COWLEY, J. M. (1969). *The Chemistry of Extended Defects in Non-metallic Solids*, edited by L. EYRING and M. O'KEEFE, p. 259. Amsterdam: North Holland.

COWLEY, J. M. (1971). *Advanc. High Temp. Chem.* **3**, 35.

ERN, V. & SWITENDICK, A. C. (1965). *Phys. Rev.* **137A**, 1927.

FROIDEVAUX, C., & ROSSIER, D. (1967). *J. Phys. Chem. Solids*, **28**, 1197.

LIN, W., SPRUIELL, J. E. & WILLIAMS, R. O. (1970). *J. Appl. Cryst.* **3**, 297.

LYE, R. G. (1971). RIAS Technical Report 71–21c.

MOSS, S. C. (1964). *J. Appl. Phys.* **35**, 3547.

NECKEL, A., RASTL, P., WEINBERGER, P. & MECHTLER, R. (1972). *Theor. Chim. Acta (Berlin)*, **24**, 170.

NOWOTNY, H. & NECKEL, A. (1969). *J. Inst. Metals*, **97**, 161.

SOMMERFELD, A. & BETHE, H. (1933). *Handbuch der Physik* **24**/2. second ed., p. 400. Berlin: Springer.

VENABLES, J. D. & MEYERHOFF, M. H. (1971). NBS Symposium on Novel High Temperature Materials, Gaithersburg, Md. (Proceedings to be published in 1972).

WARREN, B. E. (1969). *X-ray Diffraction*, p.p 227, 232 ff. Reading: Addison–Wesley.

A Lattice-Dynamical Treatment of the Thermal-Motion Bond-Length Correction

BY C. SCHERINGER

Institut für Kristallographie der Universität, Karlsruhe, Germany

The effect of the thermal motions of the atoms on interatomic distances is treated in terms of lattice dynamics. It is not only shown how the anisotropic vibration tensors of the atoms can be derived from the dynamical matrices of the crystal but also how mean binary-product coupling tensors are obtained. Each of these tensors expresses the coupling of the motions of two atoms in the unit cell as an average over time and lattice and thus is suitable for formulating the bond-length correction. Hence the discussion centres around the coupling tensors. The coupling tensors cannot be determined by experiment; but in order to calculate them and the bond-length correction, one is forced to conceive dynamical models of motion for the atoms in the unit cell. The corrections for the known models of uncorrelated motion, rigid-body motion and riding motion are rederived by using the coupling tensors.

1. Introduction

The effect of the thermal motions of the atoms on interatomic distances has been discussed by Cruickshank (1956, 1961), Busing & Levy (1957, 1964), Schomaker & Trueblood (1968), and Johnson (1970). Structure refinement with X-ray and/or neutron data provides the mean positions of the atoms in the unit cell. The distance between the mean positions of the atoms is generally considered as a good approximation of the 'true' distance between the atoms. It is, however, more exact to define the 'true' distance to be the time and lattice average of all instantaneous distances, whereby this distance is usually larger because the atoms usually do not vibrate in phase in the planes perpendicular to the distance vector. Diffraction methods applied to crystals do not provide any phase relationships for the motions of neighbouring atoms. Hence one is forced to conceive dynamical models of motion for which the phase relationships are defined. These allow one to calculate the bond-length correction. The models, which have been used in the past, are the models of rigid-body motion, riding motion, and uncorrelated motion.

Two methods have been applied to derive the bond-length correction from a given dynamical model. Cruickshank (1956, 1961) investigated how rigid-body motion effects the electron-density distribution of the

atoms in question. The calculation of the correction is based on determining the correct positions of the electron-density maxima which represent the atoms. As a new concept Busing & Levy (1957, 1964) introduced the joint distribution of the atoms in question and thus defined the 'true' distance as the average over the joint distribution of the two atoms. The actual calculation of the correction is thus based on the solution of convolution integrals. The concept of the joint distribution also plays the prominent part in Johnson's (1970) review.

Our approach to determining the correction will be derived from a lattice-dynamical investigation of the anisotropic vibration tensors. A central concept in describing the dynamics of a crystal is the dynamical matrices. In a preceding paper (Scheringer, 1972) we showed how the anisotropic vibration tensors can be expressed by way of the dynamical matrices of the crystal. In a similar manner one can also obtain mean binary-product coupling tensors. Each of these tensors expresses the coupling of the motions of two atoms in the unit cell as an average over time and lattice and thus contains the respective phase relationships. Hence the coupling tensors are suitable for formulating the bond-length correction, and in this paper our discussion will centre around them.

Unfortunately, the coupling tensors cannot be deter-

mined by experiment. Hence in order to calculate them and the bond-length correction, we are also forced to conceive dynamical models of motion for the atoms in the unit cell.

In this paper we first give the definition and discuss the meaning of the coupling tensors. Then we express the general equations for the bond-length correction in terms of the coupling tensors. Finally, we show how the correction can be derived concisely for the known dynamical models of the rigid-body motion, riding motion, and uncorrelated motion by using the coupling tensors.

2. The coupling tensors

In a preceding paper [Scheringer, 1972 equations (10) and (15)] we showed that the coupling tensors are the 3×3 off-diagonal blocks of a $3n \times 3n$ mean-square amplitude matrix $\mathbf{U}$ which is uniquely determined by the dynamical matrices of the crystal. n is the number of atoms in the unit cell. If we order the atoms r and s in sequence the 6×6 diagonal block $\mathbf{G}$ of the matrix $\mathbf{U}$, which refers to the atoms r and s, has the form

$$\mathbf{G} = \left(\begin{array}{c|c} \mathbf{U}_r & \mathbf{U}_{rs} \\ \hline \mathbf{U}_{sr} & \mathbf{U}_s \end{array} \right). \qquad (2.1)$$

Formally the matrices $\mathbf{U}_{rs}$ represent components of second rank tensors since the elements of $\mathbf{U}_{rs}$ transform like the components of the tensors $\mathbf{U}_r$ when transforming the base vectors of the crystal. Since $\mathbf{G}$ is symmetric we have $\mathbf{U}_{sr} = \mathbf{U}_{rs}^T$. (The superscript T denotes the transposed matrix.) In general, the coupling tensors are not symmetric, whereas $\mathbf{U}_r = \mathbf{U}_r^T$. The explicit lattice-dynamical expression for the coupling tensors can be derived from the dynamical matrices of the crystal as follows: The calculation, which has been performed in a preceding paper (Scheringer, 1972), has to be reversed beginning from equation (15) and ending at equation (4). Then one obtains

$$U_{rs}^{ik} = \frac{1}{2\sqrt{m_r m_s}} \sum_{\mathbf{q}j} \frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})}$$
$$\times [e_i(r|\mathbf{q}j)e_k^*(s|\mathbf{q}j) + e_i^*(r|\mathbf{q}j)e_k(s|\mathbf{q}j)]. \qquad (2.2)$$

$\mathbf{q}$ denotes the wave vector, and $j = 1 \ldots 3n$. m_r and m_s are the masses of the atoms r and s. $\bar{E}(\mathbf{q}j)$ is the energy of mode $\mathbf{q}j$ in thermal equilibrium, $\omega_j(\mathbf{q})$ the circular frequency of mode $\mathbf{q}j$, $e_i(r|\mathbf{q}j)$ the ith component of polarization of mode $\mathbf{q}j$, which specifies the motions of the atom r in this mode in the direction i, and N is the number of cells in the crystal. The components U_{rs}^{ik} usually cannot be calculated from equation (2.2) since the quantities in the sum over all modes $\mathbf{q}j$, or the dynamical matrices are usually unknown.

Let all tensors be referred to an orthonormal metric. The components are then in Å^2. Let Δx_r^i be the instantaneous displacement of the atom r from its mean position in the direction i, then the components of the tensors $\mathbf{U}_{rs}$ represent the time and lattice average

$$U_{rs}^{ik} = \langle \Delta x_r^i \Delta x_s^k \rangle; \quad i,k = 1,2,3. \qquad (2.3)$$

Thus the coupling tensors describe the extent of in-phase or out-of-phase motions of the atoms r and s, as the average over time and lattice.

3. The equations for the bond-length correction

Busing & Levy (1964), cf. also Johnson (1970), showed that the time and lattice average of a bond-length in the quadratic approximation, is given by

$$d_{corr} = d + (\overline{r^2} - \overline{z^2})/2d. \qquad (3.1)$$

The subscript 'corr' indicates that we consider this bond-length as the corrected one. d is the distance between the mean positions of the atoms. $\overline{r^2}$ is the sum of the relative mean-square displacements of the atoms r and s along the three axes of the Cartesian reference system, and $\overline{z^2}$ is the relative mean-square displacement of the atoms r and s in the direction of the bond vector, $\mathbf{d}$. Thus $\overline{r^2} - \overline{z^2}$ is twice the relative mean-square displacement in the plane perpendicular to the bond vector. In the following we calculate $\overline{r^2} - \overline{z^2}$ in terms of the vibration tensors $\mathbf{U}_r$, $\mathbf{U}_s$, and the coupling tensors $\mathbf{U}_{rs}$.

The instantaneous relative displacement of the atoms r and s from their mean positions in the direction i is given by

$$\Delta x_r^i - \Delta x_s^i.$$

The time and lattice average of the product of the relative displacements in the directions i and k is then given by

$$\langle (\Delta x_r^i - \Delta x_s^i)(\Delta x_r^k - \Delta x_s^k) \rangle$$
$$= U_r^{ik} + U_s^{ik} - U_{rs}^{ik} - U_{sr}^{ik}. \qquad (3.2)$$

We put

$$\mathbf{U}_r + \mathbf{U}_s - \mathbf{U}_{rs} - \mathbf{U}_{rs}^T = \mathbf{A}_{rs} \qquad (3.3)$$

and obtain for the average of the sum of the squared displacements along the three axes of the Cartesian reference system

$$\overline{r^2} = \left\langle \sum_{i=1}^{3} (\Delta x_r^i - \Delta x_s^i)^2 \right\rangle = \text{trace } (\mathbf{A}_{rs}). \qquad (3.4)$$

In order to express $\overline{z^2}$ we need the components l_i of the unit vector which points in the direction of the bond, $\mathbf{d}$. $l_i = d_i/d$. Then we obtain for the average of the atoms r and s in the direction of the bond

$$\overline{z^2} = \left\langle \sum_{i,k=1}^{3} l_i l_k (\Delta x_r^i - \Delta x_s^i)(\Delta x_r^k - \Delta x_s^k) \right\rangle$$
$$= \sum_{i,k=1}^{3} l_i l_k (U_r^{ik} + U_s^{ik} - U_{rs}^{ik} - U_{sr}^{ik})$$
$$= \mathbf{d}^T \mathbf{A}_{rs} \mathbf{d}/d^2. \qquad (3.5)$$

Thus we obtain for the correction term

$$\overline{r^2} - \overline{z^2} = \overline{w^2} = \text{trace } (\mathbf{A}_{rs}) - \mathbf{d}^T \mathbf{A}_{rs} \mathbf{d}/d^2. \qquad (3.6)$$

In a non-Cartesian coordinate system with metric tensor $\mathbf{g}$ in crystal space equation (3.6) becomes

$$\overline{w^2} = \text{trace} \, (\mathbf{A}_{rs}\mathbf{g}) - \mathbf{d}^T\mathbf{g}\mathbf{A}_{rs}\mathbf{g}\mathbf{d}/d^2. \tag{3.7}$$

Although the formulation in terms of the coupling tensors in a general coordinate system may be of advantage in some cases we should point out that, for evaluating the bond-length correction, it is sufficient to know only the two diagonal components U_{rs}^{11} and U_{rs}^{22} in a Cartesian coordinate system with the z axis in the direction of the bond vector.

4. The known dynamical models

The equations (3.1), (3.3), and (3.6) show that one only needs to know the tensors $\mathbf{U}_r$, $\mathbf{U}_s$ and $\mathbf{U}_{rs}$, or $\mathbf{A}_{rs}$ in order to calculate the correction. We now derive $\mathbf{U}_{rs}$ and $\mathbf{A}_{rs}$ for those models which were frequently used in the past.

(a) Uncorrelated motion

Obviously

$$\mathbf{U}_{rs} = 0 , \tag{4.1}$$

hence $\mathbf{A}_{rs} = \mathbf{U}_r + \mathbf{U}_s$ in agreement with the results obtained by Busing & Levy (1964).

(b) Rigid-body motion

We first express the tensors $\mathbf{U}_r$ by way of the rigid-body vibration tensors $\mathbf{T}\,\mathbf{L}\,\mathbf{S}$, and quote Pawley's (1968) formulation

$$\mathbf{U}_r = \mathbf{T} + \mathbf{V}_r\mathbf{L}\mathbf{V}_r^T - \mathbf{V}_r\mathbf{S} - (\mathbf{V}_r\mathbf{S})^T. \tag{4.2}$$

$\mathbf{V}_r$ is the antisymmetric tensor

$$\mathbf{V}_r = \begin{pmatrix} 0 & -Z_r & Y_r \\ Z_r & 0 & -X_r \\ -Y_r & X_r & 0 \end{pmatrix}, \tag{4.3}$$

where X_r, Y_r, Z_r are the Cartesian coordinates of the atom r, referred to an arbitrary origin in the molecular system. [The meaning of the components of $\mathbf{V}_r$ in a non-Cartesian system is discussed by Hirshfeld & Rabinovich (1966).] The coupling tensors $\mathbf{U}_{rs}$ for the rigid-body motion are now obtained by substituting the atom s in equation (4.2) for half the positions of the atom r. This procedure can be deduced by comparing the definitions of $\mathbf{U}_{rs}$ given in equation (2.2) and $\mathbf{U}_r$ given in equation (4) of Scheringer (1972). Thus

$$\mathbf{U}_{rs} = \mathbf{T} + \mathbf{V}_r\mathbf{L}\mathbf{V}_s^T - \mathbf{V}_r\mathbf{S} - (\mathbf{V}_s\mathbf{S})^T. \tag{4.4}$$

Using equations (3.3), (4.2) and (4.4) we obtain

$$\mathbf{A}_{rs} = (\mathbf{V}_r - \mathbf{V}_s)\mathbf{L}(\mathbf{V}_r - \mathbf{V}_s)^T. \tag{4.5}$$

Inserting the result (4.5) in equation (3.6) shows that the second term in equation (3.6), $\overline{z^2} = \mathbf{d}^T\mathbf{A}_{rs}\mathbf{d}/d^2$, is al-

ways zero, since the matrix product $(\mathbf{V}_r - \mathbf{V}_s)\mathbf{d}$ corresponds to the vector product $\mathbf{d}\wedge\mathbf{d}$. The correction only depends on the libration tensor $\mathbf{L}$. Equations (3.6) and (4.5) are identical with the result obtained by Schomaker & Trueblood [1968, equation (22)]. This can be shown by first expressing all vector and tensor components in a Cartesian coordinate system and then multiplying out all terms explicitly. We further remark that Schomaker & Trueblood's derivation suffers from the fact that they were forced to make two special assumptions ($\overline{\lambda} = 0$ and $\overline{t} = 0$ in their notation) which could not be proved to hold generally.

(c) Riding motion

If the atom s 'rides' on the atom r all motions of the atom r are transferred to the atom s. Hence

$$\mathbf{U}_{rs} = \mathbf{U}_r , \quad \mathbf{A}_{rs} = \mathbf{U}_s - \mathbf{U}_r , \tag{4.6}$$

in agreement with the results obtained by Busing & Levy (1964). Johnson (1970) states 'that the riding model gives the same corrected distance as the rigid-body model if and only if the origin of the atom r, on which s rides, is on a true centre of libration with no correlated rigid translation'. This can immediately be shown to hold from equations (4.2), (4.4), and (4.6): Since the axes of libration pass through the atom r we have $\mathbf{V}_r = 0$. Furthermore, $\mathbf{S} = 0$. Then $\mathbf{U}_r = \mathbf{U}_{rs} = \mathbf{T}$ and $\mathbf{U}_s = \mathbf{T} + \mathbf{V}_s\mathbf{L}\mathbf{V}_s^T$, which proves the statement.

(d) Lower and upper bounds

For determining the lower and upper bounds Busing & Levy's (1964) equations, cf. also Johnson (1970), are more suitable since they contain only scalar quantities, whereas in our condition for obtaining the bounds,

$$\det (\mathbf{G}) = 0 , \tag{4.7}$$

a 6×6 matrix is involved. $\mathbf{G}$ is defined in equation (2.1). The two possible cases which satisfy (4.7) are the maximum possible in-phase and out-of-phase motions. In general, it is not possible to solve equation (4.7) explicitly in terms of the tensors $\mathbf{U}_r$, $\mathbf{U}_s$, and $\mathbf{U}_{rs}$ and this prevents its numerical use. Only in the special case of $\mathbf{U}_r = \mathbf{U}_s$ we obtain $\mathbf{U}_{rs} = \pm\mathbf{U}_s$ as solutions of (4.7), as can easily be shown by the Laplace expansion of $\det(\mathbf{G})$.

5. Conclusions

The advantage of the approach described in this paper seems to lie in the fact that the bond-length correction is derived from the dynamical matrices of the crystal which may lead to a better physical understanding of the correction. The remaining formal limitations arise only from the harmonic approximation used in lattice dynamics and from the quadratic approximation used in equation (3.1).

The main practical problem with actual structures is the estimation of the values of the coupling tensors which in some cases may be deduced from dynamical models. However, often one is not sure if the models

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.

References

BUSING, W. R. & LEVY, H. A. (1957). J. Chem. Phys. 26, 563.

BUSING, W. R. & LEVY, H. A. (1964). Acta Cryst. 17, 142.

CRUICKSHANK, D. W. J. (1956). Acta Cryst. 9, 757.

CRUICKSHANK, D. W. J. (1961). Acta Cryst. 14, 896.

HIRSHFELD, F. L. & RABINOVICH, D. (1966). Acta Cryst. 20, 146.

JOHNSON, C. K. (1970). In Crystallographic Computing, pp. 220–226. Copenhagen: Munksgaard.

PAWLEY, G. S. (1968). Acta Cryst. B24, 485.

SCHERINGER, C. (1972). Acta Cryst. A28, 512.

SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). Acta Cryst. B24, 63.

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

BY C. SCHERINGER

Institut für Kristallographie der Universität, Karlsruhe, Germany

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, 1972a) 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