

conceived can largely, or only roughly, be applied to the actual structure. This holds, of course, for any other approach to the question of bond-length correction.

In the succeeding paper we shall develop dynamical models for diatomic and triatomic molecules.

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## The Thermal-Motion Bond-length Correction for Diatomic and Triatomic Molecules

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The bond-length correction which is needed to correct for the effects of thermal motion is derived for diatomic and triatomic molecules. We treat the molecules as rigid-body oscillators and assume that the correlation tensor  $S$  is symmetric when the origin of the librations is at the centre of gravity. For diatomic molecules consisting of atoms of different masses and for linear triatomic molecules a simple solution is obtained. For diatomic molecules consisting of equal atoms and for angular triatomic molecules one can determine the correction only by introducing an unknown lattice-dynamical parameter. The value of this parameter can be assessed to a certain extent and can be determined from the vibration tensors of the atoms of asymmetric diatomic and linear triatomic molecules. Thus one obtains an experimental distribution of the lattice-dynamical parameter which is also likely to hold for symmetric diatomic and angular triatomic molecules. The corrections are calculated for 11 water molecules for which very accurate structural data are available.

### 1. Introduction

The thermal bond-length correction for diatomic and triatomic molecules can, in principle, be determined from the model of rigid-body motion (to a very good approximation). If one atom in the molecule is much heavier than the others, the riding model (*cf.* Busing & Levy, 1964) also provides an essentially correct value of the correction. However, for many diatomic and triatomic molecules the assumptions made in the riding model do not hold. Even for the  $H_2O$  molecule the riding model does not seem to be appropriate and for the  $D_2O$  molecule it is certainly inappropriate.

If one wants to determine the correction by applying the rigid-body model the question arises to what extent the validity of this model is restricted by the internal modes of the molecule. For diatomic molecules there is only one internal mode in the direction of the bond. Since this mode does not enter into the calculation of the correction, the rigid-body model holds exactly for evaluating the correction for diatomic molecules. With triatomic molecules, however, the components of the atomic vibration tensors  $U$ , which are determined experimentally, contain contributions of the internal

modes. For light atoms these contributions attain their maximum. In a preceding paper (Scheringer, 1972*a*) we showed that, even for hydrogen atoms, they do not amount to more than about 10% of the total mean-square amplitudes. However, if one evaluates the components of the libration tensor  $L$  of the molecule from the experimentally determined components  $U^{ik}$  the actual error made is even smaller. The reason is that internal and external modes often have nearly the same mean-square amplitudes so that the libration tensor also contains the internal modes to a large extent. We shall discuss these relations in detail for the water molecule.

If the rigid-body model is applied to diatomic and triatomic molecules further investigation will then show that it is expedient to divide the molecules into two classes. For the molecules of the first class the correction can be determined directly from the vibration tensors  $U$  of the atoms. It is to this class that the diatomic molecules with unequal masses and the linear triatomic molecules belong. For the molecules of the second class the thermal rigid-body parameters cannot be fully determined from X-ray or/and neutron data, *i.e.* the components  $U^{ik}$  of the atoms are not sufficient

to determine uniquely the libration tensor  $\mathbf{L}$ , which is needed to calculate the correction. It is to this second class that the diatomic molecules with equal masses and the angular triatomic molecules belong. We shall treat the molecules of the second class in the following way: we introduce an unknown lattice-dynamical parameter and formulate the correction in terms of it. This parameter can be assessed to a certain extent by virtue of its definition and from experimental evidence. Furthermore, it can be determined from the vibration tensors  $\mathbf{U}$  of the molecules of the first class. If one calculates the lattice-dynamical parameter from various structures one obtains an experimentally established distribution of this parameter. The mean value of this distribution can – with some caution – be applied to the molecules of the second class. The correction for these molecules thus remains uncertain within certain limits but in many cases it is more accurate than the correction which one would obtain with the riding model.

In this paper we derive the equations for the bond-length correction of diatomic and triatomic molecules. We shall not discuss the case of the asymmetric angular triatomic molecule since the formulae become too cumbersome and the rare occurrence of this case in crystals does not warrant its explicit treatment. Furthermore, we calculate the corrections for 11 water molecules for which very accurate structural data, obtained by neutron diffraction, are available.

## 2. The diatomic molecule with unequal masses

We consider the molecule to be a rigid-body oscillator and choose the centre of gravity of the molecule as origin for describing the librations. We assume that the rigid-body correlation tensor  $\mathbf{S}$  is symmetric for this origin, *i.e.*  $\mathbf{S}=\mathbf{S}^T$ . This assumption has proved to be nearly true for several molecules and thus does not seem to imply a severe loss of generality. We call our model the ‘centre-of-gravity’ model, hereafter abbreviated to COG model. In order to simplify description in the following we choose a Cartesian coordinate system with the  $z$  axis pointing in the direction of the bond. The two atoms have the coordinates  $z_r$  and  $z_s$ , the  $x$  and  $y$  coordinates are zero. Thus the distance between the two atoms is  $d=|z_r-z_s|$  and the correction term,  $\overline{w^2}=\text{trace}(\mathbf{A}_{rs})$  [equation (3.6) of Scheringer, (1972c) – hereafter referred to as SCHE (3.6)] is equal to

$$\overline{w^2}=d^2(L_{11}+L_{22}), \quad (2.1)$$

*cf.* SCHE (4.5). Hence we have to determine  $L_{11}$  and  $L_{22}$  from the components  $U_r^{ik}$  and  $U_s^{ik}$ . From SCHE (4.2) we obtain in our special coordinate system

$$U_r^{11}=T^{11}+z_r^2L_{22}+2z_rS_2^1, \quad (2.2a)$$

$$U_r^{22}=T^{22}+z_r^2L_{11}-2z_rS_1^2. \quad (2.2b)$$

Similar equations hold for the atom  $s$ . There are 6 components of TLS in the equations (2.2a) and (2.2b)

but we have only 4 components,  $U_r^{ii}$  and  $U_s^{ii}$ , to determine them. Now we take advantage of our assumption that the tensor  $\mathbf{S}$ , referred to the centre of gravity, is symmetric, *i.e.*  $S_2^1=S_1^2$ . If we form the sums  $U_r^{11}+U_r^{22}$  the parameter  $S_2^1=S_1^2$  cancels out and we obtain

$$L_{11}+L_{22}=\frac{U_s^{11}+U_s^{22}-U_r^{11}-U_r^{22}}{z_s^2-z_r^2}. \quad (2.3)$$

Equation (2.3) yields a reasonable result only if  $z_s^2 \neq z_r^2$ , *i.e.* if the centre of gravity is not at the geometrical centre of the molecule, in other words if the masses  $m_r$  and  $m_s$  are not equal. In the following we choose  $m_r > m_s$ . Let  $m_r+m_s=M$ ; then

$$z_r^2=\frac{d^2m_s^2}{M^2}, \quad z_s^2=\frac{d^2m_r^2}{M^2}, \quad (2.4)$$

and we obtain with equations (2.1), (2.3) and (2.4)

$$\overline{w^2}=(U_s^{11}+U_s^{22}-U_r^{11}-U_r^{22})\frac{m_r+m_s}{m_r-m_s}. \quad (2.5)$$

Neglecting our special coordinate system and defining  $\overline{w_r^2}$  ( $\overline{w_s^2}$ ) by analogy to  $\overline{w^2}$  of SCHE (3.6), we can substitute  $\mathbf{A}_{rs}$  by  $\mathbf{U}_r(\mathbf{U}_s)$  and write

$$\overline{w^2}=(\overline{w_s^2}-\overline{w_r^2})\frac{m_r+m_s}{m_r-m_s}. \quad (2.6)$$

Hence the COG model gives a correction which can be obtained directly from that of the riding model,  $\overline{w_s^2}-\overline{w_r^2}$ , by multiplication with a mass factor. For an  $\text{OH}^-$  ion this factor is  $17/15=1.13$ , a value which will scarcely be significant on an absolute scale. But, in principle, we believe the COG model to be the more realistic approach for non-bonded diatomic molecules.

## 3. The diatomic molecule with equal masses

We now consider the case  $m_r=m_s$  for which our equations break down. With  $m_r=m_s$  the COG model demands  $\mathbf{U}_r=\mathbf{U}_s$ . Hence there are only two parameters,  $U_r^{11}$  and  $U_r^{22}$ , left and these are not sufficient to determine  $L_{11}$  and  $L_{22}$  in equations (2.2a) and (2.2b).  $\overline{w^2}$  in equation (2.6) remains undetermined since  $\overline{w_s^2}-\overline{w_r^2}$  becomes zero and the mass factor infinitely large. We get around this difficulty as follows: we introduce a lattice-dynamical parameter into the equations for the correction which describes the ratio of librational to translational motions of the molecule. This parameter can be determined from experimental data in the case  $m_r > m_s$ . The values of the parameter gained in this way will then be transferred to the case  $m_r=m_s$ .

Let  $\tau_r$  be the translational part and  $\varrho_r$  be the librational part of the lattice vibrations for the atom  $r$ , expressed as mean-square amplitudes with  $\tau_r+\varrho_r=1$ . Then we have in agreement with equations (2.2a) and (2.2b)

$$\begin{aligned} T^{11}+T^{22} &= \tau_r(U_r^{11}+U_r^{22}), \\ z_r^2(L_{22}+L_{11}) &= \varrho_r(U_r^{11}+U_r^{22}). \end{aligned} \quad (3.1)$$

Similar equations hold for the atom  $s$ . An explicit ex-

pression for the ratio  $\varrho_r/\tau_r$  can be gained from the lattice-dynamical expression for the components  $U^{ii}$  as given by Scheringer (1972*b*) equation (4). This equation refers to a single atom, but here we have to apply it to the whole molecule since we consider only the external modes of the molecule. Hence we have to substitute the masses  $m_r$  and  $m_s$  by the total mass of the molecule,  $M$ , and the moment of inertia,  $I$ . With the COG model we refer the moment of inertia to the centre of gravity of the molecule. Then we obtain the mass factor  $I/z_r^2$  instead of  $m_r$  for the librational modes of the molecule, and  $M$  for the translational modes. With equation (4) of Scheringer (1972*b*) we then obtain

$$\frac{\varrho_r}{\tau_r} = \frac{(U_r^{11} + U_r^{22})_{\text{rot}}}{(U_r^{11} + U_r^{22})_{\text{trans}}} = \frac{Mz_r^2 \{ \}_{\text{rot}}}{I \{ \}_{\text{trans}}}, \quad (3.2)$$

where

$$\{ \} = \sum_{\mathbf{q}j} \frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})} [e_1(r|\mathbf{q}j)e_1^*(r|\mathbf{q}j) + e_2(r|\mathbf{q}j)e_2^*(r|\mathbf{q}j)],$$

in our molecular coordinate system. Similar equations apply for the atom  $s$ . The notation is the same as that used in equation (4) of Scheringer (1972*b*) and in SCHE (2.2). The subscripts 'rot' and 'trans' refer to rotational and translational modes respectively. For the external modes of the molecule the high temperature approximation  $\bar{E}(\mathbf{q}j) = k_B T$  is nearly valid so that the expressions  $\{ \}_{\text{rot}}$  and  $\{ \}_{\text{trans}}$  in equation (3.2) are essentially proportional to averages  $\langle 1/\omega_{\text{rot}}^2 \rangle$  and  $\langle 1/\omega_{\text{trans}}^2 \rangle$  taken over all modes  $\mathbf{q}j$ . We define the ratio of the curly-bracket expressions in equation (3.2) to be

$$\{ \}_{\text{rot}}/\{ \}_{\text{trans}} \equiv W \equiv \frac{1}{\eta^2}, \quad (3.3)$$

which is approximately equal to  $\langle \omega_{\text{trans}}^2 \rangle / \langle \omega_{\text{rot}}^2 \rangle$ . Hence

$$\eta \simeq (\langle \omega_{\text{rot}}^2 \rangle / \langle \omega_{\text{trans}}^2 \rangle)^{1/2} \simeq \langle \omega_{\text{rot}} \rangle / \langle \omega_{\text{trans}} \rangle$$

essentially describes the ratio of a mean rotational to a mean translational frequency of the lattice modes. Since rotations (librations) are usually more hindered than translations the rotational modes will have the higher frequencies. Thus we expect  $\eta$  to have values between 1 and 3. These figures correspond to Raman and infrared frequencies which are measured on molecular crystals and assigned to the external modes of the molecules.  $W = \eta = 1$  corresponds to the state of uncorrelated motion. A proof of this statement will be given in the Appendix.  $W$  or  $\eta$  respectively is our 'lattice-dynamical parameter'. In the following equations it will be easier to use  $W$ ; however,  $\eta$ , being more or less a frequency ratio, is the more illustrative quantity so that we prefer to use it in the general discussion.

Using the parameter  $W$ , defined in equation (3.3), we now obtain from equation (3.2)

$$\frac{\varrho_r}{\tau_r} = \frac{Mz_r^2}{I} W = \frac{m_s}{m_r} W, \quad (3.4)$$

and thus

$$\varrho_r = \frac{\frac{m_s}{m_r} W}{\frac{m_s}{m_r} W + 1}, \quad \tau_r = \frac{1}{\frac{m_s}{m_r} W + 1}. \quad (3.5)$$

We obtain the corresponding equations for  $\varrho_s$  and  $\tau_s$  by exchanging the subscripts  $r$  and  $s$ . Using equations (2.1), (2.4) and (3.1) we find the correction term to be

$$\bar{w}^2 = \varrho_s \bar{w}_s^2 \left( \frac{m_r + m_s}{m_r} \right)^2, \quad (3.6)$$

and, by using equation (3.5) applied to the atom  $s$ ,

$$\bar{w}^2 = \frac{(m_r + m_s)^2 W \bar{w}_s^2}{m_r(m_r W + m_s)}. \quad (3.7)$$

Thus the correction term  $\bar{w}^2$  is represented as a function of the masses  $m_r$  and  $m_s$ , of the parameter  $W$ , and of the mean-square amplitude  $\bar{w}_s^2$  which can be calculated from the vibration tensor  $\mathbf{U}_s$ . In deriving (3.7) we first encounter  $\varrho_s$  as an unknown parameter [equations (3.5) and (3.6)] because  $\varrho_s$  is immediately related to the libration tensor  $\mathbf{L}$ , *cf.* equation (3.1). However,  $\varrho_s$  is less universal than  $W$  ( $\eta$ ) since  $\varrho_s$  is referred to a distinct atom and also depends on the type of molecule considered, *cf.* §§ 4 and 5 below. These limitations do not hold for  $W$  ( $\eta$ ) and thus we prefer to express our final equations in terms of  $W$  ( $\eta$ ).

We now discuss how  $W$  can be determined from the vibration tensors  $\mathbf{U}$  in the case  $m_r > m_s$ . Since the translations of the atoms  $r$  and  $s$  must be equal for rigid-body motions we have

$$\bar{w}_r^2 \tau_r = \bar{w}_s^2 \tau_s. \quad (3.8)$$

We define a quantity  $\bar{w}_s^2/\bar{w}_r^2 = \delta$  and obtain

$$\delta = \frac{\tau_r}{\tau_s} = \frac{\frac{m_r}{m_s} W + 1}{\frac{m_s}{m_r} W + 1} \quad (3.9)$$

from equations (3.8) and (3.5).

Equation (3.9) gives

$$W = \frac{\delta - 1}{\frac{m_r}{m_s} - \frac{m_s}{m_r} \delta}. \quad (3.10)$$

From equation (3.5), applied to the atom  $s$ , and equation (3.10) we finally obtain

$$\varrho_s = \frac{(\delta - 1)m_r^2}{\delta(m_r^2 - m_s^2)}. \quad (3.11)$$

For  $m_r > m_s$  we generally will have  $\delta > 1$  so that in this case  $W$  and  $\varrho_s$  can be determined from  $\delta$ , *i.e.* from the tensors  $\mathbf{U}_r$  and  $\mathbf{U}_s$ . For  $m_r = m_s$  we have  $\delta = 1$  and  $W$  and  $\varrho_s$  remain undetermined in equations (3.10) and

(3.11) respectively. Similarly, equation (3.9) shows that, with  $\delta=1$ ,  $W$  may have any value. If we insert  $\delta=w_s^2/w_r^2$  in equation (3.11) and further use equation (3.6) we obtain equation (2.6), which shows that the development made in this section is consistent with our previous results.

We have calculated the values of  $\delta$ ,  $W$ ,  $\eta$  and  $q_s$  with 5 structures. The values obtained are based on the structural data for OH groups as reported in the literature. For the OH<sup>-</sup> ion we have  $m_r=16$  and  $m_s=1$ . The results of our calculation and the names of the authors who carried out the structure determinations are given in Table 1. To a fair approximation  $\eta$  is equal to 2; of course, the value of  $\eta$  varies for the different compounds. Using Zigan & Rothbauer's (1967) value for  $U^{11}-\beta^{11}$  in their notation - for the oxygen atom we obtain  $\eta=1.07$ , which is only about half the expected value. We conclude that these authors determined a value of  $\beta^{11}$  which was too small.  $\beta^{11}$  is only as large as its own standard deviation. If we use the double and threefold value of  $\beta^{11}$  the  $\eta$  values for Mg(OH)<sub>2</sub> fit well into the series of the  $\eta$  values for the other compounds in Table 1. The results in Table 1 show that the mean value of  $W$  is about 0.25 ( $\eta=2.0$ ). Certainly each structure will be different in detail but the figures in Table 1 show that the ratio of rotational to translational frequencies in the mean over-all lattice modes is fairly constant. This is our justification for transferring the value of  $W(\eta)$  to the case  $m_r=m_s$ . Certainly it is desirable to establish a broader experimental basis by calculating further values of  $W(\eta)$ . Unfortunately we could not find any more structures containing diatomic molecules or ions for which the vibration tensors were determined. Furthermore, the condition  $m_r/m_s \geq 4$  should be fulfilled with these molecules since with smaller values of this ratio the experimental accuracy will usually not be sufficient to determine a significant value of  $W(\eta)$ . [As can be seen from equation (3.9) the value of  $\delta$  will be smaller than 2 with  $m_r/m_s < 4$  and  $W=0.25$ . Then equation (3.10) will give unreliable results for  $W(\eta)$  if one takes into account that the experimental accuracy in determining  $\delta$  is limited.]

If one assumes a fixed value for the lattice-dynamical parameter  $W$  the correction for the diatomic molecule with atoms of equal masses ( $m_r=m_s$ ) can be calculated from equation (3.7). Assuming  $\eta=2$ ,  $W=0.25$  we obtain  $q_s=0.20$  and  $\overline{w^2}=0.80\overline{w_s^2}$ . For the COG model the

condition  $U_r=U_s$  or  $\overline{w_r^2}=\overline{w_s^2}$  must be fulfilled. This condition can be used in order to examine whether or not the COG model is appropriate and whether or not the tensors  $U_r$  and  $U_s$  are determined with sufficient accuracy.

#### 4. The linear triatomic molecule

For this type of molecule the bond-length correction can always be calculated. The procedure is similar to that for the diatomic molecule with unequal masses because the thermal rigid-body parameters are the same and the vibration tensors  $U$  are always different for the central atom and one outer atom. The equations (2.1), (2.2) and (2.3) can thus be applied to the linear triatomic molecule whereas equation (2.4) must be modified according to the masses of the atoms in the molecule. In the following we use different masses  $m_r$ ,  $m_s$  and  $m_t$  of the atoms; the subscript  $t$  denotes the central atom. We derive the correction for the distance  $d_{st}$  between the atoms  $s$  and  $t$ . The corrections  $w^2/2d$  for the two other distances  $d_{rt}$  and  $d_{rs}$  are then proportional to the corresponding distances, *i.e.*

$$\frac{\overline{w_{rs}^2}}{d_{rs}^2} = \frac{\overline{w_{rt}^2}}{d_{rt}^2} = \frac{\overline{w_{st}^2}}{d_{st}^2}. \quad (4.1)$$

This follows from equation (2.1). The correction is obtained from equation (2.3) if we replace the atom  $r$  by the atom  $t$ . Using  $m_r+m_s+m_t=M$  we obtain for the  $z$  coordinates, referred to the centre of gravity,

$$z_s^2 = \frac{(m_t d_{st} + m_r d_{rs})^2}{M^2}, \quad z_t^2 = \frac{(m_r d_{rt} - m_s d_{st})^2}{M^2}. \quad (4.2)$$

With equations (2.3) and (4.2) we obtain

$$\overline{w_{st}^2} = (\overline{w_s^2} - \overline{w_t^2}) \left\{ \frac{M}{m_r(2d_{rt}d_{st}^{-1} + 1) + m_t - m_s} \right\}. \quad (4.3)$$

Thus the correction term consists of two factors: the riding-model term  $(\overline{w_s^2} - \overline{w_t^2})$  and a mass factor, the expression in curly brackets. For the centrosymmetric molecule we have  $d_{rt}=d_{st}$ ,  $m_r=m_s$  and the mass factor is unity; *i.e.* equation (4.3) reduces to the correction obtained by using the riding model. For  $d_{rt} \rightarrow 0$ ,  $m_r \rightarrow 0$  the triatomic molecule reduces to the diatomic one, and equation (4.3) reduces to equation (2.6). Equations (4.2) and (4.3) remain true when the indices  $s$  and  $r$  are

Table 1. Values of  $\delta$ ,  $W$ ,  $\eta$ , and  $q_s$  for some compounds

For explanation see text.					
Compound	$\delta$	$W$	$\eta$	$q_s$	Reference
AlO(OH)	4.25	0.207	2.20	0.77	Busing & Levy (1958)
Ca(OH) <sub>2</sub>	5.79	0.306	1.81	0.83	Busing & Levy (1957)
Mg(OH) <sub>2</sub>	14.14	0.869	1.07	0.93	Zigan & Rothbauer (1967)
Mg(OH) <sub>2</sub>	7.07	0.390	1.60	0.86	Zigan & Rothbauer (1967). $2\beta^{11}(0)$
Mg(OH) <sub>2</sub>	4.71	0.236	2.06	0.79	Zigan & Rothbauer (1967). $3\beta^{11}(0)$
Muscovite	3.69	0.168	2.44	0.73	Rothbauer (1971)
MnO(OH)	3.41	0.153	2.56	0.71	Dachs (1963). Isotropic thermal parameters.

exchanged. For an actual determination of the correction it is suggested that the correction with both the pairs of atoms  $r, t$  and  $s, t$  be calculated and the consistency of the results checked with equation (4.1).

The linear triatomic molecule also offers the chance to determine values of the lattice-dynamical parameter  $W$ . We abbreviate the mass factor of equation (3.2)  $G = Mz_s^2/I$ , where  $M = m_r + m_s + m_t$  and  $I$  is the moment of inertia about the  $x$  or  $y$  axis of the molecule, referred to the centre of gravity. For the centrosymmetric molecule

$$G = (2m_s + m_t)/2m_s.$$

Then

$$\varrho_s = GW/(GW + 1).$$

The correction, expressed in terms of  $\varrho_s$ , is then given by

$$\begin{aligned} \overline{w_{st}^2} &= d_{st}^2 \varrho_s \overline{w_s^2} / z_s^2 \\ &= \varrho_s \overline{w_s^2} \left\{ \frac{M}{(1 + d_{rt} d_{st}^{-1}) m_r + m_t} \right\}^2. \end{aligned} \quad (4.4)$$

Let the expression in curly brackets of equation (4.3) be denoted by  $\alpha$  and the square of the curly brackets of equation (4.4) by  $\beta$ , then, from equations (4.3) and (4.4), we obtain

$$W = \frac{\overline{w_s^2} - \overline{w_t^2}}{G[(\beta\alpha^{-1} - 1)\overline{w_s^2} + \overline{w_t^2}]}. \quad (4.5)$$

For the centrosymmetrical molecule equation (4.5) reduces because  $\alpha = \beta = 1$ .

A numerical value of  $W$  is obtained from the structural data of the  $\text{CS}_2$  molecule which were gained by Baenziger & Duax (1968) at 148°K. From the values reported for the vibration tensors of the carbon and sulphur atoms we calculate  $W = 0.316$ ,  $\eta = 1.78$  and  $\varrho_s = 0.27$ . Thus the values of  $W$  and  $\eta$  fit well into the series given in Table 1 whereas  $\varrho_s$  for  $\text{CS}_2$  differs from  $\varrho_s$  for  $\text{OH}^-$  because of the different distribution of masses in the two types of molecules. Unfortunately, we could not find other examples of linear triatomic molecules or ions which were well enough refined. The  $\text{HF}_2^-$  ion (McGaw & Ibers, 1963) does not behave as a rigid body since the motions of the hydrogen atom perpendicular to the bond are larger than those of the fluorine atoms. Several structures containing  $\text{CNO}^-$ ,  $\text{OCN}^-$ ,  $\text{CNS}^-$ ,  $\text{SCN}^-$ , and  $\text{CN}_2^-$  ions have been determined (Wyckoff, 1964), but with low accuracy and without anisotropic temperature factors.

In our discussion we have so far neglected the internal modes of the molecule. The two stretching modes do not contribute to the correction since their amplitudes are in the direction of the bonds, *cf.* Herzberg (1956, p. 164). The bending modes, however, will generally contribute to the vibrations of the atoms perpendicular to the bonds and thus to the correction. For the symmetric linear molecule the amplitudes of the two outer atoms will produce mean-square amplitudes

which could also arise from rigid-body librations. Thus, if the components of the libration tensor are calculated from the experimentally determined components  $U_r^{ik}$  and  $U_s^{ik}$ , the libration tensor contains the contributions of the bending modes to a large extent. Hence, to a very good approximation, the internal modes of the symmetric molecule need not be treated explicitly. For highly asymmetric linear molecules the contributions of the bending modes will be accounted for only poorly by the libration tensor. In this case an explicit treatment of the internal modes seems to be appropriate since neglecting these modes may result in errors of about 5 to 10% of the calculated correction, *cf.* Scheringer (1972a).

### 5. The symmetric angular triatomic molecule

This type of molecule must also be treated by using a lattice-dynamical parameter. This parameter will be applied in a manner different to that of the diatomic molecule because of the different geometry in the two types of molecules. But  $\eta$  will again represent more or less a ratio of a mean rotational to a mean translation lattice frequency. For the COG model we again assume that the correlation tensor  $S$ , referred to the centre of gravity of the molecule, is symmetric.

In order to simplify description we choose a Cartesian coordinate system with the origin at the centre of gravity of the molecule. The  $z$  axis is perpendicular to the plane of the molecule and the  $y$  axis bisects the angle at the central atom. The mass of the central atom is  $m_t$  and the two outer atoms have masses  $m_r = m_s$ . Furthermore,  $2m_s + m_t = M$ . The uncorrected distances between the atoms are  $d_{rt} = d_{st}$ . The angle at the central atom is  $2\varphi$ , see Fig. 1. The symmetry of the molecule in this coordinate system is  $m2m$  (we use orthorhombic Hermann-Mauguin symbols referred to the Cartesian coordinate system of the molecule). Possible site symmetries are  $m2m$ ,  $m11$ ,  $11m$ , and  $121$ . The following relations hold for the coordinates of the atoms, *cf.* Fig. 1:

$$\begin{aligned} x_r &= -x_s, & x_t &= 0, & x_s &= d_{st} \sin \varphi, \\ y_r &= y_s, & y_s &= -d_{st} \frac{m_t}{M} \cos \varphi, \\ y_t &= d_{st} \frac{2m_s}{M} \cos \varphi, & z_r &= z_s = z_t = 0. \end{aligned} \quad (5.1)$$

Using SCHE (3.6), SCHE (4.5), and equation (5.1) we obtain for the correction term

$$\begin{aligned} \overline{w_{st}^2} &= d_{st}^2 \{ L_{11} \cos^2 \varphi + L_{22} \sin^2 \varphi + L_{33} \\ &\quad - 2x_s(y_s - y_t)L_{12} \}. \end{aligned} \quad (5.2)$$

The corresponding equation is valid if one replaces the subscript  $s$  by  $r$  whereby the  $L_{12}$  term changes its sign. The components  $L_{ik}$  of equation (5.2) now have to be determined from the components  $U_r^{ik}$ ,  $U_s^{ik}$ ,  $U_t^{ik}$ . From

SCHE (4.2) we obtain the following relations, valid in our Cartesian coordinate system:

$$U^{11} = T^{11} + y^2 L_{33} - 2y S_3^1, \quad (5.3a)$$

$$U^{22} = T^{22} + x^2 L_{33} - 2x S_3^2, \quad (5.3b)$$

$$U^{33} = T^{33} + y^2 L_{11} + x^2 L_{22} - 2xy L_{12} + 2y S_1^3 - 2x S_2^3. \quad (5.3c)$$

For site symmetries  $m2m$ ,  $m11$ , and  $121$  we have  $L_{12} = S_2^3 = S_3^2 = 0$ . For the COG model we assume  $S_2^3 = S_3^2$  and  $S_1^3 = S_3^1$ . From equations (5.1), (5.3a) and (5.3b) we obtain

$$L_{33} = \frac{U_r^{22} + U_s^{22} - 2U_t^{22}}{2x_s^2}, \quad S_3^2 = S_2^3 = \frac{U_s^{22} - U_r^{22}}{4x_s}, \quad (5.4)$$

from equation (5.3c)

$$L_{12} = -\frac{U_s^{33} - U_r^{33} + U_s^{22} - U_r^{22}}{4x_s y_s}, \quad (5.5)$$

and from equations (5.3a) and (5.4)

$$S_3^1 = S_1^3 = -\frac{U_s^{11} - U_t^{11}}{2(y_s - y_t)} + \frac{U_r^{22} + U_s^{22} - 2U_t^{22}}{2x_s} \cdot \frac{y_s + y_t}{2}. \quad (5.6)$$

We cannot, however, determine  $L_{11}$  and  $L_{22}$  from equation (5.3c) and so have to introduce a lattice-dynamical parameter. For the atom  $t$  we write

$$U_t^{33} = (\tau_t + \varrho_t + 2\sigma_t) U_t^{33}, \quad (5.7)$$

hence

$$\tau_t + \varrho_t = 1 - 2\sigma_t.$$

Observing equation (5.1) we now obtain from equation (5.3c)

$$\tau_t U_t^{33} = T^{33}, \quad \varrho_t U_t^{33} = y_t^2 L_{11}, \quad \sigma_t U_t^{33} = y_t S_1^3. \quad (5.8)$$

By analogy with equations (3.2) and (3.3), and by using equation (5.1), we obtain

$$\frac{\varrho_t}{\tau_t} = \frac{M y_t^2}{I_x} W = \frac{2m_s}{m_t} W, \quad (5.9)$$

where  $I_x$  is the moment of inertia about the  $x$  axis. Then

$$\varrho_t = \frac{\frac{2m_s}{m_t} (1 - 2\sigma_t) W}{\frac{2m_s}{m_t} W + 1}. \quad (5.10)$$

The value of  $W$  is about 0.25, cf. § 3. With equation (5.8) we obtain  $\sigma_t = y_t S_1^3 / U_t^{33}$ , where  $S_1^3$  is determined from equation (5.6). Then  $\varrho_t$  is determined from equa-

tion (5.10) and we obtain from equation (5.8)  $L_{11} = \varrho_t U_t^{33} / y_t^2$ . With the known values of  $L_{11}$ ,  $S_1^3$  and  $\varrho_t$  we can now solve equation (5.3c) for  $L_{22}$  and obtain

$$L_{22} = \frac{1}{x_s^2} \left\{ \frac{U_r^{33} + U_s^{33}}{2} - U_t^{33} - \frac{U_s^{22} - U_r^{22}}{2} - \varrho_t U_t^{33} (y_s^2 y_t^{-2} - 1) + U_s^{11} - U_t^{11} - \frac{U_r^{22} + U_s^{22} - 2U_t^{22}}{2x_s^2} (y_s^2 - y_t^2) \right\}. \quad (5.11)$$

Now all terms are determined which are needed for the correction according to equation (5.2). Applying equation (5.1) to the equations above we replace the coordinates of the atoms by the distance  $d_{st}$ , the angle  $\varphi$  and the masses  $m_s$  and  $m_t$  and define an auxiliary quantity

$$\left(2 + \frac{m_t}{m_s}\right) \varrho_t = \frac{MW}{m_s W + m_t/2} \equiv \mu. \quad (5.12)$$

Then, after rearranging all terms, we finally obtain

$$\begin{aligned} \bar{w}_{st}^2 = & (\mu - 1) U_t^{33} + \frac{U_r^{33} + U_s^{33}}{2} + \frac{U_r^{22} + U_s^{22} - 2U_t^{22}}{2 \sin^2 \varphi} \\ & + \frac{M}{2m_t} (U_s^{33} - U_r^{33} + U_s^{22} - U_r^{22}) \\ & + \left\{ U_s^{11} - U_t^{11} - \frac{(U_r^{22} + U_s^{22} - 2U_t^{22})}{2} \cdot \frac{(m_t - 2m_s)}{M} \right. \\ & \left. \times \operatorname{ctg}^2 \varphi \right\} \left(1 - \mu \frac{2m_s}{M}\right). \end{aligned} \quad (5.13)$$

The correction term  $\bar{w}_{st}^2$  is now represented as a function of the angle  $\varphi$ , of the masses  $m_s$  and  $m_t$ , of the vibration tensors  $U_r$ ,  $U_s$ ,  $U_t$  and of the lattice-dynamical parameter  $W$ , which is contained in the quantity  $\mu$ . The first 3 terms on the right-hand side of equation (5.13) give the main contribution to the correction, they arise – only in total – from  $L_{11}$ ,  $L_{22}$  and  $L_{33}$ . The 4th term arises from  $L_{12}$  and generally is small. The final term is due to  $S_1^3$ . It is small in general but was observed to amount to about a quarter of the total correction in a few cases. If we exchange the subscripts

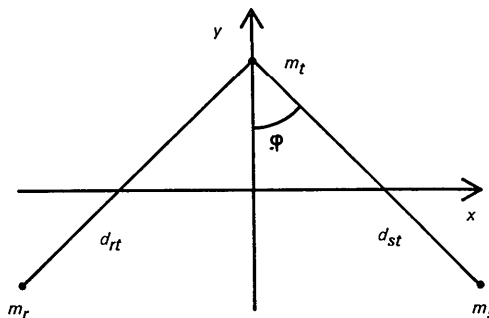


Fig. 1. Notation used in the Cartesian coordinate system of the molecule.

$r$  and  $s$  in equation (5.13) we obtain the expression for  $\overline{w_{rt}^2}$ , whereby the  $L_{12}$  term changes its sign.

If we put  $\varphi = 90^\circ$  equation (5.13) reduces to the correction for the linear symmetric molecule, the  $x$  axis being the molecular axis, and thus  $\varrho_t = W = 0$ . If we put  $\varphi = 0^\circ$ ,  $S_1^3 = 0$ ,  $m_t > 2m_s$  and eliminate the lattice-dynamical parameter  $W$  in  $\varrho_t$ , as discussed with the asymmetric diatomic molecule, equation (5.13) reduces to the correction term for the diatomic molecule with masses  $m_t$  and  $2m_s$  where the  $y$  axis is the molecular axis. This shows that the development made in this section is in agreement with our previous results obtained in §§ 4 and 2.

For the COG model three conditions must be fulfilled which one can use to examine whether or not the COG model can be applied and whether or not the experimentally determined components  $U^{ik}$  are sufficiently accurate. The conditions are

$$(1) \quad U_r^{11} = U_s^{11}, \quad (5.14a)$$

$$(2) \quad (U_r^{22} + U_s^{22}) \geq 2U_t^{22}, \quad (5.14b)$$

$$(3) \quad \sigma_t / \sqrt{\tau_t \varrho_t} \leq 1, \quad \sigma_t \leq 0.25, \quad (5.14c)$$

where the components  $U^{ii}$  are referred to the Cartesian coordinate system of the molecule. The conditions (2) and (3) are not very stringent however. The condition (1) is more suitable for examining the applicability of the COG model. For the site symmetries  $m2m$ ,  $m11$  and  $121$  we further have  $L_{12} = 0$ ,  $S_2^3 = 0$ ,  $U_r^{22} = U_s^{22}$ ,  $U_r^{33} = U_s^{33}$ .

In the program that we have written for the numerical calculation of the correction the components  $\beta^{ik}$ , which are usually reported in the literature, are first transformed to components  $U^{ik}$  in  $\text{\AA}^2$  referred to a fixed Cartesian reference system. With a second transformation the  $U^{ik}$  are calculated in the coordinate system of the particular molecule. Then  $\overline{w_{st}^2}$  and  $\overline{w_{rt}^2}$  of equation (5.13) and the actual corrections are calculated. The three conditions (5.14) are all examined. No matter what the result for condition (1) will be, it is regarded as being fulfilled within the limits of experimental error, *i.e.* in equation (5.13)  $U_s^{11}$  is replaced by the average of  $\frac{1}{2}(U_r^{11} + U_s^{11})$  so as to use two equivalent experimental data. Furthermore, the corrections for the riding model and for uncorrelated motion are calculated. Also the standard deviations of the components  $U^{ii}$  in the molecular coordinate system are evaluated.

## 6. Results on water molecules

We have calculated the bond-length corrections for 9  $\text{H}_2\text{O}$  and 2  $\text{D}_2\text{O}$  molecules in 5 structures. The compounds and the authors who carried out the structure determinations are given in Table 2. Also a serial number for identification is listed. For all molecules the atomic parameters were determined with neutron diffraction data. With the molecules 1 to 7 the components of the  $U$  tensors seemed to be most accurately

determined. The standard deviations of the  $U^{ii}$ 's are, in the mean over the molecules 1 to 7, about  $0.00055 \text{\AA}^2$  for the oxygen atoms and about  $0.00135 \text{\AA}^2$  for the hydrogen atoms. For molecule 8 the respective values are  $0.0014$  and  $0.0017 \text{\AA}^2$ , for molecule 9  $0.0009$  and  $0.0022 \text{\AA}^2$ , and for the two  $\text{D}_2\text{O}$  molecules 10 and 11 the standard deviations of the  $U^{ii}$ 's are about  $0.0009 \text{\AA}^2$  for all atoms. These values were computed by us from the standard deviations of the  $\beta^{ik}$  as given by the authors listed in Table 2. All water molecules are linked to their neighbouring molecules by two hydrogen bonds formed through the H or D atoms of the water molecules. The hydrogen bonds are weak. The  $\text{O-H}\cdots\text{O}$  distances range from  $2.68$  to  $2.96 \text{\AA}$  and the two  $\text{O-H}\cdots\text{Cl}$  distances with the molecules 2 and 4 are  $3.16$  and  $3.29 \text{\AA}$ . The molecules 1 and 3 form a very weak bifurcated hydrogen bond over the bond  $b$  of Tables 2 and 3, the uncorrected bond  $b$  is very short and the components  $U^{ii}$  of the hydrogen atom in these bonds have extremely large values. Hence one would assume that the COG model is not fully appropriate to the molecules 1 and 3.

Table 2. *Serial number, compound and reference pertaining to the 11 water molecules discussed in the text*

The letters  $a$  and  $b$  refer to the two bonds in the molecule respectively.

1a—4b	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ . El Saffar & Brown (1971).
5a—7b	$\text{Cu}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Tutton salt). Brown & Chidambaram (1969).
8a—8b	$(\text{COOK})_2 \cdot \text{H}_2\text{O}$ , site symmetry 2. Sequiera, Srikantha & Chidambaram (1970).
9a—9b	$\alpha$ - $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$ . Sabine, Cox & Craven (1969).
10a—11b	$\alpha$ - $(\text{COOD})_2 \cdot 2\text{D}_2\text{O}$ and $\beta$ - $(\text{COOD})_2 \cdot 2\text{D}_2\text{O}$ . Coppens & Sabine (1969).

In our calculations we have neglected the internal modes of the water molecules. This gives rise to errors which we want to discuss before we present our results. The two stretching modes practically do not contribute to the correction since the hydrogen atoms vibrate in the direction of the bonds and nearly in this direction respectively, and the amplitude of the oxygen atom is small, *cf.* Herzberg (1956, pp. 146, 171). A noticeable contribution, however, arises from the bending mode since in this mode the hydrogen atoms vibrate nearly perpendicular to the direction of the bonds. The mean-square amplitudes of the bending mode are very similar to those of the librations of the molecule about the  $z$  axis, which passes through the centre of gravity, because the phases of the vibrations do not occur in the mean-square amplitudes. Hence it is to be expected that the libration tensor, which is calculated from the experimentally determined components  $U^{ik}$ , contains the mean-square amplitudes of the bending mode to a large extent. Thus with a correction, which according to equation (5.13) employs the experimentally determined components  $U^{ik}$ , the internal modes should have largely been taken into account. That this is the case

will be shown by the following calculation: let  $A$  be the correction due to the bending mode,  $B$  the correction due to the external modes of the molecule, then the full correction is  $A+B$ . Let the correction obtained with the aid of equation (5.13) be  $C$ , when using the experimentally determined values of the  $U^{ik}$ 's. Let that part of the  $U^{ik}$ 's due to the bending mode which contributes to the correction *via* equation (5.13) be  $D$ . Then the total correction  $C$  is equal to  $B+D$ , whereas the correct value of the total correction is  $B+A$ . In the following we show that  $A-D$  is so small that it can well be neglected. First we calculate  $A$ : we put  $2\varphi=110^\circ$  and use  $\nu_2=1620\text{ cm}^{-1}$  for the bending mode, *cf.* Nakamoto (1963, p. 83). From Herzberg's (1956, p. 171) data we deduce that the hydrogen atom vibrates with an angle of  $83.8^\circ$  with the direction of the bond. For the mean-square amplitude of this vibration we calculate

$$\overline{u^2} = \frac{h}{8\pi^2\nu_2 m_H} \cdot \frac{m_O}{2(m_O + 2m_H)} = 0.00458 \text{ \AA}^2.$$

The component perpendicular to the bond is then  $0.00453 \text{ \AA}^2$ . Similarly, we find  $0.00003 \text{ \AA}^2$  for the normal component of the oxygen atom. The correction due to the bending mode can now be obtained approximately by using the riding model since the oxygen atom is nearly at rest, or by using the (diatomic) COG model since the bending mode behaves similarly to a libration. We obtain corrections of  $A=0.00237 \text{ \AA}$  and  $A=0.00269 \text{ \AA}$  respectively. Now we calculate the correction  $D$ : in the molecular coordinate system only the components  $U^{11}$  and  $U^{22}$  are involved in the bending mode. The only important term in equation (5.13) is

$$(U_r^{22} + U_s^{22} - 2U_i^{22})/2 \sin^2 \varphi.$$

With  $\nu_2=1620\text{ cm}^{-1}$  this term yields  $D=0.00200 \text{ \AA}$ . Hence  $A-D=0.0007 \text{ \AA}$  at the most which we can well neglect as stated above.

We have calculated the corrections for the 11 water molecules with the riding model, with the COG model for  $\eta=1.6, 2.0$ , and  $2.4$ , and for uncorrelated motion. The riding-model corrections and the corrections for uncorrelated motion will be used to judge the COG corrections by comparison. The corrections for the three values of  $\eta$  are given to obtain an impression of how much the values of the COG correction scatter, since the value of the lattice-dynamical parameter  $W(\eta)$  is not exactly known. The results of our calculations are summarized in Table 3. The final column in Table 3 gives the deviations from condition (1),  $U_r^{11}=U_r^{22}$ , in terms of one standard deviation of  $U_r^{11}$  or  $U_s^{11}$ .

For all molecules the condition (1) is rather well fulfilled, *cf.* Table 3. The larger deviations occur, as expected, with the molecules 1 and 3 since these molecules are bound in an asymmetric manner through the hydrogen bonds to their neighbouring molecules. Also for the molecules 9, 10, and 11 the deviations from condition (1) are larger but an obvious structural effect cannot be found to serve as an explanation. On an absolute scale the deviations from condition (1) still seem to be tolerable. For the molecule 8 the condition (1) is exactly fulfilled because of the site symmetry 121. Hence, for this molecule, all values in Table 3 are the same for the bonds  $a$  and  $b$ . The conditions (2) and (3) were always found to be fulfilled.

For all molecules the correction for uncorrelated motion is larger than the COG correction, even when using the extreme value of  $\eta=1.0$ . The mean value of the correction for uncorrelated motion over all molecules is  $0.1047 \text{ \AA}$  with a mean deviation of  $0.0180 \text{ \AA}$ .

Table 3. Bond lengths of 11 water molecules ( $\text{\AA}$ ), corrected with various models

	Uncor- rected	Riding model	Centre-of-gravity model			Uncorre- lated motion	Deviation from condition (1)
			$\eta=1.6$	$\eta=2.0$	$\eta=2.4$		
1 <i>a</i>	0.967	0.999	1.016	1.012	1.010	1.053	1.0 $\sigma$
1 <i>b</i>	0.944	1.021	1.040	1.036	1.034	1.081	
2 <i>a</i>	0.971	0.995	1.011	1.007	1.004	1.054	0.1 $\sigma$
2 <i>b</i>	0.963	0.999	1.008	1.003	1.000	1.056	
3 <i>a</i>	0.955	0.986	1.013	1.005	1.000	1.067	1.6 $\sigma$
3 <i>b</i>	0.923	0.989	1.021	1.013	1.008	1.078	
4 <i>a</i>	0.941	0.973	1.000	0.993	0.988	1.054	0.3 $\sigma$
4 <i>b</i>	0.953	0.978	1.004	0.997	0.993	1.054	
5 <i>a</i>	0.964	0.982	1.003	0.997	0.993	1.058	0.3 $\sigma$
5 <i>b</i>	0.963	0.983	1.004	0.998	0.994	1.058	
6 <i>a</i>	0.977	0.993	1.012	1.007	1.004	1.059	0.4 $\sigma$
6 <i>b</i>	0.978	0.993	1.011	1.006	1.003	1.059	
7 <i>a</i>	0.980	1.002	1.018	1.014	1.011	1.055	0.1 $\sigma$
7 <i>b</i>	0.976	0.991	1.007	1.003	1.001	1.045	
8 <i>a</i>	0.963	0.959	0.996	0.984	0.978	1.061	0.0 $\sigma$
8 <i>b</i>	0.963	0.959	0.996	0.984	0.978	1.061	
9 <i>a</i>	0.964	0.986	1.012	1.005	1.001	1.073	1.5 $\sigma$
9 <i>b</i>	0.956	0.985	1.015	1.007	1.003	1.066	
10 <i>a</i>	0.955	0.967	0.998	0.989	0.984	1.064	1.5 $\sigma$
10 <i>b</i>	0.954	0.982	1.012	1.003	0.998	1.074	
11 <i>a</i>	0.944	0.942	0.997	0.980	0.970	1.089	2.0 $\sigma$
11 <i>b</i>	0.947	0.940	0.993	0.976	0.966	1.082	



The corresponding mean value of the COG correction for  $\eta=2.0$  is  $0.0420 \text{ \AA}$  with a mean deviation of  $0.0130 \text{ \AA}$ . The difference of the mean values is  $0.0627 \text{ \AA}$ . For  $\eta=1.0$  the mean value of the COG correction is  $0.0794 \text{ \AA}$ .  $\eta=1.0$  closely corresponds to the state of uncorrelated motion. This will be shown in the Appendix. That the COG mean value for  $\eta=1.0$  is smaller than that for uncorrelated motion can be explained as follows: with equations (5.8) and (5.9) we have referred the parameter  $W(\eta)$  only to the librations about the  $x$  axis and the translations along the  $z$  axis of the molecular system, and with equations (5.8) and (5.10) the motions of the oxygen atom only are involved. Hence, observing (5.12),  $W$  occurs only in the first and last term of equation (5.13). The other terms in equation (5.13) are directly derived from the libration tensor and do not depend on  $W$ . Thus  $\eta=1.0$  means uncorrelated motion only for the specified part of the vibrations of the molecule and in this sense  $\eta=1.0$  affects the calculated correction. The smaller value of the COG correction for  $\eta=1.0$  shows that that part of the vibrations of the molecule, for which the correction is not determined with the aid of  $W(\eta)$ , cannot be interpreted as uncorrelated motion. Hence for this part of the vibrations of the molecule we have to assume a value of  $\eta$  which is larger than unity. This shows that, also for the water molecule, the librations are more strongly hindered than the translations. Thus we conclude that  $\eta=1.0$  is not an appropriate assumption for the remaining part of the vibrations of the molecule whose contribution to the correction can only be calculated with the aid of  $W(\eta)$ .

For all molecules the corrections calculated with the riding model are smaller than the COG corrections, even for the extreme value of  $\eta=3.0$ . Qualitatively this corresponds to our result for diatomic molecules; however, the difference is larger for  $\text{H}_2\text{O}$  molecules than for  $\text{OH}^-$  ions. In some cases the riding model breaks down completely: for the molecules 8 and 11 ( $\text{D}_2\text{O}$ ) negative corrections are calculated, and for the bonds 6a, 6b, 7b, 10a ( $\text{D}_2\text{O}$ ) the corrections are positive but very small. In these cases a fairly large amplitude of the oxygen atom is found which begins to violate the assumptions inherent in the riding model. If one considers only those molecules for which the riding model seems to yield reasonable results (all molecules except 6, 8, 11 and the bonds 7b and 10a) one obtains a mean value of the correction of  $0.0330 \text{ \AA}$  with a mean deviation of  $0.0114 \text{ \AA}$ . The mean value of the COG correction ( $\eta=2.0$ ) for the same molecules and bonds is  $0.0500 \text{ \AA}$  with a mean deviation of  $0.0121 \text{ \AA}$ . The COG mean value is larger by  $0.0170 \text{ \AA}$ . Hence the COG model yields corrections which are substantially larger than those of the riding model including those cases where the riding model does not obviously break down. However, the obvious failure of the riding model in some cases leads one to conclude that the other values of the corrections obtained with the riding model will also not be appropriate.

To sum up: The COG correction is larger than the riding-model correction and smaller than the correction for uncorrelated motion. Since the physical assumptions inherent in the COG model fit best to the actual vibrations of the water molecules, we conclude that the corrections which are calculated with the COG model are essentially correct.

The molecules 2, 4, 5, 6 and 7 are very accurately determined, the condition (1) is very well fulfilled and the values of the corrected bond lengths do not scatter much. Thus these molecules offer the chance of determining a likely value for the bond length of the 'weakly hydrogen-bonded symmetric water molecule'. With the COG model we find the following mean values and mean deviations for the 10 bonds:

$$\begin{aligned} \eta=1.6 & \quad 1.0078 \pm 0.0042 \text{ \AA} \\ \eta=2.0 & \quad 1.0025 \pm 0.0050 \text{ \AA} \\ \eta=2.4 & \quad 0.9991 \pm 0.0057 \text{ \AA} . \end{aligned}$$

As the best value we consider the bond length of  $1.002 \pm 0.006 \text{ \AA}$ . This value is larger by  $0.045 \text{ \AA}$  than the value of the bond length for the water molecule in the gaseous state, which is  $0.957 \text{ \AA}$  as given by Herzberg (1956, p. 489). We consider the difference of  $0.045 \text{ \AA}$  as physically significant. It is well known that the O-H bonds of water molecules are lengthened when the molecules form hydrogen bonds in the crystalline state. The experimental proofs as to the magnitude of this effect were not very precise however, because of the disturbances caused by the thermal motions. We believe that the calculations made with the COG model uniquely establish the lengthening of the O-H bond in the solid state.

Unfortunately, with the COG model there remains the uncertainty that the value of the parameter  $W(\eta)$  is not exactly known. The figures in Table 3 show that the scattering of the bond lengths in the region  $\eta=1.6$  to  $\eta=2.4$  is not equal for all molecules. The reason is that  $\eta(W)$  is referred only to the component  $U_{33}^2$ . If this component is very large the COG correction will scatter most for a fixed region  $\Delta\eta$ . This is the case with the molecules 8 and 11. In the region from  $\eta=1.6$  to  $\eta=2.4$  the scattering of the correction is  $0.018 \text{ \AA}$  for molecule 8, and  $0.027 \text{ \AA}$  for molecule 11. For all other molecules the scattering is smaller, the minimum value is  $0.006 \text{ \AA}$  (molecule 1), and the mean value over all 11 molecules is  $0.012 \text{ \AA}$ . This scattering is not very large compared to the magnitude of the COG correction so that the COG correction remains meaningful in principle. So far we consider  $\eta=2.0$  as the most appropriate value. With respect to the remaining uncertainty for the value of the lattice-dynamical parameter we invite other workers to report anisotropic temperature factors of asymmetric diatomic and linear triatomic molecules, which we may have overlooked or which were recently determined. With these data the statistics on the distribution of the  $\eta(W)$  parameter can be

improved, *cf.* equations (3.8) and (4.6), and the COG correction can be more reliably performed.

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## APPENDIX

### Proofs that $\eta=1.0$ corresponds to uncorrelated motion

#### (a) The diatomic molecule

The condition for uncorrelated motion is  $U_{rs}=0$ .  $U_{rs}$  is the coupling tensor for the atoms  $r$  and  $s$ , *cf.* SCHE (2.2) and SCHE (4.1). In the molecular coordinate system the weaker condition

$$U_{rs}^{11} + U_{rs}^{22} = 0 \quad (A1)$$

will hold, since  $U_{rs}^{33} = T^{33}$  does not contribute to the correction and since, with  $\bar{w}_{rs}^2 = \text{trace}(\mathbf{A}_{rs})$ , only the sum  $U_{rs}^{11} + U_{rs}^{22}$  must be zero and not the single components, *cf.* SCHE (3.3), SCHE (3.6) and SCHE (4.5). Using SCHE (4.4) and equations (2.2a) and (2.2b) we obtain in the molecular coordinate system

$$\begin{aligned} U_{rs}^{11} &= T^{11} + z_r z_s L_{22} + (z_r + z_s) S_2^2, \\ U_{rs}^{22} &= T^{22} + z_r z_s L_{11} - (z_r + z_s) S_1^2. \end{aligned} \quad (A2)$$

The condition (A1) and  $S_2^2 = S_1^2$  now results in

$$T^{11} + T^{22} = -z_r z_s (L_{11} + L_{22}). \quad (A3)$$

$z_r$  and  $z_s$  have opposite signs. Using equation (2.4) we obtain

$$T^{11} + T^{22} = d^2 (L_{11} + L_{22}) \frac{m_r m_s}{M^2} \quad (A4)$$

as the condition of uncorrelated motion for the diatomic molecule.

We now show that equation (A4) is satisfied if we put  $W = \eta = 1$ . Observing equation (3.1) and putting  $W = 1$ , we obtain from equation (3.2)

$$\frac{\rho_r}{\tau_r} = \frac{z_r^2 (L_{11} + L_{22})}{T^{11} + T^{22}} = \frac{M z_r^2}{I}, \quad (A5)$$

or

$$T^{11} + T^{22} = \frac{I}{M} (L_{11} + L_{22}). \quad (A6)$$

Since  $I = m_r z_r^2 + m_s z_s^2 = d^2 m_r m_s / M$  the condition (A4) for uncorrelated motion is obviously fulfilled for  $W = \eta = 1$ .

#### (b) The water molecule

$W(\eta)$  only refers to the librations about the  $x$  axis and to the translations along the  $z$  axis. Hence the general condition for uncorrelated motion,  $U_{st} = 0$ , reduces in the molecular coordinate system to

$$U_{st}^{33} = 0. \quad (A7)$$

Using SCHE (4.4) and equation (5.3c) we obtain for the specified modes of vibration

$$U_{st}^{33} = T^{33} + y_s y_t L_{11} + (y_s + y_t) S_1^3. \quad (A8)$$

$y_s$  and  $y_t$  have opposite signs. Observing equation (5.1), we obtain from equations (A7) and (A8)

$$T^{33} = d_{st}^2 \cos^2 \varphi \left[ \frac{2m_s m_t L_{11}}{M^2} + \frac{2m_s - m_t}{M} S_1^3 \right] \quad (A9)$$

as the condition of uncorrelated motion for the specified modes of vibration.

We show that equation (A9) is fulfilled for  $W = \eta = 1$  if we assume  $S_1^3 = 0$ . Since  $S_1^3$  is usually small and the difference  $2m_s - m_t$  tends to cancel the  $S_1^3$  term, this assumption is not very stringent. Observing equation (5.8) and putting  $W = 1$ , we obtain from equation (5.9)

$$\frac{\rho_t}{\tau_t} = \frac{y_t^2 L_{11}}{T^{33}} = \frac{M y_t^2}{I_x}, \quad (A10)$$

or

$$T^{33} = \frac{I_x}{M} L_{11}. \quad (A11)$$

Since  $I_x = m_t y_t^2 + 2m_s y_s^2 = d_{st}^2 2m_s m_t \cos^2 \varphi / M$  the condition (A9) for uncorrelated motion is fulfilled for  $W = \eta = 1$ , if the  $S_1^3$  term is neglected.

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