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The Bonded Water Molecule. I. The Effect of the Vibratory Motion on the Observed Geometry

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Correction terms are derived for a water molecule bound in a crystal, making it possible to calculate the mean OH and HH distances and the mean HOH angle from the corresponding quantities determined experimentally from neutron-diffraction data or by means of proton magnetic resonance. The correction terms depend on the matrix elements of a 9×9 generalized mean square matrix, $\langle x_i x_j \rangle$, where x_i is the Cartesian displacement coordinates of the three atoms in a molecule. The matrix elements are given for different models of the motion and numerical values have been obtained for intercomparison. The numerical values have been calculated from a new model of the motion based on a normal coordinate analysis in a combined intramolecular and isotropic external potential. The riding corrections usually applied to OH distances are shown to be much smaller than physically more reasonable corrections. The mean HOH angle is found to be smaller than the observed value. Correcting for the motion as shown results in a typical water molecule in which the mean OH distance is elongated by 0·02 Å to 0·98 Å and the HOH angle is enlarged to 106° when the molecule is bonded. The correction term calculated for the H–H distance observed in a proton magnetic resonance study is shown to be different from a correction term derived earlier.

Introduction

In recent years a large amount of information on the geometry of molecules in crystals has accumulated. When one tries to organize this material for selected molecules looking for specific effects, one rapidly detects sources of systematic errors that complicate the analysis.

The main purpose of this paper is to discuss the effects of motion on the observed geometry of a water molecule when bound in a crystal. The effects are expected to be large for water with its small moments of inertia, introducing apparent distortions of the geometry.

The geometry of a bonded water molecule can be determined in detail from neutron diffraction (n.d.) data, and to date the geometries of about 100 water molecules have been determined by this method (Ferraris & Franchini-Angela, 1972). The H–H distance can also be found from a proton magnetic resonance (p.m.r.) study and approximately the same number of cases have been studied by p.m.r.

The data presented by Ferraris & Franchini-Angela (1972) show that the reported OH distances are generally shorter and the HOH angles are generally larger in a bound water molecule compared with the mean dimensions of the free water molecule. Furthermore, the geometry varies within fairly large limits. In the free molecule at room temperature the mean OH distance is 0·9743 Å and the mean HOH angle 104·52°. (Kuchitsu, 1971). The observed OH distances in the bonded water molecules are distributed about an average value of 0·956 Å with $\frac{2}{3}$ of the distances within $\pm 0{\cdot}024$ Å of this value. For the HOH angles the average is 107·8° with $\frac{2}{3}$ of the angles within 105° to 111° (Ferraris & Franchini-Angela, 1972).

It is generally agreed that the shortening of the OH distance can only be apparent. The observed distances are averages over the thermal motion of the molecule in the crystal. It is well known that the observed distance will always be shorter than the mean distance (Busing & Levy, 1964).

To calculate the effect of motion quantitatively, however, requires a model of the motion. We shall in this paper make an intercomparison of the various models proposed earlier. Following Busing & Levy (1964) we shall give equations making it possible to calculate the mean OH and H–H distances from the observed distances, but the equations are in a form valid for any harmonic model of the motion. We also derive a similar equation relating the mean H–H distance to the observed H–H distance from a p.m.r. study. This equation is shown to be different from an equation derived earlier for a specific model (Pedersen, 1964). The equations derived make it possible to relate H–H distances observed with p.m.r. and n.d. directly.

The enlargement of the H–O–H angle by on the average 3° is interesting if real. However, the effects of motion on this parameter have never been calculated. We shall show that the mean H–O–H angle is smaller than the observed value, at least for the simple situation to be treated here.

We attempt here to analyse trends and not water molecules in specific structures. The numerical values to be given have been calculated from a new model of the motion of a bonded water molecule. This model is presented in detail elsewhere (Pedersen, 1975).

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Geometry corrections in n.d.

In a crystal structure determination by diffraction methods the atoms are generally treated as independent. The atomic positions arrived at are, within the harmonic approximation, close to the mean atomic positions averaged over the motion of the atoms. Busing & Levy (1964) showed that the mean distance between two atoms $\langle S\rangle$ is not equal to the distance between the mean positions of the atoms, but equal to

$$\langle S\rangle = S_0 + \langle w^2\rangle/(2S_0)\,. \tag{1}$$

Here S_0 is the separation between the mean positions of the two atoms, *i.e.* the value usually reported as the observed interatomic distance, w is the relative vector displacement of the two atoms projected on the plane normal to the line between the two mean positions. To evaluate $\langle w^2\rangle$ one has to know the relative motion of the two atoms. Only partial information on this motion is available from diffraction data; to calculate $\langle w^2\rangle$ requires a model of the motion. Busing & Levy (1964) proposed one model called the riding model which has been much used in correcting OH distances. They also proposed an independent motion model and analysed the rigid-body molecular motion model earlier proposed by Cruickshank (1956). This model, in the generally valid form (Schomaker & Trueblood, 1968), has recently been applied to the water molecules in ice IX by La Placa, Hamilton, Kamb & Prakash (1973). We shall return to these models below.

The same problem, as discussed by Busing & Levy (1964) concerning interatomic distances in solids determined by diffraction methods, has also been extensively discussed by groups working on the determination of interatomic distances of gaseous molecules spectroscopically or by means of electron diffraction (Robiette, 1973). The quantity S_0 given in equation (1) is equal to what Robiette and others call R_α. However, the interatomic distances observed in the gas phase are more accurately defined than the distances observed in solids. The correction terms derived below are formally $(\langle S\rangle - S_0)$, but the corrections can also be regarded as an estimate of the uncertainty in the interatomic distances and angles due to the atomic motion.

Equation (1) was derived by expanding the instantaneous separation S of the two atoms in a Taylor series, averaging and keeping terms to second order. It is instructive to write the equation in the following form:

$$\langle S\rangle = S_0 + \tfrac{1}{2}\sum_{i=1}^{9}\sum_{j=1}^{9}\left(\frac{\partial^2 S}{\partial x_i \partial x_j}\right)_0 \langle x_i x_j\rangle. \tag{2}$$

x_i is the Cartesian displacement coordinates for the atoms defined in Fig. 1. $\langle x_i x_j\rangle$ is a typical element in a 9×9 generalized mean-square amplitude matrix. We give the matrix this name because the three diagonal 3×3 blocks are equal to the familiar **U**-matrices for the three atoms in the molecule referred to the axes defined in Fig. 1.

The coordinate system in Fig. 1 has been chosen so that the mean position of H_1 is at $u_1,0,0$; H_2 at $u_2,0,0$ and O at $0,u_3,0$. We then define r_{10}, r_{20}, α_1 and α_2 by

$$r_{10} = (u_1^2 + u_3^2)^{1/2} \tag{3}$$

$$r_{20} = (u_2^2 + u_3^2)^{1/2} \tag{4}$$

$$\sin\alpha_1 = -u_1/r_{10} \tag{5}$$

$$\sin\alpha_2 = u_2/r_{20}\,. \tag{6}$$

The second derivatives needed in equation (2) have been calculated from the expressions for the instantaneous separations of the atoms and by inserting we obtain:

$$\langle R\rangle = R_0 + (\langle y^2\rangle + \langle z^2\rangle)/(2R) \tag{7}$$

where

$$\langle y^2\rangle = \langle (x_5 - x_2)^2\rangle = \langle x_2^2\rangle + \langle x_5^2\rangle - 2\langle x_2 x_5\rangle \tag{8}$$

$$\langle z^2\rangle = \langle (x_6 - x_3)^2\rangle = \langle x_3^2\rangle + \langle x_6^2\rangle - 2\langle x_3 x_6\rangle \tag{9}$$

$$\begin{aligned}\langle r_1\rangle = r_{10} + [&\cos^2\alpha_1\langle (x_1 - x_7)^2\rangle + \sin^2\alpha_1\langle (x_2 - x_8)^2\rangle \\ &+ \langle (x_3 - x_9)^2\rangle + \sin 2\alpha_1(\langle x_1 x_8\rangle + \langle x_2 x_7\rangle \\ &- \langle x_1 x_2\rangle - \langle x_7 x_8\rangle)]/(2r)\,.\end{aligned} \tag{10}$$

Analogously r_2 is given by changing 1 to 2 in the r's and x_1 to x_4, x_2 to x_5 and x_3 to x_6.

The mean H–O–H angle, $\langle 2\alpha\rangle$, can also be calculated from equation (2) setting $S = 2\alpha$. A short analytical expression for $\langle 2\alpha\rangle$ has not been derived, but utilizing quantities needed above we can calculate the necessary second derivatives from:

$$\begin{aligned} r_1 r_2 \cos 2\alpha = &(x_7 - x_1 - u_1)(x_7 - x_4 - u_2) \\ &+ (u_3 + x_8 - x_2)(u_3 + x_8 - x_5) \\ &+ (x_9 - x_3)(x_9 - x_6)\,.\end{aligned} \tag{11}$$

Then

$$\begin{aligned}\left(\frac{\partial^2(2\alpha)}{\partial x_i \partial x_j}\right)_0 = \{&r\cos 2\alpha(R_{ij}^{(1)} + R_{ij}^{(2)}) \\ &+ \cos 2\alpha(L_{1i}L_{2j} + L_{1j}L_{2i}) \\ &- r\sin 2\alpha[H_i(L_{1j} + L_{2j}) + (L_{1i} + L_{2i})H_j] \\ &- r^2\cos 2\alpha H_i H_j + A_{ij}\}/(r^2 \sin 2\alpha)\,.\end{aligned}$$

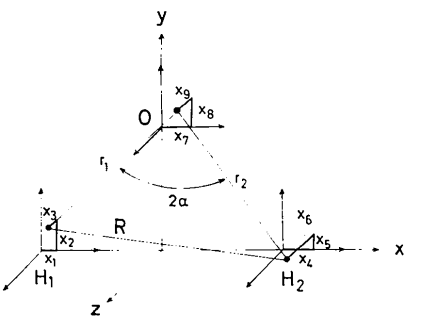

Fig. 1. The Cartesian displacement coordinates for an H_2O molecule used in the text.

Here

$$L_{kj}=\left(\frac{\partial r_k}{\partial x_j}\right)_0$$

$$H_j=\left(\frac{\partial(2\alpha)}{\partial x_j}\right)_0$$

$$R_{ij}^{(k)}=\left(\frac{\partial^2 r_k}{\partial x_i \partial x_j}\right)_0$$

$$A_{ij}=\left(\frac{\partial^2(r_1 r_2 \cos 2\alpha)}{\partial x_i \partial x_j}\right)_0 .$$

The H–H distance from p.m.r.

The H–H distance, R, can also be determined by proton magnetic resonance (Dereppe & Van Meerssche, 1968). This is due to a coupling between the nuclear magnetic dipole moments of the two protons that depends on a value of R. The coupling splits the magnetic resonance spectrum to a doublet with a splitting, ΔH, given by

$$\Delta H=\left\langle \frac{3\mu}{R^3}(3\cos^2\theta-1)\right\rangle . \qquad (12)$$

μ is the magnetic dipole moment of a proton and θ the angle between **R** and the external magnetic field. The observed splitting is the average over the thermal motion. This average was calculated earlier (Pedersen, 1964) by assuming that

$$\Delta H=\left\langle \frac{3\mu}{R^3}\right\rangle_{\text{intramol. modes}} \langle(3\cos^2\theta-1)\rangle_{\text{librational modes}} . \qquad (13)$$

The averaging was then performed on the basis of a specific model of the motion. We will here proceed differently. We define a direct observed H–H distance R_N by

$$\Delta H_{\text{obs}}=\frac{3\mu}{R_N^3}(3\cos^2\theta-1) . \qquad (14)$$

We define the direction of the magnetic field in the coordinate system in Fig. 1 by the unit vector $\mathbf{e}_H=(A,B,C)$ where A, B and C are the direction cosines. We can use equation (2) for calculating the relation between R_N and R_0 setting $S=\Delta H$.

After some calculation and rearrangements we obtain:

$$R_N=R_0+(\langle y^2\rangle+\langle z^2\rangle)/(2R)-2\langle x^2\rangle/R+P \qquad (15)$$

$$\begin{aligned}P=[&(A^2-B^2)\langle y^2\rangle+(A^2-C^2)\langle z^2\rangle\\&+8AB(\langle x_1x_2\rangle-\langle x_1x_5\rangle-\langle x_2x_4\rangle+\langle x_4x_5\rangle)\\&+8AC(\langle x_1x_3\rangle-\langle x_1x_6\rangle-\langle x_3x_4\rangle+\langle x_4x_6\rangle)\\&-2BC(\langle x_2x_3\rangle-\langle x_2x_6\rangle-\langle x_3x_5\rangle+\langle x_5x_6\rangle)]/\\&[(3A^2-1)R]\end{aligned} \qquad (16)$$

$$\langle x^2\rangle=\langle(x_1-x_4)^2\rangle=\langle x_1^2\rangle-2\langle x_1x_4\rangle+\langle x_4^2\rangle . \qquad (17)$$

This expression reduces to a similar expression recently evaluated by Diehl & Niederberger (1973) for a specific case. However, as shown below this expression is different from the expression derived earlier.

Substituting equation (7) in equation (15) we obtain

$$\langle R\rangle=R_N+2\langle x^2\rangle/R-P . \qquad (18)$$

Usually R_N is determined in the orientation where the splitting is maximum. Then $A=1$, $B=C=0$ and $P=(\langle y^2\rangle+\langle z^2\rangle)/(2R)$, *i.e.*

$$\langle R\rangle=R_N+2\langle x^2\rangle/R-(\langle y^2\rangle+\langle z^2\rangle)/(2R) . \qquad (19)$$

Discussion

By comparing equation (7) with equation (19) we see that:

$$R_N-R_0=(\langle y^2\rangle+\langle z^2\rangle)/R-2\langle x^2\rangle/R . \qquad (20)$$

As shown below, the mean square amplitude along the H–H direction, $\langle x^2\rangle$, is small compared to the perpendicular amplitudes, $\langle y^2\rangle$ and $\langle z^2\rangle$. Therefore, $R_N>R_0$, *i.e.* the directly observed H–H distance in a n.d. study, R_0, will be smaller than the same distance determined by p.m.r. This is in agreement with El Saffar (1966) who noted that R_0 on the average was 0·04 Å smaller than R_N.

We shall now discuss the motional corrections obtained from different models of the motion. The justification for introducing the independent motion model and the riding model is that the models are simple and that the corrections can be calculated from diffraction data. $\langle w^2\rangle$ in equation (1) is simply

$$\langle w^2\rangle=\langle w_1^2\rangle\pm\langle w_2^2\rangle \qquad (21)$$

with + for the independent motion model and − when atom 1 rides on atom 2. The consequences for the generalized mean square matrix $\langle x_ix_j\rangle$ are also simple. If the water molecule is assumed to consist of atoms moving independently of each other, then $\langle x_ix_j\rangle=0$ when i and j are on different atoms. If H_1 is assumed to ride on the oxygen atom then $\langle x_ix_j\rangle=\langle x_{i+6}x_j\rangle$ when $i=1$, 2 or 3 and $j=7$, 8 or 9. However, it is questionable whether either of these two models approximates to the true motion of the bound water molecule.

A physically more reasonable model is the rigid-body motion model (RBM). In the RBM model the fact that the main contribution to the **U** matrices comes from the translational and torsional modes is utilized, and the higher-frequency intramolecular modes are either ignored or corrected for in a semiquantitative way. The elements of the **U** matrices can be built up from contributions from the three 3×3 matrices **T**, **L** and **S**. The translational motion of the molecule is described by the **T** matrix, and for the water molecule this is approximately equal to the **U** matrix for the O atom. The **L** matrix describes the torsional oscillations of the

water molecule and the unsymmetrical **S** matrix couples the translational and the torsional motion. The corrections to the observed distances depend only on the elements of the **L** matrix.

We assume that the water molecule sits in a position with $2mm$ symmetry. Then the **L** matrix is a diagonal matrix and we write:

$$L(1,1)=\langle\theta_w^2\rangle$$
$$L(2,2)=\langle\theta_t^2\rangle$$
$$L(3,3)=\langle\theta_r^2\rangle \tag{22}$$

where w, t and r stand for respectively the wagging, twisting and rocking mode of the molecule. Then it follows from the general expression given by Busing & Levy (1964):

$$\langle r_1\rangle=r_{10}[1+\tfrac{1}{2}(\cos^2\alpha_1\langle\theta_w^2\rangle+\sin^2\alpha_1\langle\theta_t^2\rangle+\langle\theta_r^2\rangle)] \tag{23}$$

$$\langle R\rangle=R_0[1+\tfrac{1}{2}(\langle\theta_t^2\rangle+\langle\theta_r^2\rangle)]\,. \tag{24}$$

It follows from the general theory for the RBM model that for a simple molecule such as the water molecule it is not possible to obtain the elements of the **L** matrix from the observed **U** matrices. [This point is discussed in detail by La Placa *et al.* (1973).] The elements of the $\langle x_ix_j\rangle$ matrix are easily written down. Schomaker & Trueblood (1968) introduced the rotational displacement matrix **D** which we shall write to first order:

$$\mathbf{D}=\begin{bmatrix}0 & \bar\theta_r & \theta_t\\ \theta_r & 0 & \bar\theta_w\\ \bar\theta_t & \theta_w & 0\end{bmatrix}. \tag{25}$$

The displacement coordinate x_i is then

$$x_i=\sum_{k=1}^{3}D_{ik}r_k+t_i \tag{26}$$

where the sum is the contribution from the rotation and t_i from the translation. We change the coordinate system in Fig. 1 so that the oxygen atom is at the origin, then H_1 is at $\bar u_2$, $\bar u_3$, 0 and H_2 at u_2, $\bar u_3$, 0.

We can then calculate $\langle x_ix_j\rangle$ keeping only diagonal terms in **L** and **T** and ignoring all terms belonging to **S**. (A typical matrix element in **L** is $\langle\theta_i\theta_j\rangle$ in **T** $\langle t_it_j\rangle$ and in **S** $\langle t_i\theta_j\rangle$.) We then obtain the following non-zero terms:

$$\langle x_1^2\rangle=\langle x_4^2\rangle=\langle x_1x_4\rangle=\langle\theta_r^2\rangle u_3^2+T_{11}$$
$$\langle x_1x_2\rangle=-\langle x_1x_5\rangle=\langle x_2x_4\rangle=-\langle x_4x_5\rangle=-\langle\theta_r^2\rangle u_2u_3$$
$$\langle x_1x_7\rangle=\langle x_4x_7\rangle=\langle x_7^2\rangle=T_{11}$$
$$\langle x_2^2\rangle=\langle x_5^2\rangle=\langle\theta_r^2\rangle u_2^2+T_{22}$$
$$\langle x_2x_5\rangle=-\langle\theta_r^2\rangle u_2^2+T_{22}$$
$$\langle x_2x_8\rangle=\langle x_5x_8\rangle=\langle x_8^2\rangle=T_{22}$$
$$\langle x_3^2\rangle=\langle x_6^2\rangle=\langle\theta_t^2\rangle u_2^2+\langle\theta_w^2\rangle u_3^2+T_{33}$$
$$\langle x_3x_6\rangle=-\langle\theta_t^2\rangle u_2^2+\langle\theta_w^2\rangle u_3^2+T_{33}$$
$$\langle x_3x_9\rangle=\langle x_6x_9\rangle=\langle x_9^2\rangle=T_{33}\,. \tag{27}$$

If we insert these matrix elements in the general equations for $\langle R\rangle$ [equation (7)] and $\langle r_1\rangle$ [equation (10)] we obtain respectively equation (24) and equation (23), *i.e.* the equations are consistent.

It follows from equation (27) that only $\langle\theta_r^2\rangle$ and $(\langle\theta_t^2\rangle u_2^2+\langle\theta_w^2\rangle u_3^2)$ can be obtained from the observed **U** matrices. This is sufficient to calculate $\langle r_1\rangle$ from equation (23), but not sufficient to calculate $\langle R\rangle$ from equation (24). To be able to calculate $\langle R\rangle$ we must take a look at the potential energy of the bound water molecule. We will return to this point below

Inserting $\langle x_ix_j\rangle$ from equation (27) in equation (18) we obtain:

$$\langle R\rangle=R_N\{1-[(A^2-B^2)\langle\theta_r^2\rangle+(A^2-C^2)\langle\theta_t^2\rangle]/(3A^2-1)\}\,. \tag{28}$$

Earlier we analysed the effects of motion on p.m.r. data differently starting from the basic assumption made in equation (13). We then found:

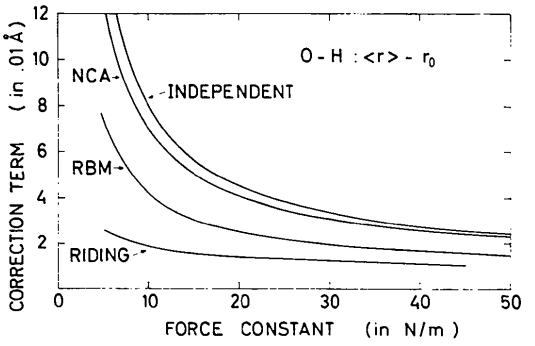

Fig. 2. The calculated difference between the mean OH distance and the observed distance – the correction term – as a function of the force constant in an isotropic external potential at 300 K. The correction term is calculated for different models of the vibratory motion of the water molecule as discussed in the text.

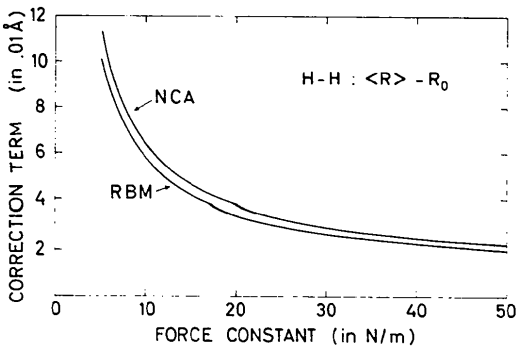

Fig. 3. The calculated difference between the mean H–H distance and the observed distance – the correction term – as a function of the force constant in an isotropic external potential at 300 K. The correction term is calculated for two models of the vibratory motion: rigid-body motion (RBM) and a normal coordinate analysis model (NCA). The independent motion model would give a result intermediate between the two curves given and is therefore omitted.

$$\left\langle \frac{3\mu}{R^3} \right\rangle = \frac{3\mu}{R_e^3}\left[1 - \frac{3\langle x\rangle}{R_e} + \frac{6\langle x^2\rangle}{R_e^2}\right] \quad (29)$$

$$\langle 3\cos^2\theta - 1\rangle = 3(1 - \langle\theta_r^2\rangle - 2\langle\theta_t^2\rangle)A^2 + 3(1\langle\theta_r^2\rangle - \langle\theta_t^2\rangle)B^2 + 3\langle\theta_t^2\rangle - 1\,. \quad (30)$$

Inserting this in equation (13), rearranging and using the definition of R_N in equation (14) and $\langle R\rangle$ in equation (7) we obtain:

$$\langle R\rangle = R_N[1 + 2\langle x^2\rangle/R^2 + \tfrac{1}{2}(B^2 - C^2) \times (\langle\theta_r^2\rangle - \langle\theta_t^2\rangle)/(3A^2 - 1)]\,. \quad (31)$$

$\langle x^2\rangle$ depends only on the intramolecular modes ($\langle x^2\rangle$ is zero in the RBM model). We therefore clearly see that the result obtained here – equation (28) – is markedly different from the 1964 result: equation (31). This lack of agreement shows that the assumption made in equation (13) cannot be valid.

We shall conclude this discussion by giving numerical values for the correction term – the difference between the observed interatomic distance or angle and the mean interatomic distance or angle. The numerical values have been obtained from a more general model of the motion discussed in more detail elsewhere (Pedersen, 1975). In this model of the motion we calculate $\langle x_i x_j\rangle$ from a normal coordinate analysis of the water molecule in a combined intramolecular and external potential – we therefore call the model the NCA model. The intramolecular potential used is a harmonic potential in internal coordinates. As the external potential is used

$$2V = \sum_{i=1}^{9}\sum_{j=1}^{9} k_{ij}x_i x_j\,. \quad (33)$$

The force constants, k_{ij} and the intramolecular force constants, can be adjusted to what is known in a specific case. Here, we shall use the simplest possible situation: intramolecular force constants as in the isolated water molecule [taken from Fifer & Schiffer (1970)], and

$$2V = k\sum_{i=1}^{9} x_i^2. \quad (34)$$

As judged from the calculated $\langle x_i x_j\rangle$ and frequencies of the normal modes a reasonable range for k is 0–50 N m^{-1}.

We have also calculated the corrections from the RBM model as a function of k. The frequency of one of the modes is generally in the harmonic approximation:

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{m}}$$

where f is the force constant and m the mass being moved in that mode. Inserting the expressions for x_i given in equation (26) in equation (33) and keeping only diagonal terms we then find that both the translational and the torsional rigid-body modes will be degenerate.

Translational modes:

$$f = 3k,\ m = M,\ i.e.\ \nu_{\text{trans}} = \frac{1}{2\pi}\sqrt{\frac{3k}{M}}$$

Torsional modes:

$$f = 2k,\ m = 2m_{\text{H}},\ i.e.\ \nu_{\text{tors}} = \frac{1}{2\pi}\sqrt{\frac{k}{m_{\text{H}}}}\,.$$

m_{H} is the mass of a H atom and M the molecular mass. When k increases from 5 to 50 N m^{-1} then ν_{tors} increases from 291 to 921 cm^{-1} (ν_{trans} from 119 to 376 cm^{-1}). The mean square amplitudes are then (Born & Huang, 1954):

$$T_{11} = T_{22} = T_{33} = F(\nu_{\text{trans}})/M$$
$$u_3^2\langle\theta_w^2\rangle = u_2^2\langle\theta_t^2\rangle = r_0^2\langle\theta_r^2\rangle = F(\nu_{\text{tors}})/(2m_{\text{H}})$$

where

$$F(\nu) = \frac{\hbar}{2\pi\nu}\,(0{\cdot}5 + 1/[\exp(h\nu/(k_B T)) - 1])\,.$$

$\hbar$ is Planck's constant divided by 2π, k_B the Boltzman constant and T the temperature in K.

The results of the calculations are given in Figs. 2, 3 and 4. We see that in the simple external potential chosen here the riding correction in the O–H distance is very much smaller than the more realistic corrections. For the H–H distance the RBM model and the NCA model give about the same correction. The independent motion correction is found between the RBM-correction and the correction calculated for the NCA model. (For reasons of clarity, however, this is not given in Fig. 3.) Therefore, somewhat surprisingly, the independent correction is close to the result obtained from the NCA model both for the OH and the H–H distances. Whether this is generally true remains to be seen when the NCA model is applied to specific cases.

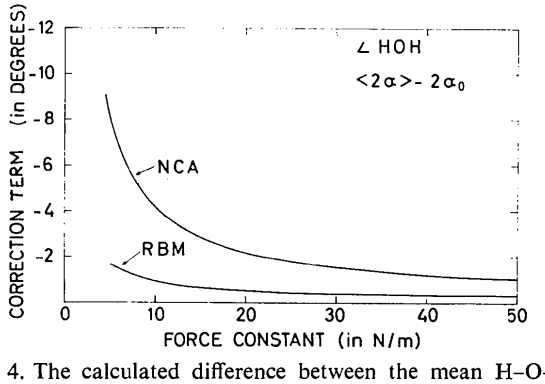

Fig. 4. The calculated difference between the mean H–O–H angle and the observed angle – the correction term – as a function of the force constant in an isotropic external potential at 300 K. The correction term is calculated for the rigid-body motion (RBM) model and the normal coordinate analysis (NCA) model.

The mean value of the HOH angle, $\langle 2\alpha \rangle$, is smaller than the observed value (Fig. 4) for both the NCA and the RBM model. This might at least partly explain why the H–O–H angle is generally observed to be about 3° larger when bound compared to the free molecule as pointed out in the Introduction. However, the correction factor is much larger for the NCA model than the RBM model.

Comparing calculated and observed normal mode frequencies and **U** matrices for the atoms a representative value for k seems to be 20 N m^{-1} (Pedersen, 1974). For this value of k the observed value of the OH distance will be 0·04 Å shorter than the mean value and the observed HOH angle will be 2° larger than the mean. Compared to the average values reported by Ferraris & Franchini-Angela (1972) this implies that the corrected OH distance on the average is stretched 0·02 Å and the corrected HOH angle is only enlarged 1·5° when the molecule is bonded. However, large variations have been observed in the geometry from one structure to another. It turns out to be difficult to systematize the observed variations. It is hoped that more reliable relations will be discovered from the geometry when the effect of motion has been corrected for. The correction must then be done as outlined above on the basis of a realistic potential fitted to the available information for each structure.

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The Bonded Water Molecule. II. A Simple Model of the Vibratory Motion

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A simple, quantitative model describing the vibratory motion of a water molecule bound in a condensed phase is presented. The model is based on a normal coordinate analysis of a bent XY_2 molecule in a combined internal and external potential. The potential can be used to simulate the potential at a specific site in a crystal. Numerical values of the frequencies and eigenvectors, referred to Cartesian coordinates, are calculated from an isotropic external potential. The range of force constant in the external potential covered is from 0 to 50 N m^{-1}. The force constants in the internal potential can be chosen to make the calculated frequencies of the internal modes equal to the observed values. The nine calculated normal modes can be divided into groups of three: intramolecular, torsional and translational. The calculated frequencies of the torsional and translational modes are in the range observed for librational modes. The translational and the intramolecular modes are coupled making the calculated intramolecular frequencies increase with the strength of the external potential using a constant internal potential. From the model, the mean square amplitudes of vibration of the individual atoms are calculated. The calculated values are found to be in the range observed in neutron-diffraction studies of hydrates.

Introduction

The free water molecule is a bent triatomic molecule with symmetry $2mm$ (C_{2v}). The dimensions of the isolated molecule and the rotary and vibratory energy levels are known in detail (Kern & Karplus, 1972). We focus the attention on the water molecule when bound in a crystal and propose a simple quantitative model as a framework for discussing experimental results obtained in spectroscopic investigations and in neutron-diffraction studies. The results obtained with the

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