

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 XY₂ 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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different techniques are interrelated – the molecular shape observed in diffraction studies is an average over the vibratory motion studied spectroscopically – but generally the results are discussed in highly different terms.

The general theory of the dynamics of a crystal lattice in the harmonic approximation is well known (Born & Huang, 1954). However, the theory is complicated to use on more complex solids and the results obtained on one crystal are difficult to generalize. This is clearly shown in the analysis of potassium oxalate monohydrate by Fukushima (1970). We shall therefore use a simpler approach and regard the crystal as consisting of stationary atoms except one water molecule. We shall discuss the motion of a single water molecule in the field of stationary atoms. In this paper we describe the first step in which the model itself is presented. Here we shall only use an isotropic external potential to show the main features of the model. Later the model will be used for discussing specific cases in which the external potential is calculated from the crystal structure by semi-empirical expressions for the interatomic potentials.

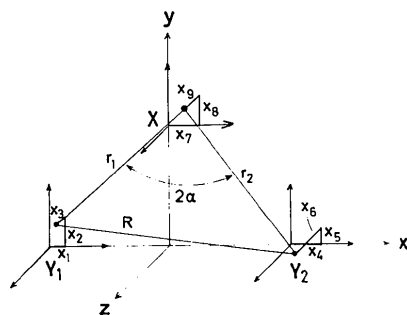


Fig. 1. The Cartesian displacement coordinates for an XY_2 molecule as used in the text.

NORMAL MODES OF A WATER MOLECULE IN AN ISOTROPIC POTENTIAL

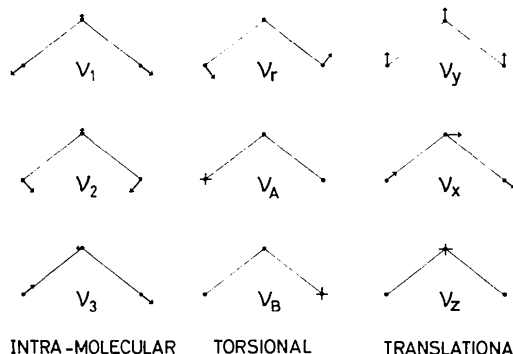


Fig. 2. The normal modes of a water molecule in an isotropic external potential. The force constant is 12 Nm^{-1} . The force constants in the internal potential have been taken from Fifer & Schiffer (1970). The amplitudes shown by the length of the arrows are not scaled correctly and do not show either the correct relative amplitudes in one mode or the correct relative amplitudes of the modes.

Our starting point will be the dynamics of the free water molecule. It is well known that the vibratory motion of the free molecule can be described in terms of the three normal modes: the symmetric stretch (v_1), the antisymmetric stretch (v_2) and the bend (v_3). As discussed by Herzberg (1945) it is possible to find reasonable force constants in the harmonic approximation to calculate normal mode frequencies in good agreement with the observed values. However, as shown by Darling & Dennison (1940) and later refined by Benedict, Gailar & Plyler (1956) the anharmonic contribution is significant. For example: the mean value of the O–H distance in the lowest vibrational state is 0.0173 \AA larger than the value at equilibrium: 0.9572 \AA (Kuchitsu, 1971).

When the water molecule is bound in a condensed phase the two stretching modes are shifted to lower frequencies indicating a weakening of the O–H bond due to hydrogen-bond formation. Again, as shown by Fifer & Schiffer (1970), it is possible to find reasonable force constants in the harmonic approximation to calculate normal mode frequencies in good agreement with the observed infrared absorption bands. However, the spectroscopic information is not detailed enough to make it possible to get information on the anharmonic part of the lattice perturbed intramolecular potential. We shall therefore assume, following Fifer & Schiffer (1970), that the anharmonicity is not significantly changed from what it is in the vapour.

To find the normal modes one has to carry through a normal coordinate analysis of the motion of the molecule. This was earlier a major operation to do numerically. However, with the aid of a modern computer the calculation is quickly done. As pointed out by Gwinn (1971) the approach should depend on the tools available for the calculation. Gwinn showed that, with a computer, it is faster and simpler to go back to the basic equations formulated in Cartesian coordinates and avoid much of the later developments mainly introduced to simplify the calculation by hand. In the Gwinn approach the analysis of an N -atom molecule will lead to $3N$ normal modes. If the molecule is linear five of these modes will have frequency equal to zero; if the molecule is non-linear six modes will have frequency zero. This is as expected and follows from the fact that the molecule will have three translational and three, or two, rotational degrees of freedom. These degrees of freedom will have zero frequency when the molecule is in a constant potential as it by definition is when the molecule is free. However, when the molecule is bound in a solid the potential is not constant. We shall therefore extend the Gwinn approach to cover a molecule bound in a condensed phase by simply adding to the intramolecular potential an external potential.

Normal coordinate analysis

The task in a normal coordinate analysis is to find a set of coordinates – the normal coordinates – such that

the total energy written in terms of these coordinates is in diagonal form (Herzberg, 1945; Born & Huang, 1954). The major obstacle for doing this is the potential energy of the molecule which is usually expressed in terms of internal coordinates. For the water molecule a commonly used intramolecular potential V_a is

$$2V_a = F_r(\Delta r_1^2 + \Delta r_2^2) + F_\alpha(2r_0\Delta\alpha)^2 + 2F_{rr}\Delta r_1\Delta r_2 + 2F_{r\alpha}(\Delta r_1 + \Delta r_2)(2r_0\Delta\alpha) \quad (1)$$

Δr_1 , Δr_2 and $r_0(2\Delta\alpha)$ are displacements of the bonds and apex angle of the water molecule from their equilibrium values: $r_1=r_2=r_0$ and 2α . We shall describe the displacements with the use of the Cartesian coordinate system shown in Fig. 1. We collect the three internal coordinates in the matrix \mathbf{q} then

$$\mathbf{q} = \mathbf{L}\mathbf{x} \quad (2)$$

where \mathbf{L} is the transformation matrix connecting the nine Cartesian displacement coordinates \mathbf{x} to \mathbf{q} (see Appendix 1). Equation (1) can be written in matrix notation

$$2V_a = \tilde{\mathbf{q}}\mathbf{F}_a\mathbf{q} \quad (3)$$

where

$$\mathbf{F}_a = \begin{pmatrix} F_r & F_{rr} & F_{r\alpha} \\ F_{rr} & F_r & F_{r\alpha} \\ F_{r\alpha} & F_{r\alpha} & F_\alpha \end{pmatrix}.$$

Substituting \mathbf{q} with \mathbf{x} in equation (3) by means of equation (2):

$$2V_a = \tilde{\mathbf{x}}(\tilde{\mathbf{L}}\mathbf{F}_a\mathbf{L})\mathbf{x}. \quad (4)$$

The external potential V_e can be written

$$2V_e = \tilde{\mathbf{x}}\mathbf{F}_e\mathbf{x}. \quad (5)$$

\mathbf{F}_e is a symmetric matrix of the order (9,9) consisting of the various force constants characteristic for a specific site in a particular crystal.

The total potential energy is then

$$2V = 2V_a + 2V_e = \tilde{\mathbf{x}}\mathbf{F}\mathbf{x} \quad (6)$$

where

$$\mathbf{F} = \mathbf{F}_e + \tilde{\mathbf{L}}\mathbf{F}_a\mathbf{L}.$$

We can now follow Gwinn (1971) and introduce the mass-weighted Cartesian displacement coordinates X_i :

$$X_i = m^{1/2}x_i.$$

In matrix notation

$$\mathbf{x} = \mathbf{M}\mathbf{X} \quad (7)$$

where \mathbf{M} is a diagonal matrix with $m_i^{-1/2}$ on the diagonal. The normal coordinates Q_i are then found by diagonalizing the matrix \mathbf{MFM} , i.e. we look for a matrix \mathbf{B} such that

$$\mathbf{X} = \mathbf{B}\mathbf{Q} \quad (8)$$

and

$$\tilde{\mathbf{B}}(\mathbf{MFM})\mathbf{B} = \mathbf{A} \quad (9)$$

where \mathbf{A} is a diagonal matrix with ω_i^2 on the diagonal. $\omega_i = 2\pi\nu_i$ where ν_i is the frequency of the i th normal mode.

To find \mathbf{B} and \mathbf{A} we use the Jacobi method as given as a subroutine written by Kuo (1965) where a detailed discussion of the Jacobi method can be found. Faster and perhaps better subroutines exist, but the one chosen functions satisfactorily with computer time of the order of seconds. (Program in Basic on a Norwegian minicomputer NORD-1.)

In the following discussion we have chosen the simplest possible external potential. \mathbf{F}_e in equation (5) is simplified to a diagonal matrix with all diagonal elements equal to k . The numerical values presented below have been calculated for k in the range $0 \leq k \leq 50 \text{ N m}^{-1}$ and values of the intramolecular

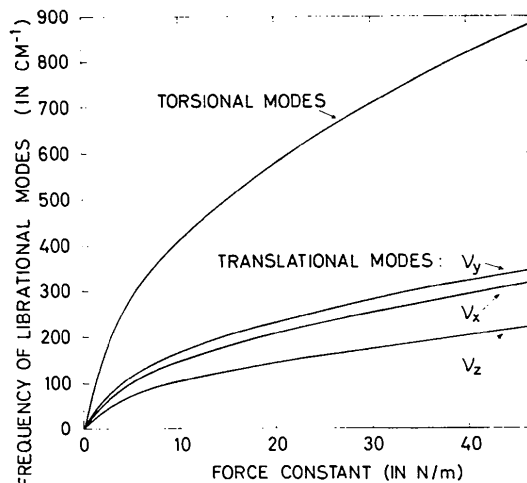


Fig. 3. The calculated frequencies of the librational modes of an H_2O molecule as a function of the force constant when the molecule is in an external isotropic potential. The internal potential is constant.

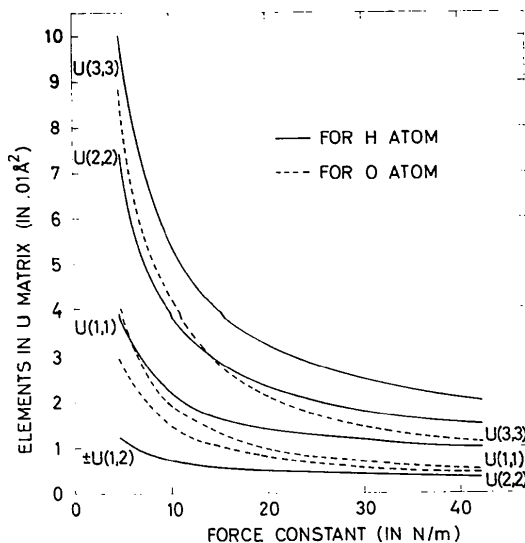


Fig. 4. The calculated elements of the \mathbf{U} matrix describing the vibratory motion of the individual atoms as a function of the force constant when the molecule is in an external isotropic potential. The internal potential is constant.

force constants (in N m^{-1}) as given by Fifer & Schiffer (1970): $F_r = 845.00$; $F_{rr} = -10.47$; $F_{r\alpha} = 16.72$; $F_\alpha = 75.40$.

Discussion

The normal modes

In the classical picture the atoms move with a constant phase relative to each other in a normal mode as shown in Fig. 2. Three of the modes can clearly be referred to the intramolecular modes. Of the remaining six which we shall call librational modes, we can choose three which are mainly torsional and three which are mainly translational.

The three torsional modes constitute a degenerate set of modes. Hence, a linear combination of them is also a normal mode. One of the modes is clearly the rocking mode – oscillation about an axis normal to the plane of the molecule. Making the simple linear combination ‘sum’ and ‘difference’ between the other two modes, we see that the ‘sum’ is the wagging mode and the ‘difference’ the twisting mode. (In the wagging mode the atoms oscillate about an axis in the plane of the molecule parallel to H–H and in the twisting mode about the twofold axis.)

The three translational modes are not degenerate and they are clearly not pure translational modes.

In Fig. 3 is shown the dependence of the frequencies of the normal modes on the force constant k . The calculated frequencies are in the range observed in hydrates: translational bands in the region $100\text{--}300\text{ cm}^{-1}$ and torsional bands in the region $400\text{--}700\text{ cm}^{-1}$ (Boutin & Yip, 1968).

For a harmonic oscillator the resonance frequency is

$$\nu = \frac{1}{2\pi} \sqrt{\frac{f}{m}} \quad (10)$$

where f is the force constant and m is the mass being moved in that mode. When f is given in N m^{-1} and m in atomic mass units then we have

$$\nu \text{ (in cm}^{-1}\text{)} = 130.28 \sqrt{\frac{f}{m}}. \quad (11)$$

The torsional frequency given in Fig. 3 is obtained if $f = 2k$ and $m = 2m_{\text{H}}$, where m_{H} is the mass of a hydrogen atom. We obtain ν_r by setting $f = 3k$ and $m = M$ in equation (11) (M is the mass of the molecule). The interpretation of these relations is that these two frequencies are the normal modes of the water molecule regarded as a rigid body (Pedersen, 1974). For a rigid body moving in an isotropic potential the three torsional and the three translational modes are two degenerate sets. As shown in Fig. 3 the translational modes are coupled differently to the intramolecular modes lifting this degeneracy.

The coupling between the translational and intramolecular modes is also manifested in a linear increase of the intramolecular frequencies with k :

$$\begin{aligned} \nu_1 \text{ (cm}^{-1}\text{)} &= 3830.4 + 2.098k \text{ (N m}^{-1}\text{)} \\ \nu_2 \text{ (cm}^{-1}\text{)} &= 1647.4 + 4.609k \text{ (N m}^{-1}\text{)} \\ \nu_3 \text{ (cm}^{-1}\text{)} &= 3942.0 + 1.979k \text{ (N m}^{-1}\text{)} \end{aligned} \quad (12)$$

This result is important. It is well known that the frequencies of the two stretching modes decrease when the water molecule is bound in a condensed phase (Falk & Knop, 1973). This frequency decrease is interpreted as being due to hydrogen-bond formation weakening the OH bond, *i.e.* the intramolecular force constants are reduced. However, the frequencies of the free molecule are always used as a reference. But, apparently, one should instead use the free molecule vibrating at the crystal site as the reference. From the results just given the frequency decrease due to bonding is significantly greater than that obtained using the free molecule as reference.

Similar calculations have been performed on D_2O . The results obtained are consistent with the picture given above taking into account the difference in mass between D and H.

The mean square amplitudes of vibration

In a diffraction study of a crystal the atoms are generally treated independently (Lipson & Cochran, 1966). For each atom a temperature factor matrix \mathbf{B} is determined. From \mathbf{B} can be calculated a \mathbf{U} matrix such that the mean amplitude of vibration of the atom in a direction \mathbf{N} , u^2 , is given as

$$u^2 = \mathbf{NUN}. \quad (13)$$

The components of the \mathbf{U} matrix for each atom can be calculated very simply. In terms of the Cartesian displacement coordinates introduced in Fig. 1 a typical element in \mathbf{U} , U_{ij} , is:

$$U_{ij} = \langle x_i x_j \rangle \quad (14)$$

when \mathbf{U} is referred to the coordinate system used in Fig. 1. Generalizing a result found by Stølevik, Seip & Cyvin (1972) it is easy to show that

$$\langle x_i x_j \rangle = \sum_{k=1}^9 F(\nu_k) V_{ik} V_{jk}. \quad (15)$$

The mean square amplitude is the thermal average over the molecular vibrations regarding the molecules as an ensemble of harmonic oscillators. $F(\nu)$ is the so called frequency factor:

$$\begin{aligned} F(\nu) &= \frac{\hbar}{2\nu} \coth \left(\frac{\hbar\nu}{2k_B T} \right) \\ &= \frac{\hbar}{\nu} (0.5 + 1/\{\exp[\hbar\nu/(k_B T)] - 1\}). \end{aligned} \quad (16)$$

Here \hbar is the Planck constant divided by 2π , k_B the Boltzmann constant and T the temperature in K.

V_{ij} in equation (15) are the elements of a matrix \mathbf{V} given as:

$$\mathbf{V} = \mathbf{M}\mathbf{B} \quad (17)$$

because as \mathbf{B} connects \mathbf{Q} and the mass weighted coordinates \mathbf{X} , \mathbf{V} will then connect \mathbf{Q} and the Cartesian displacement coordinates \mathbf{x} . Using equation (15) we have calculated the elements of the \mathbf{U} matrix for the O and the H atoms as a function of k . The results are given in Fig. 4.

In an isotropic external potential the symmetry of the water molecule is still $2mm$. Hence the oxygen atom sits at a site with symmetry $2mm$ and therefore the \mathbf{U} matrix for the oxygen atom only contains diagonal elements in the coordinate system used. The H atoms sit at a site with symmetry m ; therefore the only non-zero off-diagonal element is $U(1,2)$. These symmetry requirements are fulfilled by the results of the calculations.

Owing to the functional dependence of the frequency factor [equation (16)] the low-frequency normal modes give the largest contribution to the mean square amplitude of vibration of the atoms. Furthermore the elements of the \mathbf{U} matrix will grow beyond all limits when $k = 0$ which is correct, as the molecule then is free and not bound to any particular site. However, when $k=0$, equation (15) can still be used eliminating the modes with zero frequency. We then find at 300 K for the non-zero elements:

for the O atom:

$$U_{11} = 1.95 \times 10^{-5} \text{ \AA}^2$$

$$U_{22} = 5.66 \times 10^{-5}$$

for the H atom:

$$U_{11} = 0.00448 \text{ \AA}^2$$

$$U_{12} = \pm 0.00036$$

$$U_{22} = 0.00430.$$

The contribution from the intramolecular modes to the amplitudes of vibration in the crystal is therefore small but not negligible for the H atoms.

It is interesting to note in Fig. 4 that the three non-zero elements in \mathbf{U} for oxygen are not equal, *i.e.* the motion is anisotropic even though the molecule moves in an isotropic potential. (This is shown even more pronounced by the hydrogen atoms.) The out-of-plane motion has a larger amplitude than the in-plane motion. This follows from the fact that the translational mode moving the oxygen atom normal to the plane of the molecule is the mode with lowest frequency.

The calculated \mathbf{U} matrix for D_2O is closely similar to the results obtained for H_2O . Owing to the increased mass the amplitudes are somewhat reduced but only by about 0.003 to 0.005 \AA^2 .

Observed values of the elements of \mathbf{U} referred to the same coordinate system as used in Fig. 1 are given in Table 1. From the data in Table 1 it follows that the calculated values of \mathbf{U} given in Fig. 4 cover the range observed experimentally.

The symmetric mean-square amplitude matrix $\langle x_i x_j \rangle$ is a 9×9 matrix but only the 3×3 diagonal blocks can be given a direct physical interpretation as described above. Elsewhere the influence of the motion on the observed geometry is discussed and then the correction factor is based on this generalized mean square amplitude matrix $\langle x_i x_j \rangle$ (Pedersen, 1974).

It is interesting to compare $\langle x_i x_j \rangle$ calculated here with the corresponding matrix computed from the rigid-body motion model of Schomaker & Trueblood (1968). In the RBM model $\langle x_i x_j \rangle$ is expressed as a linear function of the matrix elements of three 3×3 matrices \mathbf{T} , \mathbf{L} and \mathbf{S} . For a water molecule at a site with $2mm$ symmetry \mathbf{S} is zero and \mathbf{T} and \mathbf{L} are diagonal matrices. Shifting the origin in Fig. 1 to the oxygen

Table 1. Observed elements of the mean square amplitude matrix \mathbf{U} for the atoms in the water molecules in some accurately determined hydrates

Compound	U_{ij} for O (in 0.01 \AA^2)							U_{ij} for H (in 0.01 \AA^2)						References	
	Atom	(1,1)	(2,2)	(3,3)	(1,2)	(1,3)	(2,3)	Atom	(1,1)	(2,2)	(3,3)	(1,2)	(1,3)		(2,3)
$\alpha\text{-COOH} \cdot 2\text{H}_2\text{O}$	O(3)	3.6	3.2	5.6	0.2	0.5	1.3	D(2)	4.7	3.5	7.7	0	0.5	-0.1	Coppens & Sabine (1969)
								D(3)	4.5	5.6	7.7	-1.2	0.9	0.9	
$\beta\text{-COOH} \cdot 2\text{H}_2\text{O}$	O(3)	3.7	2.7	10.6	0.2	0.3	-0.5	D(2)	4.6	5.0	7.4	1.3	0.8	-0.4	La Placa <i>et al.</i> (1973)
								D(3)	4.7	4.1	7.2	-0.5	0.4	-0.3	
Ice IX	O(2)	2.8	1.7	2.5	0	-0.3	0	D(7)	3.2	2.5	3.2	0.3	0.3	-0.1	La Placa <i>et al.</i> (1973)
	O(1)	2.2	1.8	2.6	0.1	0	0.1	D(5)	2.6	2.6	3.2	0.3	0.3	0	
$\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$	O(3)	2.3	2.6	7.4	0	0	0	D(6)	2.2	2.8	3.4	-0.4	0.1	-0.1	Sequiera <i>et al.</i> (1970)
								H	3.3	3.9	5.1	0.5	0.3	0	
$\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	O(7)	2.9	3.1	4.2	0.1	0.4	-0.1	H(15)	3.9	4.5	5.6	1.0	0	-0.4	Brown & Chidambaram (1969)
								H(16)	4.0	5.0	5.5	-0.9	0.1	-0.9	
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	O(8)	2.7	2.9	3.7	0	-0.3	0.1	H(17)	3.8	4.1	4.9	0.7	-0.4	0.4	Padmanabhan <i>et al.</i> (1963)
	O(9)	2.6	2.3	2.8	0	0.1	-0.6	H(18)	3.8	4.1	4.6	-0.8	-0.3	0.3	
	O(1)	2.4	1.7	2.4	0	0.1	-0.2	H(19)	3.3	4.0	5.1	0.6	0.3	-1.0	
	O(2)	2.5	1.9	2.5	-0.3	0.3	-0.2	H(20)	3.3	3.6	4.4	-0.4	0	-0.6	
								H(6)	4.1	3.7	6.3	-1.3	0.3	-0.4	
								H(7)	4.2	3.3	5.5	-1.2	0	0.1	
								H(8)	4.5	4.2	4.4	1.4	0.1	-0.4	
								H(9)	4.8	4.8	5.7	-2.2	0.1	-0.1	

atom, we obtain the matrix elements given in Table 2 (Pedersen, 1974). In this table also numerical values are given calculated for $k=20 \text{ N m}^{-1}$ for both models. We see that the two matrices are very similar with a few notable differences: $\langle x_3x_6 \rangle$, $\langle x_3x_9 \rangle$ and $\langle x_6x_9 \rangle$ are zero in the model presented here but equal to a translation in the RBM model. The origin of these differences can be understood from looking at the normal modes in Fig. 2.

Table 2. *The elements of mean square amplitude matrix $\langle x_i x_j \rangle$ for the rigid-body motion model*

The numerical values obtained for the model presented in this paper are given for comparison below ($k=20 \text{ Nm}^{-1}$, $T=300 \text{ K}$). All numbers are in 0.01 \AA^2 .

i/j	1	2	3	4	5	6	7	8	9
1	a	$-d$	0	0	d	0	e	0	0
	1.42	-0.50	0	0.79	0.31	0	0.60	0.04	0
2		b	0	$-d$	f	0	0	e	0
		2.35	0	-0.31	-0.28	0	0.46	0.70	0
3			c	0	0	e	0	0	0
			3.25	0	0	0	0	0	0
4				a	d	0	e	0	0
				1.42	0.49	0	0.60	-0.04	0
5					b	0	0	e	0
					2.35	0	-0.04	0.70	0
6						c	0	0	e
						3.25	0	0	0
7							e	0	0
							1.00	0	0
8								e	0
								0.81	0
9									e
									2.14

$a=U_{11}=1.37$; $b=U_{22}=1.78$; $c=U_{33}=4.02$; $d=U_{12}=0.79$;
 $e=U_0=0.76$; $f=2e-b=-0.26$.

APPENDIX

Evaluation of the transformation matrix L

We are working under the assumption of small displacements from the equilibrium position. To find the matrix L in equation (2) we use a Taylor expansion of the $q(I)$ about the mean position.

$$q_i = \sum_{i=1}^9 \left(\frac{\partial r_i}{\partial x_i} \right)_{0} x_i$$

$$q_1 = \Delta R_1, \quad q_2 = \Delta R_2, \quad \text{and} \quad q_3 = r_0 \Delta(2\alpha)$$

From Fig. 1 it follows that

$$r_1^2 = [x_7 - (x_1 - r_0 \sin \alpha)]^2 + [(x_8 + r_0 \cos \alpha) - x_2]^2 + (x_9 - x_3)^2$$

$$r_2^2 = [(x_4 + r_0 \sin \alpha) - x_7]^2 + [x_5 - (x_8 + r_0 \cos \alpha)]^2 + (x_6 - x_9)^2$$

$$R^2 = [(x_4 + r_0 \sin \alpha) - (x_1 - r_0 \sin \alpha)]^2 + (x_5 - x_2)^2 + (x_6 - x_3)^2$$

$$2r_1 r_2 \cos 2\alpha = r_1^2 + r_2^2 - R^2.$$

For example, to find $\partial r_2 / \partial x_7$ we differentiate the equation for r_2^2 :

$$2r_2 \frac{\partial r_2}{\partial x_7} = -2(x_4 + r_0 \sin \alpha - x_7)$$

$$\left(\frac{\partial r_2}{\partial x_7} \right)_0 = -\sin \alpha.$$

Applying this systematically we obtain

$$q_1 = -\sin \alpha \cdot x_1 - \cos \alpha \cdot x_2 + \sin \alpha \cdot x_7 + \cos \alpha \cdot x_8$$

$$q_2 = \sin \alpha \cdot x_4 - \cos \alpha \cdot x_5 - \sin \alpha \cdot x_7 + \cos \alpha \cdot x_8$$

$$q_3 = -\cos \alpha \cdot x_1 + \sin \alpha \cdot x_2 + \cos \alpha \cdot x_4 + \sin \alpha \cdot x_5 - 2 \sin \alpha \cdot x_8.$$

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