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Inelastic incoherent neutron scattering study of ice Ih, II, IX, V and VI in the region from 50–500 meV

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Abstract. Inelastic incoherent neutron scattering spectra of ice Ih and recovered high-pressure ice II, IX, V and VI were measured in the range of energy transfer from 50 to 500 meV at 20 K using the high-energy transfer (HET) spectrometer at ISIS. The excellent resolution and large-Q range of this instrument enable us to examine the vibration modes of these ices in great detail. The results clearly show that the low-energy cut-offs of the librational bands shift towards lower energy transfers by amounts ranging from 4 meV for ice IX to 12 meV for ice VI as compared with ice Ih. There is no clear high-energy cut-off for this band for ice V and VI. For the intramolecular stretching modes, the main peak at about 414 meV for ice Ih is shifted towards higher energy transfer for these recovered ices while there is no clear evidence of any shift in the intramolecular bending modes at about 200 meV.

1. Introduction

The large variety and complexity of the exotic phases of ice is in clear contrast to the simplicity of the water molecule. The properties of these phases are crucially dependent on the nature of the hydrogen bond. The understanding of this bond in different phases of ice, i.e. how it behaves with different bond lengths and inter-bond angles is important, not only for our understanding of water but also with respect to the behaviour of related hydrogen-bonded systems. In the relatively narrow pressure range from 2 to 10 kbar there are at least six solid forms of ice (ice II, III, IV, V, VI and IX) reflecting the versatility of the tetrahedral coordination of water molecules under different conditions. Most of the phases can be 'recovered' by cooling down to liquid nitrogen temperature before releasing the pressure. This provides convenient conditions for neutron scattering experiments because the large volume of sample needed would be difficult to pressurise in the neutron beam. It is important to distinguish between recovered ice and ice measured under pressure because of the possibility that the structure might change when the pressure is released. In the past the structures of these phases have been extensively studied by both x-ray (Kamb 1964, 1965; Kamb and Prakash 1968) and neutron diffraction (Kamb *et al* 1971; LaPlaca *et*

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al 1973) techniques, although some details of the structures, such as proton ordering, are still not clear from phase-to-phase. The dynamical properties of these phases of ice have also been extensively studied in the past by infra-red (IR) absorption (Bertie and Whalley 1964; Bertie 1968, Bertie and Bates 1977) and Raman scattering (Taylor and Whalley 1964; Marckmann and Whalley 1964; Bertie and Francis 1980; Sukarova *et al* 1984), but because of the ambiguous selection rules for the disordered phases of ice, some essential information is missing from both techniques and a clear understanding of the vibrational behaviour has not yet been reached. Also, little is known about the influence of the structure on the fundamental stretching and bending modes, particularly for high-pressure phases of ice such as ice II and IX. For this problem, inelastic incoherent neutron scattering (IINS) provides an ideal tool for the study of the dynamics of ices for the following reasons:

(i) no selection rules are involved;
(ii) the amplitude-weighted phonon density of states (PDOS) derived from IINS can be rigorously calculated for a particular model of the lattice dynamics.

In our previous papers, the IINS spectra for ice II, IX, V, VI and VIII, obtained from the TFXA spectrometer at ISIS, were reported (Li *et al* 1991; Kolesnikov *et al* to be published). The data provide unprecedented information on the translational and on parts of the librational modes. However, because of the small final neutron energy (4 meV) used on this spectrometer—necessary for obtaining the very good energy resolution at low-energy transfers (better than 2%)—the higher energy information (above 150 meV) is attenuated by the Debye–Waller factor and hence is submerged in the multi-phonon contribution at these large momentum transfers ($Q^2 \propto \hbar\omega$). Thus, all that is seen is a smoothly varying intensity due to multi-phonon effects. In order to obtain information on the high-energy features of the spectra, including the intramolecular bending and stretching modes of the water molecules, the high energy transfer chopper spectrometer, HET, has to be used because it can measure high-energy transfers at low Q. This is particularly valuable in solids such as ice where the intermolecular bonding is much weaker than the intramolecular bonding so that the fundamental modes have little dispersion and hence can be easily separated from the multi-phonon and multiple scattering contributions to the measured spectra by analysis of the Q-dependence of the intensity. Such measurements on the different phases of ice will then provide important information on the interatomic pair potentials via a suitable lattice dynamic model. In this paper, which is a continuation of our previous publication (Li *et al* 1991), we briefly report our recent HET experimental results for ice Ih and the recovered phases of ice II, IX, V and VI. Lattice dynamical calculations for these structures will be published later.

2. Experimental details

The HET (high energy transfer) spectrometer on the ISIS pulsed neutron source at the Rutherford-Appleton Laboratory is a direct-geometry chopper spectrometer (Boland 1990), i.e. the incident neutron energy is fixed and the energy transfer is obtained by measuring the total time-of-flight of individual neutrons from the sample to the detectors. The incident energy is fixed using a rapidly rotating slit package, phased with respect to the neutron pulse from the moderator to select a single neutron velocity. The resolution in $\Delta E/E_0$ is about 1% over an effective incident energy

range of 20–1000 meV depending on which slit package is used. The detectors are all He^3 tubes mounted in two banks at 4 m (angles from 3° to 7°) and at 2.5 m (angles from 10° to 30°) from the sample. This gives HET a background-to-signal ratio that is negligible for strongly scattering samples such as ice.

The sample of ice Ih was a slab of normal polycrystalline H_2O ice. The polymorphs of ice, ice II, XI, V and VI were prepared using the recovered technique i.e. by quenching the pressurized sample to liquid-nitrogen temperature and then releasing the pressure. It is important to distinguish between structures found in 'recovered' samples and structures obtained actually under pressure *in situ* as they may not be the same. The details of the sample preparation were described in our previous paper (Li *et al* 1991), the same samples being used in the present experiment. The samples were packed in aluminium cans and consisted of slabs 1.5×3 cm^2 in area and about 1 mm in thickness. The slit package was chosen to give an incident energy of 600 meV, in order to cover the stretching ($\sim$ 410 meV) and bending modes ($\sim$ 200 meV) of the ices with good energy resolution and intensity. A very-high-energy chopper was also used to give an incident energy of 1000 meV for measuring the combination bands above the O–H stretching frequency. To study the librational modes in the energy transfer range from 60 to 120 meV, a low-energy chopper was used to give an incident energy of 170 meV. Ice Ih (H_2O) was measured for 24 h and the other recovered samples for 16 h (or less), for both incident energies at a temperature of 20 K. An empty can and a vanadium slab were also measured for background subtraction and detector efficiency correction.

3. Experimental results

3.1. Ice Ih

Although the vibrational spectrum of ice Ih has been investigated several times using inelastic neutron scattering (Prask and Boutin 1968; Renker 1978; Andreani *et al* 1983), the limited resolution and intensity available to these authors has meant that it was not possible to measure the detailed structure of the fundamental stretching and bending modes and their sidebands, and also of the librational band which contains the features that are most sensitive to the structure. It is our intention to eventually reproduce these features for each phase starting from a general model of the lattice dynamics.

Figure 1 shows the IINS spectrum for polycrystalline ice Ih at an incident energy of 600 meV. The continuous curve is a sum of the data from detectors at angles between 3° and 7° and the curve with dots is the sum of the data obtained for the rest of the higher angle detectors between 10° and 30°. The intensity of the data for the higher-angle detectors decreases as the energy transfer increases due to the larger Debye–Waller factor at higher Q. The hump at about 280 meV increases more dramatically on going from low to high angle than do the peaks at about 80, 200 and 410 meV indicating that it is a combination band (intensity $\propto Q^4$), i.e. the hump at 280 meV is a combination of the bending mode of 200 meV and the librational band at about 80 meV. The fundamental intramolecular bending and stretching modes at 200 and 410 meV are very strong. Both peaks are rather broad which is clearly not due to the resolution of the instrument. The physical origin of this width is still not very clear and considerable efforts have been made to understand it (Andreani *et al* 1983). The improved resolution of the instrument clearly shows splitting of the

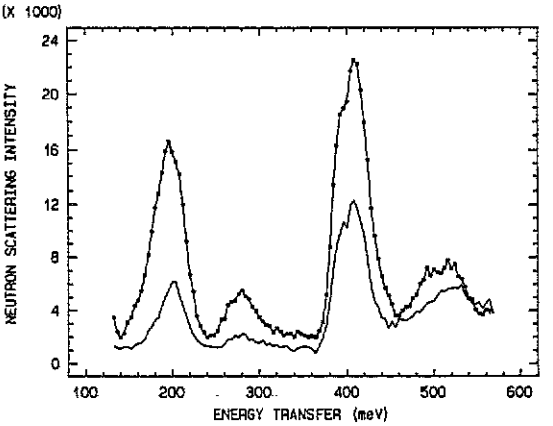

Figure 1. IINS spectra from polycrystalline ice Ih (H_2O) on HET ($E_i = 600$ meV). The smoothed curve is a spectrum summed over all angles from 3° to 7° (i.e. 4 m detector bank) and the dotted curve is a spectrum summed over all angles from 10° to 30° (i.e. 2.5 m detector bank).

two stretching modes, ν_1 (397 meV) and ν_3 (414 meV) in the spectrum from the 4 m detector bank (smoothed curve in figure 1). This is the first neutron scattering observation of this splitting. The measured splitting agrees well with earlier Raman and IR measurements.

When a very-high-incident energy, $E_i = 1000$ meV is used, the stretching combination bands are clearly visible above 410 meV (see figure 2). The small peak at 461 meV is presumably a combination of the stretching mode with the highest energy molecular optical modes at 38 meV (Li *et al* 1989), having a similar shape to these modes—although the energy transfer is somewhat higher than expected. The next peak is a combination with the librational band and appears, as expected, in the range from 479 to 540 meV, having a width of 61 meV, very close to the actual width of the librational band. The peak at 609 meV is clearly assigned to a combination with the bending mode ν_2. The last peak at 790 meV is again slightly less than twice the stretching frequency, which might indicate some anharmonicity in the system. A detailed comparison with the IR measurements is given in table 1.

In order to achieve better resolution in the region of the librational band, the incident energy was reduced to 170 meV. With this incident energy, sharp cut-offs are observed on both sides of the librational band as shown in figure 3 (70 and 125 meV). There is a minimum at 92 meV, subdividing the librational band into two. The spectrum also differs from the measurement on TFXA at high-energy transfer, demonstrating clearly the limitations of the TFXA scan in (Q, ω) space for these solids beyond about 100 meV.

It is interesting to compare these results with IR and Raman. Both electromagnetic techniques show a weak response to the bending modes and only the IR spectrum shows absorption in the librational region for ice Ih but without any detail. In contrast, the IINS data show all the modes of H that are involved in the vibrations and integrated over the whole Brillouin Zone (BZ). However, the resolutions of IR and Raman spectroscopies are still far better than neutron scattering at high-energy transfers, giving more information on the intramolecular stretching modes (see table 1).

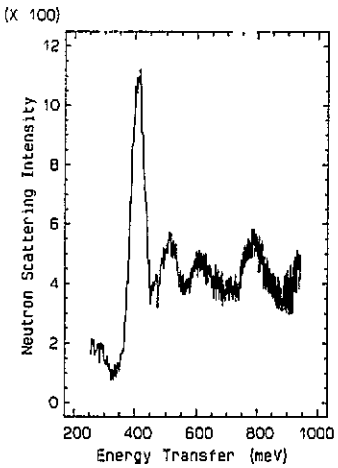

Figure 2. IINS spectrum from ice Ih (H_2O) on HET ($E_i = 1000$ meV) summed over all detectors from 3° to 30° in the range from 300 to 900 meV.

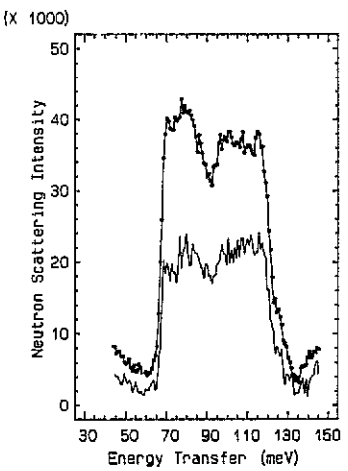

Figure 3. IINS spectra from polycrystalline ice Ih (H_2O) on HET ($E_i = 170$ meV). The smoothed curve is the spectrum summed over the angles from 3° to 7° and the dotted curve is the spectrum summed over the angles from 10° to 30°.

Table 1. Comparison of the main features of the vibration spectra of ice Ih (H_2O) as observed with IINS, IR and Raman techniques.

	Neutron meV (cm^{-1})	Infra-red meV (cm^{-1})	Raman[c] meV (cm^{-1})
Librational band	70–125 (563–1006)	68–112[a] (555–900)[a]	62–118 (500–950)
Bending mode ν_2	200(1610)	205(1650)[a]	205(1650)
Stretching ν_1	397(3196)	400(3220)[a]	391(3150)
Stretching ν_3	414(3333)	420(3380)[a]	420(3380)
Stretching + tran.	461(7311)	—	—
Stretching + Lib.	470–540 (3784–4347)	491–516[b] (3955–4150)[b]	—
Stretching + bending	609(4902)	622(5005)[b]	—
Stretching + stretching	790(6360)	831(6690)[b]	—

[a] Bertie and Whalley (1964).
[b] Ockman (1958).
[c] Scherer and Snyder (1977).

3.2. Ice II, V, VI and IX

In the pressure range up to 10 kbar, there are four recovered phases of ice namely, IX, II, V and VI. The structural differences between these phases are reflected in the IINS spectra and have a dramatic effect on the intermolecular modes (i.e. in the translational region) (Li *et al* 1991). The extent of any corresponding effect on the librational and intramolecular modes is of considerable interest although such effects are likely to be small, the H-bond being almost an order of magnitude weaker than the O–H covalent bond. The influence of the ice structure on these modes is

certainly visible in the IR and Raman spectra (Sukarova *et al* 1984). Comparison of these data with neutron scattering is also useful if one wants to build up a complete picture of the dynamics of different ices. Figure 4 shows the spectra of ice IX, II, V and VI, measured using an incident energy of 600 meV. The smoothed curve is the spectrum of ice Ih for comparison. The differences between the spectra in both the stretching modes at about 410 meV and the bending modes at about 200 meV are obvious. The two stretching modes, ν_1 and ν_3, (symmetric and anti-symmetric stretch) are clearly separated for ice Ih, at 397 and 414 meV, respectively, but they gradually come together in the higher pressure phases and small shifts towards higher energy transfers (to 418 meV for ice IX, 420 meV for ice II, 421 meV for ice V and 424 meV for ice VI) are observed. For the bending modes, the neutron data show that the peaks are at 200 meV for ice Ih, 210 for ice IX, 205 for ice V and 202 for ice VI. Also the peaks get gradually narrower, from 40 meV for ice Ih to 25 meV for ice VI (measured at half maximum), as the formation pressure increases. The humps at 280 meV, seen for all the phases of ice measured, are clearly due to the combination of the bending and librational modes because of the variation of intensity with angle, i.e. the intensities vary with $Q^4 \exp(-2W(Q))$ instead of $Q^2 \exp(-2W(Q))$ as expected for fundamental vibrational modes. In the IR and Raman spectra, the structures of the molecular stretching modes show more features than are seen in the neutron data. This may be partly due to the higher resolution of the IR and Raman spectrometers and partly due to the fact that IR and Raman measure the vibrational spectrum at BZ centre (i.e. $q = 0$). For the bending modes, neither IR nor Raman provide useful information for comparison with the present data.

In a previous paper (Li *et al* 1991), we published the librational spectra for pure ice as measured on TFXA and, as mentioned above, the intensity at the high-energy end of the band is reduced, presumably due to the Debye–Waller factor. Using HET, we could choose the incident energy just above the upper edge of the librational bands to give both good resolution and intensity to investigate this point at lower Q. Figure 5 shows the IINS spectra for ice IX, II, V and VI, plotted with that of ice Ih for comparison, for an incident energy of 170 meV. The spectra show that the whole librational band is shifted towards lower energy as compared with ice Ih—by about 4 meV for ice IX, 8 meV for ice II, 9 meV for ice V and 12 meV for ice VI, following the sequence of the increase in the formation pressure; also the right side of the bands are clearly defined for ice Ih and IX, but not for ice V and VI. The structure of the band for ice IX is rather like ice Ih, having two sub-bands and a minimum at about 90 meV. For ice II, the band is clearly divided into three sub-bands rather than two as in ice Ih. This may be due to the proton ordering in the ice II structure. The extra minimum at 68 meV is located at almost the same position as the low-energy edge of the band for ice Ih, although the second minimum is at the same position as ice IX and its first minimum has the same position as the left edge of the librational band of ice Ih. Indeed, it looks almost as if the missing phonon states at the highest energy sub-band have been removed to the first sub-band. For ice V, the structure of the librational band is not clearly defined which may be partly due to the poor statistics. For ice VI, the width of the librational band is about 60 meV—rather wider than for ice Ih, which has a similar width to ice II and ice IX (about 55 meV). The structure of the librational band for ice VI is like ice II, having two minima. The first minimum at 67 meV is at the same energy as for the similar feature in ice II and the low-energy edge for ice Ih. Although Raman spectroscopy is unable to

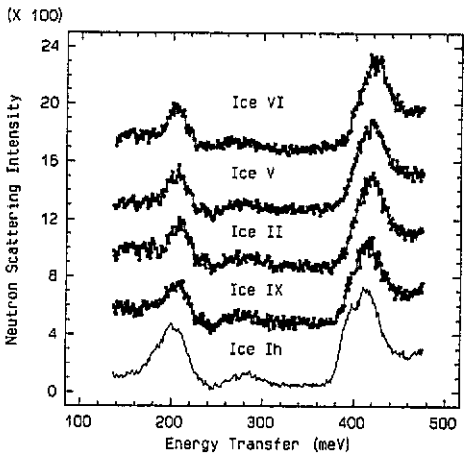

Figure 4. IINS spectra from ice II, IX, V and VI (H_2O) on HET (E_i = 600 meV) summed over the angles from 3° to 30° in the range from 100 to 500 meV. The lowest smoothed curve is the IINS spectrum of ice Ih for comparison.

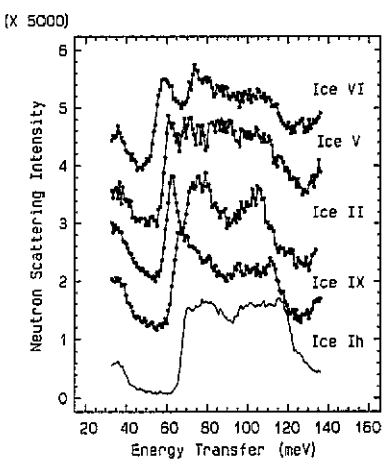

Figure 5. IINS spectra from ice II, IX, V and VI (H_2O) on HET (E_i = 170 meV) summed over the angles from 3° to 30° in the range from 20 to 150 meV. The lowest smoothed curve is the IINS spectrum of ice Ih for comparison.

provide information in this region, IR data are available. However, because of the disordering of proton in most phases of ice, the measurement and interpretation of IR is as difficult as for ice Ih. The measurements of Bates and Bertie (1977) were concentrated on the ordered and partially ordered phases of ice II and ice IX. These results show sharp features in the rotational region which can be related to zone centre frequencies.

4. Conclusion

In this paper, we have presented the first inelastic neutron scattering measurements

on ice Ih in the energy transfer region from 50 to 1000 meV and on several recovered phases of ice in the energy transfer region from 50 to 500 meV. These data provide some information on the fundamental intramolecular and librational modes, some of which cannot be seen in IR and Raman spectrum. The combination of these spectroscopies is essential for the theoretical modelling we have carried out for the translational region only, where we can regard the molecule as a point mass, i.e. for energy transfers of less than 40 meV (Li and Ross 1991). We are currently extending these calculations to describe the hydrogen motions in the librational and internal modes.

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