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Acta Cryst. (1970). **A26**, 289

Rigid-Body Molecular Motion in Crystals. The Centre of Libration

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(Received 17 June 1969 and in revised form 27 October 1969)

It is shown that the concept of the molecular centre of libration in the description of the average rigid-body thermal behaviour of molecules is a useful approximation. A restriction is made on the full theory, making the centre of libration model a constrained version of the complete model. The relationship between the models is discussed. Some examples are chosen to demonstrate the closeness of the approximation. These results show that for data reaching a reliability factor of no better than 7% an analysis using the full theory might yield a meaningless result. Some data of much higher accuracy does, however, show the need for the full theory.

Introduction

In a recent paper Schomaker & Trueblood (1968) show that the correct description of the average motion of rigid molecules in a crystal is furnished by a model with 20 parameters. These determine the mean-square translational and librational tensors **T** and **L**, each with six independent coefficients, and the screw rotation tensor **S** with eight independent coefficients. Throughout the present paper this will be called the TLS model. Before this theory was developed a model with 15 parameters had been used by Hirshfeld, Sandler & Schmidt (1963), Pawley (1963) and Cruickshank, Jones & Walker (1964). To the twelve coefficients of **T** and **L** were added three coordinates for the centre of molecular libration **X**. This will be called the TLX model.

The TLX model has proved most successful, especially when applied during structure factor least-squares (SFLS) refinement (Pawley, 1966). This procedure requires a constrained SFLS refinement, resulting in rigid-body parameters giving the best least-squares fit to the diffraction data. The alternative procedure is to perform the standard SFLS refinement, and then fit

the model to the independent atomic vibration tensors U_x thus found. The fit by this method cannot be the better; for anthracene the least-squares errors from this procedure were almost twice those obtained from the constrained SFLS refinement (Pawley, 1967). Another constrained SFLS program is therefore called for to test the data available in the literature to find examples where the TLS model provides a significant improvement over the TLX model. First let us establish the relationship between the TLS and the TLX models and find the transformation equations governing this relationship.

The TLX and TLS models

Let us examine the equations relating the U_x for the atom at the point **x** in a molecule to the three tensors **T**, **L** and **S**. These are given by Pawley (1968) equations (3):

$$\begin{aligned}(U_x)_{11} &= T_{11} + L_{22}x_3^2 + L_{33}x_2^2 - 2L_{23}x_2x_3 + 2S_{21}x_3 - 2S_{31}x_2 \\ (U_x)_{23} &= T_{23} + L_{31}x_1x_2 + L_{12}x_3x_1 - L_{23}x_1^2 - L_{11}x_2x_3 \\ &\quad + S_{33}x_1 - S_{13}x_3 + S_{12}x_2 - S_{22}x_1.\end{aligned}\quad (1)$$

We must now compare these with the equations relating the U_x to the two tensors **T** and **L** and the molecular centre of libration **X**. These can be obtained from the

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equations above by substituting $x_i - X_i$ for x_i and putting $S_{ij} = 0$. On expansion and rearrangement we get

$$\begin{aligned} (\mathbf{U}_x)_{11} = & T_{11} + L_{22}X_3^2 + L_{33}X_2^2 - 2L_{23}X_2X_3 + L_{22}X_3^2 + L_{33}X_2^2 \\ & - 2L_{23}x_2x_3 + 2(L_{23}X_2 - L_{22}X_3)x_3 \\ & - 2(L_{33}X_2 - L_{23}X_3)x_2 \end{aligned}$$

$$\begin{aligned} (\mathbf{U}_x)_{23} = & T_{23} + L_{31}X_1X_2 + L_{12}X_3X_1 - L_{23}X_1^2 - L_{11}X_2X_3 \\ & + L_{31}x_1x_2 + L_{12}x_3x_1 - L_{23}x_1^2 - L_{11}x_2x_3 \\ & + (2L_{23}X_1 - L_{31}X_2 - L_{12}X_3)x_1 \\ & + (L_{11}X_2 - L_{12}X_1)x_3 + (L_{11}X_3 - L_{31}X_1)x_2. \end{aligned} \quad (2)$$

The form of these equations exactly matches equations (1) with the following identities, where the primes indicate the tensor coefficients of \mathbf{T} and \mathbf{L} of equations (2).

$$\begin{aligned} T_{11} = & T'_{11} + L'_{22}X_3^2 + L'_{33}X_2^2 - 2L'_{23}X_2X_3 \\ T_{23} = & T'_{23} + L'_{31}X_1X_2 + L'_{12}X_3X_1 - L'_{23}X_1^2 - L'_{11}X_2X_3 \\ L_{ij} = & L'_{ij} \\ S_{12} = & L'_{11}X_3 - L'_{31}X_1 \\ S_{13} = & L'_{12}X_1 - L'_{11}X_2 \\ S_{33} - S_{22} = & 2L'_{23}X_1 - L'_{31}X_2 - L'_{12}X_3. \end{aligned} \quad (3)$$

The coefficients which are not given above can be obtained from these by cyclic permutation of all the indices.

The expressions for S_{12} and S_{13} are obtained twice, once from the diagonal coefficient equations and once from the off-diagonal coefficient equations. It is satisfying that these agree, and also that

$$(S_{33} - S_{22}) + (S_{22} - S_{11}) = (S_{33} - S_{11}).$$

Thus we see that the use of the molecular libration centre is equivalent to using a constrained TLS model, and the equations (3) above are the transformation equations.

In the TLS model Schomaker & Trueblood show that a unique shift of origin can be made, rendering \mathbf{S} symmetric and minimizing the trace of \mathbf{T} . This origin is also discussed by Johnson (1969) and we now show that it is exactly the 'centre of libration'. Writing Johnson's equation (47*b*) for the coordinates of this centre we have

$$\begin{pmatrix} \varrho_1^0 \\ \varrho_2^0 \\ \varrho_3^0 \end{pmatrix} = \begin{pmatrix} L_{22} + L_{33} & -L_{12} & -L_{13} \\ -L_{12} & L_{33} + L_{11} & -L_{23} \\ -L_{13} & -L_{23} & L_{11} + L_{22} \end{pmatrix}^{-1} \begin{pmatrix} S_{23} - S_{32} \\ S_{31} - S_{13} \\ S_{12} - S_{21} \end{pmatrix}$$

where L_{ij} and S_{ij} have the same meaning as in the present paper. Using the inverse of the matrix involv-

ing L_{ij} we can write out three equations, the first of which is

$$(L_{22} + L_{33})\varrho_1^0 - L_{12}\varrho_2^0 - L_{13}\varrho_3^0 = S_{23} - S_{32}.$$

From equations (3) we easily get

$$(L'_{22} + L'_{33})X_1 - L'_{12}X_2 - L'_{13}X_3 = S_{23} - S_{32}$$

and using $L_{ij} = L'_{ij}$ we see $\varrho_i^0 = X_i$, establishing the unique origin as the centre of libration.

The TLX model is thus a constraint on a TLS model in such a way that the libration tensor, $\mathbf{L} = \mathbf{L}'$, is unmodified. That it is a constraint on the TLS model is evident from equations (3) which define a transformation with no definite inverse.

Search for an example

We wish to find an example where the TLS model can be successfully fitted to the diffraction data using the constrained SFLS procedure. The method of computation has already been described (Pawley, 1968). Possible examples fall into two categories. The first are those where the anisotropic temperature factors, themselves obtained from the diffraction data, have been used as the basis of a TLS fit, following Schomaker & Trueblood (1968), and where the result has been deemed significant. The second are those which have refined successfully by SFLS using the TLX constraint.

In the first category there is one possibility from Schomaker & Trueblood (1968), namely benzo[*c*]phenanthrene, and one from Burns, Ferrier & McMullan (1968), namely phenylcyclobutenedione. We reject the latter on the following grounds. The improvement obtained by Burns *et al.* is hardly significant, and the comparison they make, that is between the TLS model and the TLX model with \mathbf{X} fixed, does not test the full TLX model.

Benzo[*c*]phenanthrene was studied by Hirshfeld *et al.* (1963) who obtained an *R* index of 11.1% for this structure using block-diagonal least-squares refinement with anisotropic temperature factors. To these parameters they fitted \mathbf{T} , \mathbf{L} and \mathbf{X} , needing as many as 15 cycles to achieve convergence. This result was compared by Schomaker & Trueblood (1968) to their fit of \mathbf{T} , \mathbf{L} and \mathbf{S} , based on the same anisotropic temperature factors, and the difference is highly significant.

Two SFLS refinements were attempted, the TLX and TLS models. The former was started very near the values given by Hirshfeld *et al.*, but both attempts diverged wildly and refinement was impossible. There is therefore no reason to believe that there is any physical significance in the TLX fit obtained by Hirshfeld *et al.* or in the TLS fit of Schomaker & Trueblood. This is disappointing, especially as Hirshfeld *et al.* continue by using their result to suggest evidence for the contributions from the internal modes. However, the reason for Schomaker & Trueblood's improved fit may

indeed lie in the existence of such modes with low frequencies and correspondingly large amplitudes.

The second category of examples contains the unsymmetrical boron hydrides (Pawley, 1966). The first to be tried, B_4H_{10} had been refined using the TLX model, reaching an R index of 7.6%. The centre of libration was found to be 0.26 ± 0.17 Å from the molecular centre of mass. Refinement was quick and stable.

The first attempt to include S in the refinement started with the best T and L previously obtained and $S_{ij}=0$. This refinement soon diverged, L_{33} becoming negative. Further attempts using reduced shifts gave a slight improvement but again L_{33} went negative. The R index dropped to 7.50%, but for any improvement to be significant even on the 25% level of the F distribution we expect $R < 7.1\%$ (616 observations, 63 parameters).

In a final attempt equations (3) were used on the best values for T , L and X to provide starting parameters but the shifts diverged again, L_{11} becoming very small. However, this provided a check on the new program as the anisotropic temperature factors were calculated the same before and after the transformation (3).

It was suggested to the author that starting at $S_{ij}=0$ might have been the cause of trouble, but this would not explain failure when starting from the point obtained from the transformation (3).

Another suggestion was that there might be a weak column(s) in the least-squares matrix. If encountered this can be overcome by changing the units of the parameter(s) concerned. The matrix was duly printed out, showing a variation in the diagonal elements over less than two orders of magnitude with no weak columns in evidence. This matrix was tested for ill-conditioning by rounding off its coefficients severely, but this produced little difference on inversion. All calculations were performed on the KDF9 at the Edinburgh Regional Computing Centre, which has a 48-bit word length, and the matrix inversion routine used double-length accumulation. There can be little doubt that matrix ill-conditioning is not the source of the trouble and that the difficulties are inherent in the TLS model. An eigenvector study of the least-squares matrix was not done. If successful this would result in a certain combination of parameters being important and other combinations being ill-defined. The latter combinations would define regions in parameter space where the function to be minimized in the SFLS process has very little variation. The extra space provided by TLS over TLX is thought to be such a space.

Johnson (1969) has pointed out that the analysis of the U_x becomes a singular problem if all the positions x of the molecule lie on a conic section. In this event the constrained SFLS would probably also give a singularity, and it might be a near singularity of this sort which makes the B_4H_{10} problem unstable. In the hope that the above difficulties could be due to the particular example investigated both B_8H_{12} and $B_4C_2H_8$ were

tried. Both these were successful with the TLX model (Pawley, 1966), reaching R indices of 9.6 and 7.9% respectively. However, these examples behaved in a similar manner to B_4H_{10} , giving values for parameters which were physically meaningless.

Conclusion

If the examples studied above are typical, we must conclude that for diffraction data whose accuracy will not permit a fit considerably better than $R=7\%$ it is probably meaningless to calculate the screw tensor of Schomaker & Trueblood (1968). The approximation of a 'centre of libration' should be adequate at this level of accuracy. A positive result of this work is therefore that the TLX model is not theoretically invalid. It is shown that this is simply a constraint on the TLS model about which there is no theoretical doubt.

To gain an understanding of why the SFLS refinements constrained for TLS proved unstable we should investigate the surface of

$$R_w = \sum_{\text{obs}} w(F_{\text{obs}} - F_{\text{calc}})^2 \quad (w = \text{weight})$$

in the multidimensional parameter space. S provides eight dimensions of this space. If there are directions in this space where R_w varies very slowly then the corresponding parameters cannot be well determined. The least-squares procedure would suggest large shifts in these directions, and the problem is controllable only by shift reduction. There cannot be any such directions parallel to any S_{ij} axes otherwise these would have shown up as weak columns in the least-squares matrix. So we are faced with the problem of finding directions where this flatness occurs, and when this is accomplished we must restrict the parameter values in these directions and only allow variations in the lower dimensional space which remains. Fortunately this does not call for parameter space exploration as the TLX model provides exactly what is demanded: a subspace of the TLS space in which R_w has a well defined minimum.

What then are the future prospects? For crystals composed entirely of molecules we must await results of higher accuracy, but such results are available for crystals containing molecular ions. Professor D. W. J. Cruickshank (private communication) cites the examples of the NO_3^- ion in $NaNO_3$ (Cherin, Hamilton & Post, 1967) and of the SO_4^{2-} ion in sodium alum (Kay & Cromer, 1969). In the case of $NaNO_3$ he argues that the occurrence of $U_{23} \neq 0$ must imply $S_{33} \neq 0$ which is outside the TLX restriction. The difference between the value of U_{23} and zero is highly significant, and a TLS study of this structure would therefore be well worth while. Finally both Dr F. L. Hirshfeld and Dr C. Scheringer (private communications) claim some success with a TLS constrained SFLS procedure, but again using data of higher than usual accuracy.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

Acta Cryst. (1970). A26, 292

Anharmonic thermal vibrations in Mg₂Si. By M. J. COOPER, *Materials Physics Division, A.E.R.E., Harwell, Berkshire, England* and D. PANKE, *Institut für physikalische Chemie der Universität Mainz, Germany*

(Received 5 June 1969)

The recent X-ray diffraction data from Mg₂Si, obtained by Panke & Wölfel (*Z. Kristallogr.* (1969), 129,9) show systematic differences in the structure factors from those predicted by a model which assumes harmonic thermal vibration of the atoms. These differences indicate an anharmonic component in the thermal vibration of the magnesium atoms, consistent with their tetrahedral site symmetry. An analysis of these data has therefore been carried out in terms of a model which includes anharmonic thermal vibration and a least-squares refinement gave a value of the anharmonicity parameter ($\beta_{Mg} = -2.39 \times 10^{-12}$ erg.Å⁻³) which is similar in magnitude to those found for other systems with the fluorite structure.

The significance of anharmonic thermal vibrations in materials with the fluorite structure has been established by a series of recent accurate neutron diffraction studies on UO₂ (Rouse, Willis & Pryor, 1968), BaF₂ (Cooper, Rouse & Willis, 1968) and CaF₂ and SrF₂ (Cooper & Rouse, 1970). In this structure the anion has a tetrahedral environment which allows an anharmonic contribution to the thermal vibration of the anion, consistent with the introduction of a cubic term βxyz in the potential, where x , y and z are the coordinates defining the instantaneous displacement of the anion (see Dawson, Hurley & Maslen, 1967). The magnitude of the anharmonicity parameter β in these materials is of the order of -3×10^{-12} erg Å⁻³ and the anharmonic component of the thermal vibration results in significant deviations in the Bragg intensities from those predicted by a harmonic model.

For X-ray diffraction the angular dependence of the scattering factors and the predominance of the cation scattering result in the X-ray Bragg intensities for these materials being less dependent on the anharmonic effects, although a detailed analysis of recent accurate X-ray diffraction measurements on CaF₂ (Cooper, 1970a) has shown that these also are consistent with an anharmonicity of this magnitude. Panke & Wölfel (1969) have recently carried out a careful X-ray diffraction study of Mg₂Si, which also has the fluorite structure and which has a more favourable scattering factor ratio. It is interesting to note, therefore, that their results show systematic differences from the predictions of a model which assumes harmonic

thermal vibration of the atoms, for example the different values obtained for the structure factors of the 933, 771 and 755 reflexions are indicative of anharmonic effects as described above, whereas a harmonic model would require these three reflexions to have equal structure factors. Because of these apparent systematic effects we have therefore reconsidered the experimental data in terms of an anharmonic model.

The X-ray measurements on Mg₂Si were made on both single crystals and powder samples and a comprehensive correction for extinction was carried out. Care was also taken to minimize errors due to multiple diffraction (Panke & Wölfel, 1968). No correction was made for the contribution of thermal diffuse scattering, but it is most probable that such a correction would result only in a change in the derived temperature factors (Cooper & Rouse, 1968; Cooper, 1970b). The electron density, which was calculated from the experimental structure factors, indicates spherical magnesium ions but shows that the outer electrons of the silicon ions are distorted towards the nearest magnesium neighbours. The ionic charges were found to be approximately Mg^{1.5+} and Si¹⁻ and the temperature factors were determined to be $B_{Mg} = 0.764$ Å² and $B_{Si} = 0.548$ Å².

The experimental data were reanalysed using a least-squares computer program which can refine parameters associated with both anharmonic thermal vibration and extinction (see Cooper, 1970a). The experimental structure factors, as given in the last column of Panke & Wölfel's Table 5 (Panke & Wölfel, 1969), were used, weighted in