Low-frequency Raman scattering in normal and deuterated ice I_h

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Low-frequency Raman spectra of H_2O and D_2O single crystals at different temperatures have been measured by using a DMDP2000 spectrometer. Thanks to the performances of the spectrometer, we have been able to measure spectra very close to the elastic line. Present data extend those already measured by Briganti *et al.* [Solid State Commun. **42**, 493 (1982)] to a lower frequency range and to deuterated samples. We demonstrate the existence of a quasielastic component in both deuterated and nondeuterated samples which does not show any appreciable isotopic effect. This allows us to rule out the assignment of the quasielastic component to a relaxing dynamics of the proton- (deuteron) disordered sublattice. On the contrary, the temperature dependence of the intensity of this component suggests to assign it to the quasielastic contribution of the second-order Raman scattering. [S0163-1829(98)05813-5]

I. INTRODUCTION

Ice dynamics has been extensively studied in the last 20 years because of the interest in hydrogen-bonded systems of scientists working in a variety of research fields such as biology, biochemistry, chemistry, and physics. The structural model proposed by Pauling[2] in 1935 puts ice I_h in the category of orientationally disordered crystals. The basic idea of Pauling's model is to preserve the structure of H_2O molecules even in the solid, because of the high energy required to create OH^--H_3O^+ couples. While oxygens are arranged on a perfect hexagonal structure, hydrogens are located along the O-O bonds in a way that determines a disordered orientation of H_2O molecules, thus breaking the spatial translational invariance of the crystal. Therefore the elementary cell of the crystal can be depicted as composed by four water molecules with six possible orientations each, with oxygen atoms placed on the hexagonal lattice. This model has many consequences, both from the theoretical and the experimental points of view. Indeed ice I_h shows peculiarities in the Raman and infrared-absorption (IRA) spectra which are typical of disordered systems. The pioneering work of Whalley and Bertie[3] introduced the orientational disorder of Pauling's model in the calculation of the IRA and Raman cross sections. The authors showed that orientational disorder breaks the momentum selection rule and all the crystal excitations become active both in IRA and Raman scattering. This explains qualitatively the broadband covering the entire frequency range up to about 4000 cm^{-1}, which is an ''anomalous'' feature present in both absorption and scattering spectra. The suggestion of Whalley *et al.* was followed by some of us in 1981 by performing a quantitative analysis of the ice I_h Raman spectrum in the translational frequency region[4,5] and extracting from the spectroscopic data the vibrational density of states, which compares well with that calculated by Bosi *et al.*[6] In Ref. 5 and in a subsequent

paper[1] the authors found evidence of a quasielastic spectral component, very similar to that observed in glasses; in the latter systems it has been tentatively assigned to slowly relaxing energy states (see Ref. 7 and references quoted therein). In this view, the possibility to assign the quasielastic component of ice to the dynamics of the proton sublattice was discussed[1] but the authors recognized that the quality of their low-frequency spectral data as well as the lack of measurements on deuterated samples did not allow one to draw any reliable conclusion about the physical origin of the phenomenon. Indeed, if the assignment of the low-frequency spectrum of ice to the proton dynamics were correct, one had to expect a strong spectral narrowing of the quasielastic component for deuterated samples and the spectral quality required to observe it was unreachable at that time. More recently the development of a new class of light-scattering spectrometers[8,9] has strongly improved the quality of low-frequency scattering data, thus making possible the extension of the spectral analysis even in the case of features narrower than that observed in Ref. 1. In this paper, we present the Raman data of the low-frequency region of H_2O and D_2O single crystals as a function of temperature. A DMDP2000 monochromator[8] is employed as the analyzer. The instrumental contrast and resolution characteristic of this spectrometer allow us to measure the whole frequency range of interest, including the Brillouin lines and the Raman spectrum from 0.1 up to 80 cm^{-1} frequency shift. Brillouin scattering has been used as an internal standard of intensity, in order to compare different temperature data. The data analysis results will be discussed on the basis of the knowledge recently gained on light-scattering spectra of disordered crystals and glasses.

II. EXPERIMENTAL

The measure of light-scattering spectra close to the exciting line requires the use of large optically pure crystals in order to minimize spurious elastic contributions. Ice crystals

were obtained from twice distilled deionized water, and from commercial deuterium oxide (supplied by Merck with 99.8% purity). Growing an ice crystal took place in several steps. At first, in the case of H_2O, liquid water was filtered using a 0.22 μm filter to remove suspended particles. In both cases, for normal and deuterated samples, the liquid was kept for at least 30 min in an ultrasonic cell, maintained at 330 K and slightly depressurized. Then the liquid was placed into a vertically positioned pyrex tube (20 mm diameter, 200 mm height), opened at the top and softly ending up in a thin pipe (about 0.5 mm diameter) at the bottom. The lower end was kept in thermal contact with a copper plate, held at 240 K by means of a Peltier cooler. The whole tube was surrounded with an insulating wrapping to minimize radial thermal gradients, and it was kept at 278 K inside a refrigerator. Growing a 10 cm long ice crystal typically lasted five days. The crystals were then immersed into liquid n-hexane and stored at about 265 K for several weeks in order to anneal point defects and mechanical stresses. Cylindrical samples, about 15 mm in length, were cut from the lower half of the crystals inside a refrigerator using a blade saw, lapped with sand paper and silk cloth to obtain flat surfaced parallelepipeds, and then stored again in liquid n-hexane for a few hours. The single-crystal form of the samples was roughly tested using polarized light, the long edge of the parallelepiped being approximately parallel to the c-axis. The sample was placed into a vacuum stainless-steel optical cell, completely filled with n-pentane of high purity and kept at 268 K, in order to reduce thermal stresses. Moreover, liquid n-pentane preserves the optical ice surfaces from damage due to sublimation, assures a good matching of the refractive index and reduces the scattering and spurious reflections from the sample surfaces. The cell was placed inside a Leybold RG210 cryo-generator, in thermal contact with a cold finger; it was surrounded by a radiation shield and, finally, was slowly cooled down to the chosen temperature. Measurements have been carried out at three different temperatures, namely 170, 225, and 252 K for both normal and deuterated samples; the temperature stability was better than 1 K.

Spectra have been measured using the Raman spectroscopy apparatus already described elsewhere[8,9] and the 488 nm line of a CW Ar ion laser as the exciting line (typical output power about 1 W, in single mode operation). The scattered light was collected in the usual 90° configuration and focused into the monochromator without polarization analysis because of the difficulty in aligning the c axis of the crystal with respect to the scattering geometry; in any case this configuration allows one to collect the maximum scattered signal. Since high resolution is required close to the Brillouin peaks only, each final spectrum, ranging from -80 to 80 cm^{-1} with respect to the exciting line, has been obtained by pasting data of several scans carried out with different frequency ranges, monochromator resolutions, integration times, and frequency steps. Each scan has been corrected for dark counts and monochromator efficiency and then pasted with the procedure described in Ref. 10 to get a single spectrum for each temperature. Typical spectra are shown in Figs. 1 and 2.

III. DATA ANALYSIS AND DISCUSSION

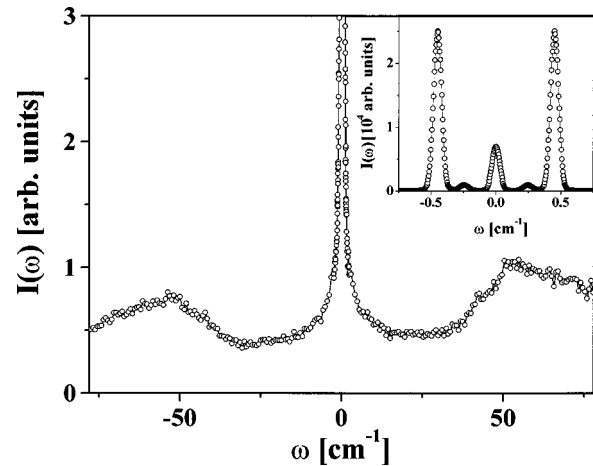Figure 1 shows, as an example, the spectrum of nondeuterated ice at $T=252$ K. The optical quality of the sample is

FIG. 1. Light-scattering spectrum of ice$_{I_h}$ ($T=252$ K) as obtained by the pasting procedure described in the text. The inset shows the low-frequency part of the spectrum (Brillouin component) on a different intensity scale.

evident looking at the inset, where the high-resolution Brillouin spectrum is reported: both transverse- (TA) and longitudinal- (LA) acoustic peaks are present, and, thanks to the optical purity of the sample, the intensity of the elastic line is lower then the LA intensity. Note that the intensity scale of the Brillouin spectrum is 10^4 times that of the extended spectrum. The wide band peaked around 50 cm^{-1} in the extended spectrum is the contribution of the transverse-acoustic density of states, mixed with that of the lower transverse-optical modes.[5] The peculiar shape of the quasi-elastic contribution can be recognized in the frequency range between approximately 1 and 40 cm^{-1}; as a matter of fact, in this range the tails of the sharp and intense LA Brillouin peaks (centered at about ± 0.45 cm^{-1}) become negligible with respect to the observed background, while the contribution of the TA density of states is expected to vanish, according to the prediction for orientational disordered crystals.[3,11] Experimental evidence of this quasielastic contribution appears when two symmetrized spectra taken at different tem-
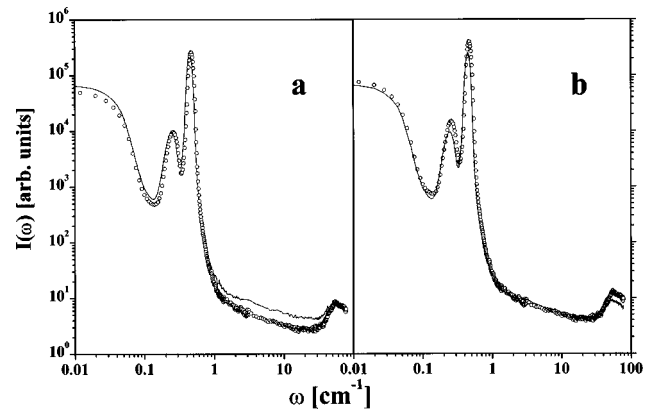

FIG. 2. Light-scattering spectrum of ice taken at two different temperatures: open circles are for $T=170$ K, while full line represent data at $T=252$K. Spectra are symmetrized with the procedure explained in the text. In (a) spectra have been normalized to have the same Brillouin-integrated intensity. In (b) the same low-temperature spectrum of (a) ($T=170$ K, open circles) has been multiplied by the temperature ratio $R=252/170$.

peratures are compared. Symmetrized spectra are obtained by multiplying the experimental data by the factor $K_B T/(\hbar\omega)/[n(\omega)+1]$, where K_B is Boltzmann's constant, T is the sample temperature, and $n(\omega)$ is the Bose population factor. In this way the effect of the detailed balance disappears and spectra looks symmetric with respect to the exciting line. In Fig. 2(a) the Stokes side of spectra at 252 and 170 K are shown. The two spectra have been normalized to have the same Brillouin-integrated intensities. This normalization accounts for the trivial temperature dependence of the first-order Raman scattering (FORS). In other words, if the dynamics of the crystal is temperature independent the symmetrized FORS spectra, normalized to the Brillouin intensity, have to superimpose each other in the whole frequency range. In the case of ice, it has been already reported that the crystal dynamics is almost temperature independent in the temperature region we are dealing with.[5] It can be observed that the width of the LA Brillouin component at both temperatures is just the spectral resolution, while its position only slightly depends on temperature, being 0.451 ± 0.001 cm^{-1} for $T=252$ and 0.472 ± 0.001 cm^{-1} for $T=170$ K. This small frequency shift can be used to determine the spectral region where the Brillouin line contribution becomes negligible with respect to the Raman spectrum. Indeed, looking at spectra in log-log scale [see Fig. 2(a)], it is possible to recognize that the effect of this frequency displacement is completely lost at 0.75 cm^{-1} where the lower temperature spectrum crosses the higher temperature one. Thus we can derive that at about 1 cm^{-1} the tails of the Brillouin component do not affect the spectral shape at both temperatures. On the other hand, if we compare the spectra in the 50 cm^{-1} range, they almost superimpose on each other, showing that the FORS spectrum is dominating at these frequencies. These observations allow us to conclude that the spectral contribution found between 1 to 40 cm^{-1} cannot be ascribed either to the Brillouin tails or to the one-phonon density of states.

To obtain more information on the origin of the quasielastic contribution, in Fig. 2(b) the normalized spectrum at 170 K of Fig. 2(a) is reported, with the intensity multiplied by the factor (252/170): now the entire quasielastic components coincide, thus showing that their intensity scales approximately with the square of the absolute sample temperature, while its shape is almost temperature independent.

In Fig. 3 a comparison has been made between the spectra taken at the same temperatures (252 and 170 K) in deuterated and nondeuterated samples. The quasielastic component overlaps at both temperatures, thus excluding any effect on its shape and intensity due to deuteration. On the contrary a trivial isotopic effect is clearly present in the 40–50 cm^{-1} frequency range, where the one-phonon density of states dominates the spectrum. This is exactly what we expect for intermolecular translational mode frequencies, because of the change in the molecular mass on deuteration which softens by about 5% the energy of all translational modes. Thus in deuterated samples the frequencies of acoustic modes are scaled with respect to those of the nondeuterated one by the square root of the inverse ratio of the molecular masses.

In summary, the temperature behavior of the low-frequency (0–100 cm^{-1}) Raman spectrum of deuterated and nondeuterated ice can be described in three frequency
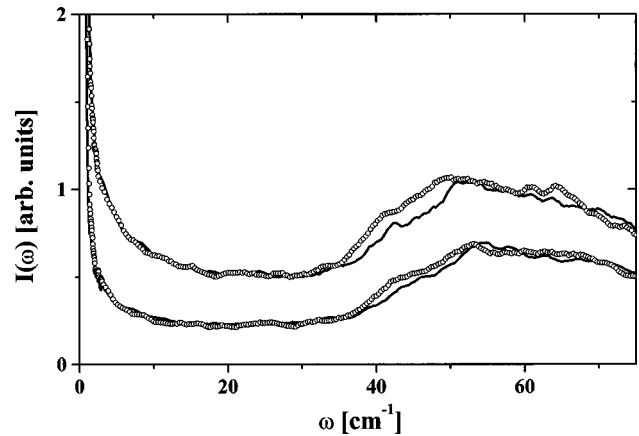

FIG. 3. Raman spectra of H_2O (full line) and D_2O (open circles) ice crystals taken at two different temperatures: upper curves for $T=252$ K while lower curves are for $T=170$ K. Spectra have been handled as those shown in Fig. 2(a).

ranges: (1) The very low-frequency range where the Brillouin spectrum dominates with intensity proportional to the sample temperature according to the thermal activation of single excitation spectra; (2) the quasielastic scattering which dominates in the frequency region between 1 and 40 cm^{-1}; its shape looks almost temperature independent while its intensity scales approximately as the square of the absolute sample temperature; (3) the frequency range $\omega>40$ cm^{-1} where the one-phonon disordered induced vibrational density of states describes exhaustively the spectral shape, as already found in Refs. 1 and 5.

This phenomenology closely resembles that of the low-frequency extra scattering in glasses[7] as well as that of the quasielastic contribution observed in mixed crystals of alkali halides.[12] The temperature behavior is very similar to that of ice and can be interpreted as due to second-order Raman scattering (SORS). As a matter of fact, a strong contribution to SORS is given by its elastic component, which is originated by all those processes which simultaneously create and annihilate the same crystal excitation. The integral of this elastic contribution has been evaluated in the case of KCl crystals to be about 20% of the total SORS intensity. In a harmonic crystal this contribution is rigorously elastic, while on anharmonic crystals it is broadened by the finite lifetime of all phonons: thus the shape of this contribution is not easily predictable, but its width is related to some ''average'' phonon broadening. The origin of the broadening has to be searched in the disorder itself and therefore it is almost temperature independent. On the other hand, the phonon broadening is largely independent of crystal deuteration: thus the assignment of the observed spectral feature to the quasielastic SORS contribution explains the observed absence of the isotopic effect (see Fig. 3) as well as its temperature behavior.

[1] G. Briganti, V. Mazzacurati, M. A. Ricci, G. Signorelli, and M. Nardone, Solid State Commun. **42**, 493 (1982).

[2] L. Pauling, J. Am. Chem. Soc. **57**, 2680 (1935).

[3] E. Walley and J. E. Bertie, J. Chem. Phys. **46**, 1264 (1967).

[4] G. Briganti, V. Mazzacurati, G. Signorelli, and M. Nardone, Mol. Phys. **43**, 1347 (1981).

[5] V. Mazzacurati, C. Pona, G. Signorelli, M. A. Ricci, E. Mazzega, M. Nardone, A. De Santis, and M. Sampoli, Mol. Phys. **44**, 1163 (1981).

[6] P. Bosi, R. Tubino, and G. Zerbi, J. Chem. Phys. **59**, 4578 (1973).

[7] J. Jackle, in *Amorphous Solids. Low Temperature Properties*, edited by W. A. Phyllips, Topics in Current Physics, Vol. 24 (Springer, Berlin, 1981), p. 135.

[8] V. Mazzacurati, P. Benassi, and G. Ruocco, J. Phys. E **21**, 798 (1988).

[9] L. Crescentini and A. Amoruso, Rev. Sci. Instrum. **67**, 3044 (1996).

[10] P. Benassi, A. Fontana, and P. A. M. Rodriguez, Phys. Rev. B **43**, 1756 (1991).

[11] P. Benassi, O. Pilla, V. Mazzacurati, M. Montagna, G. Ruocco, and G. Signorelli, Phys. Rev. B **44**, 11 734 (1991).

[12] P. Gallo, V. Mazzacurati, G. Ruocco, and G. Signorelli, Phys. Rev. B **47**, 11 830 (1993); P. Benassi, P. Gallo, G. Ruocco, V. Mazzacurati, and G. Signorelli, in *Induced Spectroscopy: Advances and Applications*, edited by G. C. Tabisz, NATO-ASI (Kluwer, New York, 1995), p. 307.