Acta Cryst. (1985). A**41**, 356-361

Thermal Motion for Non-Rigid Molecules in Crystals: Symmetry of the Generalized Mean-Square Displacement Tensor W

BY CARLO MARIA GRAMACCIOLI

Dipartimento di Scienze della Terra, Università, Via Botticelli 23, *I*-20133 *Milano, Italy*

AND GIUSEPPE FILIPPINI

Dipartimento di Chimica Fisica e Centro CNR, Università, via Golgi 19, *I*-20133 *Milano, Italy*

(*Received* 3 *July* 1984; *accepted* 15 *January* 1985)

Abstract

A lattice-dynamical evaluation of the mean-square displacement tensor **W** for a non-rigid molecule is not a difficult problem in the harmonic approximation, provided appropriate potentials are known; from it, essential information for bond-length correction can be easily derived. The symmetry transformations and the site-symmetry requirements for **W** are discussed on the basis of group theory: for the rigid body, they coincide with the requirements for **T**, **L** and **S**.

Introduction

Thermal motion analysis is becoming more and more important when particularly accurate results concerning crystal structure are wanted. For cases involving rigid molecules, the interpretation of atomic temperature factors (**B**'s) in terms of two or three molecular tensors **T**, **L** and **S** is quite useful (Cruickshank, 1956; Schomaker & Trueblood, 1968, here onwards ST; Pawley, 1972*a*). However, for small or highly symmetrical molecules, there are difficulties in deriving **T**, **L** and **S**, because of a singularity or ill-conditioning of the least-squares matrix (Johnson, 1970, 1980; Filippini, Gramaccioli, Simonetta & Suffritti, 1974*a*). Sometimes the molecule can hardly be considered as 'rigid', even if the fit of the **B**'s to **T**, **L** and **S** is good.

For all these cases, a lattice-dynamical evaluation of thermal motion seems to be a promising solution (Pawley, 1967, 1968, 1972*a*, *b*; Cochran & Pawley, 1964; Willis & Howard, 1975; Kroon & Vos, 1979; Filippini, Gramaccioli, Simonetta & Suffritti, 1973, 1974*a*, *b*, 1976*a*, *b*, 1978; Bonadeo & Burgos, 1982; Gramaccioli, Filippini & Simonetta, 1982; Gramaccioli & Filippini, 1983, 1984, 1985; Scheringer, 1982*a*, *b*, *c*). In our generalized treatment for a non-rigid molecule (Gramaccioli & Filippini, 1983, hereafter GF), the best description of molecular motion is obtained in terms of the normal coordinates of the isolated molecule (Taddei, Bonadeo, Marzocchi & Califano, 1973; Bonadeo & Taddei, 1973; Neto, Righini, Califano & Walmsley, 1978; Bonadeo & Burgos, 1982). The set of normal coordinates should include the ones corresponding to zero frequency, if the routine that has been proposed by Wilson, Decius & Cross (1955) or Gwinn (1971) is used: in this way, rotations and translations can be given the same mathematical treatment as for the internal motion.

In GF, we proposed the use of a mean-square displacement tensor (**W**) relative to all the molecule. This tensor includes external and internal modes together, and can be obtained as

$$\mathbf{W}=\langle \mathbf{v}\mathbf{v}^T\rangle = N^{-1}\sum_{\psi\mathbf{k}} E_\psi(\mathbf{k})\omega_\psi(\mathbf{k})^{-2}\mathbf{p}(\psi\mathbf{k})|\mathbf{p}^*(\psi\mathbf{k})|^T, \tag{1}$$

where $E_\psi(\mathbf{k})$ is the average energy of the ψ mode for a certain value of the wave vector $\mathbf{k}$, $\mathbf{p}(\psi\mathbf{k})$ are the eigenvectors of the dynamical matrix $\mathbf{D}(\mathbf{k})$, and $\mathbf{v}$ indicates the displacement in terms of normal (mass-weighted) coordinates of the free molecule. From **W**, all the 'usual' crystallographic tensors, such as the **B**'s or **T**, **L**, **S** can be easily obtained (see GF, equation 6.4 in Willis & Pryor, 1975, or below); also, the so-called 'coupling tensors' $\mathbf{U}(ij)=\langle \mathbf{u}(i)|\mathbf{u}(j)|^T\rangle$ between the atoms i and j can be derived from **W** by a simple transformation [see (3) below]. Such tensors are essential. for bond-length correction in the most general case (Johnson, 1970, 1980; Scheringer, 1972*b*) and cannot be obtained from the usual diffraction data. Obviously, the advantages of using **W** *in lieu* of **T**, **L** and **S** are especially evident for the non-rigid body, when the latter tensors are not sufficient for describing the molecular motion.

If the molecule is in a special position, **W** is subject to site-symmetry requirements, which may be interesting to ascertain. The problem is not only of academic interest, because a considerable restriction of the Brillouin-zone sampling in our calculations can be achieved. For a rigid body we have, for instance (Filippini, Gramaccioli, Simonetta & Suffritti,

0108-7673/85/040356-06$01.50

1976*a*),

$$\mathbf{T}=\sum_j \mathbf{M}_j\mathbf{T}_1\mathbf{M}_j^T;\ \mathbf{L}=\sum_j \mathbf{M}_j\mathbf{L}_1\mathbf{M}_j^T;$$

$$\mathbf{S}=\sum_j |\mathbf{M}_j|\mathbf{M}_j\mathbf{S}_1\mathbf{M}_j^T, \tag{2}$$

where the $\mathbf{M}_j$'s are the transformation matrices of the site-symmetry group, and the summation is extended to all the operations in the group. $\mathbf{T}_1$, $\mathbf{L}_1$ and $\mathbf{S}_1$ are the contributions to **T**, **L** and **S** obtained from sampling the asymmetric part of the Brillouin zone, and $|\mathbf{M}_j|$ is the determinant of $\mathbf{M}_j$. The results are in complete agreement with ST.

On extending our calculations to a non-rigid model, our first routine for calculating the **B**'s from **W** (which was used in GF) involved applying symmetry transformations directly to temperature factors. However, this routine becomes considerably cumbersome when the coupling tensors $\mathbf{U}(ij)$ are also wanted, whereas the other way, implying symmetry transformations of **W** as for **T**, **L** and **S** [see (2) to (5)], is much simpler.

Therefore, we decided to examine such symmetry transformations in detail, as well as the site-symmetry requirements. Some of these are quite simple, according to group theory, and can be applied to a general case involving any kind of site symmetry and internal coordinates. As a particular case, they should include (or be compatible with) the site-symmetry requirements, or the transformations, of **T**, **L**, **S** and of any atomic temperature factor.

Method of calculation

Let us first recall the relationships between **W** and temperature factors, as given by GF:

$$\mathbf{\Omega}=\mathbf{V}\mathbf{m}^{-1/2}\mathbf{W}\mathbf{m}^{-1/2}\mathbf{V}^T. \tag{3}$$

Here **V** is a matrix whose columns are the eigenvectors of the mass-adjusted dynamical matrix of the isolated molecule, **m** is the so-called 'mass matrix', which contains each one of the atomic masses repeated three times, in sequence along the main diagonal, and having all other elements equal to zero.

The 3×3 blocks along the main diagonal of $\mathbf{\Omega}$ are the atomic mean-square displacement tensors $\mathbf{U}(i)$; the off-diagonal blocks are the coupling tensors $\mathbf{U}(ij)$.

If the molecule is in a non-trivial symmetric site, for obtaining **W** a procedure similar to (2) can be adopted:

$$\mathbf{W}=\sum_j \mathbf{W}'_{1j}=\sum_j \mathbf{Q}_j\mathbf{W}_1\mathbf{Q}_j^T, \tag{4}$$

where $\mathbf{W}_1$ is the contribution to **W** in the asymmetric part of the Brillouin zone with respect to the site-symmetry group, $\mathbf{W}'_{1j}$ is the transformed counterpart of $\mathbf{W}_1$ with respect to the *j*th symmetry operation, and $\mathbf{Q}_j$ is the corresponding transformation matrix of $\mathbf{W}_1$ (and **W**). Since $\mathbf{W}=\langle\mathbf{v}\mathbf{v}^T\rangle$, we have

$$\mathbf{W}'_j=\langle\mathbf{v}'_j\mathbf{v}'^T_j\rangle=\mathbf{Q}_j\langle\mathbf{v}_j\mathbf{v}_j^T\rangle\mathbf{Q}_j^T$$

$$=\mathbf{Q}_j\langle\mathbf{v}\mathbf{v}^T\rangle\mathbf{Q}_j^T=\mathbf{Q}_j\mathbf{W}\mathbf{Q}_j^T. \tag{5}$$

Therefore, from (5) it is evident that $\mathbf{v}'_j=\mathbf{Q}_j\mathbf{v}$, *i.e.* the transformation matrices for **W** are the same as for the displacement vectors **v**. Since the components of such vectors here refer to the normal coordinates of the free molecule, $\mathbf{Q}_j$ will be a block-diagonal matrix. In $\mathbf{Q}_j$ each block refers to one normal coordinate (or more if symmetry degenerate) and can be deduced from symmetry labelling of such normal modes with respect to the *site* symmetry group. In other words, the set of $\mathbf{Q}_j$'s is the direct sum of representations of the group that are carried by all the normal coordinates.

According to (4), an element $\mathbf{W}_{rs}$ of **W** occurring for a particular site symmetry can be written as

$$\mathbf{W}_{rs}=\sum_j\sum_{kl=1,n}\mathbf{Q}_{rk(j)}\mathbf{Q}_{sl(j)}\mathbf{W}_{1kl}, \tag{6}$$

where the summation on the index *j* is referred to all the site-symmetry group operations, and *n* is the order of **W**. Owing to the nature of **Q**, a non-zero element $\mathbf{Q}_{rk(j)}$ or $\mathbf{Q}_{sl(j)}$ will correspond to an element $\mathbf{M}_{tu(j\rho)}$ or $\mathbf{M}_{vw(j\sigma)}$ of a matrix belonging to a certain representation Γ_ρ or Γ_σ of the site-symmetry group relative to the normal coordinates *r* or *s*, respectively. It will be, in general: $t=r-m_1$; $u=k-m_1$; $v=s-m_2$; $w=l-m_2$, where m_1 and m_2 are the sum of the orders of the preceding blocks in the diagonal of the $\mathbf{Q}_j$'s. Therefore, we have

$$\mathbf{W}_{rs}=\sum_{kl}\sum_j\mathbf{Q}_{rk(j)}\mathbf{Q}_{sl(j)}\mathbf{W}_{1kl}$$

$$=\sum_{\substack{kl\\(uw)}}\sum_j\mathbf{M}_{tu(j\rho)}\mathbf{M}_{vw(j\sigma)}\mathbf{W}_{1kl}. \tag{7}$$

Because of the orthogonality relationship,

$$\sum_j\mathbf{M}_{tu(j\rho)}\mathbf{M}^*_{vw(j\sigma)}=\delta_{\rho\sigma}\delta_{tv}\delta_{uw}h/g, \tag{8}$$

where *g* is the dimension of the representation and *h* is the order of the group. Consequently, if **M** is real:

$$\mathbf{W}_{rs}=\sum_{\substack{kl\\(uw)}}\mathbf{W}_{1kl}\sum_j\mathbf{M}_{tu(j\rho)}\mathbf{M}_{vw(j\sigma)}$$

$$=h/g\sum_{kl}\mathbf{W}_{1kl}\delta_{\rho\sigma}\delta_{tv}\delta_{uw}. \tag{9}$$

If q_r, q_s are symmetry-related degenerate coordinates, we have $m_1=m_2$ and (7) can be written as

$$\mathbf{W}_{rs}=\sum_{kl}\sum_j\mathbf{M}_{tu(j\rho)}\mathbf{M}_{vw(j\rho)}\mathbf{W}_{1kl}$$

$$=h/g\sum_{kl}\delta_{rs}\delta_{kl}\mathbf{W}_{1kl}$$

$$=h/g\,\delta_{rs}\sum_k\mathbf{W}_{1kk}. \tag{10}$$

Expressions (8) to (10), however, have been derived with the assumption that $\mathbf{M}$'s are matrices belonging to *irreducible* representations. This happens for the great majority of cases; the only exceptions occur for the E representations of the groups C_k, C_{kh}, S_k, T or T_h, where some elements are complex when they are irreducible.

For such cases, we could define $\mathbf{P}_{(j\rho)}$ as a 2×2 matrix, where $\mathbf{P}_{12}=\mathbf{P}_{21}=0$, and $\mathbf{P}_{11}=\mathbf{P}^*_{22}=\exp(2\pi i\varphi)$, φ being the rotation angle corresponding to the matrix $\mathbf{M}_{(j\rho)}$. Therefore, the representations concerning the $\mathbf{P}$ matrices are the direct sum of two irreducible monodimensional representations, which are complex conjugate to each other. An element $\mathbf{M}_{tu(j\rho)}$ will be a linear combination of the elements of $\mathbf{P}_{(j\rho)}$, according to the transformation

$$\mathbf{M}_{(j\rho)}=\mathbf{U}\mathbf{P}_{(j\rho)}\mathbf{U}^{\dagger}, \tag{11}$$

where

$$\mathbf{U}=1/2^{1/2}\begin{pmatrix}1 & 1\\ -i & i\end{pmatrix}.$$

Also,

$$\mathbf{U}\mathbf{P}^*_{(j\rho)}\mathbf{U}^{\dagger}=\mathbf{M}^{-1}_{(j\rho)}=\mathbf{M}^{T}_{(j\rho)}. \tag{12}$$

Here $\mathbf{P}^*_{(j\rho)}$ corresponds to $\mathbf{P}_{(j\rho)}$, where non-zero elements are exchanged. By developing (7), and knowing (8), (11) and (12), even in such cases we have

$$\mathbf{W}_{rs}=0 \text{ for } \Gamma_\rho\neq\Gamma_\sigma. \tag{13}$$

For any block $\mathbf{A}$ of $\mathbf{W}$ corresponding to cross terms between normal coordinates carrying the same representation, by developing the same expressions we have:

$$\begin{aligned}\mathbf{A}_{11}&=\mathbf{A}_{1(11)}+\mathbf{A}_{1(22)}\\ \mathbf{A}_{22}&=\mathbf{A}_{1(11)}+\mathbf{A}_{1(22)}\\ \mathbf{A}_{12}&=-\mathbf{A}_{1(21)}+\mathbf{A}_{1(12)}\\ \mathbf{A}_{21}&=\mathbf{A}_{1(21)}-\mathbf{A}_{1(12)}.\end{aligned} \tag{14}$$

Here, $\mathbf{A}_{tv}=\mathbf{W}_{rs}$ and $\mathbf{A}_1$ is the block of $\mathbf{W}_1$ corresponding to $\mathbf{A}$.

Therefore, if $\mathbf{A}$ lies on the main diagonal of $\mathbf{W}$, it is symmetric (as well as $\mathbf{A}_1$) and $\mathbf{A}_{1(12)}=\mathbf{A}_{1(21)}$. Consequently, (10) still holds. Then, we may conclude that (10) and (13) are of general use, and some important laws can be stated:

(1) *Any element of* $\mathbf{W}$ *relative to normal coordinates with non-equivalent site-symmetry irreducible representation is zero.*

(2) *Any off-diagonal element of* $\mathbf{W}$ *involving cross terms between normal coordinates that are related to each other by symmetry degeneracy is zero. All the diagonal elements involving such coordinates are equal.*

Another important point concerns the cross terms between normal coordinates that belong to the same two- or three-dimensional (E or T) representations, without being related to each other by symmetry degeneracy. In other words, this is the problem of *off-diagonal* 2×2 or 3×3 *blocks* of $\mathbf{W}$ in connection with symmetry-degenerate normal coordinates: for the rigid body, this may concern the so-called $\mathbf{S}$ tensor for some sites of high symmetry.

Here, a more subtle distinction must be made between the various possibilities. For instance, if the representations of the symmetry-degenerate sets of coordinates are the same, and are also *irreducible*, (8), (9) and (10) hold:* consequently, in each block of $\mathbf{W}$ that is relative to such degenerate coordinates all the diagonal elements are equal, and all off-diagonal elements will be zero. This is the reason why the $\mathbf{S}$ tensor for groups like 23 (T), or 432 (O) is diagonal with all equal non-zero elements, as shown by ST.

For groups where the real E representations are reducible, (14) can be applied when such representations are the same; however, since we are not on the main diagonal of $\mathbf{W}$, for such blocks $\mathbf{A}_{1(12)}\neq\mathbf{A}_{1(21)}$, and (10) does not hold for this reason. Anyway, by applying (14), we have $\mathbf{A}_{12}=-\mathbf{A}_{21}$ and $\mathbf{A}_{11}=\mathbf{A}_{22}$.

A particular problem occurs when the normal coordinates carry *different*, though *equivalent*, representations. Here (9) cannot be applied, and the value of the sums $\sum_j \mathbf{M}_{tu(j\rho)}\mathbf{M}_{vw(j\sigma)}$ depends on each particular case. For this reason, simple laws such as (1) and (2) cannot be stated. Therefore, for symmetry-degenerate coordinates, *it is necessary not only to find the symmetry label (or the character) of a particular set of equivalent representations, but we should know also the representation itself.* This is different from most spectroscopic applications of group theory.

Relationships to T, L and S

As we have already mentioned, the use of $\mathbf{W}$ *in lieu* of $\mathbf{T}$, $\mathbf{L}$ and $\mathbf{S}$ is essential for non-rigid motion. However, the relationships of $\mathbf{W}$ to $\mathbf{T}$, $\mathbf{L}$ and $\mathbf{S}$ can be interesting to examine: such relationships are also a good check for our generalized treatment, which should be identical with ST for a rigid molecule.

According to GF (see their equations 6 and 9), $\mathbf{W}$ is connected with $\mathbf{T}$, $\mathbf{L}$ and $\mathbf{S}$ by the following transformation:

$$\left(\begin{array}{c|c}\mathbf{T} & \mathbf{S}\\ \hline \mathbf{S}^{\dagger} & \mathbf{L}\end{array}\right)=\mathbf{D}^{-1/2}\mathbf{W}_{\text{ext}}\mathbf{D}^{-1/2}, \tag{15}$$

where $\mathbf{D}$ is a diagonal matrix that is formed by repeating the molecular mass three times and from the principal moments of inertia, and $\mathbf{W}_{\text{ext}}$ is the translational-rotational part of $\mathbf{W}$, corresponding to the first 6×6 (or 5×5) block along the main diagonal. Since,

---

* Equation (10) holds with respect to row and column indices (r, s) referred to the *block*.

for any jth symmetry transformation,

$$\mathbf{Q}_j\mathbf{W}_{\text{ext}}\mathbf{Q}_j^T=\mathbf{W}'_{j(\text{ext})}=\mathbf{D}^{-1/2}\left(\begin{array}{c|c}\mathbf{T}' & \mathbf{S}'\\ \hline \mathbf{S}'^{\dagger} & \mathbf{L}'\end{array}\right)\mathbf{D}^{-1/2}, \tag{16}$$

this necessarily implies that

$$\left(\begin{array}{c|c}\mathbf{T}' & \mathbf{S}'\\ \hline \mathbf{S}'^{\dagger} & \mathbf{L}'\end{array}\right)=\mathbf{Q}\left(\begin{array}{c|c}\mathbf{T} & \mathbf{S}\\ \hline \mathbf{S}^{\dagger} & \mathbf{L}\end{array}\right)\mathbf{Q}^T. \tag{17}$$

Since S is real, $\mathbf{S}^{\dagger}=\mathbf{S}^T$ also.

Let us consider now the symmetry labelling of the translational and rotational normal modes, *i.e.* the ones corresponding to $\mathbf{W}_{\text{ext}}$. In our procedure, the first three eigenvectors relative to the translational motion of the isolated molecule are:

$$\mathbf{q}_1=\begin{pmatrix}\alpha_1\\0\\0\\ \vdots\end{pmatrix}\qquad \mathbf{q}_2=\begin{pmatrix}0\\ \alpha_1\\0\\ \vdots\end{pmatrix}\qquad \mathbf{q}_3=\begin{pmatrix}0\\0\\ \alpha_1\\ \vdots\end{pmatrix}.$$

Here, $\alpha_i=(m_i/m)^{1/2}$, where m_i is the mass of the ith atom in the molecule, and m is the mass of the molecule; the sequence of three numbers is repeated for each atom. In this way, the first three modes and normal coordinates q_1, q_2 and q_3 are defined: these coordinates correspond to motion along the three principal axes of inertia x, y and z, respectively.

For the rotational normal coordinates, we have

$$\mathbf{q}_4=\begin{pmatrix}0\\-z_1\beta_{11}\\y_1\beta_{11}\\ \vdots\end{pmatrix}\qquad \mathbf{q}_5=\begin{pmatrix}z_1\beta_{21}\\0\\-x_1\beta_{21}\\ \vdots\end{pmatrix}\qquad \mathbf{q}_6=\begin{pmatrix}-y_1\beta_{31}\\x_1\beta_{31}\\0\\ \vdots\end{pmatrix}.$$

Here, $\beta_{1i}=(m_i/I_1)^{1/2}$; $\beta_{2i}=(m_i/I_2)^{1/2}$; and $\beta_{3i}=(m_i/I_3)^{1/2}$, where x_i, y_i, z_i are the atomic coordinates referred to the principal axes of inertia, and I_1, I_2, I_3 are the principal moments of inertia corresponding to the x, y and z axes. As for translational coordinates, the sequence is repeated for each atom.

If such eigenvectors ($\mathbf{q}_1$ to $\mathbf{q}_6$) do not result directly from diagonalization of the dynamical matrix of the isolated molecule, following Wilson *et al.* (1955) or Gwinn (1971), they are replaced by the eigenvectors shown above. This is equivalent to choosing purely translational or rotational motion along (or around) the principal axes *in lieu* of their combinations in the space of the six- (or five-) fold degeneracy occurring for zero frequency. If the molecule is linear, and z is chosen as the axis corresponding to the least moment of inertia (here zero), $\mathbf{q}_6$ is omitted, and the calculation is carried on as for the general case.

Since the first three normal coordinates are translational, the first 3×3 diagonal block in $\mathbf{Q}_j$ corresponds to $\mathbf{M}_j$, the point-group symmetry operation: if the coordinates are referred to the principal axes of inertia, the representation of the group corresponding to the $\mathbf{M}_j$'s is irreducible, provided no transformations involving complex bases are considered.

The components of the vectors $\mathbf{q}_4$ to $\mathbf{q}_6$, which define the rotational normal coordinates, are for each atom equal to $\hat{\boldsymbol{\lambda}}x\mathbf{r}_i$, where $\hat{\boldsymbol{\lambda}}$ is a unit rotation vector around the x, y or z axis, and $\mathbf{r}_i$ is the distance of the atom from the origin. According to the transformation rules for a vector product, the corresponding diagonal block of $\mathbf{Q}_j$ is $\mathbf{M}_j|\mathbf{M}_j|$. If (15) to (17) are considered, this necessarily implies that (2) must follow, in complete agreement with ST.

On these grounds, a general review concerning **T**, **L** and **S** for all the possible sites in crystals can be obtained quite easily. For monodimensional representations, the cases are trivial (see the examples given below); for higher-dimensional representations, a distinction should be made between the groups with complex irreducible representations, and the others. For the holoaxial groups like 422 (D_4), 32 (D_3), or 622 (D_6), the irreducible E representations are real, and the representations of translations and rotations, when such 'E' degeneracy occurs, are the same, since no improper rotations are there. Therefore, in S the 2×3 block involving x and y is diagonal, with $S_{11}=S_{22}$, as from law 2. The third line and column of S will have all off-diagonal elements equal to zero, according to law 1. These results are the same as in ST. A rather similar result with respect to the 3×3 'T' degenerate representations can be obtained for the cubic holoaxial groups 23 and 432 (see above).

For cubic groups, such as T_h, T_d or O_h (*i.e.* $m3$, $\bar{4}3m$ and $m3m$) the representations of the translational normal coordinates are not equivalent to the representations of the rotational coordinates, and therefore **S** is zero. For **T** and **L**, owing to the three-dimensional 'T' degeneracy, law 2 holds, and the results are as in ST.

For holoaxial groups with real reducible representations, such as 4 (C_3), 3 (C_3), or 6 (C_6), (14) can be applied, and $S_{12}=-S_{21}$.

The last point to be dealt with is the case of real irreducible representations for non-holoaxial groups, such as $C_{4v}(4mm)$, $C_{3v}(3m)$, $C_{6v}(6mm)$, $D_{2d}(\bar{4}2m)$, $D_{4h}(4/mmm)$, *etc.* Here, the representation of the 'E'-labelled rotational and translational normal coordinates are sometimes different (C_{4h}, D_{4h}, *etc.*), and in other instances they are equivalent, but not equal. For the former cases, according to law 1, **S** is zero; for the latter, laws 1 and 2 can be applied to **T** and **L**, but not to **S**.

A detailed analysis must be therefore carried on, for each site symmetry. For such considerations, which involve only a very limited number of cases, all the results that are shown in ST can be obtained.

Table 1. *The tensor* **W** *for* α*-sulfur* (*atomic mass units* $\times$Å^2; *referred to the principal axes of inertia*)

For q_7, q_8 and q_9, q_{10}, which are the internal mode frequencies considered here, the calculated frequency for the free molecule is reported in the first column. In the crystal, these frequencies become 82 to 99 cm^{-1} for the first two, and 162 to 171 cm^{-1} for the other two (Gramaccioli & Filippini, 1984).

	$q_1(B)$	$q_2(A)$	$q_3(A)$	$q_4(B)$	$q_5(A)$	$q_6(A)$	$q_7(A)$	$q_8(B)$	$q_9(A)$	$q_{10}(B)$
q_1	6.420	0.000	0.000	−0.193	0.000	0.000	0.000	−0.119	0.000	0.035
q_2		8.637	−0.743	0.000	1.207	−1.349	−0.445	0.000	0.079	0.000
q_3			5.486	0.000	−0.980	0.075	0.128	0.000	−0.044	0.000
q_4				3.447	0.000	0.000	0.000	0.045	0.000	−0.054
q_5					3.713	−1.026	−0.023	0.000	−0.016	0.000
q_6						6.662	0.457	0.000	0.018	0.000
q_7 } (E_2; 67 cm^{-1})							1.084	0.000	0.011	0.000
q_8								0.984	0.000	−0.017
q_9 } (E_2; 156 cm^{-1})									0.280	0.000
q_{10}										0.285

Applications and discussion

(*a*) *Anthracene*

As an example, let us consider the tensor **W** for anthracene, which is reported in Table 5 of GF.* In this table, the rows and columns refer to the normal coordinates q_1 to q_{14}, in sequence, from the lowest to the highest frequencies. The elements of further rows and columns referring to q_{15} onwards are close to zero (especially if non-diagonal), because frequencies are high. The representations of the internal coordinates q_7 to q_{14} are, in sequence: B_{3u}, A_u, B_{2u}, B_{2g}, B_{1g}, B_{3u}, A_g, B_{3g}, according to Mulliken's labelling. However, such classification is referred to the $D_{2h}(mmm)$ symmetry of the free molecule, whereas for our purpose only the *u*, *g* labels referring to the $C_i(\bar{1})$ site are effective. The representation of the translational normal coordinates q_1 to q_3 is '*u*', whereas that of the rotational normal coordinates q_4 to q_6 is '*g*'. As a first consequence, because of law 1, the **S** tensor will be zero, as in all cases of centrosymmetric molecular sites.

Apart from the elements of **W** corresponding to **S**, we can extend our considerations to all the region concerning internal modes and their interaction with translational or rotational modes. We accordingly notice that all the elements that are relative to cross terms between the '*g*' rotational modes involving coordinates q_4 to q_6 and the '*u*' internal modes corresponding to q_7, q_8, q_9 and q_{12} are zero. For the same reason, all the cross terms between the '*u*' translational modes q_1–q_3 and the '*g*' internal modes corresponding to q_{10}, q_{11}, q_{13} and q_{14} are zero, as well as any cross term between internal '*g*' and '*u*' modes.

(*b*) α*-Sulfur*

Similar observations can be made with respect to the **W** tensor for α-sulfur. This tensor has recently been calculated by us and is reported in Table 1: the temperature factors that are deduced from it are reported elsewhere (Gramaccioli & Filippini, 1984), and are in excellent agreement with the experimental values (Pawley & Rinaldi, 1972). The elements corresponding to the high-frequency internal modes (q_{11} onwards) are very small and are not reported here.

The representation of the internal coordinates q_7 and q_8 is E_2; the same representation is carried by q_9 and q_{10} (Gramaccioli & Filippini, 1984). The site symmetry of the S_8 molecule is C_2 (the free molecule has a non-crystallographic D_{4d} symmetry). In our calculations, the twofold axis of the site symmetry has been chosen as *x*.

With respect to the site symmetry, q_1 and q_4 carry the *B* representation, whereas q_2, q_3, q_5 and q_6 carry the *A* representation. According to our first law, therefore, the cross terms between *A* and *B* coordinates are zero: this leads to **T**, **L** and **S** tensors in agreement with ST. Of the internal modes, the E_2 representation for the isolated molecule splits into an *A* and a *B* representation in the crystal. This effect can be seen quite easily in a character table for the group D_{4d}: since the crystallographic twofold axis of the C_2 site symmetry for α-sulfur is normal to the $\bar{8}$ axis of the free molecule, the characters corresponding to the C_2' operations are important for our purposes. These are zero, thereby implying the presence of opposite elements in the diagonal, *i.e.* in the corresponding 1×1 representations. In our particular case, q_7 and q_9 carry the *A* representation, whereas q_8 and q_{10} the *B* representation: the results in Table 1 are in agreement with our first law.

(*c*) *Adamantane*

Let us consider now the crystals of the $\bar{4}2m$ form of adamantane: here the molecule lies in a site of $\bar{4}(S_4)$ symmetry. The translational coordinates q_1 and q_2 along *x* and *y* carry an *E* representation, as well as the rotational coordinates q_4 and q_5. Instead, the translation along $z(q_3)$ carries an *A* representation, and the rotation involving $z(q_6)$ a *B* representation.

Because of our first law, the off-diagonal elements of **W** corresponding to L_{13}, L_{23}, T_{13} and T_{23} are zero. For the same reason, all the components of **W** corre-

---

* The values of **W** reported in GF for anthracene and other hydrocarbons with site symmetry $\bar{1}$ should be doubled.

sponding to the third row and column of S are zero. According to our second law, it will be: $T_{12} = L_{12} = 0$, and $T_{11} = T_{22}$; $L_{11} = L_{22}$. From (9), since $g = 2$ and $h = 4$, we also have: $T_{11} = 2(T_{1(11)} \pm T_{1(22)}) = T_{22}$, and similarly for $L_{11} = L_{22}$. This is in agreement with our results (Filippini, Gramaccioli, Simonetta & Suffritti, 1976*a*) and with ST.

References

Bonadeo, H. & Burgos, E. (1982). *Acta Cryst.* **A38**, 29-33.

Bonadeo, H. & Taddei, G. (1973). *J. Chem. Phys.* **58**, 979-984.

Cochran, W. & Pawley, G. S. (1964). *Proc. R. Soc. London Ser. A*, **280**, 1-22.

Cruickshank, D. W. J. (1956). *Acta Cryst.* **9**, 747-753, 754-756, 757-758.

Filippini, G., Gramaccioli, C. M., Simonetta, M. & Suffritti, G. B. (1973). *J. Chem. Phys.* **59**, 5088-5101.

Filippini, G., Gramaccioli, C. M., Simonetta, M. & Suffritti, G. B. (1974*a*). *Acta Cryst.* **A30**, 189-196.

Filippini, G., Gramaccioli, C. M., Simonetta, M. & Suffriti, G. B. (1974*b*). *Chem. Phys. Lett.* **26**, 301-304.

Filippini, G., Gramaccioli, C. M., Simonetta, M. & Suffritti, G. B. (1976*a*). *Acta Cryst.* **A32**, 259-264.

Filippini, G., Gramaccioli, C. M., Simonetta, M. & Suffriti, G. B. (1976*b*). *Chem. Phys. Lett.* **39**, 14-18.

Filippini, G., Gramaccioli, C. M., Simonetta, M. & Suffritti, G. B. (1978). *Mol. Phys.* **35**, 1659-1667.

Gramaccioli, C. M. & Filippini, G. (1983). *Acta Cryst.* **A39**, 784-791.

Gramaccioli, C. M. & Filippini, G. (1984). *Chem. Phys. Lett.* **108**, 585-588.

Gramaccioli, C. M. & Filippini, G. (1985). *Acta Cryst.* **A41**, 361-365.

Gramaccioli, C. M., Filippini, G. & Simonetta, M. (1982). *Acta Cryst.* **A38**, 350-356.

Gwinn, W. D. (1971). *J. Chem. Phys.* **55**, 477-481.

Johnson, C. K. (1970). In *Crystallographic Computing*, edited by F. R. Ahmed, pp. 207-226. Copenhagen: Munksgaard.

Johnson, C. K. (1980). In *Computing in Crystallography*, edited by R. Diamond, S. Ramaseshan & K. Venkatesan, pp. 14.01-14.85. Bangalore: The Indian Academy of Sciences.

Kroon, P. A. & Vos, A. (1979). *Acta Cryst.* **A35**, 675-684.

Neto, N., Righini, R., Califano, S. & Walmsley, S. H. (1978). *Chem. Phys.* **29**, 167-179.

Pawley, G. S. (1967). *Phys. Status Solidi*, **30**, 347-360.

Pawley, G. S. (1968). *Acta Cryst.* **B24**, 485-486.

Pawley, G. S. (1972*a*). In *Advances in Structure Research by Diffraction Methods*, Vol. 4, edited by W. Hoppe & R. Mason, pp. 1-64. Oxford: Pergamon Press.

Pawley, G. S. (1972*b*). *Phys. Status Solidi* **B49**, 475-488.

Pawley, G. S. & Rinaldi, R. P. (1972). *Acta Cryst.* **B28**, 3605-3609.

Scheringer, C. (1972*a*). *Acta Cryst.* **A28**, 512-515.

Scheringer, C. (1972*b*). *Acta Cryst.* **A28**, 516-522.

Scheringer, C. (1972*c*). *Acta Cryst.* **A28**, 616-619.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63-76.

Taddei, G., Bonadeo, H., Marzocchi, M. P. & Califano, S. (1973). *J. Chem. Phys.* **58**, 966-978.

Willis, B. T. M. & Howard, J. A. K. (1975). *Acta Cryst.* **A31**, 514-520.

Willis, B. T. M. & Pryor, A. N. (1975). *Thermal Vibrations in Crystallography*. Cambridge Univ. Press.

Wilson, E. B. Jr., Decius, J. C. & Cross, P. C. (1955). *Molecular Vibrations* pp. 22-25. New York: McGraw-Hill.

Acta Cryst. (1985). **A41**, 361-365

Thermal Motion Analysis in *o*-Terphenyl: a Lattice-Dynamical Approach

By Carlo Maria Gramaccioli

Earth Science Department, University of Milan, Via Botticelli 23, *I*-20133 *Milano, Italy*

and Giuseppe Filippini

Department of Physical Chemistry and CNR Centre, University of Milan, Via Golgi 19, *I*-20133 *Milano, Italy*

(*Received* 15 *September* 1984; *accepted* 15 *January* 1985)

Abstract

A 'non-rigid' harmonic lattice-dynamical model has been used for calculating thermal motion in crystals of *o*-terphenyl. For this purpose, empirical internal and external force fields, derived from a series of other aromatic hydrocarbons have been employed. The agreement between calculated anisotropic temperature factors and corresponding neutron-diffraction data is excellent (10%); it becomes decidedly worse if intramolecular van der Waals interactions are neglected in our model. Bond-length corrections for the general case of non-rigid thermal motion are made: the differences with respect to the 'ordinary' rigid-body model are particularly evident for the C–H bonds.

Introduction

The need to know thermal motion in crystals on a rational basis is rapidly developing nowadays. This may be essential for improving the empirical force fields, which too often do not distinguish between the free and the packed molecules. Other important applications are in electron density measurements, and even for establishing the mechanism of movement

0108-7673/85/040361-05$01.50