The Proton Distribution in Ice – Ih Investigated by Light Scattering

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(Z. Naturforsch. **31 a**, 1526 – 1531 [1976]; received October 22, 1976)

Oriented single crystalline samples of Ih-ice have been investigated by light scattering. The lack of observable phonon directional dispersion effects shows that ferroelectric domains with dimensions of the order of light wave lengths as stated earlier in the literature, do not exist. The depolarization ratio of the phonons originating from O-H stretching vibrations is found to be independent of the wave vector direction. This demonstrates clearly that the proton distribution is statistical.

Introduction

Although ten different phases of ice have become known up to now [1] the only ones which seem to play an important role in our environment are the hexagonal and cubic phases Ih and Ic. Other ordered phases such as e.g. II, III and IX may be produced at pressures well above 1000 at [1]. These phases might exist in certain extreme situations e.g. at the bottom of moving glaciers where local mecanical forces of this amount may occur, but generally Ih-ice is the most important phase in geophysics.

Early X-ray studies on Ih-ice have been published by Dennison in 1921 [2], and possible orientations of the water molecules in the unit cell were first experimentally determined by Barnes [3]. These studies clarified the structure of the oxygen lattice and the possible orientations of the O – H bonds. They left open, however, the detailed positions of the individual protons. Ih-ice was found to belong to the space group D_{6h}^4 (= C 6/mmc). There are four oxygen atoms in the unit cell at the coordinates ± (1/3, 2/3, 1/16) and ± (2/3, 1/3, 9/16). Every oxygen atom is tetrahedrally surrounded by four other oxygen atoms at distances = 2.76 Å. The positions of the protons could not be identified by X-ray spectroscopy.

Barnes proposed the protons to be located half way between the oxygen atoms. The water molecules thus would be ionized in Ih-ice. This structure required the static dielectric constant to be as small as ≈ 10 whereas the experimental value was found to be about 100 [4]. The experiment can be understood only if ice is built up essentially by water molecules with dipole moments as in the liquid and gaseous states.

From Raman- and infrared spectroscopic studies, on the other hand, the O – H bond length of free water molecules was derived to be ≈ 0.96 Å [5]. The frequencies $\omega_1 = 3651$, $\omega_2 = 1595$ and $\omega_3 = 3750$ cm^{-1} recorded in the liquid state are not changed drastically in the solid state, compare Figures 1 to 4. This confirmed the assumption of the existence of water molecules in ice.

In 1933 Bernal and Fowler proposed an ice model with intramolecular O – H bonds of ~ 1 Å and intermolecular H . . . O bonds to the next neighboring molecule of ~ 1.76 Å [6]. Their model is determined by two rules: a) Only one proton is located between every pair of oxygen atoms. b) The four O – O bond directions of every oxygen atom are occupied by two protons at 1 Å distance and two protons at 1.76 Å distance. Taking into account only a), there would be $4^2 = 16$ possible proton configurations around every O-atom. b) Excludes 10 of these possibilities which would imply the existence of ions. The remaining 6 configurations allow a large number of different water-molecule-orientations in the crystal. Most of these do not show a periodical structure. The simplest periodical structure has an elementary cell with 12 molecules, is hexagonal, and belongs to the space group C_{6v}^3 (= P 6_3 cm). The simplest periodical structure with an inversion centre, on the other hand, would require an elementary cell with 96(!) molecules which seems to be quite unrealistic. Due to Bernal

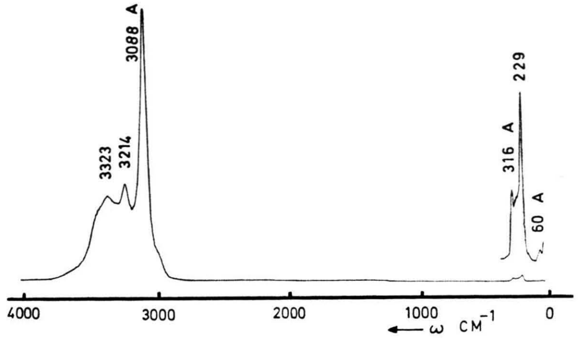

Fig. 1. Survey Raman spectrum of Ih-ice.

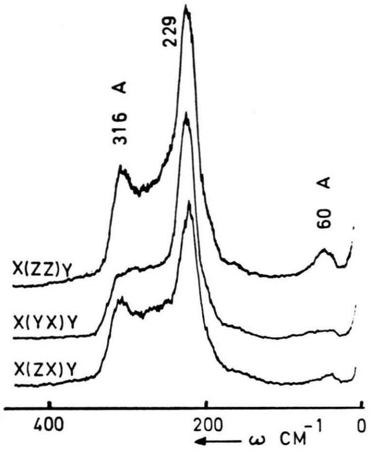

Fig. 2. Low frequency polarized Raman spectra of single crystalline Ih-ice recorded with different scattering geometries allowing the separation of modes with different symmetries.

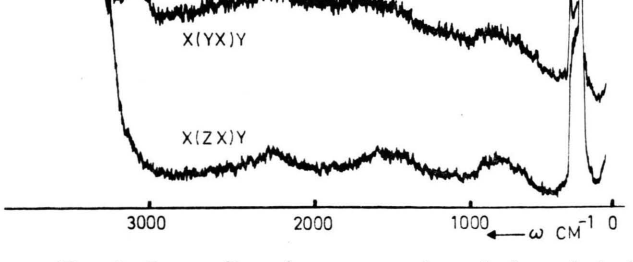

Fig. 3. Intermediate frequency region of the polarized Raman spectra of Ih-ice.

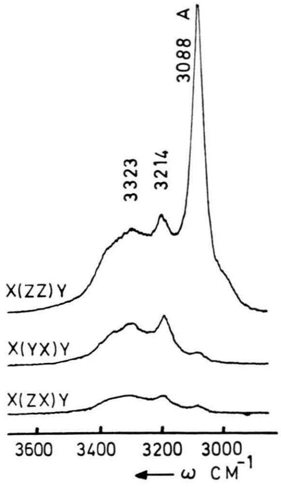

Fig. 4. High frequency polarized Raman spectra of single crystalline Ih-ice.

and Fowler the most likely proton configuration is the statistic distribution without a periodical structure. This picture is supported by the fact that the C_{6v}^3-symmetry would cause piezoelectricity in Ih-ice which is generally not observed.

The picture of a statistical proton distribution furthermore is supported by zero-entropy measurements carried out by Giauque and Ashley[7] and Giauque and Stout[8] in 1933 and 1936, respectively. The experimental results could be verified theoretically by Pauling in 1935[9] using the model of Bernal and Fowler. Furthermore, lattice dynamical calculations by Zerbi and coworkers[10] provide phonon dispersion curves which are in good agreement with neutron scattering data. Nevertheless the existence of ferroelectric polar domains belonging to the factor group C_{6v} has been stated or assumed by different authors within the last few years[11–15]. The dimensions of the domains are supposed to be of the order of light wave lengths. It was the aim of the present Raman spectroscopic study on single crystalline Ih-ice to check the evidences for the assumed domains. The result is completely negative. The light scattering spectra discussed by Refs.[11, 12] seem to have been somewhat overinterpreted by the authors in this context. The directional independent depolarization ratio of the phonons originating from O – H stretching vibrations shown and discussed in the following demonstrates in a quite direct way that the protons are arranged statistically.

Experimental

The growth and orientation of the ice crystals was performed in the following way. Pure ice single crystals were grown by a zone refining technique [16]. Preoriented ice cubes were frozen onto a goniometer head mounted on a lathe in a coldroom. Humidity from the surrounding air did condense as small frost crystals which grew epitactically on the freshly cut surfaces. These small epitactical crystals were illuminated with a He – Ne laser beam oriented at right angle to the lathe. The orientation of the sample was readjusted by means of the goniometer head until the reflected light from the epitactical crystal facettes was reflected exactly towards the incident beam. After having found the exact orientation of the c- and a-axes, the sample was machined.

Our Raman spectra were excited by an Ar^+-laser with ~800 mW output power at the laser lines 488 and 514.5 nm. The scattered radiation was analyzed with a double monochromator (RSV-Hechendorf) and the electronic signals from the photomultiplier were processed by a photon couting system. The samples were kept in a cryostat at liquid nitrogen temperatures. A maximum of 6 samples cut with different orientations of the optic axes to the surfaces could alternatively be changed by a turrethead without being taken out of the cryostat. The samples were approximately cubic with edges of ~7 mm length. Thin microscopy cover glasses were frozen onto the surfaces in order to attain a maximum of transparency. Raman spectra in forward- and right angle-scattering geometries were then recorded and analyzed.

Results and Discussion

The space group $D^4_{\sigma h}$ has an inversion centre causing alternative Raman- and IR-selection rules. The material, when belonging to this space group, would show only Raman-active modes of A_{1g}-type and IR-active modes of A_{2u}-type. If, on the other hand, there are domains in ice belonging to the factor group C_{6v} there should be A_1-modes which are simultaneously Raman- and infrared-active. The problem is to decide whether the observed (totally symmetric) Raman-lines are simultaneously IR-active or not. Although the problem seems trivial the experimental decision in practice is not. A coincidence of bands in the Raman- and IR-spectra might be accidental and does not give a definitive argument. Severe differences of the intensities, on the other hand, might prevent the detection of real coincidences. The only realistic way seems to be a search for dispersion effects which are typical for polar (infrared active) modes in the Raman spectra. Such dispersion effects are directional- and polariton-dispersion, see [17]. The observation of polaritons by light scattering strongly depends on the refractive indices of the material and the laser frequency used for excitation. Thus if light scattering experiments in order to find polariton-dispersion fail this must not necessarily indicate that there are no Raman-active polar modes. Directional dispersion on the contrary will be found independently from such experimental effects. The dependence of phonon frequencies on the wave vector direction relative to the optic axis can be investigated by all suitable scattering geometries using arbitrary laser lines.

The Raman spectrum of Ih-ice has been studied by different authors in the past. We especially cite [12, 18, 19] and the literature therein. Most of these investigations were concerned with polycrystalline samples and only a few with oriented single crystals [11, 12]. In the latter type of studies, on the other hand, normally only certain line groups are discussed in detail. We therefore show a survey-spectrum of Ih-ice in Fig. 1 and reproduce detail spectra recorded with different sensitivities and the scattering geometries $x(zz)y$, $x(yx)y$ and $x(zx)y$ in Figures 2, 3, 4. As easily can be verified from Table 1 these scattering geometries are adequate to allow the identification of modes of different symmetries for both factor groups D_{6h} and C_{6v}. Phonons which could be identified as totally symmetric have been indicated by the corresponding symbol (A) in the spectra. Wave numbers of the most significant features are given in the figures too, see also [20]. The A-mode at 1081 cm^{-1} in Fig. 3 clearly shows some interference with the background, see e. g. [21]. A future more detailed study of this effect might provide ad-

Table 1. Raman scattering tensors for the factor groups C_{6v} and D_{6v}. Letters in brackets after the mode symmetry symbols show IR-activity for dipole moments in the directions indicated, respectively. This table is somewhat condensed. For more detailed information see e.g. Ref. [17], Appendix 4.

	$\begin{pmatrix} a & & \\ & a & \\ & & b \end{pmatrix}$	$\begin{pmatrix} & & -c \\ & & \\ -c & & \end{pmatrix}$	$\begin{pmatrix} & & \\ & & c \\ & c & \end{pmatrix}$	$\begin{pmatrix} & d & d \\ & d & -d \\ & & \end{pmatrix}$
C_{6v}	$A_1(z)$	$E_1(-x)$	$E_1(y)$	E_2
D_{6h}	A_{1g}	E_{1g}	E_{1g}	E_{2g}

ditional information on the origin of the broad structures in the region from ~ 500 to ~ 3000 cm^{-1}.

We shall restrict our discussion on the totally symmetric modes essentially for two reasons: a) The A-modes can easily be distinguished from the others by light scattering due to the tensorelement α_{zz}, see again Table 1. On the contrary E$_1$- and E$_2$-modes are not easily separated. A comparison of the $x(yx)y$ and $x(zx)y$-spectra, Figs. 2, 3, 4 clearly shows this. b) The assumed (fluctuating) ferroelectric domains imply ordered O – H . . . O bonds along the optic axis (z) [11]. Pure A-modes have lattice displacements parallel to the z-axis. Directional dispersion and intensity measurements of these modes therefore should give the most direct information on the problem in question.

The basic condition for the assumed ferroelectric domains to be detected by light scattering is that they must have linear dimensions of the order of ~ 0.25 μm: light scattering processes from polar modes grouptheoretically required for the C$_{6v}$-symmetry must be possible. When considering a right angle scattering geometry and an exciting laser line at 488 nm the wave numbers of the observed phonon modes in the material become ~ 40500 cm^{-1} and their actual wave lengths of the order cited above. These dimensions, on the other hand, are not too far from the limit where domains generally can be attributed as polar. Long range electric fields typical for polar crystals show wave lengths "large" compared with the lattice constant. The medium must behave as a continuum where Maxwells electrodynamics is valid. This requires a ratio of lattice wave length to lattice constant of ~ 10^2 to 10^3 and thus domains with linear dimensions of the order of ~ 10^{-5} cm.

A second condition for the fluctuating domains to be detected by light scattering is that their life times must be large compared to those of the phonons (~ 10^{-12} s). This generally should be fulfilled.

Directional dispersion of polar modes in polyatomic uniaxial crystals is quantitatively described by the relation

$$\sin^2\Theta\cdot\varepsilon_{\perp\infty}\prod_{i=1}^{n_\perp}(\omega^2_{\perp \mathrm{L}i}-\omega^2)\prod_{j=1}^{n_\parallel}(\omega^2_{\parallel \mathrm{T}j}-\omega^2)$$
$$+\cos^2\Theta\cdot\varepsilon_{\parallel\infty}\prod_{j=1}^{n_\parallel}(\omega^2_{\parallel \mathrm{L}j}-\omega^2)\prod_{i=1}^{n_\perp}(\omega^2_{\perp \mathrm{T}i}-\omega^2)=0\,. \tag{1}$$

$n_\perp$ and $n_\parallel$ are the number of modes for wave vector directions perpendicular and parallel to the optic axis, respectively. $\varepsilon_{\perp\infty}$ and $\varepsilon_{\parallel\infty}$ are the high frequency dielectric constants, respectively. Θ denotes the angle between the optic axis and the wave vector and the indices L and T distinguish between the frequencies of the longitudinal and transversal modes, see [17]. According to the classical LST-relation

$$\varepsilon_0/\varepsilon_\infty=\prod_i \omega^2_{\mathrm{L}i}/\omega^2_{\mathrm{T}i} \tag{2}$$

the TO – LO-splittings directly determine the ratio of the dielectric constants. For totally symmetric modes with lattice displacements parallel to the z-axis in Ih-ice this ratio becomes $\varepsilon_0/\varepsilon_\infty \approx 80$. The value has been extrapolated for 85 K from the data of Johari and Whalley [4], page 278. Thus, if this ratio were determined only by the lattice dynamical mechanism of polar modes, large TO – LO splittings leading to strong directional dispersion effects should be recorded in the Raman spectra provided the A-modes are simultaneously Raman- and IR-active! Detailed corresponding studies of samples allowing for scattering geometries with $\Theta = 0°, 15°, 30°, 60°, 75°$ and $90°$, see (1), did not give the slightes hint of any directional dispersion effects [20, 22].

The ratio of the dielectric constants may be determined to a large extent by the dynamics of point defects and fluctuating dipole relaxations too. The corresponding generalized LST-relation becomes in this case

$$\frac{\varepsilon_0}{\varepsilon_\infty}=\prod_i\frac{\tau_{\mathrm{T}i}}{\tau_{\mathrm{L}i}}\prod_j \omega^2_{\mathrm{L}j}/\omega^2_{\mathrm{T}j}\,, \tag{3}$$

see e. g. [17, 23, 24]. $\tau_{\mathrm{T}i}$ and $\tau_{\mathrm{L}i}$ therein are relaxation times of fluctuating dipoles. There are severe arguments for the fact that the high $\varepsilon_0/\varepsilon_\infty$-ratio of Ih-ice is mainly caused by the latter type of processes [25]. Our above arguments against the existence of polar domains therefore are not definitive. We must admit, however, that at least some percents of the $\varepsilon_0/\varepsilon_\infty$-ratio have to originate from lattice dynamical effecs. Otherwise the existence of the type of long range electric fields which are normally used to characterize polar lattices becomes questionable. An easy calculation shows that even a ratio that makes up only a small part of the value $\varepsilon_0/\varepsilon_\infty = 80$ should cause TO – LO-splittings well above the resolution of our experimental set up, see also [20]. We omit the reproduction of spectra series.

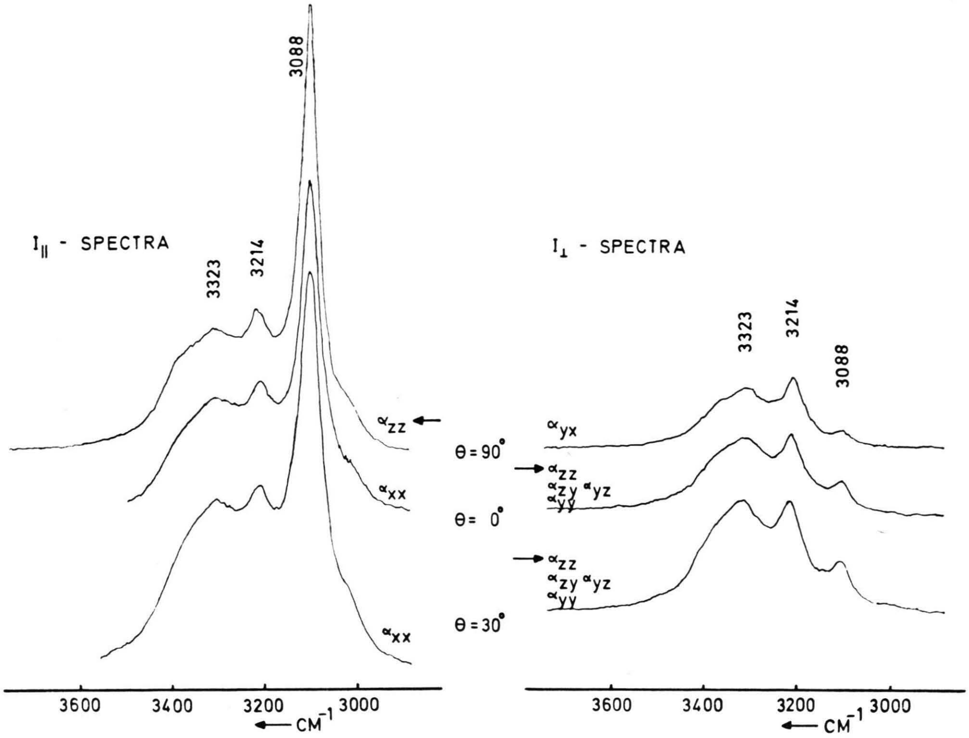

Fig. 5. Polarized high frequency Raman spectra of Ih-ice recorded for phonon wave vectors forming the angles $\Theta = 90°$, $0°$ and $30°$ with the optic axes of the samples. The spectra clearly show the directional independence of the depolarization ratio of the strong phonon at 3088 cm^{-1} originating from O–H stretching vibrations. This is unexpected in ordered crystals. The spectra directly demonstrate the disorder of the protons in Ih-ice, see text.

Forward scattering experiments in order to find polariton dispersion effects on the Raman-active phonon modes failed too. As already pointed out above, however, this does not definitely exclude the existence of Raman-active polaritons. By obvious reasons we omit the reproduction of spectra series[22] here too.

We now have to comment on the work of Fauré et al.[11, 12]. These authors claim to have found some directional dispersion on the Raman line at 316 cm^{-1}, see Figure 2. The shift recorded by these authors was from 310 cm^{-1} for $\Theta = 0°$ to 316 cm^{-1} for $\Theta = 45°$ and back to 310 cm^{-1} for $\Theta = 90°$, see Fig. 5 in their paper[11]. They correctly comment that "the usual formula" to describe directional dispersion could not be applied to this result. The formula cited by them in fact is the most rough approximation of Eq. (1) that is known as the "Poulet-Loudon-approximation". It is derived from (1) by setting $\varepsilon_{\perp\infty} = \varepsilon_{\|\infty}$ and by neglecting all directional dispersion branches except for the one of interest[17, 26]. The origin of the Poulet-Loudon formula was not too well known a few years ago. Equation (1) is rigorous except for the approximated influence of exciton states on the phonon directional dispersion as long as the $\varepsilon_0/\varepsilon_\infty$-ratio allowed for is caused by lattice dynamics. From (1) it can be verified that the dispersion curves $\omega = \omega(\Theta)$ have the shape of tg$^2\,\Theta$-functions. That means that $\omega = \omega(\Theta)$ is unique. Back turning curves as those reported by Fauré and Chosson therefore cannot be interpreted as directional dispersion of polar phonon modes. The effect reported by these authors originates from sums of the spectra reproduced in Fig. 2 which appear different for different wave vector directions because of a varying weight of the three components for different Θ. The large half widths of the lines relative to their distance suggest a continuous frequency shift.

We finally turn our attention to the scattering intensities recorded as a function of Θ, see Figure 5. All the spectra in this figure were recorded by right angle scattering. The upper two scans recorded for wave vectors propagating in the optically isotropic plane ($\Theta = 90°$) show strong α_{zz}-scattering from the O–H mode at 3088 cm^{-1}. This mode is unambiguously of A-type because it almost vanishes for α_{yx} and α_{zx}-scattering, see also Figure 4. The $\Theta = 0^\circ$-scan on the left hand side shows similarly strong light scattering due to the diagonal tensor element α_{xx}. The $\Theta = 0^\circ$-spectrum on the right hand side was recorded with the incident and scattered beams both polarized perpendicularly to the x-axis. As a result the α_{zz}-tensor element of the phonon in question again should contribute. Simultaneously the α_{yy}-element which is identical to the α_{xx}-element should contribute scattering intensity too, see Table I. Nevertheless the spectrum shows essentially the same shape as the α_{yx}-scan above. This is a unique result for a single crystal. It is a well known fact that strong totally symmetric phonons normally are difficult to eliminate from the other weaker phonon spectra and that they will aways appear dominantly whenever the selection rules allow this. The situation for $\Theta = 30^\circ$ is the same. The depolarization ratio $I_{\|} : I_{\perp}$[27] of this line in fact generally showed to be independent of the wave vector direction relative to the optic axes of the samples. This is not the typical behaviour of a single crystal but merely that of a liquid. These experiments therefore give strong arguments against the existence of polar domains and for the purely statistical proton distribution in Ih-ice.

Acknowledgement

We want to thank J. Brandmüller for discussions, Chr. Schwägerl for technical assistance and the Deutsche Forschungsgemeinschaft for financial support.

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