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Abstract. We have determined the normal modes of ice VIII, a 16-molecule supercell, using *ab initio* calculations. The dynamical matrices so obtained are diagonalized and the eigenvectors projected on to the stretching, bending and libration modes of each water molecule in turn. We can therefore accurately correlate the symmetry assignments of the zone centre modes and the corresponding frequencies of these dynamical results with Raman, infrared and neutron scattering data. In particular, using neutron scattering data, we obtain excellent agreement with the frequencies of the $\upsilon_{R_y} B_{1u}$ phonon mode which is inactive in Raman or infrared spectroscopy.

1. Introduction

The vibrational spectra of the various forms of ice are of considerable interest from a variety of experimental and theoretical points of view [1]. In particular, it has proven difficult to understand the inelastic incoherent neutron scattering (IINS) of the proton-disordered ices [2]. We have therefore attempted the first complete analysis of the vibrational modes of ice VIII which, being proton-ordered and having a relatively high symmetry unit cell, is relatively accessible to *ab initio* methods. A previous attempt at such a comparison was made by Silvi *et al* [3]. The present results for all of the modes of vibration largely agree with these limited results and yield values that compare well with the best Raman, infrared and IINS data.

Ice VIII belongs to the space group $I4_1/amd$ (D_{4h}^{19}) with a supercell of 16 molecules [4]. It is stable at high pressures and the protons show antiferroelectric ordering [5]. The structure consists of two independent interpenetrating $I4_1md$ ferroelectric ice Ic sublattices (with all D-type [2] hydrogen bonds) with dipole moments oppositely directed along the c-axis. The structures of these sublattices separately satisfy the Bernal–Fowler ice rules [6]. The two sublattices are not perfectly centred with respect to one another; however, the situation of perfect centring would cause the oxygen atoms in each sublattice to lie in a body centred arrangement (with $z_0 = 0.125$). Instead, the oxygen atoms of each lattice are displaced a distance 0.5δ along the z-axis, 'downwards' in one lattice and 'upwards' in the other, so that the two lattices are displaced by δ (0.23 Å) from the centred positions. This causes each water molecule to possess two non-hydrogen bonded neighbours at separations of 2.86 Å (at zero pressure and temperature) that are shorter than for the four hydrogen bonded neighbours (2.99 Å). The experimentally determined [7] lattice parameters were $a = 4.80$ Å

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and $c = 6.99$ Å and we have calculated equivalent values of $a = 4.85$ Å and $c = 7.05$ Å There are seven other water molecules within a O–O distance of 3.43 Å. This nearly closed-packed arrangement makes the density high: 1.56 g cm^{-3} at zero pressure for H_2O–ice VIII.

Wong and Whalley [8] have analysed the measured Raman spectra of H_2O and D_2O ice VIII recovered at $\sim$100 K and zero pressure in the frequency range 50–4000 cm^{-1}. Also, more recently, Tay *et al* [9] have used the same conditions to study the infrared spectrum of ice VIII in the range 50–500 cm^{-1}. We have also compared the calculations with the IINS data [10], and these are generally in closer agreement with our calculated results (see table 2). The neutron modes are summed over all frequencies in the Brillouin zone (BZ) and so are expected to peak at the zone edge. Fortunately, all but one of the IINS peaks in the data are very narrow, hence the corresponding dispersion curve must be very flat (i.e. dispersion is not important). This means that the zone centre frequency is virtually coincident with the zone edge. From considerations of symmetry [11], ice VIII has 26 zone centre normal modes belonging to ten irreducible representations (see table 1),

$$\Gamma R = 3A_{1g} + 3B_{1g} + 3A_{2u} + 3B_{2u} + A_{2g} + A_{1u} + B_{1u} + B_{2g} + 5E_g + 5E_u.$$

From these 26 modes, 12 are Raman active (A_{1g}, B_{1g}, B_{2g} and E_g), eight are infrared active (A_{2u}, B_{1u}, A_{1u} and A_{2g}) while six are totally inactive to Raman or infrared (B_{2u}, B_{1u}, A_{1u} and A_{2g}) but are observable with neutron scattering.

Table 1. Correlation of the point groups of the intra- and inter-molecular motions in ice VIII. $\upsilon_1 \upsilon_3$ and υ_2 denote the symmetric stretch, anti-symmetric stretch and bending motions, respectively, and these correspond to the intra-molecular modes. T_x, T_y and T_z denote translations of the molecules parallel to their x, y and z axes; and R_x, R_y and R_z denote rotations about the x, y and z axes, defined for each molecule; the y axis of rotation being coincident with the C_v axis, the z axis of rotation being normal to the plane of the water molecule and passing through its centre of mass and the x axis of rotation being defined as the cross product of the y and z axes of rotation. The translational and rotational motions correspond to inter-molecular modes.

Molecular motions	Molecular point group and site symmetry group symmetry species	Space group symmetry species
$\upsilon_1, \upsilon_2, T_z$	A_1	$A_{1g} + B_{1g} + A_{2u} + B_{2u}$
R_z	A_2	$A_{2g} + A_{2u} + B_{1u} + B_{2g}$
R_y, T_x	B_1 ⎫	$E_g + E_u$
υ_3, R_x, T_y	B_2 ⎭	

2. Computational methods

The electronic properties of the ice VIII lattice have been described using the *ab initio* pseudopotential method as implemented in the CASTEP code [12]. Here Kohn–Sham electronic states are described within a plane wave basis set, and the generalized gradient approximation (GGA) [13] to density functional theory is used to describe electron–electron correlations. This level of approximation has been shown to give a good description [14] of the properties of hydrogen bonds which are central to this study. A norm-conserving pseudopotential is used to describe the oxygen atoms and a bare Coulomb potential to describe the proton. The kinetic energy cut-off of the plane-wave basis set is relatively high (800 eV) in order to ensure convergence. In each case, the total energy was minimized with respect to all the structural parameters, including atomic positions and lattice vectors (but without allowing for the zero point energy of the protons).

The dynamical properties of the lattices under consideration are then modelled within the harmonic approximation. The zone centre dynamical matrix associated with the supercells is obtained [15, 16] by a finite-difference method, based on the evaluation of the atomic forces when atoms are shifted from their equilibrium positions. Each of the ionic degrees of freedom is shifted in both directions about its relaxed position in order to obtain the rows of the dynamical matrix as follows. We first write the total energy of the lattice as a Taylor expansion [17]:

$$E = E_0 + \frac{1}{2} \sum_{ij} A_{ij} u_i u_j + \frac{1}{6} \sum_{ijk} B_{ijk} u_i u_j u_k \tag{1}$$

where E_0 represents the equilibrium lattice energy and u_i is a general coordinate of an ion relative to the minimum energy configuration (i labels both the ion and a particular Cartesian direction). A_{ij} describes the harmonic response of the lattice and is used to construct the dynamical matrix from:

$$D_{ij} = \frac{1}{m_j m_j^{1/2}} A_{ij} \tag{2}$$

where the m_i represent the ionic masses.

The force on the general coordinate is written as:

$$F_i = -\frac{\mathrm{d}E}{\mathrm{d}u_i} = -\sum_j A_{ij} u_j - \frac{1}{2} \sum_{jk} B_{ijk} u_j u_k. \tag{3}$$

We now independently shift each general coordinate by an amount $\pm\Delta$ and minimize the total energy with respect to electronic degrees of freedom in order to obtain forces on all the ions in this distorted configuration. Taking differences of the $F_i^{\pm\Delta m}$ we now obtain:

$$F_i^{-\Delta m} - F_i^{+\Delta m} = \Delta A_{im}. \tag{4}$$

This shift in opposite directions ensures cancellation of any cubic terms of the expansion whilst the quartic terms will be small enough to ignore. The magnitude of the shift must be large enough to overcome errors in the forces due to the noise produced by grid errors and small enough to ensure that the response of the ions is still harmonic. The shift is chosen to be 0.1 Å in all cases [18].

3. The frequencies of the zone centre vibrations in ice VIII

For ice VIII (with all D-type hydrogen bonds) the water molecules are on sites of C_{2v} (mm^2) symmetry which is also the symmetry of the isolated water molecule. As a result of this, anti-symmetric stretch and symmetric stretch motions will not couple to each other at the zone centre. This geometrical constraint was necessary for the experimental (Raman and infrared) interpretation of the total spectra of the zone centre modes, since a less restrictive geometry would have allowed mixing of the symmetric and anti-symmetric motions making it impossible to tell if the total spectra was pure or mixed.

In the approach we have adopted, it is not necessary to rely on this high symmetry, since we are splitting the total spectra into the stretching, bending, rotational and translational regions of the vibrational spectrum. If we relied on examining the total for the computed spectra, we would only be able to accurately study ice VIII and ice Ic (with all D-type hydrogen bonds). In fact, in addition to these two phases, we have studied ice Ih, ice IX, ice II, ice VI and an interpretation of ice VII, all modelled within the supercell approach [4]).

For ice VIII, we have found the eigenvectors of the zone centre modes for the symmetry coordinates of all the stretching, bending, rotational and translational bands. These are listed

in table 2, as are the corresponding frequencies. Because these four main spectral regions are well separated from each other in frequency and because the two stretching frequencies do not mix at the zone centre, the symmetry coordinates are found to be a good approximation to the normal coordinates. The exceptions to this situation are the two E_g translational symmetry coordinates, which couple together, as do the two E_g and the two E_u rotational coordinates.

The symmetry coordinates for the modes υ_{Ry} A_{2g}, υ_{Ry} A_{1u}, υ_{Ry} B_{2g} and υ_{Ry} B_{1u} are normal coordinates since they are alone in their class. Diagrams of the symmetry coordinates as well as the presentation of the measured Raman spectra of ice VIII are available in the paper Wong and Whalley [8], and the far infrared spectra of ice VIII are presented in the paper by Tay *et al* [9].

The superscripts on the symmetry coordinates in table 2 represent the four distinct molecules in ice VIII, where the pairs of superscripts (1 and 2), (3 and 4) always represent the molecules appearing in the same sublattice. Symbols (R) and (IR) appearing next to a given frequency denote measured Raman and infrared frequencies respectively.

4. Discussion

4.1. The zone centre modes of ice VIII

The symmetry coordinates of all the stretching, bending, rotational and translational bands and the corresponding zone centre frequencies are listed in table 2. Comparisons with the experiment are made in the columns headed [19] and [10]. In all cases, the calculated frequencies and the vibration symmetries coincide with the experimental assignments with reasonable accuracy.

4.1.1. The O–H stretching vibrations. Of the six modes in this region, we find three modes with the same assignments and in the same order of frequency as did Wong and Whalley when they investigated the three Raman bands in this part of the spectra of ice VIII (see table 2). The $\upsilon_1 B_{1g}$, $\upsilon_3 E_g$ and $\upsilon_1 A_{1g}$ modes were found by calculation to have isotopic ratios of 1.3867, 1.3610 and 1.3875, respectively, whereas Wong and Whalley obtained experimental isotopic ratios for these modes of 1.365, 1.342 and 1.364, respectively.

The order of the $\upsilon_1 B_{1g}$ and $\upsilon_3 E_g$ bands are reversed between H_2O and D_2O. This is due to a difference in the isotope shifts and is also in agreement with Wong and Whalley.

4.1.2. Bending vibrations. We disagreed with the (tentative) assertion of Wong and Whalley in the sequence of the frequencies of the two Raman active bands. The Raman-active vibrations were found to be [8] the $\upsilon_2 B_{1g}$ and $\upsilon_2 A_{1g}$ vibrations with frequencies 1677 cm^{-1} and 1346 cm^{-1}, with isotope ratios of 1.365 and 1.335, respectively. We found these same assignments and they had frequencies 1523 cm^{-1} and 1583 cm^{-1} with isotope ratios 1.3703 and 1.3663, respectively.

4.1.3. Rotational vibrations. The three calculated frequencies, with the equivalent experimental values in brackets are: 840.6 (874.2), 481.1 (494.0) and 473.7 (548.4) (see table 2). These were considered by Wong and Whalley to be the three bands due to the rotational vibrations and were described as being the rotational fundamentals occupying an octave of frequency. The modes determined in our calculation also have this behaviour. The frequency of the IINS corresponding to the middle of these values was 483.9, which is very close to our calculated value. We found good agreement with the IINS data for the Raman,

Table 2. The symmetry assignments and the zone centre frequencies.

Vibration	Symmetry coordinate[a]	H$_2$O This paper	H$_2$O [8]	H$_2$O IINS data [10][d]	D$_2$O This paper	D$_2$O [8]	D$_2$O IINS data [10]	$\frac{\nu\mathrm{H_2O}}{\nu\mathrm{D_2O}}$ This paper	[8]	IINS data [10]
$\nu_1 A_{1g}$	$\frac{1}{2}(Q_1^1 + Q_1^2 + Q_1^3 + Q_1^4)$	3282.9	3358.8 (R)		2366.0	2462.7 (R)		1.3875	1.3640	
$\nu_1 A_{2u}$	$\frac{1}{2}(Q_1^1 + Q_1^2 - Q_1^3 - Q_1^4)$	3273.1			2359.9			1.3870		
$\nu_1 B_{1g}$	$\frac{1}{2}(Q_1^1 - Q_1^2 + Q_1^3 - Q_1^4)$	3410.7	3477.4 (R)		2457.6	2548.0 (R)			1.3867	1.3650
$\nu_1 B_{2u}$	$\frac{1}{2}(Q_1^1 - Q_1^2 - Q_1^3 + Q_1^4)$	3393.9						1.3739		
$\nu_2 A_{1g}$	$\frac{1}{2}(Q_2^1 + Q_2^2 + Q_2^3 + Q_2^4)$	1583.4	1346 (R)		1158.9	1008 (R)		1.3663	1.3350	
$\nu_2 A_{2u}$	$\frac{1}{2}(Q_2^1 + Q_2^2 - Q_2^3 - Q_2^4)$	1482.0			1083.3			1.3680		
$\nu_2 B_{1g}$	$\frac{1}{2}(Q_2^1 - Q_2^2 + Q_2^3 - Q_2^4)$	1523.1	1677 (R)		1111.5	1229 (R)		1.3703	1.3650	
$\nu_2 B_{2u}$	$\frac{1}{2}(Q_2^1 - Q_2^2 - Q_2^3 + Q_2^4)$	1651.5			1193.7			1.3835		
$\nu_3 E_g$	$\frac{1}{2}(Q_3^1 + Q_3^2 - Q_3^3 - Q_3^4)$	3377.5	3447.6 (R)		2480.0	2568.7 (R)		1.3610	1.3420	
$\nu_3 E_u$	$\frac{1}{2}(Q_3^1 - Q_3^2 - Q_3^3 + Q_3^4)$	3376.4			2481.0			1.3617		
$\nu_{R_x}, \nu_{R_z} E_g$ (wagging, rocking)	$\frac{1}{2}(R_x^1 - R_x^2 + R_x^3 - R_x^4)$	840.6	874.4 (R)	863.0	614.0	652.2 (R)	645.2	1.3699	1.2990	1.3370
$\nu_{R_x}, \nu_{R_z} E_g$ (wagging, rocking)	$\frac{1}{2}(R_x^1 + R_x^2 + R_x^3 + R_x^4)$	481.1	494.0 (R)	483.9	350.0	365.5 (R)	355.7	1.3746	1.3520	1.3610
$\nu_{R_x}, \nu_{R_z} E_u$	$\frac{1}{2}(R_x^1 + R_x^2 - R_x^3 - R_x^4)$	840.1	610^c (IR)		613.6	421 (IR)		1.3691		
$\nu_{R_x}, \nu_{R_z} E_u$	$\frac{1}{2}(R_x^1 - R_x^2 - R_x^3 + R_x^4)$	406.4	455 (IR)	451.6	289.8	322 (IR)		1.4023		
$\nu_{R_y} A_{2g}$	$\frac{1}{2}(R_y^1 + R_y^2 + R_y^3 + R_y^4)$	602.6			426.1		402.4	1.4142	1.3730	1.3630
$\nu_{R_y} A_{1u}$	$\frac{1}{2}(R_y^1 + R_y^2 - R_y^3 - R_y^4)$	987.8		1026 [19]	698.5		726 [19]	1.4142	1.4130	
$\nu_{R_y} B_{2g}$ (twisting)	$\frac{1}{2}(R_y^1 - R_y^2 + R_y^3 - R_y^4)$	473.7	548.4 (R)	552.5	335.0	398.9 (R)		1.4140	1.3750	
$\nu_{R_y} B_{1u}$	$\frac{1}{2}(R_y^1 - R_y^2 - R_y^3 + R_y^4)$	465.9		451.6	329.4		334.7	1.4144	1.3250	1.3250
$\nu_{T_x}, \nu_{T_z} E_g$	$\frac{1}{2}(T_x^1 + T_x^2 - T_x^3 - T_x^4)$	158.4	172.0 (R)		152.2	166.4 (R)		1.0401	1.0340	1.0328
$\nu_{T_x}, \nu_{T_z} E_g$	$\frac{1}{2}(T_x^1 - T_x^2 - T_x^3 + T_x^4)$	195.5	214.3 (R)	215.3	187.9	207.5 (R)	205.7	1.0405	1.0330	1.0330
$\nu_{T_x}, \nu_{T_z} E_u$	$\frac{1}{2}(T_x^1 + T_x^2 + T_x^3 + T_x^4)$	89.2	162 (IR)	118.5	81.15	162 (IR)	116.9	1.0992		
$\nu_{T_z} A_{1g}$	$\frac{1}{2}(T_z^1 + T_z^2 - T_z^3 - T_z^4)$	158.0	169.2 (R)		150.0	161.6 (R)		1.0533	1.0460	
$\nu_{T_z} B_{1g}$	$\frac{1}{2}(T_z^1 - T_z^2 - T_z^3 + T_z^4)$	240.8	214.3 (R)		229.0	249.1 (R)		1.0515		
$\nu_{T_z} B_{2u}$	$\frac{1}{2}(T_z^1 - T_z^2 + T_z^3 - T_z^4)$	226.5			217.3			1.0423	1.0470	

[a] Q$_1$, Q$_2$, Q$_3$ represent the normal coordinates for the vibrations of the individual molecules; R_x and T_x, etc represent rotations about and translations along the crystal axes.
[b] The Raman frequencies and assignments are from Wong and Whalley [8].
[c] Frequencies at 22 °C and ~30 kbar from Klug *et al* [20].
[d] Unless otherwise stated.

infrared inactive $\upsilon_{Ry}B_{1u}$ (H_2O) mode and also excellent agreement for the fully deuterated structure.

4.1.4. Translational vibrations.   If the sublattices of ice VIII were centrally located to each other (which they are not), then the rigid body motions of the sublattices would form a threefold degenerate vibration at the edge of the Brillouin zone, and there would be no Raman activity. The lowering of the symmetry moves these vibrations to the zone centre and splits them into $\upsilon_{T_z}A_{1g}$ and υ_{T_x}, $\upsilon_{T_z}E_g$ vibrations. The A_{1g} and E_g modes correspond to the relative displacement along and perpendicular to the *c*-axis. We have recently analysed this motion in detail [4]. These particular motions do not involve any variation of either internal or hydrogen bond-related coordinates; see table 2. The IINS data for Raman active modes in this region for ice VIII have been obtained by Li and Adams [21]. These workers reported a peak at 147.6 cm^{-1} which could either be the A_{1g} or the E_g mode. Our results are in closer agreement with the Hartree–Fock calculations of Silvi *et al* [3], who obtained the zero pressure frequencies 156.1 (148.0) and 159.3 (150.4) cm^{-1} for the hydrogenated A_{1g} and E_g modes, respectively, where the corresponding fully deuterated result is given in brackets, with frequency differences 3.2 and 2.4 cm^{-1}. We calculated the same set of frequencies as 158.4 (150.0) and 158.0 (152.2) cm^{-1}, with frequency differences 0.4 and 2.2 cm^{-1}. The lowest neutron peak is at 118.5 cm^{-1}.

5. Conclusions

We have carried out extensive *ab initio* calculations of the modes of vibration of ice VIII. The calculated frequencies and the related displacement symmetries are in excellent agreement with the Raman/infrared measurements. In general, the calculated frequencies are some 3–10% lower than the measured values except for the mode where the calculation is actually higher than in the experiment. The isotopic shifts also follow the experimental trends. The calculation also correctly identifies all the IINS peaks, including those that are inactive to Raman and infrared. This calculation has thus effectively simulated the hydrogen bonding and non-hydrogen bonding interactions in ice VIII. The small residual errors are probably due to zero point energy effects (anharmonicity in the energy surface).

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