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Isotopic quantum effects on the structure of low density amorphous ice

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Abstract

Careful neutron diffraction measurements on deuterated low density amorphous (LDA) ice confirm that at 120 K it can be considered a fully ‘annealed’ structure, as no significant changes are observed in the amorphous spectra until crystallization occurred over time at 130 K. On this basis, the measurement of structural differences between the hydrogenated and deuterated forms of LDA ice at 120 K, have been carried out using 98 keV electromagnetic radiation diffraction techniques. The maximum observed isotope effect in LDA ice is $\sim 3.4\%$ at 40 K when compared to the magnitude of the first peak in the electronic structure factor at $Q = 1.70 \text{ \AA}^{-1}$. This compares to a maximum effect of $\sim 1.6\%$ previously measured in liquid water at room temperature (Tomberli *et al* 2000 *J. Phys.: Condens. Matter.* **12** 2597). The isotope effect is shown to be similar to a temperature shift in the structure of light LDA ice. However, the existence of a first sharp diffraction peak at $Q = 1.0 \text{ \AA}^{-1}$ in the isotopic difference function is not reproduced in the temperature difference and suggests that additional longer-range correlations are present in the more ordered deuterated form.

1. Introduction

The structures of low and high density amorphous ices have recently been the subject of much attention [1–3]. Conventional x-ray diffraction studies of low density amorphous (LDA) ices have previously been made on samples formed by vapour deposition of H₂O [4] and by the heating of high density D₂O amorphous ice produced by the compression of ice-*Ih* [5]. However, at low temperatures isotopic quantum effects are expected to have a significant influence on the structure arising from the differences in zero-point vibrations of the H₂O and

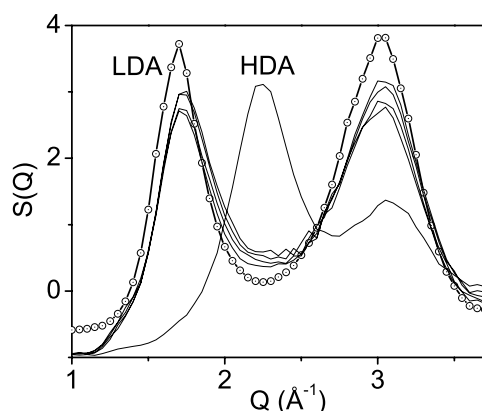


Figure 1. The pseudonuclear x-ray structure factors for a H₂O HDA ice form and the 120 K LDA ice form (circles) are shown in the region of the FSDP. Intermediate forms close to the 120 K LDA ice form are also shown.

D₂O molecules [6]. This work follows high energy electromagnetic radiation measurements of isotopic quantum effects on room temperature liquid water [7, 8] which are in qualitative agreement with quantum molecular dynamics simulations [9, 10] and show H₂O to be a slightly more disordered liquid than D₂O at room temperature. The simulations demonstrate that isotope effects have a quantum mechanical origin: for example, a classical simulation using the same potential for two different isotopes would obtain the same structure for all isotopes of a particular molecule, whereas a quantum simulation does not. In water, the simulations predict that isotopic quantum effects due to orientational disorder are largest in the oxygen–oxygen partial structure factor, which is close to the x-ray function measured here [11]. Experimentally it has been shown that the structure of liquid D₂O is similar to that of H₂O if its temperature is raised by 5.5 °C.

Quantum simulations on high density amorphous (HDA) ice [12] predict considerable changes in intermolecular structure due to isotopic effects. There appear to be no such calculations for LDA ice in the literature. Due to the difficulty in making reproducible HDA ice samples and their tendency to relax into intermediate forms [2], the objective of this study was focused on investigating the differences in structure of H₂O and D₂O LDA ice at the same temperature and below ambient pressure. As in our previous studies [2] the LDA ice samples were formed by warming HDA ice, which leads to major changes in the region of the first sharp diffraction peak (FSDP) for both neutron and x-ray structure factors. These changes in the FSDP are directly related to changes in the intermediate-range order of the amorphous solids [1]. As an example, figure 1 shows the pseudonuclear x-ray structure factors (i.e. the electron cloud has been deconvoluted using atomic form factors to give the nuclear interactions) for HDA ice and LDA ice in the FSDP region. The spectra for previously reported forms close to LDA ice are also shown [2]. The final, fully annealed LDA ice form is characterized by a FSDP position of 1.70 Å⁻¹ [2, 6].

2. Experimental details

Initially, samples of HDA ice (either 99.99% D₂O or 99.99% H₂O) were prepared by pressurizing ice-1*h* to 18 kbar at 77 K in a piston cylinder apparatus at the National Research Council Laboratory in Ottawa, Canada. The samples were stored in liquid nitrogen

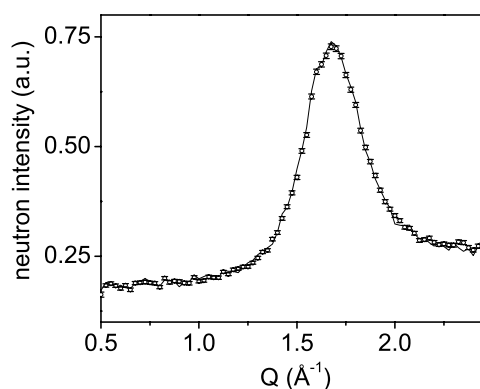


Figure 2. The measured neutron intensity for LDA ice at 120 K (circles with error bars) and 130 K (full curve) in the region of the FSDP (see text). The spectra have been corrected for background scattering, detector efficiency and normalized to a vanadium standard.

during shipment to Argonne National Laboratory in Chicago. The samples were transferred from liquid nitrogen storage into helium cryostats mounted on the high energy photon diffractometer at the 11-ID-C beamline at the Advanced Photon Source, and on the Glass, Liquid and Amorphous Materials Diffractometer at the Intense Pulsed Neutron Source. For the synchrotron experiment the HDA H₂O and D₂O powdered samples were loaded (in liquid nitrogen) into two separate compartments (5 mm apart) within the same aluminium holder. The holder had two thin kapton windows through which the high energy x-ray scattered beam passed in transmission geometry. In the neutron experiment the D₂O sample was poured into a standard vanadium container together with the liquid nitrogen and mounted in an orange cryostat at 40 K. The sample was then warmed to 80 K to boil away the nitrogen and the temperature controlled via the helium exchange gas in the cryostat.

In the neutron measurements D₂O LDA ice was formed by raising the temperature to 120 K, which is above the H₂O HDA–LDA ice transition of 113.5 K [13]. The HDA to LDA ice transition for D₂O is expected to be a few degrees higher than for H₂O, similar to the difference in freezing temperatures or in the onset of the glass transitions [14]. The LDA ice sample was annealed for 12 h at 120 K during which time neutron spectra were measured in 1 h increments, but no measurable change in the amorphous structure was observed. Further annealing at 130 K for a further 12 h started to show the growth of crystalline ice with time. In figure 2 the measured neutron spectra in the FSDP region during the second hour of the 120 K anneal are compared to that observed in the second hour of the 130 K anneal. Since these two neutron spectra show no significant changes in amorphous structure we conclude that at 120 K D₂O LDA ice can be considered the fully ‘annealed’ form.

In the x-ray experiment the helium cryostat was mounted on a translation stage, enabling the samples to be easily interchanged in the incident beam. The temperature of the samples was accurate to within ~ 0.1 K through equilibration with a low-density helium exchange gas in direct contact with both samples. Each sample was a loosely packed powder and its volume was small (~ 3 mm \times 3 mm \times 4 mm) relative to the cold He exchange gas in which it was immersed. Once loaded in the cryostat, x-ray measurements revealed a maximum 8% difference between the normalized intensities of the H₂O and D₂O HDA ice samples. However, it was not clear whether these differences were due to isotopic effects or very slight differences in sample history. Consequently, we warmed the HDA ice samples simultaneously to 120 K for 1 hour and quenched to 40 K. Measurements were then performed on the resulting LDA

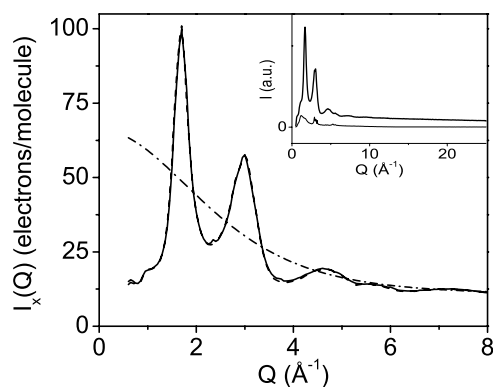


Figure 3. The electronic structure factor $I_X(Q)$ for hydrogenated (full curve) and deuterated (broken curve) LDA ice at 40 K. The independent atom model form factor and Compton contribution is also shown as a chain curve. The inset compares the background (thin full curve) to the measured data (thick full curve).

structures for H_2O and D_2O at 40 K. On the basis of the neutron and x-ray measurements described above it is argued that any difference in the measured x-ray structure factors on LDA ice samples annealed at 120 K are due to isotopic quantum effects.

3. Data reduction

The incident beam energy was 98 keV and the x-ray data presented here have been corrected for detector dead time, container scattering, varying detector distance and polarization, as previously described [15]. Multiple scattering and attenuation corrections for the small samples were found to be negligible ($\sim 1\%$) at this energy [16]. A small correction was made for crystalline ice-*Ih* scattering, which had condensed from the air onto the outside of the cryostat during the experiment⁶. The resulting electronic $I_X(Q)$ curves were normalized to the sum of the atomic form factors plus Compton scattering with a Klein–Nishina correction (later referred to as $I_0(Q)$) and are shown in figure 3. Our measured $I_X(Q)$ for D_2O LDA ice was also converted to the pseudonuclear form using the molecular form factors of Narten and Levy [17]. It was found to be generally in good agreement with the published results of Bizid *et al* [4] (see figure 4(a)), except in the region of $Q \sim 5.6 \text{ \AA}^{-1}$. Although there are slight differences between our x-ray data and the data of Bizid *et al* [4] in the region of the first two (sharpest) diffraction peaks, these could be due to instrumental resolution effects. However a careful inspection of our $S(Q)$ LDA ice curves reveal that the shoulder at $Q = 5.6 \text{ \AA}^{-1}$ becomes more pronounced as LDA ice relaxes. This is illustrated in figure 4(b). It is therefore likely that the shoulder at $Q = 5.6 \text{ \AA}^{-1}$ in the $S(Q)$ data of Bizid *et al* [4] may be due to the LDA ice form not being fully relaxed. It is also interesting to note that Bizid *et al* [4] also found discrepancies in this region between LDA ice samples made by the warming of HDA ice and vapour deposited samples [5].

⁶ A small correction to eliminate Bragg scattering in the region $Q = 1.75\text{--}6.5 \text{ \AA}^{-1}$ was applied to the isotope LDA ice difference (see figure 5). No Bragg peaks were observed below 1.75 \AA^{-1} since the frozen condensate was not at the scattering centre of the instrument. Above 6.5 \AA^{-1} no significant Bragg scattering was observed in either the isotopic difference or above the statistical noise of the measured crystalline ice-*Ih* spectra.

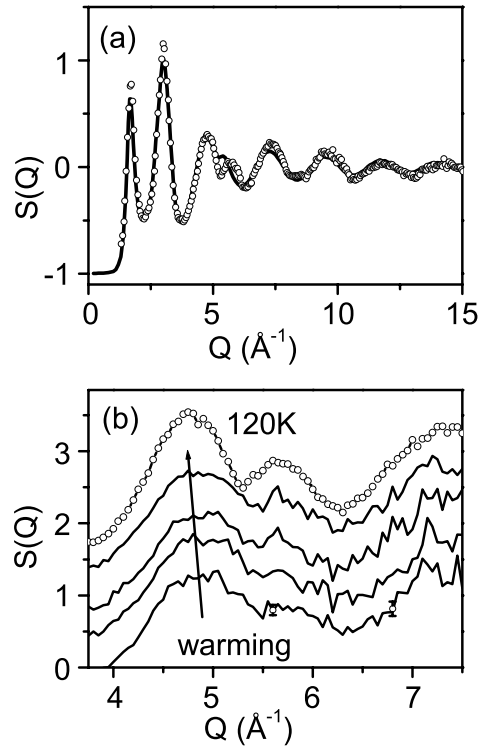


Figure 4. (a) Compares our measurements on LDA ice at 120 K (circles) with those of Bizid *et al* [5] (full curve) analysed using the molecular form factors of Narten and Levy [17]. (b) Shows the same curves shown in figure 1 blown up in the region between $Q = 4$ and 8 \AA^{-1} to investigate the growth of the feature at $Q = 5.6 \text{ \AA}^{-1}$. However, we note that the top curve at 120 K is a different sample to those marked 'warming'. Representative error bars are shown.

4. Theory

Since x-ray scattering amplitudes are unaffected by the isotopic substitution, structural differences between the hydrogenated and deuterated $S_X(Q)$ curves for LDA ice are given by

$$\Delta I_X(Q) = I_X^{\text{D}_2\text{O}}(Q) - I_X^{\text{H}_2\text{O}}(Q). \quad (1)$$

This quantity is related to differences in the electronic distribution function $\Delta G_X(r)$ by the Fourier transform

$$\Delta I_X(Q) = \frac{4\pi\rho}{Q} \int r[\Delta G_X(r)] \sin(Qr) dr \quad (2)$$

where ρ is the electronic number density of the sample.

5. Discussion

The difference, $\Delta I_X(Q)$, for deuterated minus hydrogenated LDA ice at 40 K is shown in figure 5. The observed maximum isotope effect for LDA ice is $\sim 3.4\%$ relative to the height of the first peak of the x-ray structure factor at $Q = 1.70 \text{ \AA}^{-1}$, which is somewhat larger than the value of $\sim 1.6\%$ previously observed for liquid water [7]. In liquid water at room temperature it has been shown that the isotopic quantum effect is analogous to a 5.5 K temperature change

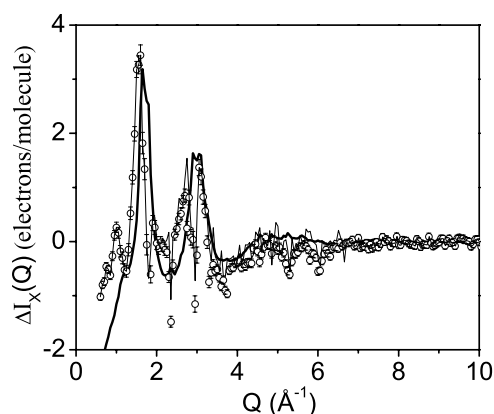


Figure 5. The measured isotopic difference in electronic structure factors for D_2O-H_2O , $\Delta I_X(Q)$, in LDA ice at 40 K (open circles with error bars). The same isotope difference corrected for a small amount of additional background scattering (see footnote 6) is shown as a thin full curve. A temperature difference curve in H_2O LDA ice is represented as a thick full curve (see text).

in the liquid structure [7]. A temperature difference curve was constructed for LDA ice data. Data taken for H_2O LDA ice at 120 K minus that taken at 40 K and divided by 9 are plotted in figure 5. Since the behaviour of $I_X(Q)$ for LDA ice with temperature is not known, the absolute values of the temperature difference should be taken with caution. We note for example that in crystalline ice-*Ih* the temperature dependence of the lattice parameter is highly non-linear and the sample exhibits negative thermal expansion below ~ 60 K [18]. Nonetheless, the temperature difference has the same general features as the isotope difference curve but is shifted slightly towards higher Q values. More importantly, the peak at 1.0 \AA^{-1} is not reproduced by the temperature difference. This peak suggests that there are significant intermediate-range order differences between the hydrogenated LDA ice and deuterated LDA ice samples, the deuterated form being the more structured. We note that a similar Q -space comparison of the isotopic and temperature difference curves for liquid water did not show this feature [7].

A real space comparison of the measured LDA quantum difference curve ($D_2O - H_2O$) and the LDA ice temperature effect, together with the water isotopic quantum difference, are shown in figure 6. Also plotted is a Fourier transform of the $I_X(Q) - I_0(Q)$ curve from figure 3. It is interesting to note that the $D_2O - H_2O$ difference in LDA ice and that found in water have the same general features in real space. There are peaks in the 2.8 and 4.5 \AA regions with a dip in between at 3.4 \AA , corresponding to an enhancement of the first and second nearest-neighbor oxygen–oxygen electron densities. However, significant differences in shape and sign between the curves are also apparent at the hydrogen bonding distance of $\sim 1.8 \text{ \AA}$ and at higher distances around 5.8 \AA . Notably, the 1.8 \AA feature is negative in the LDA ice quantum and temperature differences, and slightly positive in the water isotope difference. At 5.8 \AA the LDA ice quantum difference appears more intense than the LDA ice temperature effect. These results suggest that, although in general H_2O yields a slightly more disordered structure than D_2O , there are significant differences in the quantum mechanical behaviour of LDA ice at 40 K and liquid water at room temperature.

In summary, on the basis of careful neutron diffraction annealing measurements it is argued that at 120 K the LDA ice form is fully relaxed, since there are no significant changes in the amorphous structure compared to the spectra at 130 K. Over a period of several hours at a

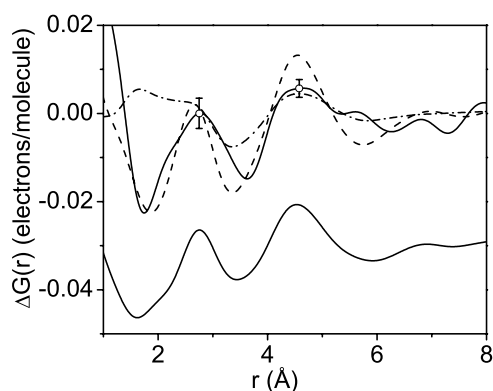


Figure 6. The real space curves ($D_2O - H_2O$) for the LDA quantum effect (full curve with representative error bars) and the LDA temperature difference in H_2O (broken curve), obtained by the Fourier transforms of the circles and the thick full curve in figure 5, respectively. A discussion on how the error bars were obtained may be found in the work of Weitkamp *et al* [20]. These are compared to the quantum effect for water at 298 K reported by Tomberli *et al* [7] (chain curve). The Fourier transform of $I_x(Q) - I_0(Q)$ (divided by 30) from figure 3 for D_2O is also shown (displaced downwards by 0.03, full curve) for comparison.

temperature of 130 K the growth of small crystallites were observed. Synchrotron diffraction measurements using 98 keV electromagnetic radiation on LDA ice annealed at 120 K for 1 h and quenched to 40 K reveal a measurable isotopic quantum effect between the electronic total structure factors of the H_2O and D_2O samples. When compared to water at room temperature the $\Delta G_x(r)$ LDA ice function has a different sign at 1.0 \AA and is approximately twice as large at 3.5 \AA . Figure 6 shows that at $r = 2.8$ and 4.8 \AA the isotopic quantum effect accounts for about 5 and 3%, respectively, of the total measured intensities. In addition, the measured isotope effect is mostly, but not completely, reproduced by an LDA ice temperature difference. In particular, the quantum effect difference has a peak at 1.0 \AA^{-1} , indicating the presence of more ordering in the D_2O LDA ice sample at distances of $r > 5 \text{ \AA}$. This may have implications on the accuracy of extracting partial structure factor information using the H/D substitution technique in neutron scattering. The very large effects in structure predicted for HDA ice [12] are not observed in the measured effect for LDA ice (which is much more experimentally accessible). However, it has been shown through a combination of reverse Monte Carlo, molecular dynamics and lattice dynamic calculations that quantum corrections have a substantial effect on the thermodynamic properties of LDA ice and supercooled water [19]. It would therefore be interesting to compare the measurements presented in this paper with future quantum mechanical simulations for LDA ice.

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