Proton Dynamics in Water and Ice Studied by Inelastic Scattering of Slow Neutrons

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The proton dynamics of water at 273.4°K and ice at 268.7°K have been studied by scattering of cold neutrons. It is shown that the sharp peaks in the ice spectrum are flattened out on melting and that the spectra from ice and water are thus significantly different. The main features of the spectra are rather independent of the scattering angle, and it is therefore concluded that multiphonon scattering cannot explain the divergency of earlier results on water close to the freezing point.

INTRODUCTION

WHEN neutrons are inelastically scattered by protons in water and ice, an exchange of energy between the neutrons and the lattice vibrations, characteristic of the proton motions, takes place. During the interaction, the energy of a phonon—that is, a quantum of the lattice vibration energy—is either absorbed or emitted by the interacting neutron. In the liquid phase there is also a contribution from the diffusional motion of the molecules. This gives rise to small-energy-transfer scattering, usually referred to as quasielastic scattering.

Thus by studying the momentum and energy changes of the neutrons on scattering, information is obtained about the corresponding quantities for the phonons. From this information, knowledge about the states of motion of the protons can be deduced.

In the scattering process, the following momentum and energy relationships must be obeyed:

$$E=(\hbar^2/2m)(k^2-k_0^2), \tag{1}$$

$$p=\hbar(\mathbf{k}-\mathbf{k}_0)=\hbar\boldsymbol{\kappa}, \tag{2}$$

where E and p are the energy and momentum of the phonon, $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors for the incident and scattered neutron, and $\hbar\boldsymbol{\kappa}$ is the momentum transferred in the scattering process.

In the case of a cubic monoatomic crystal (Bravais lattice), it is possible to calculate the phonon-frequency distribution from the observed neutron spectrum. The double-differential incoherent-scattering cross section derived by Placzek and Van Hove[1] in 1954, and by Sjölander[2] in 1958, has been used as a basis for the general interpretation of the experimental data from such measurements. Larsson and Dahlborg[3] assumed that the frequency spectrum for ice, $f(E)$, may be derived, to a first approximation, from the observed neutron spectrum by using the formula

$$f(E)\sim\frac{k_0}{k}\frac{k^2-k_0^2}{\kappa^2}(e^{E/k_BT}-1)e^{2W}I(E), \tag{3}$$

where $I(E)$ is the observed intensity per unit energy and unit solid angle at the energy transfer E, and e^{-2W} is the Debye-Waller factor, which in the Debye approximation can be written

$$2W=\tfrac{1}{2}6\hbar^2\frac{T\kappa^2}{Mk_B\Theta_D^2}. \tag{4}$$

Here Θ_D is the Debye temperature, T the sample temperature, and M the effective mass of the scattering unit.

For more complicated crystals the relation between the measured neutron energy distribution and the frequency spectrum is not as straightforward but one may still hope that useful information about the states of motion of the hydrogen atoms can be deduced. In particular, it should be possible to obtain the positions of the peaks in the frequency spectrum.

While the use of a crystal model for ice is well justified, the description of the lattice vibrations in terms of a Debye spectrum is somewhat ambiguous. The part of the spectrum of ice which consists of acoustic and soft optical vibrations may for the purpose of formulating the scattering theory be approximated by a Debye spectrum, but this is not necessarily true for the band of "hard" optical vibrations with a center of gravity around 26×10^{-3} eV. The dispersion curves for ice have been calculated by Forslind[4] for two distinct directions, the crystallographic a and c axes. He obtained nine optical and three acoustic branches. The acoustic vibrations are concentrated in an energy range around 7×10^{-3} eV, and six hard optical branches have a concentration between $(22\text{–}30)\times10^{-3}$ eV.

Many neutron investigations have been undertaken

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to study proton dynamics in water and ice; among these should be mentioned the experimental studies of Brockhouse[5] (1958 and 1959), Hughes *et al.*[6] (1960), Stearns *et al.*[7] (1961), Larsson *et al.*[8] (1961), Cribier and Jacrot[9] (1961), Stiller and Danner[10] (1961), Larsson and Dahlborg[3] (1962), Sakamoto *et al.*[11] (1962), Bajorek and Golikov and others[12,13] (1963 and 1965), and Stiller[14] (1964 and 1965).

Since Larsson and Dahlborg on the one hand and Golikov and his co-workers on the other have obtained very different results for the spectra of water close to the freezing point, we have repeated these measurements with the time-of-flight spectrometer at the reactor R2 in Studsvik. According to the observations of Larsson and Dahlborg, there should be practically no difference between the spectra scattered from water and the spectra scattered from ice at temperatures near the phase transition, and this was taken as a strong proof that the semicrystalline model of water is a physical reality.

It is evident, from the work of Sakamoto *et al.*,[11] that if these results were correct one must make the assumption of very substantial changes in the dynamics of water between the melting point and room temperature. One would, in particular, have to explain why no broadening of the elastic line is observed in the spectrum of water close to the melting point, while the spectra taken at room temperature show significant broadening. The change of the diffusion constant with temperature is not large enough to explain this difference.

Golikov *et al.* observed, on the other hand, an appreciable difference in their spectra between water and ice, especially in the low-energy-transfer region. They suggested that the discrepancy between their results and those of Larsson may arise from multiphonon processes, which should be more pronounced in their experiment because of the larger scattering angle used. The spectrum of the incident neutron was, in both cases, the full Be-filtered spectrum. Since Larsson and Dahlborg's measurements were performed at a 30° scattering angle, and Golikov's at 75°, we made our measurements at both these angles to investigate the validity of this explanation of the discrepancies.

EXPERIMENTAL

The experimental arrangement was in principle the same as that reported by Holmryd *et al.*,[15] in 1964, the spectrometer being provided in the present instance with a second flight path, which made possible simultaneous studies at two different scattering angles. The scattering target was a thin sample of water or ice, about 0.3 mm thick and 90 cm^2 in area. The sample holder was mounted in a vacuum container. The sample was maintained at constant temperature by circulating alcohol through the frame of the sample holder. The alcohol was cooled in a heat exchanger containing a mixture of solid CO_2 and alcohol. The temperature was measured by thermocouples and automatically controlled by an on-off system. The error, including both the fluctuations and the temperature gradient, was less than 0.2°C.

EXPERIMENTAL RESULTS AND DISCUSSION

The neutron spectra scattered from water at 273.4°K and ice at 268.7°K at the two scattering angles, 30° and 75°, are shown in Figs. 1 and 2. The frequency spectra calculated from these curves, after smoothing of the original points, replacing the graph by a vertical parabola passing through five consecutive points,[16] are shown in Fig. 3.

The neutron spectra in Figs. 1 and 2 are corrected for background, but not for detector efficiency, and the measured neutron intensity is given in absolute counts per channel versus the neutron time of flight in microseconds per meter. The background subtracted is plotted with open circles and is, within the statistics, rather constant over the whole inelastic region of the spectrum. The spectra include a component of low-energy neutrons, which actually belongs to the preceding frame (frame overlap).

To improve the statistical significance of the data, a moving average calculation over three consecutive channels,[16] that is, a curve smoothing by averaging three points and correcting the middle point, has been done in order to get the best average representation of the curves in Fig. 2. The moving-average procedure was also applied to the background subtracted in Fig. 2, but in Fig. 1 the original background points are plotted. This does not destroy significant structure in the curves as the time resolution of the spectrometer is of the order of three channels wide. The statistical errors appro-

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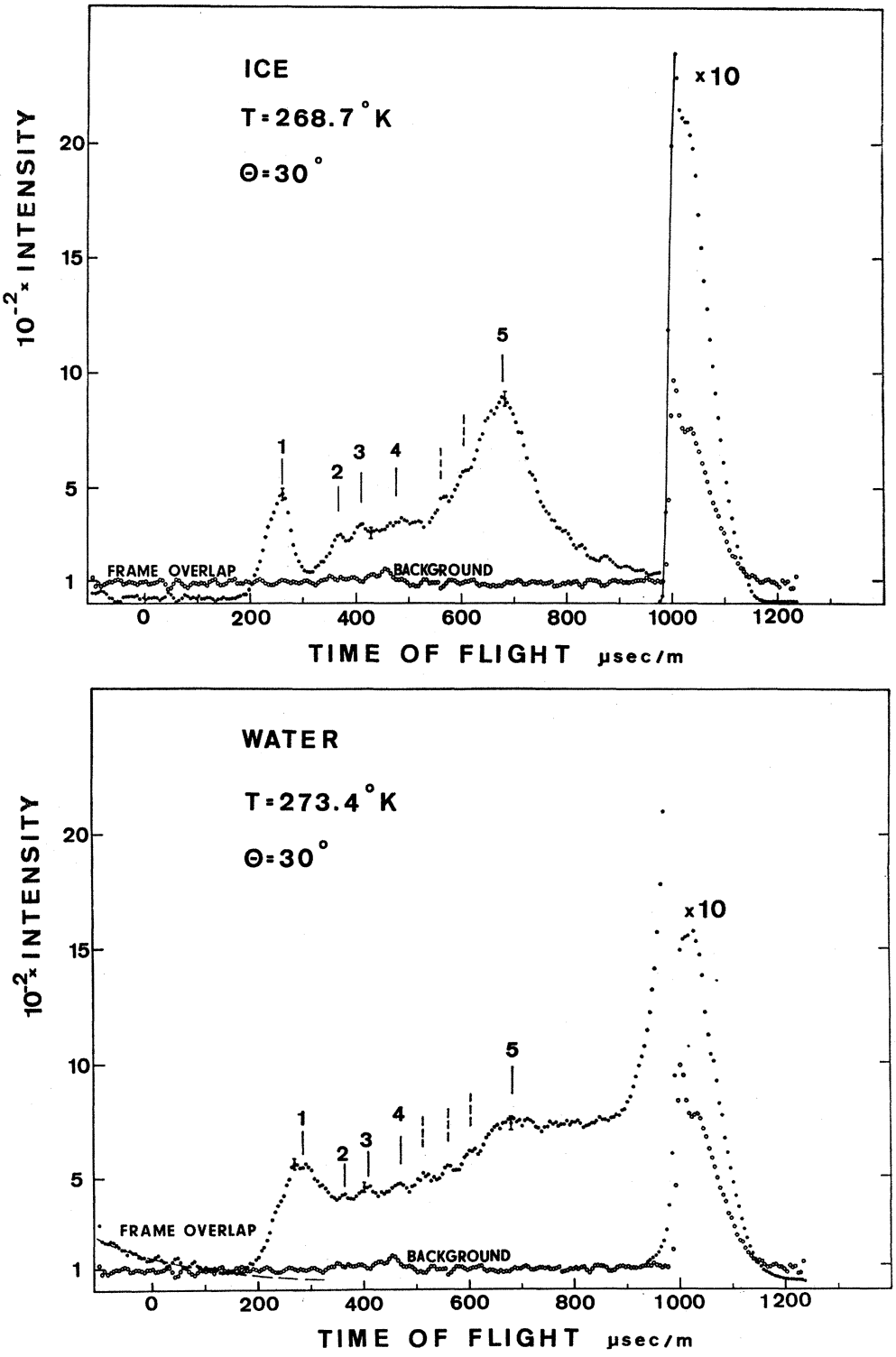
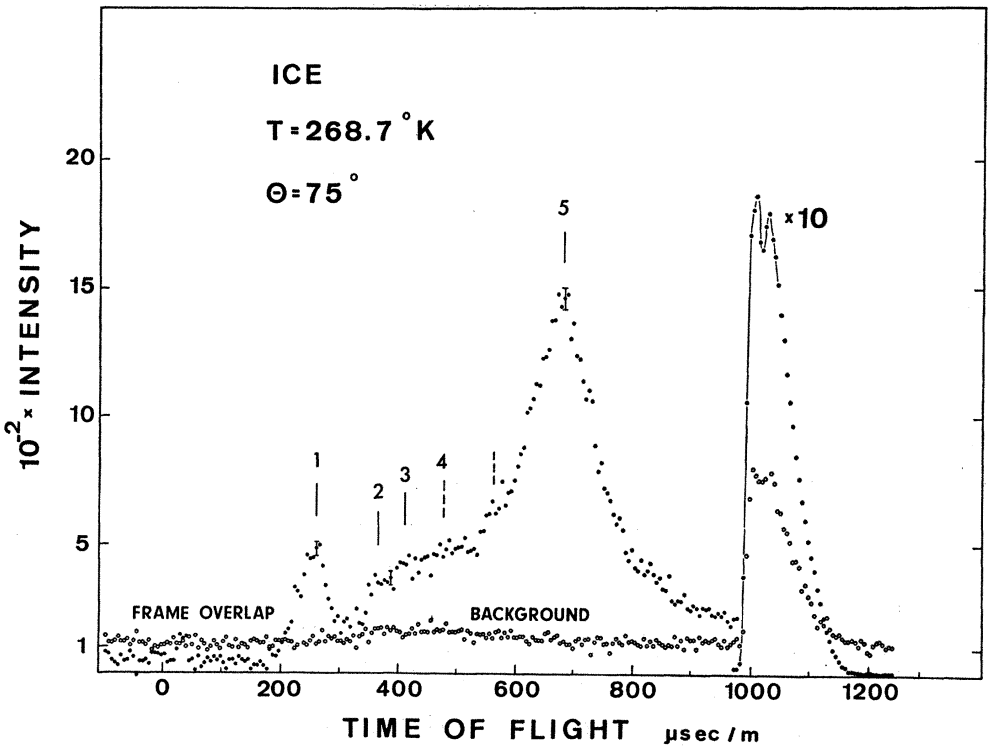


FIG. 1. Neutron intensity in absolute counts/channel versus neutron time of flight in μsec/m for water at 273.4°K and ice at 268.7°K for angles of observation $\theta=30°$, $\theta=75°$. The subtracted background is plotted with open circles. The labelled peaks are discussed in text.



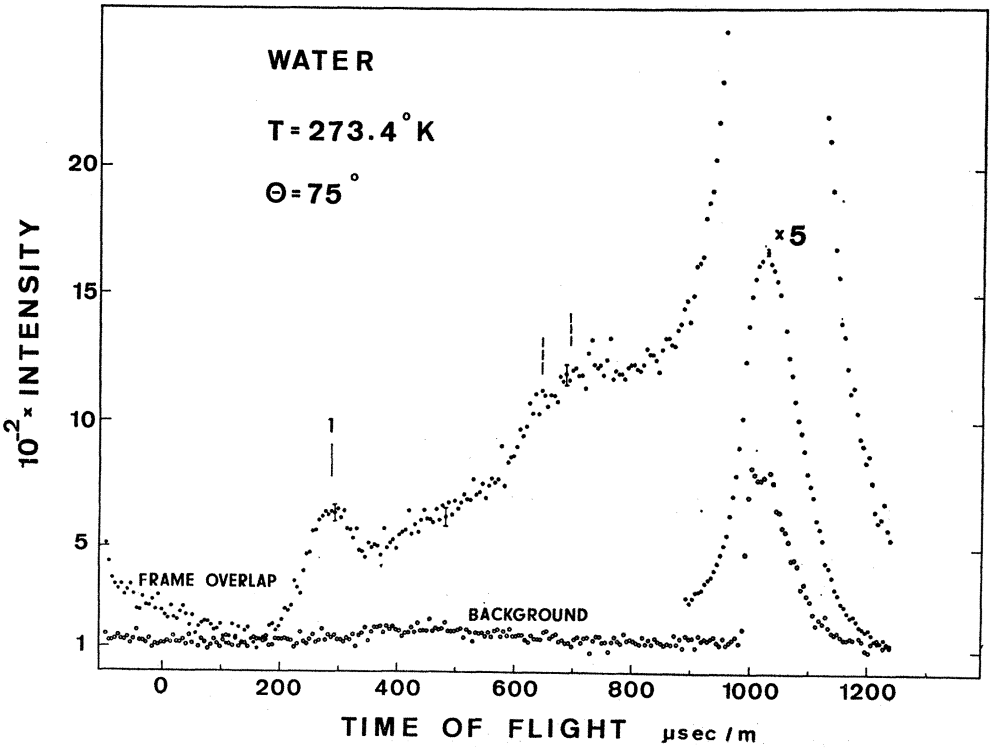


FIG. 1 (*continued*).

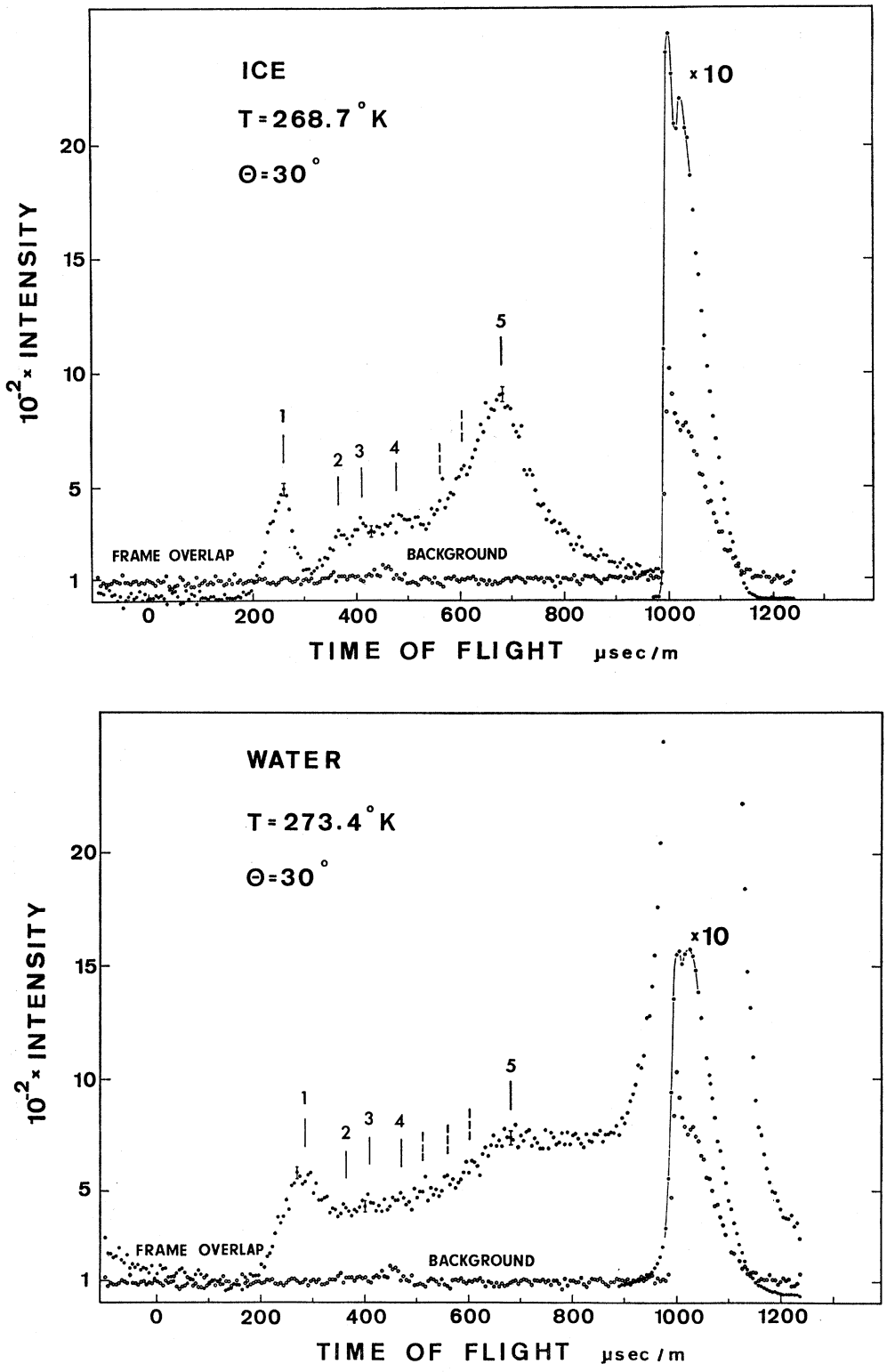
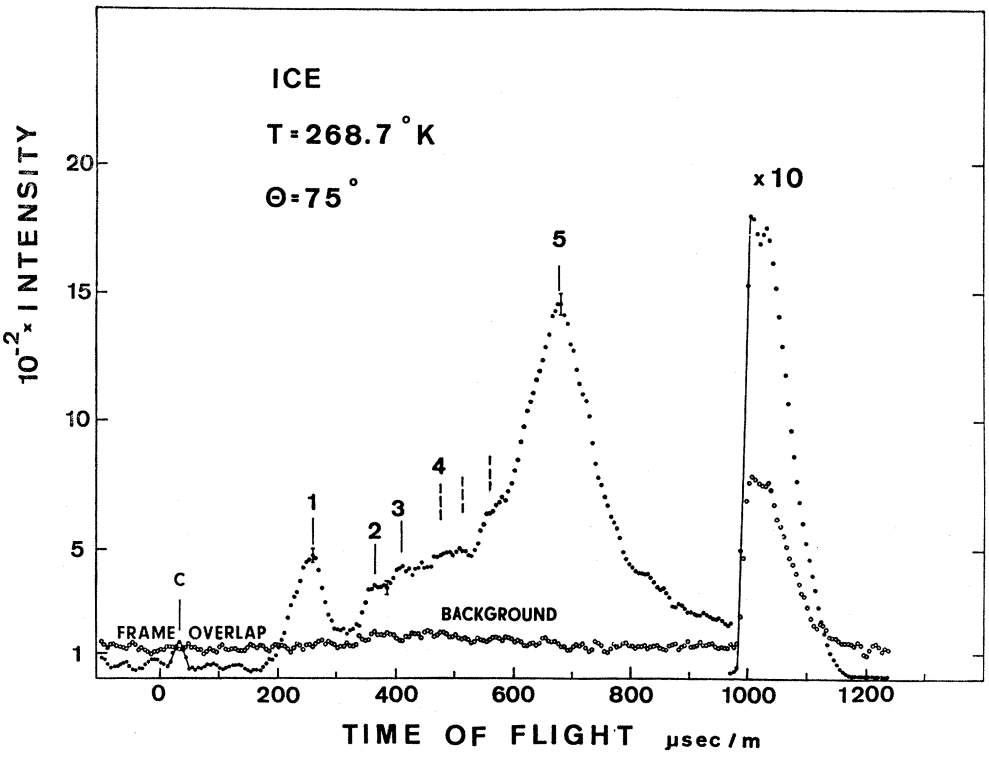


FIG. 2. Neutron spectra obtained by a moving average calculation over three consecutive channels applied to original points shown in Fig. 1. The background subtracted has also been smoothed in the above-mentioned way.



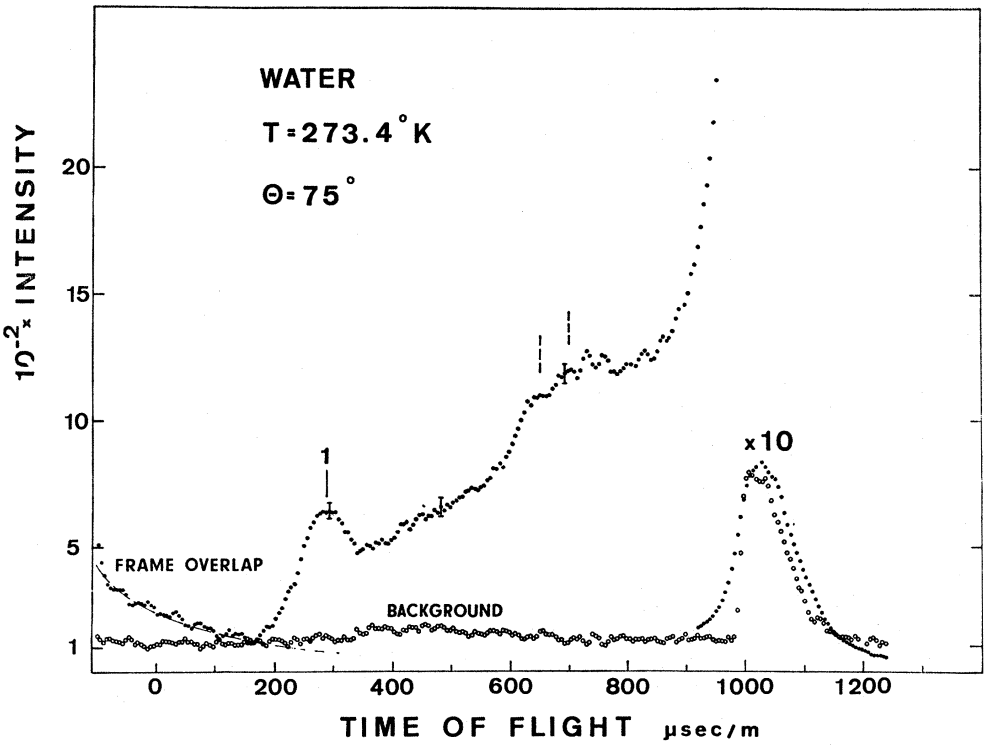


FIG. 2 (*continued*).

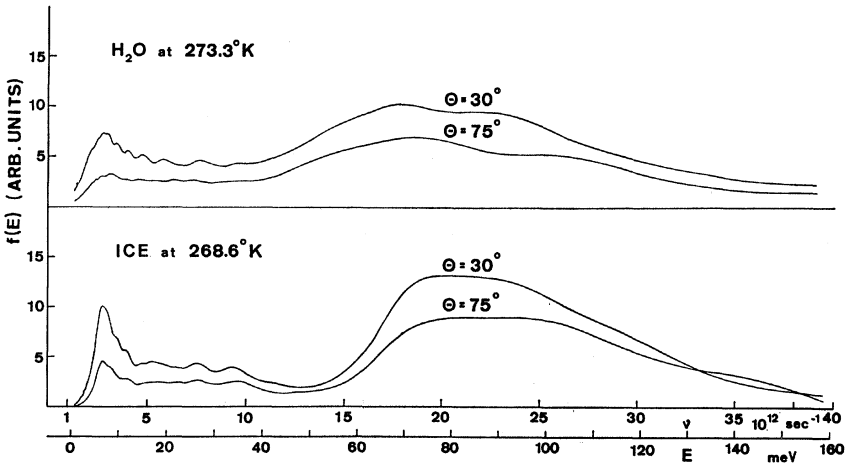


FIG. 3. Frequency spectra for water and ice calculated from the neutron spectra shown in Figs. 1 and 2. The absolute frequency of the neutron is given in sec^{-1} and the energy transferred in the scattering process in meV (10^{-3} eV).

priate to the original points are indicated with error bars in Figs. 1 and 2.

This relatively high resolution made it possible to observe detailed structure in the low-energy region of the neutron spectra from water and ice. It was therefore possible to distinguish many peaks in the energy distribution of the scattered neutrons. Confirmation was obtained for the peaks in ice earlier reported by Stearns *et al.*, at 6.5×10^{-3} eV (peak 5), at 34×10^{-3} eV (peak 2), and 72×10^{-3} eV (peak 1) or expressed in optical wave numbers 52, 275, and 580 cm^{-1}. The appearance of another peak at 26×10^{-3} eV (peak 3) or 210 cm^{-1} could possibly be related to a peak seen in the experiments of Larsson *et al.* There are also indications of a peak at 19×10^{-3} eV (peak 4) or 155-cm^{-1}, one at 11.8×10^{-3} eV or 95 cm^{-1} (~561 μsec/m), and another at 9.6×10^{-3} eV or 77 cm^{-1} (~603 μsec/m).

Golikov *et al.* have reported peaks in the ice spectra at $\sim70\times10^{-3}$, 24×10^{-3}, and 12×10^{-3} eV, and they also state that the high-energy peak is clearly shifted toward lower energy ($\sim60\times10^{-3}$ eV) when passing the melting point. The latter statement is in fact in agreement with our measurements. The existence, or nonexistence, of such peaks in the spectra from inelastic neutron-scattering experiments in water and ice has been commented upon many times in the literature and is an extremely controversial question.

A comparison of the spectra of water and ice gives the interesting information that a few low-energy peaks in water also coincide with those of ice. It is, on the other hand, also obvious from a comparison of the neutron spectra in Figs. 1 and 2 that the spectra from ice and water are rather different. A sharp elastic peak is observed in ice while the peak observed in water is considerably broadened by diffusion. The high-energy peak is at a lower energy in water and is no longer distinctly separated from the optical region around 400 μsec/m. The acoustic peak (~680 μsec/m), which is so clearly defined in the ice spectra, is almost completely smeared out in the spectra from water and overlaps both the quasielastic region and the optical region. The high-energy peak in water is at 60×10^{-3} eV (peak 1) or 480 cm^{-1} and low-energy peaks are at 34×10^{-3} eV (peak 2), 26×10^{-3} eV (peak 3), 19×10^{-3} eV (peak 4), 14.8×10^{-3} eV (~516 μ sec/m), 11.8×10^{-3} eV (561 μsec/m), 9.6×10^{-3} eV (603 μsec/m), and 6.5×10^{-3} eV (peak 5) (in water at $\theta=30°$). Hughes *et al.* reported, among other peaks, a peak in water at 61×10^{-3} eV and another at 21×10^{-3} eV. These should be compared with the peaks found by Larsson *et al.* at 59×10^{-3} and 20×10^{-3} eV.

It should be pointed out that the results for water at 273.4°K, near the freezing point, are, in the main features, in substantial agreement with earlier work for water at room temperature, especially the experiment at 90° angle by Sakamoto *et al.*, even though they did not see any evidence for discrete peaks. It is to be mentioned that we have no indications of the small energy transfers at about $\pm(5\text{–}7)\times10^{-4}$ eV observed by Hughes *et al.*, by Larsson *et al.*, and by Stiller and Danner.

Also, Cribier and Jacrot studied the quasielastic peak of neutrons scattered at 90° from light water at temperatures of 30 and 43°C. At both temperatures they observed considerable line broadening but no trace of the small discrete peaks at 7×10^{-4} eV reported by other workers.

An interesting observation in the present study is the peak which is seen at 34.9 μsec/m (peak C) in the spectra scattered at $\theta=75°$ from ice at all the temperatures studied (143–268.7°K). Both the variation with temperature of the intensity of this peak and a direct determination of the true time of flight show that the peak belongs to the preceding frame and thus is on the energy-loss side. The corresponding energy transfer is 2.2×10^{-3} eV. The peak is very intense at the lowest temperatures and is definitely not spurious. The fact that it is observed at $\theta=75°$ but not at 30° indicates that it is coherent in nature. Although the coherent scattering is expected to be smoother in water compared to ice, it seems possible that coherent scattering could explain some of the discrepancies of the earlier results,

as far as the existence of peaks at small energy transfers is concerned. Small differences in scattering angle and energy distribution of incident neutrons may give rise to rather large differences in coherent scattering.

This experiment thus verifies the results obtained by Golikov, although the differences between water and ice seem to be even more pronounced in the present study. This may be attributed, at least as far as the small-energy-transfer scattering is concerned, to the narrower incident spectrum used in the present experiment. By comparing the results obtained at the two scattering angles, we conclude that the discrepancy between the results obtained by Golikov *et al.*, and those obtained by Larsson and Dahlborg, cannot be accounted for by multiphonon scattering. The very close similarity between the water result and the ice result in the experiment by Larsson and Dahlborg seems to indicate that both results are obtained from H_2O in the solid phase.

FREQUENCY SPECTRA

Before the frequency spectra were calculated from the observed neutron spectra, corrections were made for the energy-dependent detector efficiency and for air absorption in the flight path. A conversion from time to energy distribution was also performed.

Following the procedure of Larsson and Dahlborg, and Golikov *et al.*, the Debye-Waller factor was set equal to unity as in the derivation of the spectrum from the experimental results. This was done in order to facilitate the comparison with the results obtained by these authors.

The ice spectra derived from the 30° run and the 75° run were brought to the best possible agreement in a well-defined energy interval by an adjustment of appropriate parameters, the mass M and the Debye temperature Θ_D, in the expression for the Debye-Waller factor [Eq. (4)]. This was achieved for the acoustic peak at 6.5×10^{-3} with $M=18$ amu and $\Theta_D\sim110°K$, or $M=2.1$ amu and $\Theta_D=330°K$. The same fitting for the high-energy peak (72×10^{-3} eV) gave reasonable coincidence for $M=2.3$ amu and $\Theta_D\sim850°K$. These results confirm the assignment of the high-energy peak to librational motion of the H_2O molecule and the low-energy peaks at 19×10^{-3}, 26×10^{-3}, and 34×10^{-3} eV to translational modes of the entire H_2O molecule, or, in other words, hydrogen-bond-stretching modes of vibrations, while the peak at 6.5×10^{-3} eV could be a hydrogen-bond-bending vibration (rocking motion of the H_2O molecule).

The study of ice has been extended down to 143°K and the spectra of pure ice and ice contaminated with small amounts of KOH have been compared. These measurements will be reported in a separate paper.

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