Isotopic Quantum Effects on the Structure of Low-density Amorphous Ice

C.J. Benmore,[1] J. Urquidi,[1] J. Neuefeind,[1] B. Tomberli,[2]
C. A. Tulk,[3] M. Guthrie,[1,3] P.A. Egelstaff,[2] D.D. Klug[4]
[1]Intense Pulsed Neutron Source (IPNS) and Chemistry Divisions,
Argonne National Laboratory, Argonne, IL, U.S.A.
[2]Department of Physics, University of Guelph, Guelph, Ontario, Canada
[3]Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A.
[4]National Research Council of Canada, Ottawa, Ontario, Canada

Introduction

The structures of low-density amorphous (LDA) ices and high-density amorphous (HDA) ices have recently been the subject of much attention [1]. Conventional x-ray diffraction studies of LDA ices were previously made on samples formed by the vapor deposition of H_2O and by the heating of D_2O HDA ice produced by the compression of ice-Ih. 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 H_2O and D_2O molecules. This work follows high-energy electromagnetic radiation measurements of isotopic quantum effects on room-temperature liquid water. The measurements are in qualitative agreement with quantum molecular dynamics simulations and show that H_2O is a slightly more disordered liquid than D_2O at room temperature [2]. The simulations demonstrate that isotopic 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. It has been shown experimentally that the structure of liquid D_2O is similar to that of H_2O if its temperature is raised by 5.5°C [2].

Quantum simulations on HDA ice predict considerable changes in intermolecular structure due to isotopic effects. There appear to be no such calculations for LDA ice in the literature. Because of the difficulty in making reproducible HDA ice samples and their tendency to relax into intermediate forms, the objective of this study was to investigate the differences in the structures of H_2O and D_2O LDA ices at the same temperature and below ambient pressure.

On the basis of careful exploratory neutron diffraction annealing measurements, it can be argued that at 120K, the LDA ice form is fully relaxed, since there are no significant changes in the amorphous structure when compared to the spectra at 130K. Over a period of several hours at a temperature of 130K, the growth of small crystallites is observed in the neutron data.

Methods and Materials

Initially, samples of HDA ice (either 99.99% D_2O or 99.99% H_2O) were prepared by pressurizing ice-Ih to 18 kbar at 77K in a piston cylinder apparatus at the National Research Council Laboratory in Ottawa. The samples were stored in liquid nitrogen during shipment to Argonne National Laboratory near 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 APS. The H_2O and D_2O HDA powdered samples were loaded (in liquid nitrogen) into two separate compartments (5 mm apart) within the same aluminum holder. The holder had two thin Kapton® windows through which the high-energy x-ray-scattered beam passed in transmission geometry.

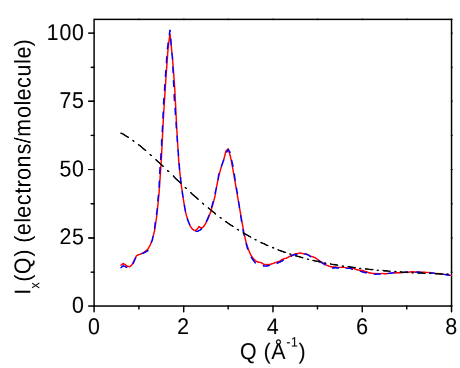

FIG. 1. The electronic structure factor $I_X(Q)$ for hydrogenated (solid red line) and deuterated (dashed blue line) LDA ice at 40K. The independent atom model form factor and Compton contribution are also shown as a dashed-dotted line.

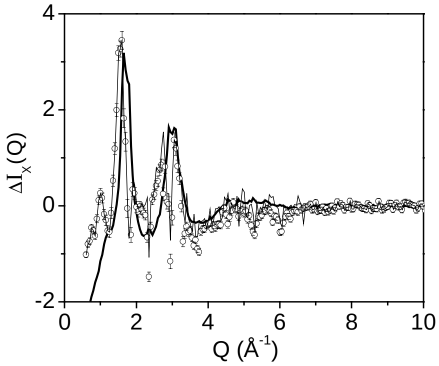

FIG. 2. The measured isotopic difference in electronic structure factors for D_2O minus H_2O, $\Delta I_X(Q)$, in LDA ice at 40K (open circles with error bars). The same isotopic difference corrected for a small amount of additional background scattering is shown as a thin solid line. A temperature difference curve in H_2O LDA ice is represented as a thick solid line.

Results and Discussion

Synchrotron diffraction measurements, made by using 98-keV electromagnetic radiation on LDA ice annealed at 120K for 1 hour and quenched to 40K, reveal a measurable isotopic quantum effect between the electronic total structure factors of the H_2O and D_2O samples (Fig. 1). The observed maximum isotopic effect for LDA ice is ~3.4% relative to the height of the first peak of the x-ray structure factor at Q = 1.70 $Å^{-1}$, which is somewhat larger than the value of ~1.6% previously observed for liquid water. A temperature difference curve was constructed for LDA ice data (Fig. 2). The peak at 1.0 $Å^{-1}$ 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 [3]. This may have implications on the accuracy of extracting partial structure factor information by using the hydrogen/deuterium (H/D) substitution technique in neutron scattering.

Acknowledgments

Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38. Support from BESSRC and the IPNS Division is also gratefully acknowledged.

References

[1] C.A. Tulk, C.J. Benmore, J. Urquidi, D.D. Klug, J. Neuefeind, B. Tomberli, and P.A. Egelstaff, *Science* **297**, 1320 (2002).

[2] B. Tomberli, C.J. Benmore, P.A. Egelstaff, J. Neuefeind, and V. Honkimäki, J. Phys.: Condens. Matter **12**, 2597 (2000).

[3] J. Urquidi, C.J. Benmore, J. Neuefeind, B. Tomberli, C.A. Tulk, M Guthrie, P.A. Egelstaff, and D.D. Klug, “Isotopic quantum effects on the structure of low density amorphous ice,” J. Phys.: Condens. Matter **15**, 3657 (2003).