A RE-CORRELATION OF THE VIBRATIONAL SPECTRA AND CRYSTALLOGRAPHIC
DATA FOR THE VARIOUS ICE POLYMORPHS

B. MINČEVA-ŠUKAROVA, G.E. SLARK*, W.F. SHERMAN* and
G.R. WILKINSON*

Institute of Chemistry, Faculty of Science, Cyril and
Methodius University, Skopje, Yugoslavia
*Department of Physics, King's College, Strand,
GB-London WC2R 2LS, Great-Britain

RÉSUMÉ. — Nous avons obtenu des spectres Raman de bonne qualité sur les glaces I_h, II, III, V, VI et IX dans leur domaine de stabilité thermodynamique à l'aide de cellule Raman, sous pression et température variables. Nous discutons des relations entre les spectres Raman dans la région dynamique du réseau, en essayant de l'interpréter par sa structure cristallographique.

ABSTRACT.— We have obtained good quality Raman spectra of ices I_h, II, III, V, VI and IX in their regions of thermodynamic stability with a variable pressure, variable temperature Raman cell. We discuss the relationships between the Raman spectra in the lattice region and attempt to interpret them in terms of the available crystal structure data.

INTRODUCTION

In the last six or seven years we have obtained a considerable amount of data on the phases of ice in their regions of true thermodynamic stability [1,2,3] up to a pressure of about 1.00 GPa, which is the highest pressure we could reach in our high pressure, low temperature Raman cell.

We have concentrated our attention on the problem of finding a correlation between the crystallographic data on the various ice phases and spectroscopic data, in particular our Raman data, and the Raman and infrared data obtained from quenched samples [4,5]. Recent neutron diffraction studies of ices VI, VII and VIII [6] and the evidence for a new, high pressure phase, ice X [7,8], provide us with additional data for use in spectral-structural correlations. We have also made use of the results of a lattice dynamical calculation based on a six-parameter rigid ion model, which is a development of our previous calculations on diamond model [9].

DISCUSSION

The form of the vibrational modes of the water molecules (bending and stretching) in the various ice phases do not differ greatly. Furthermore, the internal modes are, as usual, decoupled from the translatory lattice vibrations which lie in the range between 0 and 350 cm^{-1}. Therefore, in this paper we will not consider the internal or torsional modes of the water molecules, but only the oxygen lattice and the corresponding translatory lattice vibrations which occur at low frequencies.

In all the ice phases the oxygen atoms are hydrogen bonded to four neighbours in an arrangement which is approximately tetrahedral with a range of O···O distances (table 3 of reference 1) and bond angles. It seems, therefore, that the total ensemble of all the possible vibrational frequencies should be similar for all the phases. However, the actual vibrational spectra are highly specific to each particular phase (figure 1) indicating that even for the disordered structures the Raman spectra in the lattice dynamics region are determined by the geometry of the oxygen lattice which strongly favours some vibrational modes relative to others. For ordered phases (e.g. II, IX, VIII) the selection rules imposed by the crystal structure will obviously determine which zone centre mode become Raman active. In the disordered phases (e.g. I_h, III, V, VI) the situation is not so clear. Strictly speaking, all modes should become disordered allowed [11]
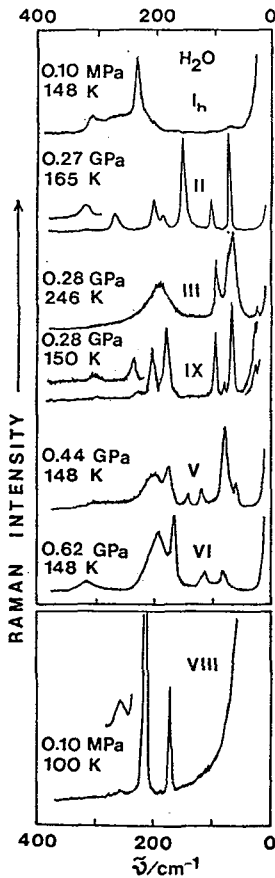
Fig.1. The Raman spectra of ices I_h, II, III, IX, V, VI and VIII in the region 0—350 cm^{-1} at pressures and temperatures as indicated. (Data for ice VIII are from reference 10).

with their intensities determined by transition moments and the density of states. An examination of the spectra of these disordered phases shows, however, that the disordering does not have nearly as great an effect on the Raman spectra as it does on the infrared spectra (figure 7 of reference 1).

These observations can be interpreted in terms of the analysis of the dependence of the polarizability tensor on the stretching of an O—H···O bond. It has been argued [12] that the intensity of the bands in the Raman spectrum which are allowed by the crystal symmetry selection rules should be large compared to the disordered allowed features. This concept can be traced back to the ideas developed in a series of papers published by Whalley and coworkers starting in 1967 [13]. However, this is only part of the problem. It answers the question as to how many bands to expect, but it does not address the equally important points of what form the vibrations have and what frequencies to expect. These two latter points are covered by the concept of similar overall vibrational properties for all ice structures.

When a simple diamond-like model is used for all ices, the O···O bond stretching force constant scales inversely with the mean O···O bond length [1]. Those force constants, more important to the acoustic modes, increase with the density [14] and the extra Γ points introduced by the larger cells can be positioned within the reciprocal space for the diamond model by considering the crystallographic data.

In our previous paper [1] we tried to interpret the Raman spectra of different ice phases in terms of modifications of a single ice I_c model. However, the actual correlation between the different ice phases is not a trivial problem and when an ice phase has a space group that is not a subgroup of the ice I_c group, there can be no direct correlation. It soon became apparent, however, that it was much easier to make convincing correlations for the structures which were closely related in symmetry.

We have not completed a full correlation of the infrared and Raman data with the crystallographic data, partly because the Raman and infrared spectra of ice IV and ice VII below 350 cm^{-1} as well as the far infrared spectra of ice VIII, have not been published yet. Nevertheless, we present some of our observations in these two sections: (A). Cubic and tetragonal ices and (B). Hexagonal and rhombohedral ices. The only ice form that is not included here is ice V, because its space group is monoclinic and as such is an 'exception' from these two sections.

The division between the (A) and (B) 'types of ices' as well as the relationships between the point groups of different structures of ices can be seen on figure 2.

(A). CUBIC AND TETRAGONAL ICES

For this group of ices it is convenient to begin with a study of ices VI and IX since the correlation could be established most easily in this case.

Crystallographic and spectroscopic relationship between ices VI and IX

The remarkable resemblance between the Raman spectra of these phases has already been noted [17]. The number of bands in the lattice region of ice VI and ice IX are about the same at low temperatures
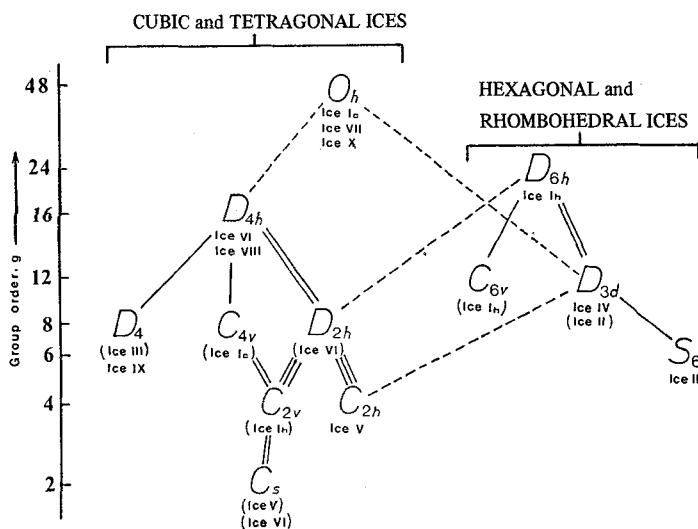
Fig.2. Schematic representation of the crystallographic point groups for different ice phases, known and hypothesized (in paranthesis) [15], as a function of group order (modified from reference 16).

(figure 3.a.). Ice VI and ice IX have tetragonal unit cells and are quite similar. The relationship between them is shown on figure 3.b. Ice VI has 10 molecules per unit cell with two types of oxygen atoms and three different O···O separations [19]. Ice IX has 12 molecules per unit cell but also has two types of oxygen atoms and three different O···O separations [20]. Although ice VI is denser than ice IX, the average O···O separation is about 3 % greater in ice VI [19] than in ice IX [20]. Spectroscopically, this is reflected in the fact that the 'optic like' mode frequencies in ice IX are higher than in ice VI because these modes are a direct measure of the O···O bond strength. The frequencies of the 'acoustic like' modes, however, are generally an increasing function of the density [14], and these modes are indeed at higher frequencies in ice VI than in ice IX (figure 3.a.).

Ice VI could be transformed into ice IX by symmetry degradation from D_{4h} to D_4. From the structural point of view this results from the movement of eight atoms which occupy sites of C_s symmetry in ice VI to asymmetric positions in ice IX. The two atoms which were on D_{2d} sites in ice VI move to positions on the C_2'' axes in ice IX and the two additional atoms 'enter' the unit cell to take up positions of C_2'' axes. The resulting structure has eight oxygen atoms on asymmetric sites which form two four-fold spiroids (type I). These atoms are hydrogen bonded to four oxygen atoms (type II) on the C_2'' axes and the structure closely resembles that of ice VI.

Therefore, despite different space groups and different number of molecules per unit cell, these two ices are locally very similar, at least with respect to the oxygen positions. It is not surprising therefore, that their Raman spectra look similar. Somewhat different values for the frequencies are expected because of the different average O···O separations in these ices.

Crystallographic and spectroscopic relationship between ices I_c and VIII

Spectral and structural comparisons can also be made for the hypothetically ordered ice I_c and ice VIII (figure 2 and figure 4). The unit cells of these two ices are very similar and they both have body-centred tetragonal Bravais cells but they have different number of molecules per unit cell and different O···O separations. The correlation between these two ice phases has been discussed by Whalley [11]. The Raman spactrum of ice VIII is well known and the bands due to the translatory modes have been assigned [10]. Therefore, the spectral and structural correlation in these two ices are even more pro-
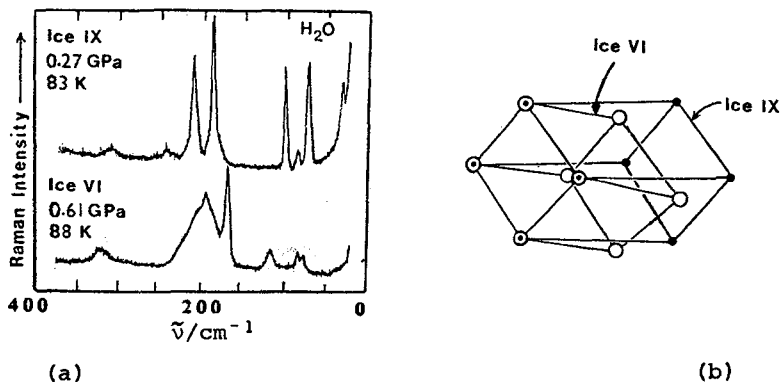
Fig. 3. (a) The Raman spectra of ice IX and ice VI at pressures and temperatures as indicated.
(b) Relation of the unit cell of ice IX with the unit cell of ice VI (from reference 18).
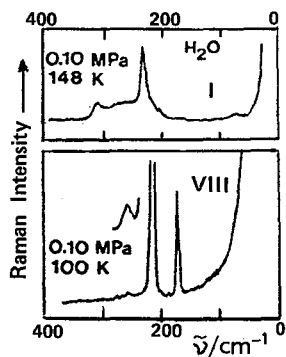

Fig. 4. The low frequency Raman spectra of ices I and VIII [10].

nounced than the ones in ices VI and IX. It is again evident that the most intense optic mode (analogous to the diamond Raman band) in ice I_c has a higher frequency than the corresponding mode in ice VIII as a result of the greater O···O separation in ice VIII than in ice I_c. The less intense zone centre mode frequency in ice VIII at about 180 cm^{-1} (figure 4) has no strict analogue in ice I_c because it is allowed by the tetragonal symmetry of the ice VIII lattice. This mode, in fact, becomes a zone boundary acoustic mode in the cubic phase, ice X [7].

Similar correlations can also be applied for the cubic disordered forms of ices, ice I_c and ice VII [11] and possibly ice I_c and ice X (figure 2).

(B). HEXAGONAL AND RHOMBOHEDRAL ICES

This group of ices contains ice I_h, ice II and ice IV (figure 2). Ice I_h is by far the most studied phase of ice; the Raman and infrared spectra are known in detail. Extensive calculations on the lattice dynamics of the hypothetically ordered ice I_h have been carried out in the past.

The Raman and infrared spectra of ice II are known in detail and have been studied down to 35 K I 21 I. Ice IV is metastable in the ice V region and its Raman and far infrared spectra have not yet been obtained. Its structure resembles that of ice II, and the structural correlation can be established most easily in these two ices.

Crystallographic and spectroscopic relationship between ices IV and II

The structures of these two ices are characterised by the net of hexagonal rings which lie more or less perpendicular to the C axis. These hexagons are connected by O—H···O bonds which run parallel to the C axis.

In the ice II structure (12 molecules per unit cell), the hexagonal rings of water molecules are stacked coaxially along the C axis which subtends the three rhombohedral axes equally. There are two types of oxygen atoms and four different O···O separations [22]. The unit cell of ice IV is also rhombohedral containing 16 molecules and has four oxygen atoms on C_3 sites (type I) and twelve on general positions (type II). These two types of oxygen atoms form, as in ice II, four types of hydrogen bonds [23]. The average O···O separation in ice IV is about 5 % greater than in ice II [22,23]. Ice IV and ice II have

about the same arrangement of oxygens and locally similar. This is not surprising since the hypothetical proton ordered modification of ice II proposed by Kamb [15] would have the same space group, D_{3d} as in ice IV. Ice IV could be transformed into ice II by symmetry degradation from D_{3d} to S_6 (figure 2). Therefore, a similar structural correlation to the one made for tetragonal ices can be made for the rhombohedral ices, ice II and ice IV. However, the lack of Raman and far infrared data for ice IV below 350 cm^{-1} made it impossible for us to confirm or refute the spectral similarities between ices II and IV. On the other hand, the Raman [17,21] and far infrared spectra [5] of ice II have been extensively investigated. We have obtained the polycrystalline and semi-polarized Raman spectra of ice II [17]. Although we were unable to establish the exact orientation of the ice II crystal inside our cell, we were able to deduce from the spectra that the ice II crystals tend to form along the pressure axis [24]. This allowed polarized data to be obtained, which is a helpful piece of information for the assignment of the bands in ice II.

In the absence of the spectroscopic data for ice IV, it could be possible to make some kind of spectral-structural correlations between ice II and ice I$_h$ (figure 1 and figure 2), but this is probably less direct and more complex way of correlating.

Crystallographic and spectroscopic relationship between ices I$_c$ and I$_h$

The two zero pressure forms of ices, ice I$_c$ and ice I$_h$ are the 'carriers' of the two sections: (A) Cubic and tetragonal ices and (B) Hexagonal and rhombohedral ices (figure 2). These two ices have been thoroughly investigated. Extensive spectroscopic studies on ice I$_c$ and ice I$_h$ have shown that they have nearly identical Raman [4,25] and far infrared [26] spectra. The structural correlation between these two zero pressure form of ices have already been discussed [18].

Ice I$_h$ and ice I$_c$ are hexagonal and cubic versions of the same proton-disordered structure. Those O—H···O bonds which are parallel to the hexagonal C axis in ice I$_h$ are parallel to the [111] direction in ice I$_c$, while the other O—H···O bonds lie perpendicular to them. These two phases of ice have the same density and the lattice spacing and only one type of O···O separation. In fact, these two phases may be superimposed on each other out to the third neighbour. (We have performed calculations on the lattice dynamics of ice I$_c$ based on a six patameter rigid ion model which was developed from diamond model [9]. These calculations show, as it is expected, that the nearest neighbour force constants are of the order of 10-100 times greater than the second nearest neighbour constants.)

Thus, despite the quite different space group and the different number of molecules per unit cell, ice I$_c$ and ice I$_h$ are locally identical. One should not, therefore, expect great differencies in their vibrational spectra and this is indeed the case [26]. We have, ourselves, studied the Raman spectra of ice I$_c$ obtained from high pressure ice phases, such as ice II and ice IX, but were unable to distinguish it from ice I$_h$.

However, in spite of all these spectral and structural similarities, there is no direct 'route' between ice I$_c$ and ice I$_h$ (as implied by figure 2). Since D_{6h} is not a subgroup of O_h, the transformation ice I$_c$ to ice I$_h$ can possibly go : $O_h \rightarrow D_{3d} \rightarrow D_{6h}$, i.e. via D_{3d} (figure 2).

We consider only ice I$_c$ to ice I$_h$ transformation (but not vice versa), because ice I$_c$ is metastable with respect to ice I$_h$*, and this is the only 'naturally' occuring transformation between these two ice forms. Ice I$_c$ can be obtained in large quantities from the high pressure ices. It is interesting to note that the crystallographic point groups of some of these ices, such as ices VI, VII and IV are subgroups of the O_h point group (figure 2).

CONCLUSIONS

In this paper we have outlined our attempt to correlate the available spectroscopic and crystallographic data for different ice phases. We believe that the fundamental similarities in the tetrahedral bonding of the various ice phases should permit the spectroscopic data to be interpreted in terms of systematic modifications to a simple diamond-like model. These modifications must be based on the crystallographic

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* Note that the cubic form of carbon, diamond, is also metastable with respect to its hexagonal form, graphite.

data of each particular phase (mean O···O distances, density, etc.) and will allow the Γ points of each phase to be defined crystallographically in the reciprocal space of the diamond-like model. This will allow the prediction of : (i) the number of modes expected to contribute significantly to the infrared and/or Raman spectrum, (ii) the form (approximate eigenvector) of each of these modes and (iii) the approximate frequencies of these modes.

Clearly, we have not yet totally justified this approach, but all the data which we have tested so far have been capable of inclusion within this scheme. We would hope soon to be able to complete these correlations and to move on to see to what extent this approach could be useful in predicting the equivalent lattice dynamical contributions to the thermodynamic properties of these ices and the transition between them.

ACKNOWLEDGEMENTS

REFERENCES

[1] B. Minčeva-Šukarova, W. F. Sherman and G. R. Wilkinson, *J. Phys. C: Solid State Phys.*, **17** (1984) 5833-5850.

[2] B. Minčeva-Šukarova, W. F. Sherman and G. R. Wilkinson, *J. Mol. Struct.*, **115** (1984) 137-140.

[3] B. Minčeva-Šukarova, G. Slark and W. F. Sherman, *J. Mol. Struct.*, **143** (1986) 87-90.

[4] M. J. Taylor and E. Whalley, *J. Chem. Phys.*, **40** (1964) 1660-1664.

[5] J. E. Bertie, *Appl. Spectrosc.*, **22** (1968) 634-640.

[6] W. F. Kuhs, J. L. Finney, C. Vettier and D. V. Bliss, *J. Chem. Phys.*, **81** (1984) 3612-3623.

[7] K. R. Hirsh and W. B. Holzapfel, *J. Chem. Phys.* **84** (1986) 2771-2775.

[8] A. Polain and M. Grimsditch, *Phys. Rev. Lett.*, **52** (1984) 1312-1314.

[9] C. Patel, W. F. Sherman and G. R. Wilkinson, *J. Phys.C : Solid State Phys.*, **17** (1984) 6063-6068.

[10] P. T. T. Wong and E. Whalley, *J. Chem. Phys.*, **64** (1976) 3259-2366.

[11] E. Whalley, *Can. J. Chem.*, **55** (1977) 3429-3441.

[12] P. T. T. Wong, D. D. Klug and E. Whalley, in *Physics and Chemistry of Ice*, Ed. E. Whalley, S. J. Jones and L. W. Gold, Royal Soc. of Canada, Ottawa, 1973, p. 87-92.

[13] E. Whalley and J. E. Bertie, *J. Chem. Phys.*, **46** (1967) 1264-1270.

[14] A. Polain, J. M. Besson and M. Grimsditch, in *Solid State Physics under Pressure : Recent Advances with Anvil Devices,* Ed. S. Minomura.

[15] B. Kamb, in *Physics and Chemistry of Ice,* Ed. E. Whalley, S. J. Jones and L. W. Gold, Royal Soc. of Canada, Ottawa, 1973, p. 28-41.

[16] G. Turell, *Infrared and Raman Spectra of Crystals,* Academic Press, London and New York, 1972.

[17] B. Šukarova, *Ph. D. Thesis,* King's College, London , 1982.

[18] A. von Hippel and E. F. Farrell, *Mat. Res. Bull.,* **8** (1973) 127-145.

[19] B. Kamb, *Science* **150** (1965) 205-209.

[20] S. J. La Placa, W. C. Hamilton, B. Kamb and A. Prakash, *J. Chem. Phys.,* **58** (1973) 567-580.

[21] J. E. Bertie and B. F. Francis, *J. Chem. Phys.* **7** (1982) 1-15.

[22] B. Kamb, W. C. Hamilton, S. J. La Placa and A. Prakash, *J. Chem. Phys.* **55** (1971) 1934-1945.

[23] H. Engelhardt and E. Kamb, *J. Glaciol.* **21** (1978) 51-53.

[24] B. Minčeva-Šukarova, W. F. Sherman and G. R. Wilkinson, *Spectrochim. Acta* **41A** (1985) 315-318.

[25] P. T. T. Wong and E. Whalley, *J. Chem.Phys.*, **65** (1976) 829-836.

[26] J. E. Bertie and S. M. Jacobs, *J. Chem. Phys.*, **67** (1977) 2445-2448.

COMMENTS

J.W. GLEN :

I was interested in your comparison between the structures of ice VI ice IX. Does not the fact that ice VI consists of two interpenetration lattices not have significance for the spectral response ?

Answer:

It may be expected, but the Raman scattering (I am not talking about the infrared) is sensitive mainly to the <u>bonded</u> oxygens (O-H...O) not the <u>unbonded</u> oxygens in different sublattices. Ice VI does have interpenatrating lattices, but it has three different O...O separations (as same is ice IX) which are all inside one single unit cell (as same as in ice IX). Therefore, in respect to the first nearest <u>bonded</u> neighbours, the lattices of ice IV and ice IX look similar. (N.B. In ice VI, as well as in ice IX, the first nearest bonded neighbours are **shorter** than the first nearest nonbonded neighbours).

In the case of ice VIII in which there are also two interpenetrating lattices, there is the feature in the Raman spectrum which could be assigned to the vibration of one sublattice against the other ; However, this feature is weak compared to the one which commes from hydrogen bond due to the intralattice.

(N.B. In ice VIII, the first nearest bonded neighbours are **longer** than the first nearest nonbonded neighbours).