

Isolated O-D stretching frequencies in ice II

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Abstract—Partially polarized Raman spectra of the four $\nu_{\text{O-D}}$ (HDO) bands for HDO solutions in H_2O ice II have been recorded under a pressure of 0.28 GPa and a temperature of 160 K. The polarization properties of the bands require a re-assignment of three out of four of these bands. Using this assignment and established spectroscopic-crystallographic correlations, we have estimated the four O-D and four O-D---O distances in ice II.

INTRODUCTION

Spectroscopists have known of the close correlation between bond length and bond-stretching force constant for over fifty years. Probably the most frequently quoted relationship is "BADGER's rule" [1].[†] With the increasing availability of high pressure spectroscopic equipment there has emerged a renewed interest in such relationships [2]. There has also been a growing awareness of the other factors which might be influencing the observed i.r. or Raman frequencies [2, 3]. Correlations for X-H bonds are, in general, limited by the lack of precision with which the X-H bond lengths are known. For a few small, gas phase molecules, the X-H bond lengths are accurately known from spectroscopically derived rotational constants. However this gives a very small data set without any examples of hydrogen bonded systems. A vast amount of spectroscopic data is available for hydrogen bonded X-H---Y systems, but the corresponding X-H bond lengths are known with relatively poor precision. This has resulted in correlations being made with the more precisely known X...Y spacings within hydrogen bonded systems in condensed phases.

We present here some data on the O-D stretching modes observed in partially-polarized Raman spectra of dilute solutions of HDO in H_2O ice II. These data suggest that previously published assignments of these modes [4, 5] are incorrect. Using our new assignment and averaged spectroscopic-crystallographic correlations (that should be relatively insensitive to the fairly large error in any one (ν_{OD} , O-D distance) or (ν_{OD} , O---O distance) point), we have estimated the four O-D distances and the corresponding O---O distances in the ice II structure.

It seems to us that ice II and, to a lesser extent, ice IX are the systems which can be made to yield results of sufficient accuracy to firmly establish the ν_{OD} vs O-D distance correlation. This would be of considerable

value in many investigations. For example all those involving water in some form—such as those meteorological, biological and medical situations within which the precise geometry and bonding of the water is important. Also, other O-H bonds within other molecules seem likely to be fairly closely described by the same relationship. This move to return to the basic correlation with the covalent bond length (rather than the covalent plus hydrogen-bond X---Y distance) seems likely to produce a more universally applicable relationship. It does leave completely unanswered the contentious questions [3] about the influence on ν_{OD} of the X---Y distance and/or the X-D---Y angle. However these questions could be reconsidered in a more tractable form if the basic ν_{OD} vs O-D distance correlation could be firmly established.

As part of a wide-ranging study [6] of the Raman spectra of high pressure ice polymorphs within their regions of true thermodynamic stability, we recorded a series of spectra for H_2O , D_2O , H_2^{18}O and dilute solutions of HDO in both H_2O and D_2O . The spectra shown in the lower part of Fig. 1 are two examples of the spectra of ice II formed from a small concentration of HDO in H_2O . Four components are seen to be present within this "isolated O-D stretching" region. The upper spectrum shows an i.r. absorption spectrum of this same region [5] for a reclaimed ice II sample at zero pressure and temperatures of 100 and 10 K.

X-Ray diffraction measurements [7] and neutron scattering [4, 8] experiments on reclaimed (zero pressure) samples of ice II have located the oxygen and, to a lower precision, the deuterons, within the D_2O ice II structure. There are two crystallographically-different oxygen atoms (labelled O(I) and O(II)) and four differently sited deuterons (D(1), D(2), D(3) and D(4)) within the ice II structure. Each oxygen atom is held by four "hydrogen bonds" to nearby oxygen atoms. The four hydrogen bonds (two O-D bonds and two O---D bonds) are approximately tetrahedrally arranged with respect to one another around any one particular oxygen atom. Within this structure, each unit cell contains six O(I), six O(II) and six deuterons of each type. Figure 2 shows the four distinct O-D---O arrangements and their orientations relative to the crystal C_h axis. There are six examples of each type of

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[†] $K(r-d)^3 = C$ (Where k is the force constant of a bond of length r and d and C are constants with predictable values).

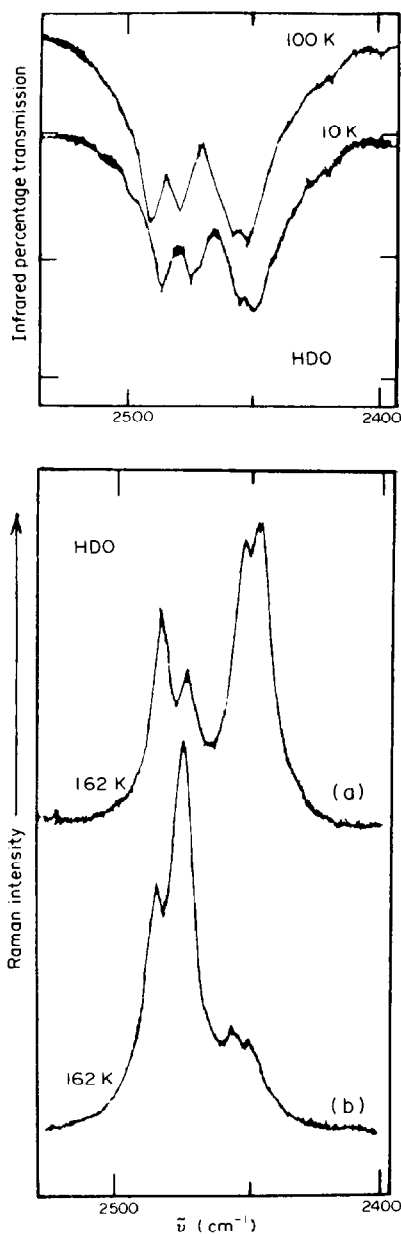


Fig. 1. The upper frame shows the i.r. transmission spectrum of HDO in H_2O ice II at zero pressure and temperatures of 100 and 10 K, after BERTIE and BATES [5]. The lower frame shows two different polarizations (a) is $X(YX)Y$ and (b) is $X(ZZ)Y$, where Z is parallel to the crystal C_h axis of our Raman spectra of HDO in H_2O ice II at a temperature of 162 K and a pressure of 0.28 GPa.

bond within each unit cell, arranged at 60° intervals around the C_h axis.

For an isolated O—D—O bond within a basically O—H—O environment, the main polarizability change associated with the O—D stretching vibration will undoubtedly be closely aligned with the O—D direction. Thus by averaging the effects of the six equivalent sites (60° intervals round C_h , three “up” and three “down”), it will be seen that for the O—D stretching vibrations:

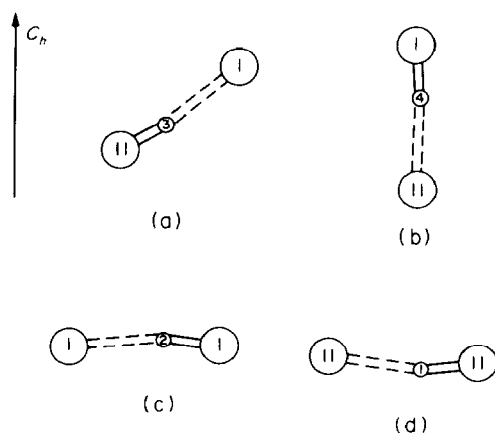


Fig. 2. (a) O(II)—D(3)—O(I) bond forms an angle of 45° with the hexagonal C_h axis. It is therefore expected to have approximately the same intensity in all six types of polarization as given in Fig. 1. (b) O(I)—D(4)—O(II) bond forms an angle of 0° with the hexagonal C_h axis and is expected to have maximum intensity in the $X(Z, Z)Y$ polarization as shown in Fig. 1. (c) and (d) O(I)—D(2)—O(I) and O(II)—D(1)—O(II) bonds form an angle of approximately 90° with the hexagonal C_h axis and are expected to show minimum intensity under $X(ZZ)Y$ polarization and maximum intensity under $X(YX)Y$ polarization (Fig. 1).

(i) the six O(II)—D(3)—O(I) bonds must produce polarizability changes that are almost independent of direction within the crystal.

(ii) the six O(I)—D(4)—O(II) bonds can be expected to show large polarizability changes parallel to C_h only.

(iii) bonds O(I)—D(2)—O(I) and O(II)—D(1)—O(II) will cause large polarizability changes within the plane perpendicular to the C_h axis only.

The details of our high pressure cell, the reasons for the preferred orientation of the ice II crystals and the limitations on the polarizability terms that could be monitored are described elsewhere [6]. However the two Raman spectra of Fig. 1 (labelled with the Porto notation where Z is parallel to the crystal C_h axis) show that the highest frequency component is virtually unpolarized and must be associated with O(II)—D(3)—O(I); the next highest component is strongly polarized parallel to the C_h axis and must be associated with O(I)—D(4)—O(II); the two low-frequency components are strongly polarized within the plane perpendicular to the C_h axis and must be associated with O(I)—D(2)—O(I) and O(II)—D(1)—O(II).

Bearing in mind the six examples of each type of bond arranged at 60° intervals around the C_h axis, there is no other acceptable assignment for these bands.

The two low-frequency components which show similar polarization properties are unambiguously assigned to the bonds within the hexagonal rings, but it is less clear which should be associated with which ring. However, in the various spectra of different samples prepared during this work, the lowest frequency

component always showed a slightly greater degree of polarization than the component just above it. The O(II)-D(I)---O(II) bond is almost linear and almost precisely perpendicular to the *C* axis, whereas the O(I)-D(2)---O(I) bond is significantly bent and is significantly off the perpendicular to the *C* axis. We have therefore assigned the lowest frequency component to O(II)-D(I)---O(II).

Having assigned the four frequencies to the four different bonds, it should now, in principle, be possible to correlate them with the bond lengths. However, the frequencies are known to an accuracy of $\pm 0.5 \text{ cm}^{-1}$ (i.e. about $\pm 0.02\%$) whereas the bond lengths are known to about $\pm 2 \text{ pm}$ for O---O distances (i.e. about $\pm 0.7\%$) and about $\pm 4 \text{ pm}$ for O-D distances (i.e. about $\pm 4\%$). Correlation of ν with the available O-D bond lengths over this range is therefore virtually to correlate with random numbers. Correlations with O---O distances might be meaningful, but there must be reservations about their significance because of the present lack of understanding about the influence of hydrogen-bond bending and other factors [3].

An alternative approach is therefore to consider whether the frequencies can be used (together with an acceptable model) to predict the bond lengths.

Wide-ranging correlations of O-D stretching frequency, ν_{OD} , vs O-D bond length, r_{OD} , and O---O bond lengths, $r_{\text{O---O}}$, suggest that the appropriate value for $d\nu_{\text{OD}}/dr_{\text{OD}}$ would lie somewhere in the range between $-50 \text{ cm}^{-1}/\text{pm}$ and $-80 \text{ cm}^{-1}/\text{pm}$ (with isolated O-D usually requiring numerically smaller values than the coupled OD frequencies) and $d\nu_{\text{OD}}/dr_{\text{O---O}} \approx 10 \text{ cm}^{-1}/\text{pm}$ (cf. NOVAK [10]).

Using $d\nu/dp$ data for the prominent lattice mode of ice Ih near 220 cm^{-1} it is possible to show (using a formalism developed earlier [11]) that the hydrogen bond can be regarded as having a bond-scaling parameter of about 1.38. The available [6] $d\nu/dp$ data for the isolated ν_{OD} can be adequately described by a series of similar models. (E.g. it can be fitted to a $kr^4 = \text{constant}$ relationship of the type that is commonly used for the different electronic states, of a given molecule [12], or a $kr^6 = \text{constant}$ relationship [11, 12], or a Morse type of potential function, or a LIPPINCOTT-SCHROEDER function [13].) When any one of these models is forced to fit the limited amount of $d\nu/dp$ and dr_{OD}/dp data, then it is

found to predict a $d\nu_{\text{OD}}/dr_{\text{OD}}$ value of about $-60 \text{ cm}^{-1}/\text{pm}$ and a $d\nu_{\text{OD}}/dr_{\text{O---O}}$ value of $+9.8 \text{ cm}^{-1}/\text{pm}$ in the frequency range considered here. These numbers are reasonably consistent with the approximate values quoted above.

A reference point is required if the above derivatives of ν_{OD} are to be used to produce equations relating frequencies to bond lengths. The most precise data that we could find for r_{OD} and $r_{\text{O---O}}$ (close to the ice II values) was for ice IX [14]. There are three sites for the deuterium atoms within the ordered ice IX structure [14] with eight atoms of each type within each unit cell. In order to have a single reference point of maximum accuracy we decided to take the average of the three isolated $\nu_{\text{O-D}}$ stretching frequencies, coupled with the average of the three r_{OD} (or $r_{\text{O---O}}$) distances.

Thus using $\nu_{\text{OD}} = 2448.3$, $r_{\text{OD}} = 98.3 \text{ pm}$ and $r_{\text{O---O}} = 276.9 \text{ pm}$ we get the relationships: $\nu_{\text{OD}} = 2448.3 - 60 (r_{\text{OD}} - 98.3) = 8346.3 - 60 r_{\text{OD}}$ or $r_{\text{OD}} = 139.105 - \nu_{\text{OD}}/60$ and $\nu_{\text{OD}} = 2448.3 + 9.8 (r_{\text{O---O}} - 276.9) = 9.8 r_{\text{O---O}} - 265.3$ or $r_{\text{O---O}} = 27.07 + \nu_{\text{OD}}/9.8$.

Using the above relationships we get the calculated r_{OD} and $r_{\text{O---O}}$ distances given in the final two columns of table 1. The values are quoted to two decimal places since the $\pm 0.5 \text{ cm}^{-1}$ accuracy of the ν_{OD} data implies a $\pm 0.01 \text{ pm}$ uncertainty in r_{OD} or ± 0.05 uncertainty in $r_{\text{O---O}}$. Even if the frequencies can be used to determine differences in bond lengths to those accuracies, the absolute values must be much less well defined. The best that could be claimed would be the accuracy of the ice IX reference point data.

There would also be problems with the temperature and pressure dependences of the Raman frequencies which are quite large ($d\nu_{\text{OD}}/dT \approx 0.14 \text{ cm}^{-1}/\text{K}$ and $d\nu_{\text{OD}}/dP \approx -40 \text{ cm}^{-1}/\text{GPa}$) and show different volume (and hence $r_{\text{O---O}}$) dependences [3]. Nevertheless, the large amount of spectroscopic data which has shown reliable frequency vs bond-length relationships leads us to believe that correlations of this type should also hold for the ν_{OD} vs r_{OD} situation. The ν_{OD} vs $r_{\text{O---O}}$ situation has been more widely used in the past, but it is far more sensitive to geometrical factors such as the non-linearity of the O-D---O bond, or the angles made by the bond in question with other bonds involving the terminal oxygens.

The use of the above linear relationships is strictly

Table 1. Assignment of the four $\nu_{\text{OD(HDO)}}$ bands in ice II

| $\nu_{\text{OD(HDO)}}$ (cm^{-1})* | Type of the O-D---O bond | $r_{\text{OD}}(\text{pm})\dagger$ | $r_{\text{O---O}}(\text{pm})\dagger$ | Calc. | Calc. |
|-------------------------------------------------|-----------------------------|-----------------------------------|--------------------------------------|-----------------------------|-------------------------------|
| | | ± 4 | ± 2 | $r_{\text{O-D}}(\text{pm})$ | $r_{\text{O---O}}(\text{pm})$ |
| 2489.2 | O(II)-D(3)---O(I) | (101.4) | (284.4) | 97.62 | 281.00 |
| 2479.1 | O(I)-D(4)---O(II) | 97.5 | (276.8) | 97.79 | 279.97 |
| 2459.0 | O(I)-D(2)---O(I) | (95.6) | (280.3) | 98.12 | 277.92 |
| 2455.4 | O(II)-D(I)---O(II) | (93.7) | (278.1) | 98.18 | 277.55 |

*Our data $P \approx 0.28 \text{ GPa}$ $T \approx 162 \text{ K}$ (cf. i.r. data [5]).

†Neutron data of KAMB *et al.* [4].

justified for relatively small deviations from the ice IX reference position only. However the work of LIPPINCOTT and SCHROEDER [13] (which in this respect has not been significantly improved upon by later workers) shows that the dv_{OD}/dr_{OD} value can be expected to change relatively slowly with r_{OD} . The dv_{OD}/dr_{O---O} relationship however can be expected to be much more curved. Our own study of such relationships, modified to agree with our variable pressure data is being prepared for publication elsewhere.

The ice II structure is built up from inter-linked hexagonal rings. Our new assignment, which shows the strong hydrogen bonds forming the rings and the weaker bonds forming the inter-ring linkages, seems inherently more satisfactory than the previous assignment which showed no such correlation.

CONCLUSIONS

The isolated O–D stretching frequencies in ice II were previously wrongly assigned, mainly because the crystallographic data was insufficiently precise. Partially polarized Raman spectra of HOD in H₂O ice II have allowed an unambiguous assignment. Using this new assignment and established spectroscopic–crystallographic relationships supported by our variable pressure data, it has been possible to suggest new O–D (and O–D---O) bond lengths. Although the absolute values of these new bond

lengths cannot be significantly better than the crystallographic data on ice IX on which they are based, the small relative changes in bond length are probably extremely precise.

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