region of an ice \(l_0\) single crystal starts to loose its long-range order at temperatures much lower than the point of the bulk ice melting. Similar conclusions were derived from sum-frequency generation (SFG) spectroscopy.\(^{[34]}\) A high-density interfacial ice structure has been recently suggested for an ice film grown epitaxially on an oxygen-pretreated Rh(111) crystal on the basis of He scattering data.\(^{[35]}\)

Furthermore, since a very intense soft X-ray beam produced by the third-generation synchrotron radiation source was utilized for the EXAFS data collection, some irradiation-induced structural or chemical modifications of the surface (e.g., recrystallization) cannot be totally ruled out.

Summary and Outlook

The Fourier transform of the O K-edge EXAFS spectrum of an amorphous ice film reveals several distinct peaks suggestively attributed in this work to:

- O–H contacts due to overlapping contributions from intramolecular covalent and intermolecular hydrogen bonds simulated with a set of three distances at 1.01 (effective coordination number \(N = 0.6\), 1.41 (\(N = 1.6\)), and 1.89 Å (\(N = 1.8\));
- closest intermolecular O–O contacts at 2.73 Å (\(N = 4\));
- longer intermolecular O–O contacts at 3.61, 5.36, and 6.57 Å.

This is the first time that both covalent and hydrogen-bridge O–H bonds in the local environment of oxygen atoms in ice were revealed by O K-edge EXAFS. A possible distortion of the reported best-fit parameters, due to a contribution from photoelectron scattering by oxygen lone pairs or other AXAFS-related effects, has yet to be evaluated.

The analysis of the longer O–O contacts suggests that the local environment around the oxygen atoms in the near-surface region of the amorphous ice film differs substantially from the bulk structure of low-density amorphous ice and crystalline ice I, and is closer to that observed in high-density amorphous ice (HDA and VHDA) or high-pressure crystalline phases of ice, (ice II, III, or IX).

The results hence demonstrate that soft X-ray EXAFS gives valuable information about the local atomic structure of molecular solids such as amorphous ice, even though they consist only of light atoms. Due to its surface sensitivity, O K-edge EXAFS makes a valuable contribution to the ongoing discussion of the structural properties of ice and water, complementary to traditional diffraction techniques.

Nevertheless, this study leaves several important questions unanswered and we plan to continue working in this field. In particular, a comparative analysis of EXAFS spectra of crystalline ice, amorphous ice, and liquid water (measured under identical conditions using the bulk sensitive X-ray fluorescence yield acquisition mode) would be very interesting.

Experimental Section

The measurements were performed in ultrahigh vacuum at the UE-52 PGM undulator beamline of the synchrotron radiation source BESSY II (Berlin). The base pressure during the measurements was lower than \(1 \times 10^{-9}\) mbar. A film of ice was grown in situ by exposure of a substrate, kept at 100 K, to water vapor at \(5 \times 10^{-6}\) mbar applying a total dose of approximately 2500 L (1 L = 1 \times 10^{-6} Torr s, which approximately corresponds to one monolayer of adsorbed water). As a substrate, a polycrystalline Au-covered Si wafer with the (111) crystal face predominantly exposed, was used. In order to promote the uniform adsorption of the first ice layers, the Au surface was modified with a highly hydrophilic, OH-terminated undecanethiol self-assembled monolayer (SAM) using the standard procedure.\(^{[34]}\) Prior to dosing, water was purified by several consecutive freeze-pump-thaw cycles. No signals from the substrate or any contaminants were detected by XPS after film preparation. All measurements were performed at 100 K. EXAFS spectra of the film were measured in the 500–1000 eV photon energy range with 1 eV step-width. The near-edge region, that is, the NEXAFS spectrum, was also measured on the same sample with the same beamline settings and an energy step-width of 0.2 eV. Slits settings of the plane grating monochromator corresponded to a resolving power of ca. 10000. Electrons in the constant kinetic energy range of 475–525 eV (including the O K Vu Auger electrons) were registered using a Scienta SES-200 analyzer and a multi-channel plate detector. The sample was placed at the "magic" incidence angle (ca. 55°) to the primary beam and normal to the electron analyzer. Some variations in the shape of the NEXAFS spectra were observed for ice samples after very long beam exposures. Thus, the beam intensity and the duration of data collection were adjusted so as to minimize these effects.
Since the intensity of the incident beam provided by the beamline is a smooth, uniformly decreasing function, without any sharp features over the entire energy range, the EXAFS spectrum was analyzed as measured without any additional normalization. Standard processing of EXAFS spectra, which includes background subtraction, forward and back Fourier transformation, and nonlinear curve fitting, was performed using the UWXAFS software package with FEFF7 ab initio scattering amplitudes and phase functions. As recommended in ref. [37], parameters of the O–H scattering path were calculated by assuming a distance of 1.4 Å in order to avoid problems with the selection of the muffin–tin radius of oxygen atoms by the potential calculation procedure of FEFF. Interatomic distances (R), effective coordination numbers (N), and Debye–Wallner parameters (σr) were used as variable structural parameters in the curve-fitting procedure, according to the standard EXAFS equation. The scaling factor, S0², was kept constant at 0.85, and Fourier transforms of model crystalline ice phases were simulated using FEFF (on the basis of literature crystallographic data) with taking all O–O single and multiple scattering contributions with lengths up to 9 Å into account, and assigning equal Debye–Wallner factors (0.01 Å) to all scattering paths.

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