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Vibration properties of low-fraction hydrogen in deuterium ices*

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Inelastic incoherent neutron scattering spectra of D_2O high-density amorphous (hda) ice, ice-VIII and ice-II mixed with small amount of H_2O (<5%) have been measured recently on high-energy transfer spectrometer at Rutherford Appleton Laboratory (UK). The hydrogen atom on D_2O ice lattices has three distinguished vibrational modes, two bending at low frequencies and one stretching at high frequencies, and their frequencies are slightly different for different phases of ice. It was found that the lower one of the bending modes is located at ∼95 meV for hda-ice, at ∼95 meV for ice-VIII and at ∼96 meV for ice-II and they are all lower than the value of 104 meV for ice-Ih. It was also measured that the O-D and O-H covalent bond stretching modes of ice-VIII are at ∼315 and ∼425 meV, ice-II at 307 and ∼415 meV, hda-ice at 312 and ∼418 meV, respectively. They are significantly higher than the values of ice-Ih at ∼299 and ∼406 meV, respectively.

Keywords: neutron scattering, defect vibration modes, Gaussian fit
PACC: 2540F, 6170, 6320M, 6320P

1. Introduction

When a defect is formed in a solid, its dynamic behaviour differs significantly from that of the host lattice. If a deuterium atom is replaced by a hydrogen atom in D_2O ice, forming a HOD molecule, the translational propagation will be broken by the hydrogen atom. For a weakly bonded defect, there will be localized modes induced by the impurity atom, which have resonance frequencies different from those of the phonon modes in a perfect crystal. Motions of the defect modes will appear on the defect atom itself and the surrounding lattice atoms will little respond to these motions, so that they decay rapidly as they depart from the defect atom. The analysis of defect modes depends on the nature of their interactions with neighbouring atoms and hence the measured frequencies can give direct information of these interactions.

Studies of H vibrations in D_2O (or D in H_2O) have been carried out for many years using Raman scattering and infrared (IR) absorption techniques.[1−3] The intermolecular coupling forces, caused by both hydrogen bonding and polarization field, give rise to the collective oscillations, ν_1 and ν_3, that dominate the IR and Raman stretching mode complexes, as shown in Fig.1. The bending mode, ν_2, is mainly determined by H–O–H bending interaction. The H defect modes in D_2O ice, unlike those stretching and bending modes in the lattice, are decoupled from their surroundings and oscillate in three degrees of freedom while the surrounding atoms are in effect stationary. The assignment of the defect modes μ_1, μ_2 and μ_3 is also indicated in Fig.1. Because of the selection rules in both IR and Raman techniques, two of the three defect modes (μ_1 and μ_2) are almost invisible, and this makes the interpretation of such spectra difficult. In the past, much effort was devoted to the studies of the stretching mode, μ_3, and its combination bands.[4−6] Compared with them, inelastic neutron scattering (INS) has a very distinct advantage in the measurement of H in D_2O, because H has a much larger incoherent cross section than D.[7] This character gives some forty times greater sensitivity for modes involving hydrogen motion than that due to deuterium. Hence very small amount of H impurity in D_2O ice can be easily detected. This is quite evident in our previ-

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ous H-contaminated D_2O samples, which provided a new insight into the hydrogen bonding in ice-Ih.[8,9] Clearly, H-contamination becomes very important for INS measurement of non-hydrogenous samples.

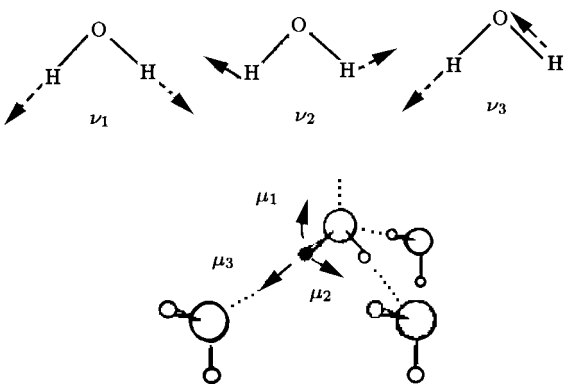


Fig.1. Schematic illustration of the bending and stretching modes, ν_1, ν_2 and ν_3, and three defect modes μ_1, μ_2, and μ_3.

Experimental data about the strength of the hydrogen bond can be obtained directly by measuring vibrational spectra. A special vibrational mode (or phonon) is determined by the interatomic force constants, which are the double differentials of the potential function. Therefore, measuring dynamic properties constitutes one of the most powerful ways of investigating water potentials that lie at the heart of our understanding in a wide range of water anomalies.[10] Studying the defect modes requires a lattice dynamical model of the unperturbed lattice, the defect mode frequencies and the displacements of all the atoms involved. These modes can easily be observed by INS measurements. In this paper a series of measurements using high-energy transfer (HET)[11] spectrometers on ISIS neutron source of Rutherford Appleton Laboratory (UK) are reported. The different measurements for the samples of ice-II, ice-VIII and hda-ice in high-purity D_2O with 5 wt, % H_2O are carried out at low temperature (15K).

2. Sample preparation and measurements

The samples of ice II and ice VIII D_2O (99.9%) mixed with 5 wt.% H_2O (99.6%, doubly distilled) were made by using a recovery technique,[9] in which the ice-Ih was pressurized to 0.3GPa and 2.2 GPa at 240 K, respectively to obtain the above two samples. Then they were cooled down to 77 K (liquid nitrogen temperature) and the pressures were released. High-density amorphous ice (hda-ice) sample was produced by pressurizing ice-Ih to ~1.2 GPa at ~80 K, and then the pressure was released. All samples were kept in liquid nitrogen for neutron measurements.

INS measurements were carried out on the HET spectrometer of the ISIS pulsed neutron source at Rutherford Appleton Laboratory (UK). Because a direct geometry was used on this instrument, it was possible to make the measurements at relatively low Q values. The incident neutron energy was fixed by using a rapidly rotating slit package and the energy transfer was obtained by measuring the total time-of-flight of individual neutrons from the sample to the detectors. The resolution is estimated to be about 1% over an effective incident energy range of 20–2000 meV, depending on which slit package is used. Thus the HET spectrometer is particularly valuable for solids, such as ice, where the intermolecular bonding is much weaker than the intra-molecular bonding, so that the fundamental modes have little dispersion and hence at low Q they can be easily separated from the multiphonon and multiple scattering contributions. Since H has a much larger incoherent cross section and larger vibration amplitude than D, this is a considerable advantage in making measurements on H in D_2O ices.

3. Results and discussion

The structural differences among the high-pressure phases of ice should reflect in the INS spectra of molecular-relative-moving vibrations (translation <40 meV), inter-molecular bending vibrations (40 meV< libration <120 meV) and intra-molecular vibrations (internal band >120 meV). The hydrogen bond is almost an order of magnitude weaker than O–H covalent bond, so that the effect of impurity on the latter can be small. Figures 2 and 3 show the INS spectra of ice-II, ice-VIII and hda-ice D_2O mixed with <5 wt.% H_2O in regions of libration and internal vibration, respectively. The spectrum of ice-Ih (10 wt.% H_2O in D_2O) is also shown for comparison. The differences among the spectra for the stretching modes μ_3 at about 406 meV, the bending modes μ_2 at about 184 meV and the rotation modes μ_1 at about 104 meV are obvious.

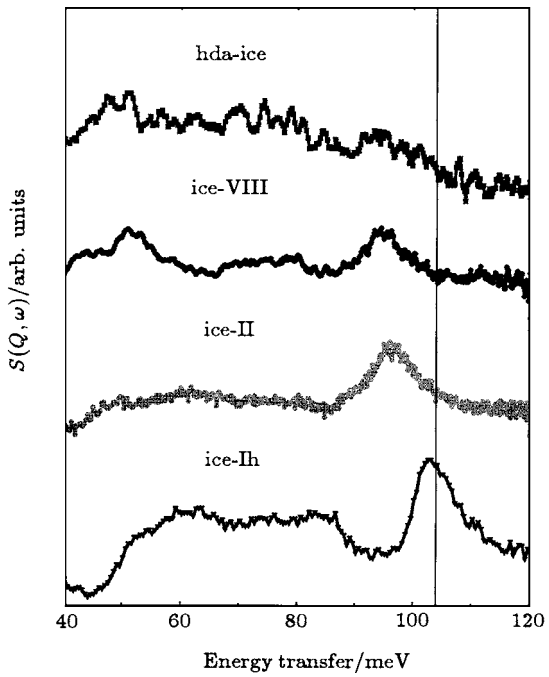


Fig.2. The librational band comparison of the INS measurements of various phase D_2O/H_2O (<5%) ices (ice II, ice VIII and high density amorphous ice) with D_2O/H_2O (~10%) ice Ih using HET spectrometer at 15K.

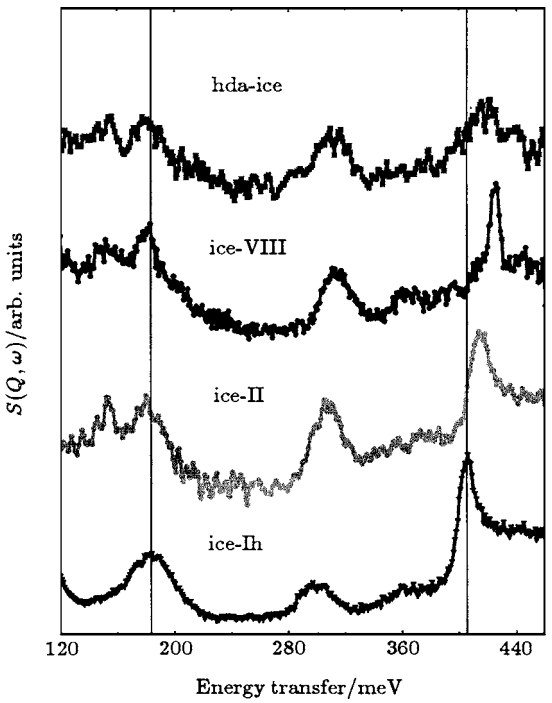


Fig.3. The internal vibrational band comparison of the INS measurements of various phase D_2O/H_2O (<5%) ices (ice II, ice VIII and high density amorphous ice) with D_2O/H_2O (~10%) ice Ih using HET spectrometer at 15K.

The μ_3 mode of ice-Ih results in the peak at 406 meV, and the peak would have different shifts for different high-pressure phases of ice, i.e. shifting to 415 meV for ice II, 425 meV for ice VIII and 418 meV for hda-ice. This is a direct evidence that the covalent bond is strengthened (two ions are closer) as hydrogen bond length or O···O distance is stretched longer.[4] The peaks in the region from ~305 to 314 meV come from O–D stretching vibrations. This mode in the high-pressure phases has the same shifting tendency as O–H. The peaks at ~180 meV result from the bending mode μ_2, and they almost keep unchanged for different phases: at about 184 meV for ice-Ih, 181 meV for ice-II and ice-VIII, 179 meV for hda-ice. From Fig.3 it can be found that in high-pressure phases these bending modes produce two peaks, which are due to two bending modes: D–O–D mode at ~150 meV and H–O–D mode at ~180 meV. For ice-Ih only the H–O–D mode is left, which is due to the higher concentration of H_2O.

The μ_1 mode of H defect in ice-Ih is located at ~104 meV, and this mode in high-pressure phases shifts toward low energy side, e.g. ~96 meV for ice-II and ~95 meV for ice-VIII and hda-ice. Their positions of ice-VIII and hda-ice are almost the same, except that the peak of hda-ice is quite flatter due to its amorphous structure.

From our previous lattice dynamic (LD) simulations and experiments for various high-pressure phases such as ice-II,[12] ice-VIII[13] and hda-ice,[14] it is known that the low-energy cut-offs of librations result from inter-molecular bending force constants and these inter-molecular bending interactions are determined by the nearest molecular distances. For example, their positions are 67.2 meV for ice-Ih (R_{O-O}=2.75Å); 63.0 meV for ice IX (R_{O-O}=2.750–2.793Å); 56.1 meV for hda-ice (R_{O-O}=2.8Å); 59.5 meV for ice-II (R_{O-O}=2.768–2.844Å); 53.6 meV for ice-VI (R_{O-O}=2.79–2.82Å) and 54.8 meV for ice-VIII (R_{O-O}=2.95Å).[2,15] It means that these inter-molecular bending interactions become weaker when the nearest O–O distances are stretched longer. It is further deduced that the defect vibration μ_1 is also related to these bending interactions. Therefore, Fig.4 shows the peaks at ~104 meV of Fig.2 fitted by numbers of Gaussian distributions for various phases of ice due to different numbers of nearest O-O distances. This peak of ice-Ih is fitted by two Gaussian functions centred at 103 and 107 meV, corresponding respectively to two nearest O–O lengths (2.75 and 2.76Å[2]). Similarly, these peaks of ice-II and ice-VIII are fitted by four (centred at 90, 94.6, 97.7 and 102 meV) and one (94.6 meV) Gaussian functions

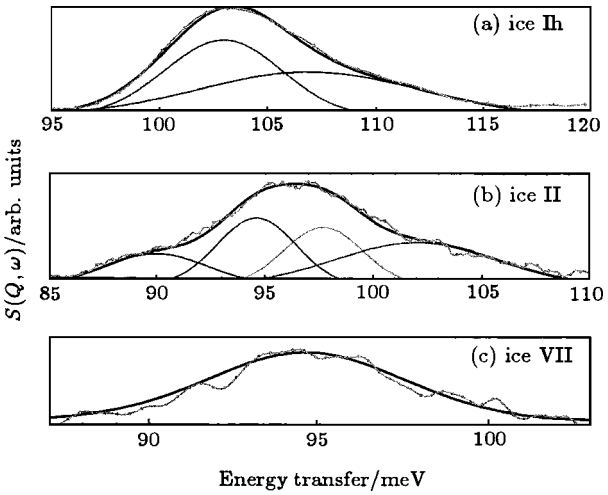


Fig.4. μ_1 of H defect modes was fitted by several gaussian functions: (a) (ice Ih) two gaussian functions centrally located at 105 meV and 107 meV; (b) (ice II) four at 90 meV, 94.6 meV, 97.7 meV and 102 meV; (c) (ice VIII) one at 94.6 meV.

related to different numbers of nearest O–O distances (2.768, 2.781, 2.803 and 2.844Å for ice-II;[16] 2.95Å for ice-VIII[17]), respectively.

4. Conclusion

In this paper, we present the neutron spectroscopic measurements of H defect modes in D_2O ice-Ih, ice-II, ice-VIII and hda-ice. These defect modes are dynamically decoupled from the lattice modes of neighbouring vibrations, and they provide direct information about the interactions of the defect atoms with other lattice atoms. From the comparison between different INS spectra, it can be found that covalent bond is strengthened and closer as its corresponding hydrogen bond is stretched longer in high-pressure phases of ice. It is straightforward that μ_1 vibrational frequencies shift towards low energy side in these high-pressure phases, which is due to the inter-molecular interactions becoming weaker when the distance between molecules is stretched longer.

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