Pergamon

Planet. Space Sci., Vol. 45, No. 4, pp. 469–473, 1997

0032-0633/97 $17.00+0.00

PII: S0032-0633(96)00131-6

Inelastic neutron scattering study of high density amorphous water ice

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Received 22 May 1996; revised 16 September 1996; accepted 16 September 1996

Abstract. The various forms of amorphous ices with trapped impurities play an important role in astrophysics. Such ices observed spectroscopically as frost on interstellar dust in dense molecular clouds and in comets require a detailed understanding of the spectroscopic properties in laboratory conditions. Using the neutron inelastic scattering technique on ISIS at Rutherford–Appleton Laboratory, the recovered high density amorphous ice is measured along with its subsequent high temperature metastable phases: low density amorphous ice, cubic and hexagonal ices under the same conditions in the energy transfer region from 2 to 500 meV (i.e. 16–4025 cm^{-1}). The results show that the spectra of low density amorphous ice have similar features to cubic and hexagonal ices. However, the spectrum for the high density amorphous ice is significantly different from the others in the translational and librational regions (<150 meV). © 1997 Elsevier Science Ltd

Introduction

Ice in the interstellar space is mostly in the form of low temperature vapour deposits, frosts on interstellar dust grains. The ice is a product of accretion and plays an important role as a source of volatility in cloud chemistry and in the production of organic residues through recombination of UV photolysis products. Such ice is observed spectroscopically as frosts on interstellar dust in dense molecular clouds and constitutes the bulk of matter in comets (Hagen *et al.*, 1981; Standford and Allamandola, 1988). A correct interpretation of the observed ice bands in terms of grain chemistry demands an understanding of the physical properties of low temperature vapour deposited ice. In order to understand the mechanism behind the complex formation of many different kinds of amorphous ices, understanding its interactions between the water molecules is essential.

At low temperature ($T<220$ K) and pressure ($P<0.2$ kbar), water ice exists in a number of metastable forms that can persist over very long timescales because of large activation energy barriers. The transitions are time-dependent. In pure water at low pressures, there are two known crystalline states: a diamond cubic form (Ic) and a hexagonal phase (Ih), as well as a number of amorphous forms. In astrophysics, more important are the two low temperature amorphous forms of water ice: the high density (I_ah or HDA) and the low density amorphous form (I_al or LDA). High density amorphous water ice can be prepared by pressure amorphizing crystalline forms at 77 K (called HDA; Mishima *et al.*, 1984, 1985), by vapour deposition (I_ah; Narten *et al.*, 1976; Jenniskens *et al.*, 1995), and by electron or ion-bombardment of crystalline forms (Heide, 1984; Heide and Zeitler, 1985; Hudson and Donn, 1991). The vapour deposition is thought to be most relevant to astrophysical ices. High density amorphous ice is formed at substrate temperatures less than some 30 K and at low enough vapour pressure (deposition rates less than 100 $\mu m\,h^{-1}$). On the other hand, the pressure induced HDA is more readily available for studies of water structure. Freshly prepared HDA has a similar diffraction pattern as freshly prepared I_ah (Jenniskens *et al.*, 1995). HDA transforms to the low density form upon warming at about 117 K, then to ice Ic at about 150 K and finally to ice Ih above 210 K (Handa *et al.*, 1986). Tse (1992) proposed from numerical modelling that the physical mechanism underlying the formation of HDA from crystalline Ih is the collapse of water molecules into the empty cages in the crystalline structure which is in many ways similar to the structure simulated for the I_ah by Jenniskens and Blake (Jenniskens *et al.*, 1995). To further advance our knowledge of the verity of amorphous structures of ice, understanding it dynamical properties (i.e. water–water interactions) is equally important.

As one knows, measurements of vibrational spectra constitute one of the most powerful ways of investigating pairwise interactions of interatomic potentials in given materials, because the frequencies of the vibrational

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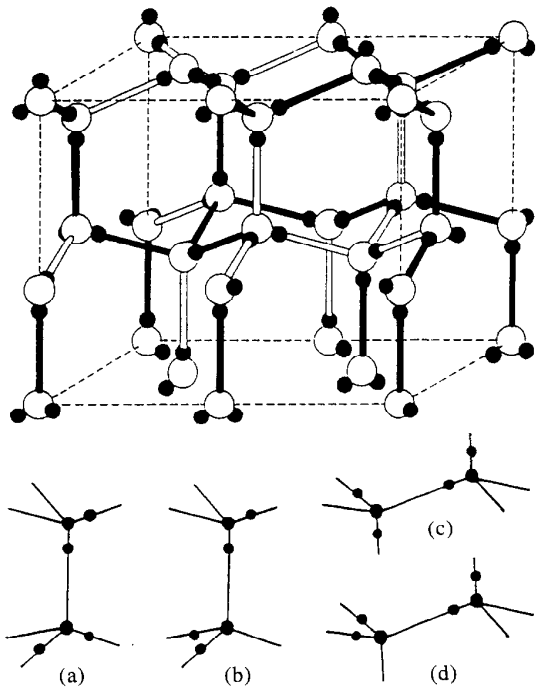

Fig. 1. Schematic diagrams for ice Ih (space group $P6_3/mmc$) and for the four possible hydrogen configurations in ice

modes are determined by the interatomic forces which in turn are determined by the double differentials of the pairwise potentials (i.e. $-d^2v/dr^2$). Inelastic Incoherent Neutron Scattering (IINS) is a powerful technique for the study of water ice, because it is sensitive to translational (lattice) modes which are controlled by the strength of hydrogen bonds. There are weak and strong bonds, depending on the nearest neighbour configuration of the hydrogen atoms in the tetrahedrally bonded network (see Fig. 1), and we have interpreted features in the IINS spectra as to be due to these two types of hydrogen bonds (Li and Ross, 1993). We now have found that this makes IINS a useful tool for probing the structure of High Density Amorphous Water Ice (I_ah), the form of amorphous water ice postulated to be present in nature both as a frost on interstellar grains (Jenniskens *et al.*, 1995) and in some Kuiper Belt comets that were formed at large heliocentric distances (Jenniskens and Blake, 1994). The IINS spectra of high density amorphous ice are found to differ dramatically from those of the low density amorphous form, to which the high density form transforms upon warming. An understanding of the physical properties of these two amorphous water ice structures is essential in interpreting the complex outgassing phenomena observed in comets and in laboratory experiments that address cometary ices (Bar-Nun *et al.*, 1985; Kouchi *et al.*, 1994; Jenniskens and Blake, 1994).

Since the recent development of high flux pulsed neutron sources and high resolution neutron scattering instruments, there is renewed interest in examining the dynamical properties of ice using these techniques (Kolesnikov *et al.*, 1992; Li *et al.*, 1991, 1992). This is because thermal neutrons are unique for the study of molecular solids. The thermal neutron energy is comparable to the phonon energy and the wavelength associated with the neutron is of the same order as the interatomic distances in the condensed materials. Also, the neutron mass is of the same order as the mass of the scattering nuclei. The scattering is, therefore, sensitive to the structure of the system. In an inelastic scattering experiment, the variation of scattering intensity with neutron energy, $\hbar\omega$, and momentum transfer is observed. Neutron scattering is characterized by the range of ω and Q in which measurements are carried out. Note that for molecular phenomena, the relevant energies are of the order of 10^{-4}–10^{-1} eV and the wavevectors are of the order of 10^{-3}–10^{-1} Å. Therefore, neutron scattering is unique in that it can probe the dynamics of molecular solids on short space scales as well as on short timescales.

In its energy and momentum transfer properties, neutrons share some features with infrared photons, as in infrared spectroscopy (Whalley and Bertie, 1967; Bertie *et al.*, 1969; Hagen *et al.*, 1981) and Raman spectroscopy (Klug and Whalley, 1972; Minceva-Sukarova *et al.*, 1984). IINS probes the density of states of the vibrational modes, producing something similar to the infrared spectra that are familiar to astronomers. In fact, all three techniques are sensitive to the intramolecular modes involving the O–H stretching and bending, but infrared and Raman spectroscopy are less sensitive to translational and librational modes in water and the spectra are hampered by optical selection rules. The higher frequencies of the translational modes at about 37 meV (320 cm^{-1}), for example, are not seen in infrared and remains weak in Raman spectroscopy. IINS is a more direct probe of such modes, because the IINS spectrum is directly proportional to the phonon density of states weighted by the mean square amplitude associated with each mode. Hence, IINS measures all modes simultaneously and these lattice modes provide direct information about the H-bond interaction. In their diffraction properties, similarly neutrons share some features with X-rays and electrons, while visible and infrared photons have significantly longer wavelength. However, because of the small charge of the proton, hydrogens are invisible to X-rays and electrons, but can be detected by neutrons.

The measurements

In the last few years, systematic studies of the dynamics of various ice phases have been carried out, including most of the "exotic" high pressure structures of water ice, ice in confined geometry and H-impurity in D_2O ice (Li *et al.*, 1992, 1993, 1994) using the IINS technique at the ISIS facility at the Rutherford–Appleton Laboratory (RAL), Oxfordshire, U.K. In this paper, we report on some newly obtained IINS data for the HDA water ice, prepared by pressure amorphization.

The HDA sample is prepared by pressuring ice Ih at 77 K to about 1.2 GPa. The structure does not change much when the pressure is subsequently reduced to ambient values if the sample is kept cool at liquid nitrogen temperature, because at this temperature protons in the structure are frozen and the orientation of the water molecules with respect to each other will not change further. In liquid nitrogen, the sample was transferred into an Al

container which is mounted on the cryostat central stick. The central stick was quickly inserted into a pre-cooled cryostat (at ~50 K) and then the cryostat cooled down further to its base temperature, ~15 K, for the neutron measurement (the sample area inside the cryostat maintains a ~20 mbar He gas pressure for thermal conduction between the sample and the cryostat). Using such lower temperature is to minimize the multiple phonon scattering and other temperature effects.

The Time Focus X-tal Analyser (TFXA) is used with a fixed scattering angle of 45 deg. This geometry is used for high pressure studies, because it allows an efficient beam collimation and neutron-shielding of the pressure cell components to increase the signal to background. The use of time and energy focusing, in conjunction with a pyrolytic graphite analyser in indirect geometry, enables us to make IINS measurements from very low energy transfer of about 2 meV (in the far-infrared region) with a resolution of about 1% ($\Delta E/E_i$) right up to energy transfers up to 150 meV or above (we would like to emphasize that a different IINS instrument will have different resolutions and intensities at different energy transfers). The LDA form is obtained by heating the sample up to 120 K in the cryostat for a few minutes at 1 K min^{-1}, at which point the HDA transforms into LDA. The sample is subsequently cooled to 15 K before measurement. Cubic and hexagonal crystalline forms are obtained by warming to 160 and 250 K, respectively.

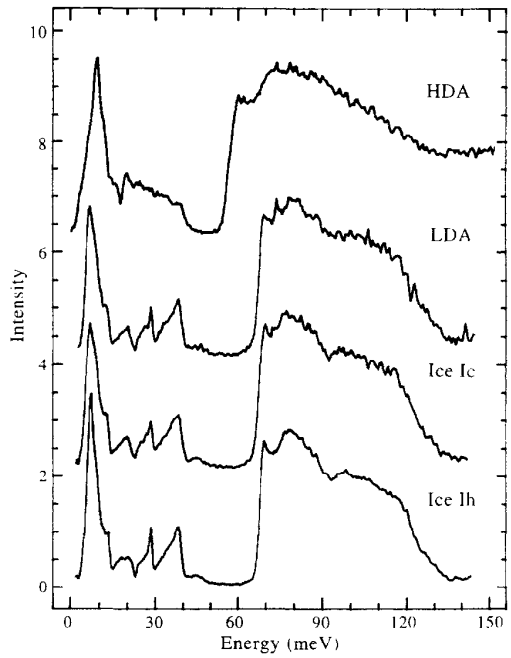

Fig. 2. IINS spectra of high density amorphous (HDA) ice, low density amorphous (LDA) ice, ice Ic and Ih. The measurements show that spectra for LDA, ice Ic and Ih are almost identical in the measured region. However, the spectrum for the HDA ice is significantly different from the others in the translational and librational regions

Results and discussion

Previous IINS measurements of LDA, Ic and Ih showed a gradual narrowing of the two peaks in the optic part of the translational band (Klug *et al.*, 1991). We find, instead, that the IINS spectra of LDA, Ic, and Ih are fundamentally the same (Fig. 2), with almost the same energy positions for peaks in the acoustic and optic part of the translational band and the same band width for the librational modes (see Table 1). We confirm that the translational band in HDA, on the other hand, is distorted and the two peaks are washed out (Klug *et al.*, 1991). What remains is a plateau of density of states. We also found that the translational acoustic band is shifted to higher energy as compared to that in the other three forms. Finally, we found the whole librational band of HDA is displaced to lower energy transfers (see Table 1).

This corroborates observations in infrared spectroscopy, where the 45 μm feature is weak for low temperature deposits and emerges upon transformation to I_aI (Klug *et al.*, 1989; van Grunsven, 1991). Upon crystallization, the feature changes further with a sharper peak emerging from the short wavelength side, which we do not confirm.

We interpret the shift of the librational band as to merely reflect the higher density of HDA. The magnitude of the shift suggests a density increase of 21%, this is based on the assumption that the shift of the librational band is mainly due to the increase of the total initial water molecules in the unit cell. A similar value can also be obtained from scattering transmission in comparison with the HDA and ice Ih, because the transmission is directly proportional to the density of the measured sample. From other experiments, a density difference of 22% was found (Mishima *et al.*, 1984, 1985), it is in good agreement with our results. The density of HDA is similar to that of ice VIII (see Fig. 3), the IINS spectrum of which we show for comparison. However, HDA is not an amorphized ice VIII because HDA misses the order in the librational band. Also, the acoustic band of ice VIII (at 14.5 meV) is at much high energy position in comparison with the same band for the HDA at 9.5 meV. The disappearance of the two peaks in the translational modes is a tell-tale feature

Table 1. The main features of the IINS spectra for the measured samples (meV)

Main features	Ice Ih	Ice Ic	LDA	HDA	Ice VIII
Acoustic peak	7.1	7.1	7.1	9.5	14.5
Molecular optic peak #1	28	28	28	—	21.0
Molecular optic peak #2	37	37	37	19–38	27.0
Librational band	68–120	69–120	69–120	57–	56–

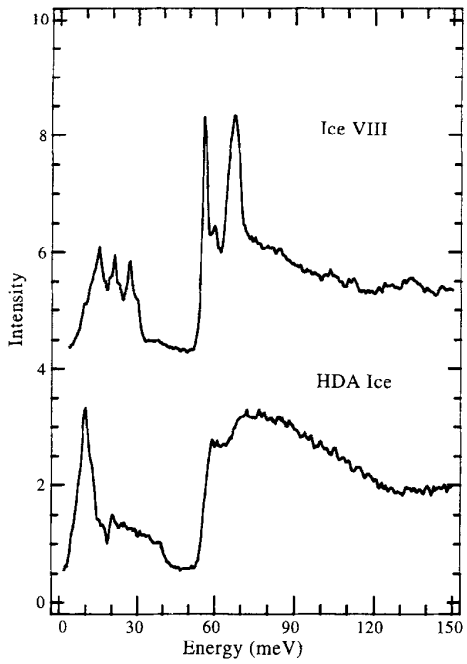

Fig. 3. Comparison of the spectra for ice VIII and HD. The translational modes are shifted to lower energy from 38 meV for HDA (and most of the other ices) to 28 meV. The left cut-off for the librational band is almost the same, i.e. both have the large shifts of about 12 meV to the low energy region from 68 meV, in comparison with LDA and ice Ic and Ih

of HDA. If the interpretation of the two features in the IINS spectra at 28 and 37 meV (220 and 310 cm^{-1}) in terms of two types of hydrogen bonds in water (Li and Ross, 1993) is correct, then this result implies that there is a significant torsion in the hydrogen bonding network, a torsion which is completely removed when the ice transforms in the (disordered) low density amorphous form. This result supports models that describe the formation of HDA from ice Ih are due to the collapse of the hydrogen bonded network (Tse, 1992). Notably, molecular dynamics calculations of HDA show a conspicuous lack of the large cavities that are characteristic for the higher temperature LDA, Ih and Ic forms of water ice (Jenniskens *et al.*, 1995). It is likely that vapour deposited high density amorphous ice has a similar torsion of hydrogen bonding, but further experiments are warranted to probe the structure of this form of ice, which is the most abundant form of water ice in the universe.

The results of our experiment suggest that the dynamical properties of water ice are dominated by the local (short range) order of the ice structures. Despite the significant differences in the long range order of ice Ic, Ih and LDA, their spectroscopic properties are almost identical. This similarity can even extend to the small water droplets or clusters (Li *et al.*, 1994) which may be present in space. The spectral features change from normal ice Ih (or Ic) only when the local structures are distorted, as it happens in HDA and other high pressure forms of ice II, III, etc., because the distortion of local structures of water ice results in changes of hydrogen strengths among the water molecules. This indeed happens in the HDA structure as suggested by the simulations of Tse (1992) and Jenniskens *et al.* (1995). The concept should equally apply to IR and Raman spectra. This implies that we can only distinguish spectroscopically the structures of water ice in space when their local structures significantly depart from normal ice Ih and Ic, such as HDA and the high pressure phases of ice.

Acknowledgements. We wish to thank David F. Blake, and the staff at RAL for making these studies possible. P.J. is with the SETI Institute and works at NASA/Ames Research Center under NASA Agreement NCC 2-572. This work is funded by Engineer Physics Science Research Council, U.K.

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