AIP | The Journal of Chemical Physics

Absolute measurements of the stretching mode density of states in polycrystalline ice Ih

C. Andreani, P. Bosi, F. Sacchetti, and C. K. Loong

Citation: The Journal of Chemical Physics **83**, 750 (1985); doi: 10.1063/1.449488
View online: http://dx.doi.org/10.1063/1.449488
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/83/2?ver=pdfcov
Published by the AIP Publishing

Absolute measurements of the stretching mode density of states in polycrystalline ice Ih[a)]

C. Andreani
ENEA Casaccia, Divisione Scienza dei Materiali, Via Anguillarese 301, Roma, Italy

P. Bosi
Gruppo Nazionale de Struttura della Materia del CNR di Roma, Italy

F. Sacchetti
Dipartimento de Fisica dell'Universitá di Perugia, Italy

C. K. Loong
IPNS, Argonne National Laboratories, Argonne, Illinois 60439

(Received 4 September 1984; accepted 27 March 1985)

An incoherent inelastic neutron scattering experiment on polycrystalline ice Ih at $T = 20$ K is reported. The experiment was performed on the high-resolution chopper spectrometer at the Intense Pulsed Neutron Source (IPNS) of the Argonne National Laboratory. Scattering functions in the angular range from 4° to 20° were converted, after analytical corrections, into density of states of the system in the stretching frequency region. Analysis of these results leads to the following conclusions: (i) the number of modes in the stretching region of ice Ih is 8.1/cell which is that expected in the case of free molecules; (ii) the general shape of the density of states is in qualitative agreement with Raman scattering results, however the high energy side of the neutron data suggests that a non-Raman active band exists at about 3500 cm^{-1}; (iii) the overall bandwidth observed in this experiment is in good agreement with what we estimated by a coherent inelastic neutron scattering study on heavy ice Ih.

I. INTRODUCTION

In the last years several experimental and theoretical studies on the static as well as on the dynamic behavior of ice Ih have been performed.

A recent crystallographic study by Kuhs *et al.*[1] on light ice completed the information previously obtained on heavy ice[2] so that the static average structure of this system can be considered fairly well assessed. In addition to this, neutron scattering studies performed by means of neutrons[3,4] shows a disordered arrangement of deuterium atoms in heavy ice so we can state that the structure of ice Ih resembles Pauling's model closely.

Ice Ih is extremely interesting since it might be considered as a prototype for systems showing ice disorder.[5] Many hydrogen-bonded systems have this structural feature and for them the hydrogen bond can also provide two equilibrium positions for a proton which is tunnel between allowed sites.[6] Nevertheless, this proton behavior in the case of ice has not been established unambiguously so far.[4]

We may expect the presence of such complex structural features to affect the internal modes of water molecules in ice, in particular the O–H stretching. In fact, the dynamics in this frequency region may be dependent on the proton positions, whereas the intermolecular modes are essentially determined by the center of mass motion of the molecules. However, as far as we are aware, no clear experimental evidence of this effect has been found.

Recent Raman scattering studies[7] indicate that most of the Raman spectra features are accounted for by a coupling of stretching modes with optical translational phonons at about 200 cm^{-1}. At the same time it seems that a rather sharp distribution of oxygen–oxygen (O· · ·O) nearest neighbor separation exists, thus giving rise to a somewhat broadened spectrum for localized OH (OD) stretching modes in D_2O (H_2O) matrices. The high quality of these data makes Raman scattering and infrared absorption[8] results extremely useful although it is clear that a theoretical interpretation is limited by the complexity of the radiation-matter coupling phenomenon. Therefore absolute experiments like those employing neutron scattering techniques are highly desirable.

The first complete analysis of the dynamical behavior of ice Ih was certainly that reported by Harling.[9] However that experiment was performed at $T = 268$ K and thereby the stretching band was clearly affected by the coupling with low energy modes. This fact has been confirmed by a recent experiment performed at 80 K[10] where a sharper stretching frequency distribution was measured. On the other hand, in the latter study no attempt was made to obtain the absolute density of states for the stretching modes. The possibility of deducing a good density of states from neutron scattering experiments is strongly connected to the availability of the scattering function at low momentum transfers. This implies a low scattering angle together with a high incoming energy. Bearing in mind these requirements we performed a measurement of the incoherent neutron scattering function of polycrystalline ice Ih using an incident energy of 800 meV. The sample was held at the temperature of 20 K in order to reduce the contribution from multiphonon processes and the effects due to the Debye–Waller factor. The latter contribution to our scattering function will be discussed in the following section.

[a)] This research was supported by the Gruppo Nazionale di Structtura della Materia (GNSM) del CNR.

The aim of the present experiment was an absolute determination of the density of states of the O–H stretching modes in order to estimate the total number of modes as well as the shape of the density function. Although the present experiment contains information on the whole dynamical behavior of the protons, in this analysis we only discuss the stretching region since, it has been more widely studied by Raman scattering and infrared absorption and therefore a comparison with these results can be attempted. In particular, it has been shown that in disordered systems the symmetry-projected density of states can be deduced, under certain assumptions, through a careful analysis of polarized and depolarized Raman spectra in a single crystal.[11]

Therefore in principle we can compare absolute density of states measured by means of either a neutron or a Raman scattering experiment, in order to obtain the relative weight of the various symmetry projected bands.

II. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

The measurements were performed using the high-resoltuion medium-energy chopper spectrometer (HRMECS) at the Pulsed Spallation Neutron Source of the Argonne National Laboratory (IPNS)[12] This neutron source provides a large amount of ephitermal neutrons at high energies which are essential to the present experiment. The sample was contained into 140 quartz capillary tubes with internal diameter 0.08 cm and wall thickness 0.01 cm. Tubes were arranged into two rows, mounted in an aluminum holder perpendicular to the beam and sealed under helium gas atmosphere. Sample area in the beam was 5×7 cm^2. During the measurement, the temperature of the sample was kept at 20 K with an accuracy of 0.05 K. A phased Fermi chopper produces pulses of monochromatic neutrons at an incident energy of 800 meV. The energy resolution is about 14 meV (FWHM) at the stretching frequency (400 meV). 96 ^{3}He gas counters were used for recording the time of flight scattered spectrum covering an angular range from 4° to 20°. The details of the IPNS chopper have been given elsewhere.[13]

We obtained an absolute scattering function by means of a standard background subtraction and normalization from the scattered intensities of the sample, empty container, and vanadium.[14] Since the incoherent scattering is not strongly momentum dependent we grouped the counters into eight groups at the following scattering angles: $2\theta = 4.3°$, 6.9°, 9.0°, 10.9°, 12.9°, 15°, 16.9°, 19.0°. The normalized scattering functions $S(Q,E)$ were then obtained and written as

$$S(Q,E) = \frac{d^2\sigma}{d\Omega dE} \frac{K_0}{K_1} \frac{4\pi}{\sigma_{\rm inc}}, \tag{2.1}$$

where $\sigma_{\rm inc}$ is the incoherent hydrogen cross section, K_0 and K_1 are the incident and outgoing wave vectors, respectively. Cross sections σ are given in b sr^{-1} meV^{-1} molecule^{-1}. Figure 1 shows the neutron weighted $G(Q,E)$ from polycrystalline ice Ih given by

$$G(Q,E) = (E^2/Q^2)S(Q,E). \tag{2.2}$$

Starting from small momentum transfer Q we observed first a narrower peak ($E \sim 40$ meV) representing translational motions, a broader peak ($E \sim 100$ meV) representing librational motions, a band corresponding to the bending modes ($E \sim 220$ meV), and on the very high energy side the O–H stretching of ice ($E \sim 417$ meV).

In Fig. 2 the scattering functions are plotted vs energy transfer in the energy range 350–480 meV for each detector angle. The latter are not the correct density of states we are looking for since all data still contain a multiple scattering contribution which is not negligible. As the total cross section of ice is dominated by the incoherent scattering of hydrogen atoms we can consider the single scattering function within the incoherent approximation.[15,16] The slab sample geometry implies that any double-scattering process is mainly composed of two single scattering processes 90° apart. At such an angle the momentum transfer is so high that the single scattering is dominated by the single particle contribution.[16] The double-scattering function of such processes can be assumed to be of the following Gaussian form:

$$S_1(E) = A \exp[-b(E - E_0)^2], \tag{2.3}$$

where A is a constant and E_0 is the incoming energy which equals the single particle energy (with neutron mass) at 90°.

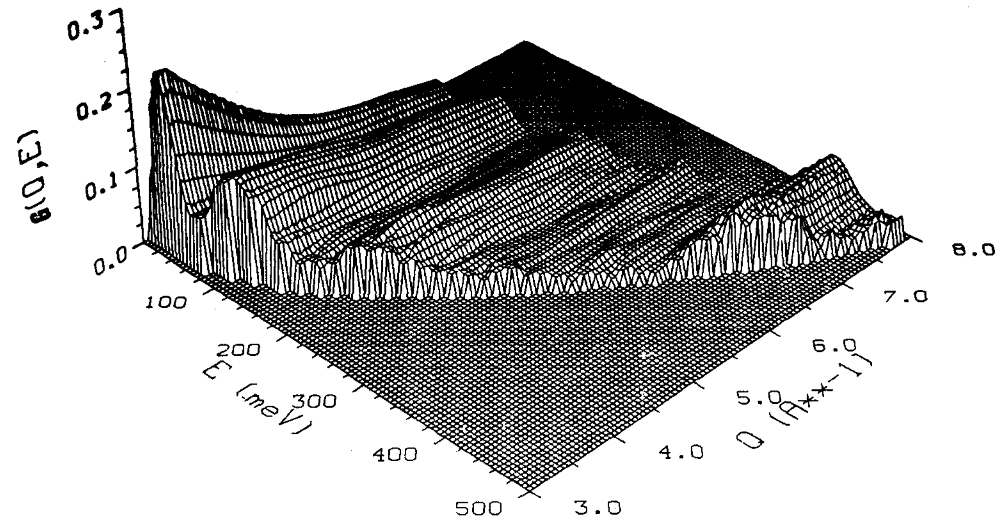

FIG. 1. The neutron weighted $G(Q,E)$ from ice Ih (20 K).

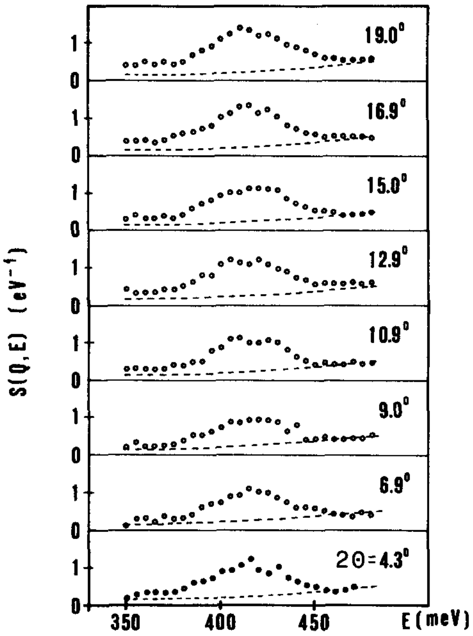

FIG. 2. Scattering functions $S(Q,E)$ at various scattering angles. Dotted line represents the multiple scattering contribution (circles are the magnitude of the error).

The value for b can be deduced by comparison with Harling's data at the same momentum transfer ($b = 4.54 \times 10^{-7}$). Using Eq. (2.3) and the experimental energy dependence of the total cross section we can deduce the double-scattering contribution.[17] In doing this we employed the approach suggested by Sears as applied to an infinite slab.[18] Within the present approximation the multiple scattering is 28% of the total scattering and completely isotropic in our range of scattering angles. In our experiment the procedure employed appears to be adequate and in agreement with the general behavior of the scattering functions as can be seen in Fig. 2.

In order to obtain the density of states of ice, with no other approximation than that implied by neglecting the oxygen motion, we employed the following approach. In general the scattering cross section can be written in the form[15]

$$\frac{d\sigma}{d\Omega dE} = \frac{1}{2\pi\hbar}\frac{K_1}{K_0}\left[\int_{-\infty}^{+\infty}\left(\frac{\sigma_{\mathrm{coh}}}{4\pi}\sum_{ll'}\langle b_l b_{l'} e^{i\mathbf{Q}\cdot\mathbf{u}_l(0)} e^{-i\mathbf{Q}\cdot\mathbf{u}_{l'}(t)}\rangle \cdot + e^{i\mathbf{Q}\cdot(\mathbf{R}_l - \mathbf{R}_{l'}} + \frac{\sigma_{\mathrm{inc}}}{4P}\sum_{l}^{H}\langle e^{i\mathbf{Q}\cdot\mathbf{u}_l(0)} e^{-i\mathbf{Q}\cdot\mathbf{u}_l(t)}\rangle\right)e^{i\omega t}dt\right],$$

where $\mathbf{Q} = \mathbf{K}_1 - \mathbf{K}_0$; b_l, R_l, and $u_l(t)$ are the coherent scattering amplitude, the equilibrium position and displacement from it respectively, and l is a position index running on the N sites of the crystal. σ_{inc} is the incoherent cross section of hydrogen atoms, while the second sum in Eq. (2.4) is restricted to hydrogen sites only. The cross section in Eq. (2.4) can be further simplified by neglecting the oxygen motion. Such an approximation is quite reasonable as far as the internal mode frequency region in concerned since hydrogen atoms are mainly responsible for the dynamics in ice at such high energy. Therefore we can write Eq. (2.4) as

$$\frac{d\sigma}{d\Omega dE} = \frac{1}{2\pi\hbar}\frac{K_1}{K_0}\sum_{l}^{H}\frac{\sigma_{\mathrm{inc}}}{4\pi}\int_{-\infty}^{+\infty}\langle e^{i\mathbf{Q}\cdot\mathbf{u}_l(0)} e^{-i\mathbf{Q}\cdot\mathbf{u}_l(t)}\rangle e^{i\omega t}dt. \tag{2.5}$$

If the phonon Hamiltonian of the system is such that anharmonic contributions can be treated in a perturbative way we have[15]

$$\left(\frac{d\sigma}{d\Omega dE}\right)_{\mathrm{inc}} = \frac{1}{2\pi\hbar}\frac{K_1}{K_0}\frac{\sigma_{\mathrm{inc}}}{4\pi}\int_{-\infty}^{+\infty} e^{-2W(\mathbf{Q})} \times\left[\sum_l e^{\langle \mathbf{Q}\cdot\mathbf{u}_l(0)\mathbf{Q}\cdot\mathbf{u}_l(t)\rangle} - 1\right]e^{i\omega t}dt, \tag{2.6}$$

where the first factor in the integrand is the Debye–Waller factor. Since from the Bragg scattering the proton Debye–Waller factor looks almost isotropic, we can write

$$\frac{d\sigma}{d\Omega dE} = \frac{1}{2\pi\hbar}\frac{K_1}{K_0}\frac{\sigma_{\mathrm{inc}}}{4\pi}e^{-\langle u_H^2\rangle Q^2/6} \times\sum_{l}^{H}\int_{-\infty}^{+\infty}\left[e^{\langle \mathbf{Q}\cdot\mathbf{u}_l(0)\mathbf{Q}\cdot\mathbf{u}_l(t)\rangle} - 1\right]e^{i\omega t}dt, \tag{2.7}$$

$\langle u^2\rangle$ being the mean-square displacement of the proton. From the data of Ref. 1 we can deduce $\langle u^2\rangle = 0.072$ Å^2 in agreement with the value deduced by Ledbetter[19] from specific heat data. Then we have a Debye–Waller factor of the order of 0.4 in the present Q range. Bearing this in mind we divide our cross section data by the isotropic Debye–Waller factor and by K_1/K_0 and eventually extrapolate and resulting contribution to zero momentum transfer. This procedure reduces considerably the uncertainty due to the extrapolation procedure. In fact a considerable part of the Q dependence in the data is accounted for by the Debye–Waller factor. In doing that the leading contribution in Eq. (2.7) is given by

$$S_0(Q,\omega) = \frac{\sigma_{\mathrm{inc}}}{4\pi}\frac{1}{3}Q^2\sum_{l\alpha}^{H}\int_{-\infty}^{+\infty}\langle u_l^\alpha(0)u_l^\alpha(t)\rangle e^{i\omega t}dt, \tag{2.8}$$

where α indicates the Cartesian coordinates. Equation (2.8) has been obtained by spherical averaging of the cross section and by neglecting the elastic contribution to the scattering. We now observe that a simple relation exists between the correlation function $\langle u_l^\alpha(0)u_l^\alpha(t)\rangle$ and the density of states even in a disordered system. In fact we have[20]

$$g(w) = -\frac{2}{3}\frac{\omega}{\pi}\mathrm{Im}\sum_\alpha\langle m_{\mathrm{H}} G^{\alpha\alpha}(ll,w)\rangle, \tag{2.9}$$

where $g(w)$ is the density of states of our system, m_{H} is the hydrogen mass, and $G(11,w)$ is the displacement–displacement Green's function, which is simply related to the corresponding correlation function. In Eq. (2.9) $\langle\cdots\rangle$ indicates the average with respect to all possible configurations of protons. Equation (2.9) also gives the hydrogen projected density of states exactly if l is a hydrogen site (however, as already observed, in the present energy range the only motion is that of the hydrogen atoms). Finally we can express Eq. (2.8) in terms of the density of states:

$$S_0(Q,w) = \frac{\sigma_{\mathrm{inc}}}{4\pi}Q^2\frac{1}{2m_{\mathrm{H}}}\frac{g(w)}{w}[m(w)+1]. \tag{2.10}$$

From Eq. (2.10) the absolute density of states is immediately obtained and the result is shown in Fig. 3. Here we see a

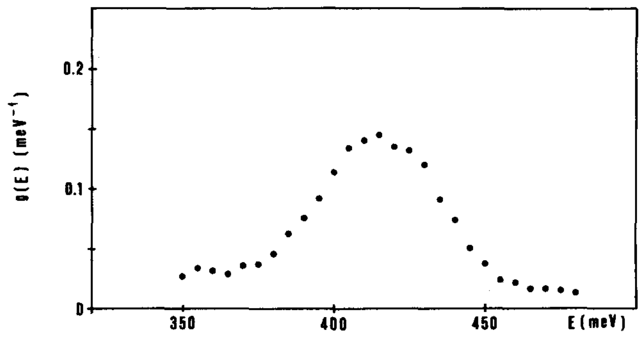

FIG. 3. Density of states of ice Ih in the stretching frequency region (full circles are the magnitude of the error).

single peak present although there is evidence of "some structure" in the high energy side of the band. In our analysis we have to bear in mind that no attempt has been made to remove the effect of the instrument resolution function which amounts to about 14 meV in the energy range of stretching modes.

III. RESULTS AND DISCUSSION

Using the present density of states data we can obtain the number of modes in the stretching region. By integrating the $g(w)$ we get

$$\int_{350}^{450} g(E)dE = 8.1/\text{cell}, \tag{3.1}$$

where the indicated energy range is in meV. This number equals that expected in a unit cell of ordered ice, therefore indicating that the intermolecular interaction does not modify the relevant characteristics of the internal modes although it is important, together with disorder, in determining the shape of the density of states. Unfortunately, the present data cannot be used to obtain the relative contribution of molecular coupling and disorder to the density of states.

The general shape of the density of states, as seen in Fig. 3, in qualitative agreement with Raman scattering results apart from the strongly polarized peaks at about 385 (3100 cm^{-1}) and 400 meV (3200 cm^{-1}) that correspond to zone center modes. Furthermore, the high energy side of the neutron data appears to be more extended than in Raman experiment. This fact suggests that a nonactive Raman band may exists at about 435 meV (3500 cm^{-1}) and the density of states extends up to 450 meV (3600 cm^{-1}). This high energy tail could be connected to the presence of a strong interaction between stretching modes and bending overtones as indicated by the calculation of Ref. 21. This latter calculations however, largely based on a comparison with Raman and IR experiments, fails to account for the shape of the total density of states. The presence of high energy modes was also observed in a coherent inelastic neutron scattering experiment performed recently on heavy ice Ih where a nondispersive branch at about 310 meV (2500 cm^{-1}) was observed.[22] Although the latter experiment did not allow any determination of the density of states we can assess that the overall bandwidth observed in heavy ice is in good agreement with the one obtained in the present study.

In conclusion we believe that further theoretical analysis is essential since new unexpected features have shown up in both coherent and incoherent neutron scattering experiments. Moreover, further experimental analysis is needed, possibly with better resolution, in both light and heavy ice Ih. In particular, the high energy tail of the stretching band needs to be more carefully understood.

ACKNOWLEDGMENTS

The authors are grateful to IPNS scientific staffs and to Dr. J. Teixeira and Dr. S.-H. Chen for their sample in use.

[1]W. F. Kuhs and M. L. Lehmann, J. Phys. Chem. **87**, 4312 (1983).
[2]S. W. Peterson and H. A. Levy, Acta Crystallogr. **10**, 70 (1957).
[3]J. Schneider and C. Zeyen, J. Phys. C **13**, 4121 (1980).
[4]F. Sacchetti, V. Mazzacurati, F. Menzinger, and M. A. Ricci, J. Phys. C **15**, 1 (1982).
[5]J. M. Ziman, *Model of Disorder* (Cambridge University, Cambridge, 1979).
[6]H. Grim, H. Stiller, and T. H. Plesser, Phys. Status Solidi **42**, 207 (1970).
[7]T. C. Sivakumar and S. A. Rice, J. Chem. Phys. **69**, 3470 (1978).
[8]J. E. Bertie and E. Whalley, J. Chem. Phys. **40**, 1637 (1964).
[9]O. K. Harling, J. Chem. Phys. **50**, 5279 (1969).
[10]C. Andreani, B. Boland, F. Sacchetti, and C. G. Windsor, J. Phys. C **16**, 2513 (1983).
[11]V. Mazzacurati, C. Pona, G. Signorelli, G. Briganti, M. A. Ricci, E. Mazzega, M. Nardone, A. De Santis, and M. Sampoli, Mol. Phys. **44**, 1163 (1981).
[12]IPNS, Progress Report 1981–1983, Argonne National Laboratory (1983).
[13]D. L. Price, J. M. Carpenter, C. A. Pellizzari, S. K. Sinha, I. Bresof, and G. E. Ostrowski, Proceedings of the Sixth Meeting of the International Collaboration on Advanced Neutron Sources, June 28–July 2, 1982, ANL-82-80 (1963), p. 207.
[14]J. R. D. Copley, D. L. Price, and J. M. Rowe, Nucl. Instrum. Methods **107**, 501 (1973).
[15]W. Marshall and S. W. Lovesey, *Theory of Thermal Neutron Scattering* (Clarendon, Oxford, 1971).
[16]J. M. F. Gunn and M. Warner, Z. Phys. B **56**, 13 (1984).
[17]K. Heinloth and T. Springer, *IAEA Inelastic Neutron Scattering Conference* (IAEA, Vienna, 1961), p. 323.
[18]V. F. Sears, Adv. Phys. **24**, 1 (1975).
[19]A. J. Leadbetter, Proc. R. Soc. London Ser. A **287**, 403 (1965).
[20]D. W. Taylor, *Dynamical Properties of Solids*, edited by G. H. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1975), Vol. 2, p. 285.
[21]M. S. Bergren and S. A. Rice, J. Chem. Phys. **77**, 583 (1982).
[22]C. Andreani, P. Bosi, E. Mazzega, F. Sacchetti, and C. G. Windsor, J. Phys. C **16**, 3055 (1983).