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A Lattice-Dynamical Interpretation of Molecular Rigid-Body Vibration Tensors

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The rigid-body motions of molecules in crystals are treated with the aid of lattice dynamics of molecular crystals. An equation is derived in which the rigid-body vibration tensors **TLS** are related to the dynamical matrices of the crystal. Then the components of **TLS** are explicitly given in lattice-dynamical terms. A procedure is developed with which the trace of **S**, which cannot be determined from diffraction data, can be approximately determined. The principal motions of the rigid-body vibrations of molecules are discussed. Which types of coordinate systems can be used to give a physically meaningful description of the rigid-body motions is examined from a dynamical point of view. A 'dynamical' interpretation of the tensors **TLS** is given which consists in relating **TLS** to the intermolecular forces of the crystal and then comparing the intermolecular forces with the packing of the molecules in the crystal. The interpretation is illustrated with the structures of maleic anhydride and 5-chloro-1,4-naphthoquinone.

1. Introduction

Cruickshank (1956*a*) was the first to show how the external vibrations of almost rigid molecules can be described by two tensors **T** and **L** which account for the translations and librations of the molecules respectively. However, Schomaker & Trueblood (1968) showed that, in general, the rigid-body motions are fully accounted for only if a (translation–libration) correlation tensor **S** with 9 components is introduced. Only 8 of these components can be determined from diffraction data. Schomaker & Trueblood's derivation was performed in geometrical and statistical terms, *cf.* also Johnson (1970). In connexion with their derivation Schomaker & Trueblood discuss (geometrical) possibilities for the actual rigid-body motions. In the main these authors consider a model in which the molecule carries out six uncorrelated simple motions; three of them are screw motions about perpendicular non-intersecting axes, and three are pure translations. Although no claim is expressed '... that the elementary motions so derived must have dynamic significance' (Johnson, 1970) the rigid-body motions described by the non-intersecting-axes model are related to the geometrical (and chemical) arrangement of the molecules in a given structure; *cf.* also the discussion of the rigid-body motions of the glycolic acid molecule as given by Ellison, Johnson & Levy (1971). This means that the screw motions about non-intersecting axes are

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considered to exist in reality and thus to be 'dynamically' relevant. Hence this model is considered as describing more than just a geometrical possibility which may or may not be realized in nature.

A further derivation of the **S** tensor, based on lattice-dynamical terms, was given by Pawley (1968). Pawley did not put forward a geometrical interpretation of the tensors **TLS**, and, in another context (Ahmed, 1970, pp. 250–251), expressed objections to the interpretation of **TLS** that was suggested by Schomaker & Trueblood (1968), and by Johnson (1970).

In this paper we try to give an interpretation of the tensors **TLS** on the basis of lattice dynamics of molecular crystals. For this purpose we derive the relation that exists between the vibration tensors **TLS** and either the dynamical matrices or the lattice frequencies and eigenvectors of the crystal. Since the dynamical matrices contain a summation over the various intermolecular forces, a relation between the tensors **TLS** and the intermolecular forces is thus established, at least in principle. This lattice-dynamical approach to formulating the tensors **TLS** allows one to: (1) make a proper choice of the coordinate system which is used to describe the molecular motions (only those systems which are suitable for a dynamical formulation of the vibrational problem are suitable for describing 'what really happens in nature' [Johnson, *cf.* Ahmed (1970), pp. 250–251]); (2) find a condition which permits the determination of the trace of **S**, which cannot be found from diffraction data, to a sufficient approximation; (3) derive the principal components of the rigid-body motions; (4) draw conclusions about the intermolecular forces from the components of **TLS** and relate the 'average forces' to the packing of the molecules in the crystal.

2. Mean-square-amplitude matrix and dynamical matrices of the crystal

In this section we shall derive a relation between the mean-square-amplitude matrix and the dynamical matrices of a molecular crystal as has already been done for atomic crystals [Scheringer, 1972*a*, equations (10) and (15)]. In establishing the relation for atomic crystals we made use of the well known lattice-dynamical expression for the Debye–Waller factors. With molecular crystals an analogous derivation cannot be performed because there are no Debye–Waller factors for molecules, but only for the single atoms of a molecule. A rigid molecule has six degrees of freedom (corresponding to three translations and three rotations) but by diffraction methods only the translations of the individual atoms of the molecule in three directions can be determined. Since there is no direct way of determining to what extent the translations and rotations of the molecule contribute to the translations of the individual atoms, one is not able to determine the forms of the molecular vibrations directly. Hence, in order to derive the desired relation, we are forced to pursue a different approach to that which is possible for atomic crystals.

In order to establish the dynamics of the molecular vibrations, we use the equations of motion for a molecular crystal and then determine the relation between the quantities which occur in the equations of motion (energy, frequency and mass) and the mean-square amplitudes, which can be obtained with the aid of diffraction methods.

First, we set up the secular equations for a molecular crystal, and for this purpose we need the dynamical matrices of the crystal and the kinetic-energy matrix. The equations are analogous to those obtained in the dynamics of atomic crystals, *cf., e.g.,* Maradudin, Montroll & Weiss (1963); Cochran & Cowley (1967). We consider a crystal with n equal molecules in the unit cell and choose a Cartesian coordinate system for each molecule. Each system is fixed relative to each molecule. There are six vibrational coordinates for each molecule $k, k=1\ldots n$, which are referred to the equilibrium position of the molecule. We denote the three translation coordinates by $\mathbf{u}_t(k)$, and the three rotational coordinates by $\boldsymbol{\theta}(k)$ for the kth molecule. As an equivalent notation for the $6n$ vibrational coordinates we use column matrices $\mathbf{y}$: then the elements y_i with $i=6(k-1)+1,2,3$ denote the three translation coordinates, and $i=6(k-1)+4,5,6$ denote the three rotational coordinates. The indices l and l' denote the cells in the crystal, and $\phi_{ij}\binom{ll'}{kk'}$, $i,j=1\ldots 6$, denote the intermolecular force and couple constants, which can be derived from the interatomic force constants of the individual atoms in the molecules (lk) and $(l'k')$, *cf.* Cochran (1963), Powell (1969). Then the elements of the $6n\times 6n$ dynamical matrix for the wave vector $\mathbf{q}$ are given by

$$L_{ij}\binom{\mathbf{q}}{kk'}=\sum_{l-l'}\phi_{ij}\binom{ll'}{kk'}\exp\{i\mathbf{q}\,.\,[\mathbf{r}(lk)-\mathbf{r}(l'k')]\}, \tag{2.1}$$

where $\mathbf{r}(lk)$ denotes the vector to the origin of the molecule (lk) in the crystal. The kinetic energy of the n molecules in a unit cell may be written as

$$E_{\text{kin}}=\tfrac{1}{2}\sum_{i,j=1}^{6n}A_{ij}\dot{y}_i\dot{y}_j,\quad A_{ij}=A_{ji}, \tag{2.2}$$

where the $6n\times 6n$ matrix $\mathbf{A}$ can be calculated from the total mass and the inertial moments of the molecules. Since the kinetic energy for the n molecules in the cell is the sum of n individual contributions, the matrix $\mathbf{A}$ is 6×6 block diagonal. Since we use the same type of coordinate system for the different molecules, each block of $\mathbf{A}$ has the same form. If the origin of the coordinate system is at the centre of gravity of the molecule, then the 6×6 block decomposes into two 3×3 blocks, one for the translations and one for the rotations. This does not, however, hold for an arbitrary origin, *cf.* Schäfer (1950), Higgs (1955). A concise expression for $\mathbf{A}$ can be obtained if the position of the centre of gravity, $\boldsymbol{\varrho}$, in the molecular coordinate system is represented by the antisymmetric tensor

$$\mathbf{V}_\varrho=\begin{pmatrix} 0 & -\varrho_z & \varrho_y \\ \varrho_z & 0 & -\varrho_x \\ -\varrho_y & \varrho_x & 0 \end{pmatrix}. \qquad (2.3)$$

Let m be the total mass of one molecule, $\mathbf{I}$ be the inertial tensor referred to the centre of gravity, and $\mathbf{E}$ be the unit matrix, then from Higgs' equation (A9) one obtains*

$$\mathbf{A}_{66}=\left(\begin{array}{c|c} m\mathbf{E} & m\mathbf{V}_\varrho^T \\ \hline m\mathbf{V}_\varrho & \mathbf{I}+m\mathbf{V}_\varrho\mathbf{V}_\varrho^T \end{array}\right) \qquad (2.4)$$

for a 6×6 diagonal block of $\mathbf{A}$. The secular equation for each wave vector $\mathbf{q}$ is now

$$\det\,[\mathbf{L}(\mathbf{q})-\lambda_j(\mathbf{q})\mathbf{A}]=0, \qquad (2.5)$$

where $\lambda_j(\mathbf{q})$ represents one of the $6n$ possible solutions of equation (2.5). The solutions are the squares of the lattice frequencies $\omega_j(\mathbf{q})$. In order to calculate the $\lambda_j(\mathbf{q})$ one usually transforms equation (2.5) so that the kinetic-energy matrix $\mathbf{A}$ is reduced to the unit matrix, *i.e.*

$$\mathbf{G}^T\mathbf{A}\mathbf{G}=\mathbf{E}. \qquad (2.6)$$

Similarly, the dynamical matrices $\mathbf{L}(\mathbf{q})$ are transformed, and the solutions $\lambda_j(\mathbf{q})$ are the eigenvalues of the transformed dynamical matrices. Often the transformation (2.6) is carried out in two steps: $\mathbf{A}$ is diagonalized with the aid of an orthogonal transformation $\mathbf{P}$, and then the diagonalized matrix is reduced to $\mathbf{E}$ with the aid of a diagonal matrix $\mathbf{Q}$, *i.e.* $\mathbf{G}=\mathbf{PQ}$, *cf.*, *e.g.*, Smirnow (1964). Since $\mathbf{A}$ is 6×6 block diagonal, $\mathbf{G}$, $\mathbf{P}$ and $\mathbf{Q}$ are also block diagonal. Whereas $\mathbf{P}$ merely describes the transformation to a new (six-dimensional) coordinate system, $\mathbf{Q}$ normalizes the masses and inertial moments to unity and at the same time normalizes the vibrational coordinates to unit-length coordinates. The mass-normalized dynamical matrix has the form

$$\mathbf{M}(\mathbf{q})=\mathbf{G}^T\mathbf{L}(\mathbf{q})\mathbf{G}, \qquad (2.7)$$

and we can represent the solutions $\lambda_j(\mathbf{q})$ of equation (2.5) by a $6n\times6n$ diagonal matrix $\mathbf{\Lambda}$ according to

$$\mathbf{M}=\mathbf{R}\mathbf{\Lambda}\tilde{\mathbf{R}}, \qquad (2.8)$$

for each wave vector $\mathbf{q}$. $\mathbf{M}$ is Hermitian and $\mathbf{R}$ is unitary, *i.e.* $\tilde{\mathbf{R}}=\mathbf{R}^{-1}$ ($\sim$ denotes the conjugate-complex transpose matrix, -1 the inverse), because the elements L_{ij} of the dynamical matrices are generally complex, *cf.* equation (2.1).

In order to establish the relation between our equations and the mean-square amplitudes of the molecules, it is now expedient to make use of a well known relation, which holds, quite generally, for oscillators in thermal equilibrium. Let $\bar{E}$ be the mean energy, ω the frequency of the oscillator, and $\overline{u^2}$ the mean-square amplitude referred to the unit mass, then

$$\bar{E}=\omega^2\overline{u^2}, \qquad (2.9)$$

cf. Bloch (1932), Born & Huang [1962, equation (16.17)]. In our problem $\bar{E}$, ω and $\overline{u^2}$ each refer to a lattice mode $\mathbf{q}j$; the explicit expression for $\bar{E}$ has been given, *e.g.* by Scheringer [1972*a*, equation (3)]. In order to be able to connect equation (2.9) with our equations, we first express it in matrix notation. Similarly to representing the $\omega_j^2(\mathbf{q})$ by a diagonal matrix $\mathbf{\Lambda}$ we represent the energies $\bar{E}(\mathbf{q}j)$ by a $6n\times6n$ diagonal matrix $\mathbf{\Gamma}(\mathbf{q})$, and the elements $\overline{u^2}(\mathbf{q}j)$, which refer to the contents of a unit cell, by a $6n\times6n$ diagonal matrix $\mathbf{D}_A(\mathbf{q})$. Let N be the number of cells in the crystal; then we can write equation (2.9) as

$$\mathbf{\Lambda}^{-1}(\mathbf{q})\mathbf{\Gamma}(\mathbf{q})=N\mathbf{D}_A(\mathbf{q}). \qquad (2.10)$$

In order to connect equations (2.10) and (2.8) we rewrite equation (2.8) as

$$\mathbf{M}^{-1}=\mathbf{R}\mathbf{\Lambda}^{-1}\tilde{\mathbf{R}}, \qquad (2.11)$$

and observe that $\mathbf{R}\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\tilde{\mathbf{R}}=\mathbf{R}\mathbf{\Lambda}^{-1}\tilde{\mathbf{R}}\mathbf{R}\mathbf{\Gamma}\tilde{\mathbf{R}}$, since $\mathbf{R}$ is unitary. Then we obtain from equations (2.10) and (2.11)

$$\mathbf{M}^{-1}\mathbf{R}\mathbf{\Gamma}\tilde{\mathbf{R}}=N\mathbf{R}\mathbf{D}_A\tilde{\mathbf{R}}. \qquad (2.12)$$

Since $\mathbf{M}^{-1}$, $\mathbf{R}\mathbf{\Gamma}\tilde{\mathbf{R}}$, and $\mathbf{R}\mathbf{D}_A\tilde{\mathbf{R}}$ are usually Hermitean and not real it is expedient to use both the wave vectors $\mathbf{q}$ and $-\mathbf{q}$ in setting up a real mean-square-amplitude matrix $\mathbf{D}$. Then we obtain from equation (2.12).

$$\mathbf{D}(\mathbf{q},-\mathbf{q})=\frac{1}{N}\,(\mathbf{M}^{-1}\mathbf{R}\mathbf{\Gamma}\tilde{\mathbf{R}}+\mathbf{M}^{*-1}\mathbf{R}^*\mathbf{\Gamma}\tilde{\mathbf{R}}^*), \qquad (2.13)$$

where the second term refers to the wave vector $-\mathbf{q}$. $\mathbf{D}$ is real and symmetric and is mass-normalized, as is $\mathbf{M}$. In order to express the mean-square amplitudes in our initial translation and librational coordinates we have to remove the mass normalization; *i.e.* we have to transform $\mathbf{D}$ corresponding to the transformation $\mathbf{M}\rightarrow\mathbf{L}$. $\mathbf{D}$ transforms as $\mathbf{M}^{-1}$, and hence with equation (2.7) we obtain

$$\mathbf{C}(\mathbf{q},-\mathbf{q})=\mathbf{G}\mathbf{D}(\mathbf{q},-\mathbf{q})\mathbf{G}^T \qquad (2.14)$$

for the mean-square-amplitude matrix. $\mathbf{C}$ refers to the initial system of translation coordinates $\mathbf{u}_t(k)$ and libration coordinates $\boldsymbol{\theta}(k)$. From equations (2.13) and (2.14) we now obtain

$$\mathbf{C}(\mathbf{q},-\mathbf{q})=\frac{1}{N}\,(\mathbf{G}\mathbf{M}^{-1}\mathbf{R}\mathbf{\Gamma}\tilde{\mathbf{R}}\mathbf{G}^T+\mathbf{G}\mathbf{M}^{*-1}\mathbf{R}^*\mathbf{\Gamma}\tilde{\mathbf{R}}^*\mathbf{G}^T). \qquad (2.15)$$

We insert the unit matrix $\mathbf{G}^T\mathbf{G}^{T-1}$ after $\mathbf{M}^{-1}$ and $\mathbf{M}^{*-1}$ in equation (2.15) and define the matrix product

$$\{\mathbf{G}^{T-1}\mathbf{R}\mathbf{\Gamma}\tilde{\mathbf{R}}\mathbf{G}^T\}_\mathbf{q}=\mathbf{\Omega}(\mathbf{q}). \qquad (2.16)$$

$\mathbf{\Omega}(\mathbf{q})$ has the dimension of energy. In the high-temperature approximation it reduces to

$$\mathbf{\Omega}(\mathbf{q})=\mathbf{\Gamma}(\mathbf{q})=k_BT\mathbf{E}, \qquad (2.17)$$

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* The existence of the off-diagonal blocks $m\mathbf{V}_\varrho$ was pointed out to me by Dr N. Brodherr, München.

where k_B is Boltzmann's constant and T is the absolute temperature. $\mathbf{\Omega}(\mathbf{q})$ is not Hermitian. In order to obtain the mean-square-amplitude matrix of the crystal, we have to sum over all wave vectors in the crystal. We insert $\mathbf{\Omega}(\mathbf{q})$ of equation (2.16) in equation (2.15), carry out the summation, and finally obtain

$$\mathbf{C}=\frac{1}{N}\sum_{\mathbf{q}}\mathbf{L}^{-1}(\mathbf{q})\mathbf{\Omega}(\mathbf{q}). \qquad (2.18)$$

An alternative form of the mean-square-amplitude matrix $\mathbf{C}$, in which $\mathbf{C}$ is related to the lattice frequencies and eigenvectors, may be useful in some cases. From equations (2.10), (2.12) and (2.15) we obtain

$$\mathbf{C}=\frac{1}{N}\sum_{\mathbf{q}}\mathbf{G}\{\mathbf{R}\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\tilde{\mathbf{R}}\}_{\mathbf{q}}\mathbf{G}^{T}. \qquad (2.19)$$

In the Appendix we use equation (2.19) to prove that $\mathbf{C}$ has only positive eigenvalues. An application of equation (2.19), in the form of the mass-normalized matrix $\mathbf{D}=\mathbf{G}^{-1}\mathbf{C}\mathbf{G}^{T^{-1}}$, has already been given (Scheringer, 1972*b*), where the contributions of the internal and external modes of molecules to the Debye–Waller factors were analysed.

Equation (2.18) is our desired result, in which the $6n\times 6n$ mean-square-amplitude matrix $\mathbf{C}$ is expressed in terms of the dynamical matrices of the crystal. Equation (2.18), which refers to molecular crystals, is fully equivalent to equation (15) of Scheringer (1972*a*), which refers to atomic crystals. The derivation which we have given in this section can, of course, be performed in an analogous manner for atomic crystals, and thus will lead to the mean-square-amplitude matrix for an atomic crystal. However, this approach cannot be considered as a complete derivation of the Debye–Waller factors, since these contain not only the mean-square amplitudes of the individual atoms but also express the way in which the lattice spectra of a crystal are affected by the thermal motions of the atoms.

3. Specification of the elements of the mean-square amplitude matrix C

After having derived our basic relations (2.18) and (2.19) we have to show which elements of the mean-square-amplitude matrix $\mathbf{C}$ are to be identified with the components of the vibration tensors **TLS**. This identification arises from our definition of the translation coordinates $\mathbf{u}_t(k)$ and librational coordinates $\mathbf{\theta}(k)$. The sequence of these coordinates for the n molecules in the unit cell determines the corresponding sequence of the elements in the dynamical matrices $\mathbf{L}(\mathbf{q})$ of equation (2.1). The same sequence holds for the inverse dynamical matrices and hence, from equation (2.18), for the mean-square-amplitude matrix $\mathbf{C}$. With the sequence $\mathbf{u}_t(1)$, $\mathbf{\theta}(1)$, $\mathbf{u}_t(2)$, $\mathbf{\theta}(2),\ldots,\mathbf{u}_t(n)$, $\mathbf{\theta}(n)$ of the vibrational coordinates, as used in § 2, we therefore find that the kth 6×6 diagonal block of $\mathbf{C}$, which refers to the mean-square amplitudes of the kth molecule, has the form*

$$\mathbf{C}_{66}(kk)=\left(\begin{array}{c|c}\mathbf{T} & \mathbf{S}^{T}\\ \hline \mathbf{S} & \mathbf{L}\end{array}\right)_{k}. \qquad (3.1)$$

The 6×6 off-diagonal blocks $\mathbf{C}$, $\mathbf{C}_{66}(kk')$, contain the coupling terms for the molecules k and k'. Although these terms are defined in terms of the dynamical matrices they cannot be determined by experiment. Only the tensors **TLS** and hence the diagonal blocks of $\mathbf{C}$ are subject to experimental investigation (except for the trace of $\mathbf{S}$). An analogous result was already found to hold for the 3×3 blocks of the mean-square-amplitude matrix of atomic crystals, *cf.* Scheringer (1972*a*).

Next we consider the question of how we can represent the components of **TLS** explicitly in terms of the lattice frequencies and eigenvectors. This we do with the aid of equations (3.1) and (2.19). Equation (2.19) contains not only the frequencies $\omega(\mathbf{q})$ and the matrices $\mathbf{R}(\mathbf{q})$ of the eigenvectors, but also the transformation matrix $\mathbf{G}$ of equation (2.6). If the principal inertial system with the origin at the centre of gravity is used as reference system, $\mathbf{G}$ is diagonal and the components of **TLS** can be given explicitly. In any other system $\mathbf{G}$ is not diagonal. If one diagonalizes $\mathbf{G}$ in a system whose origin does not coincide with the centre of gravity, one obtains only linear combinations of the components of **TLS**. If one does not choose the centre of gravity as the molecular origin then the reduction of the kinetic-energy matrix to the unit matrix usually leads to a system of eigenvectors whose base vectors do not coincide with the base vectors of the principal inertial systems of the n molecules. Before we express the components of **TLS** in terms of the lattice frequencies and eigenvectors we want to derive the transformation by which the two sets of base vectors are related to each other.

Let $\boldsymbol{\varrho}$ be the vector from the centre of gravity to the molecular origin, and let $\mathbf{L}_{\varrho}(\mathbf{q})$ be the dynamical matrix. Then the mass normalization of the $6n$ vibrational coordinates $\mathbf{y}_{\varrho}$ by means of the transformation matrix $\mathbf{G}=\mathbf{PQ}$ of § 2 can be written as

$$\mathbf{y}_{PQ}^{\text{norm}}=\mathbf{Q}^{-1}\mathbf{P}^{-1}\mathbf{y}_{\varrho}=\mathbf{G}_{PQ}^{-1}\mathbf{y}_{\varrho}. \qquad (3.2)$$

Next we have to carry out the mass normalization so that it leads to normalized coordinates $\mathbf{y}_{\text{pis}}^{\text{norm}}$ which refer to the principal inertial systems of the n molecules. We first rotate each Cartesian system so that its axes are parallel to the axes of the principal inertial system (transformation $\mathbf{H}_B$), then shift the origins of the molecular systems to the centres of gravity (transformation $\mathbf{H}_{\varrho}$), and finally normalize in the principal inertial systems (transformation $\mathbf{Q}_{\text{pis}}^{-1}$). The total transformation of the coordinates is

$$\mathbf{y}_{\text{pis}}^{\text{norm}}=\mathbf{Q}_{\text{pis}}^{-1}\mathbf{H}_{\varrho}\mathbf{H}_{B}\mathbf{y}_{\varrho}=\mathbf{G}_{\text{pis}}^{-1}\mathbf{y}_{\varrho}. \qquad (3.3)$$

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* In this paper the symbol $\mathbf{L}$ is used for the dynamical matrix $\mathbf{L}(\mathbf{q})$ and also for the libration tensor. Confusion cannot arise, however, since the two symbols are never used together.

The transformation matrices $\mathbf{H}_B$ and $\mathbf{H}_Q$ will be specified below, *cf.* equations (3.14) and (3.17). From equations (3.2) and (3.3) we obtain for the transformation between the normalized coordinates

$$\mathbf{y}_{PQ}^{\text{norm}}=\mathbf{G}_{PQ}^{-1}\mathbf{G}_{\text{pis}}\mathbf{y}_{\text{pis}}^{\text{norm}}, \tag{3.4}$$

and hence for the transformation between the respective base vector systems

$$\mathbf{a}_{PQ}=(\mathbf{G}_{PQ}^{-1}\mathbf{G}_{\text{pis}})^{T-1}\mathbf{a}_{\text{pis}}. \tag{3.5}$$

Reference to a particular molecular origin is now redundant since all normalized vibrational coordinates are expressed as translation coordinates. Finally, we show that the transformations (3.4) and (3.5) correspond to a rotation of the $6n$-dimensional coordinate system. We put $\mathbf{G}_{PQ}^{-1}\mathbf{G}_{\text{pis}}=\mathbf{W}^{-1}$ and show that $\mathbf{W}$ is orthogonal, *i.e.* $\mathbf{W}^{-1}=\mathbf{W}^T$. From equation (3.4) we obtain for the transformation between the mass-normalized dynamical matrices[†]

$$\mathbf{M}_{PQ}=\mathbf{W}^T\mathbf{M}_{\text{pis}}\mathbf{W}. \tag{3.6}$$

Since both sets of coordinates, $\mathbf{y}_{PQ}^{\text{norm}}$ and $\mathbf{y}_{\text{pis}}^{\text{norm}}$, fulfil the normalizing condition (2.6), the respective mass-normalized dynamical matrices, $\mathbf{M}_{PQ}$ and $\mathbf{M}_{\text{pis}}$ of equations (2.7) and (2.8), have the same eigenvalues $\lambda_j(\mathbf{q})$. Thus $\mathbf{M}_{PQ}$ and $\mathbf{M}_{\text{pis}}$ are similar and from equation (3.6) we deduce $\mathbf{W}^T=\mathbf{W}^{-1}$.

We obtain the expressions for the components of **TLS** in the principal inertial system with origin at the centre of gravity by evaluating equation (2.19). $\mathbf{G}$ is diagonal and for each molecule it contains three times the inverse square roots of the mass m of the molecule and the inverse square roots of the principal moments of inertia, I_i, $i=1,2,3$. Let $s=6(k-1)+t$ with $t=1\ldots6$, and let $e_t(k|\mathbf{q}j)$ be the sth component of the jth eigenvector to the frequency $\omega_j(\mathbf{q})$ [the sth element of the jth column of the unitary matrix $\mathbf{R}(\mathbf{q})$] then, for the kth molecule in the unit cell and $i,e=1,2,3$

$$T^{ie}(k)=\frac{1}{2Nm}\sum_{\mathbf{q}}\sum_{j=1}^{6n}\frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})}\times[e_i(k|\mathbf{q}j)e_e^*(k|\mathbf{q}j)+e_i^*(k|\mathbf{q}j)e_e(k|\mathbf{q}j)], \tag{3.7a}$$

$$L_{ie}(k)=\frac{1}{2N\sqrt{I_iI_e}}\sum_{\mathbf{q}}\sum_{j=1}^{6n}\frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})}\times[e_{i+3}(k|\mathbf{q}j)e_{e+3}^*(k|\mathbf{q}j)+e_{i+3}^*(k|\mathbf{q}j)e_{e+3}(k|\mathbf{q}j)], \tag{3.7b}$$

$$S_i^e(k)=\frac{1}{2N\sqrt{mI_i}}\sum_{\mathbf{q}}\sum_{j=1}^{6n}\frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})}\times[e_{i+3}(k|\mathbf{q}j)e_e^*(k|\mathbf{q}j)+e_{i+3}^*(k|\mathbf{q}j)e_e(k|\mathbf{q}j)]. \tag{3.7c}$$

In order to express the components of **TLS** in any other coordinate system (with any origin) we have to take into account that $\mathbf{G}$ is not diagonal. The simplest presentation in this case is obtained if one uses a 6×6 matrix representation instead of the component representation (3.7). We express **TLS** in the matrix $\mathbf{C}_{66}$ of equation (3.1), and we similarly express the products of the components of the eigenvectors $e_t(k|\mathbf{q}j)$, $e_{t'}(k|\mathbf{q}j)$, t, $t'=1\ldots6$, which occur in equation (3.7), in a 6×6 matrix, $\boldsymbol{\varepsilon}_{66}$. Similarly, we only need a 6×6 (diagonal) block of $\mathbf{G}$, $\mathbf{G}_{66}$. Then we can represent the relation between $\mathbf{C}_{66}$ and the mass-normalized molecular mean-square-amplitude matrix, $\mathbf{D}_{66}$, by

$$\mathbf{C}_{66}=\mathbf{G}_{66}\mathbf{D}_{66}\mathbf{G}_{66}^T. \tag{3.8}$$

Evaluation of equation (2.19) leads to

$$\mathbf{C}_{66}=\frac{1}{2N}\sum_{\mathbf{q}j}\frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})}\mathbf{G}_{66}\{\boldsymbol{\varepsilon}_{66}+\boldsymbol{\varepsilon}_{66}^*\}_{\mathbf{q}j}\mathbf{G}_{66}^T \tag{3.9}$$

for the given molecule.[‡] In the principal inertial system equation (3.9) reduces to equations (3.7).

In order to show how the transformation laws for the tensors **TLS** can be obtained from our lattice-dynamical formulation of the mean-square-amplitude matrix $\mathbf{C}$, we define a general transformation

$$\mathbf{y}_H=\mathbf{H}^{-1}\mathbf{y} \tag{3.10}$$

of the $6n$ vibrational coordinates. With equation (3.10) the corresponding transformation

$$\mathbf{C}_H=\mathbf{H}^{-1}\mathbf{C}\mathbf{H}^{T-1} \tag{3.11}$$

for the mean-square-amplitude matrix holds. First we consider a change of our three-dimensional basis in crystal space. We define the transformation of the base vectors so that we obtain

$$\mathbf{u}_{tB}=\mathbf{B}^{T-1}\mathbf{u}_t \tag{3.12}$$

[†] Spectroscopists often do not calculate the frequencies from the dynamical matrix $\mathbf{M}$ but rather from the product $\mathbf{LA}^{-1}$ ('FG-method'). $\mathbf{LA}^{-1}$ and $\mathbf{M}$ have the same eigenvalues since they are similar, for $\mathbf{LA}^{-1}=\mathbf{G}^{T-1}\mathbf{M}\mathbf{G}^T$. Since $\mathbf{G}$ is not orthogonal a corresponding transformation for the vibration coordinates and base vectors is no longer defined [in contrast to equations (3·4), (3·5) and (3·6)]. Hence for $\mathbf{LA}^{-1}$ reference to a particular coordinate system is lost. Furthermore, $\mathbf{LA}^{-1}$ is not Hermitian. This means that the phase relations, which are contained in $\mathbf{M}$, are no longer expressed in $\mathbf{LA}^{-1}$. For these reasons we consider a representation with the matrix product $\mathbf{LA}^{-1}$ unsuitable for the purpose of our analysis.

[‡] Here we refer to a special point of a previous paper (Scheringer, 1972*b*), in which we discussed the contributions of the internal and external modes of molecules to the Debye–Waller factors. In that paper we showed how the contributions of the external modes, C^{ext}, can be calculated if the vibration tensors **T L S** are referred to the principal inertial system with origin at the centre of gravity. With the equations derived in this section we can give the expression for C^{ext} when the tensors **T L S** are referred to any coordinate system. With $\mathbf{A}_{66}$ defined by equation (2.4) and $\mathbf{C}_{66}$ by equation (3.1) we obtain

$$C^{\text{ext}} = \text{trace}\,(\mathbf{C}_{66}\mathbf{A}_{66})\,.$$

The derivation is as follows. By definition of $\mathbf{G}_{66}$ we obtain $\mathbf{A}_{66} = \mathbf{G}_{66}^{T-1}\mathbf{G}_{66}^{-1}$, and with equation (3.8) we see that $\mathbf{D}_{66} = \mathbf{G}_{66}^{-1}\,\mathbf{C}_{66}\,\mathbf{A}_{66}\,\mathbf{G}_{66}$. Hence $\mathbf{D}_{66}$ and $\mathbf{C}_{66}\,\mathbf{A}_{66}$ have the same eigenvalues; thus trace $(\mathbf{D}_{66})$ = trace $(\mathbf{C}_{66}\,\mathbf{A}_{66})$. Now, by definition C^{ext} = trace $(\mathbf{D}_{66})$, which establishes the above result.

for the translation coordinates $\mathbf{u}_t(k)$ of the molecules. Then the libration coordinates transform according to

$$\boldsymbol{\theta}_B=\mathbf{B}\boldsymbol{\theta}\ \text{sign}\ (\det \mathbf{B}). \qquad (3.13)$$

For a change of the three-dimensional basis the transformation matrix $\mathbf{H}$ is 6×6 block diagonal, and every 6×6 block of $\mathbf{H}^{-1}$ has the form

$$\mathbf{H}_{66}^{-1}=\left(\begin{array}{c|c}\mathbf{B}^{T-1} & \mathbf{0}\\ \hline \mathbf{0} & \mathbf{B}\ \text{sign}\ (\det \mathbf{B})\end{array}\right). \qquad (3.14)$$

$\mathbf{0}$ is the null matrix. We insert $\mathbf{H}_{66}^{-1}$ of (3.14) into equation (3.11), multiply out all terms, and solve for the **TLS** terms. We obtain

$$\begin{aligned}\mathbf{T}_B&=\mathbf{B}^{T-1}\mathbf{T}\mathbf{B}^{-1},\\ \mathbf{L}_B&=\mathbf{B}\mathbf{L}\mathbf{B}^{T},\\ \mathbf{S}_B&=\mathbf{B}\mathbf{S}\mathbf{B}^{-1}\ \text{sign}\ (\det \mathbf{B}).\end{aligned} \qquad (3.15)$$

Equations (3.15) state the transformation laws for the rigid-body parameters **TLS** and at the same time establish the tensor properties of **TLS**. (3.15) is in agreement with the assignment of tensorial indices as given by Burns, Ferrier & McMullan (1967).

Next we show how the tensors **TLS** transform when the molecular origin is shifted by a vector $\boldsymbol{\varrho}$. Let $\mathbf{X}_r$ be the coordinates of the atoms in the old molecular system, $\mathbf{X}_{r\varrho}$ the coordinates in the new system, then

$$\mathbf{X}_{r\varrho}=\mathbf{X}_r-\boldsymbol{\varrho}. \qquad (3.16)$$

Let the components of $\boldsymbol{\varrho}$ be expressed as components of the antisymmetric tensor $\mathbf{V}_\varrho$ of equation (2.3). Then a 6×6 diagonal block of the matrix $\mathbf{H}^{-1}$ has the form

$$\mathbf{H}_{66}^{-1}=\left(\begin{array}{c|c}\mathbf{E} & \mathbf{V}_\varrho^T\\ \hline \mathbf{0} & \mathbf{E}\end{array}\right). \qquad (3.17)$$

We insert $\mathbf{H}_{66}^{-1}$ of (3.17) into equation (3.11), multiply out all terms, solve for the **TLS** terms, and obtain

$$\begin{aligned}&\mathbf{T}_\varrho=\mathbf{T}+\mathbf{V}_\varrho\mathbf{L}\mathbf{V}_\varrho^T-\mathbf{V}_\varrho\mathbf{S}-(\mathbf{V}_\varrho\mathbf{S})^T,\\ &\mathbf{L}_\varrho=\mathbf{L},\quad \mathbf{S}_\varrho=\mathbf{S}+\mathbf{L}\mathbf{V}_\varrho.\end{aligned} \qquad (3.18)$$

Equations (3.18) are identical with results derived by Schomaker & Trueblood [1968, equations (10) and (11)].

Finally, we want to comment on how the relation between the tensors **TLS** and the atomic vibration tensors can be gained from a lattice-dynamical approach. Pawley (1968) has derived this relation using the components of the eigenvectors of a molecular crystal. In our opinion two points have to be observed in this derivation. Pawley uses the symbols u_i, θ_i and v_i, φ_i and states that they stand for the real and imaginary parts of the components of the eigenvectors. Strictly speaking, these symbols stand for the mass-normalized components of the eigenvectors (or linear combinations of them) since only these are directly related to the translation and rotational mean-square amplitudes, *cf.* equation (3.19) below. The second point is related to the first and refers to the coordinate system used. In Pawley's (1968) derivation of his equation (5) one has to assume that the components of **TLS** refer to the principal inertial system with origin at the centre of gravity. For only in this system does the mass normalization give rise to simple factors for the components of the eigenvectors, thus permitting the derivation given by Pawley. In any other coordinate system the components of **TLS** are not related to a simple product of mass-normalized components but rather to a linear combination of such products, which is determined by the matrix $\mathbf{G}_{66}$, *cf.* equation (3.9). The restriction of Pawley's derivation to the principal inertial system with origin at the centre of gravity does not, however, impair the validity of Pawley's result in any coordinate system, because the invariance of Pawley's equation (5) is ensured by the form of the transformation laws (3.15) and (3.18). In order to connect our equations to Pawley's we thus have to take the mass normalization into account and we also have to refer to the principal inertial system. We then obtain with equations (3.7)

$$\begin{aligned}&e_i(k\,|\,\mathbf{q}j)\alpha(\mathbf{q}j)/\sqrt{m}=u_i+iv_i\ \text{(Pawley)},\\ &e_{i+3}(k\,|\,\mathbf{q}j)\alpha(\mathbf{q}j)/\sqrt{I_i}=\theta_i+i\varphi_i\ \text{(Pawley)},\end{aligned} \qquad (3.19)$$

where $\alpha(\mathbf{q}j)=\bar{E}(\mathbf{q}j)/N\omega_j^2(\mathbf{q})$. The $\alpha(\mathbf{q}j)$ are constant factors for the components of the eigenvectors (for this reason they are omitted by Pawley) and account for the fact that the lengths of the eigenvectors are normalized to unity.

4. The trace of S

As shown by Schomaker & Trueblood (1968) the trace of S cannot be determined from diffraction data since only the differences $S_i^i-S_k^k$ enter into the calculation. Hence only 8 of the 9 components S_i^k can be determined experimentally. The fact that the trace of S cannot be determined is to be considered as a deficiency in our experimental methods and does not imply that the rigid-body motions of molecules can be adequately described with 8 components S_i^k. According to equation (2.18) all 9 components S_i^k are uniquely determined by the dynamical matrices $\mathbf{L}(\mathbf{q})$ and the matrices $\boldsymbol{\Omega}(\mathbf{q})$, and hence have fixed values for a given structure. This may also be illustrated in the following way: the trace of S could also be determined with the aid of the coupling tensors $\mathbf{U}_{rs}$ from atomic crystals, *cf.* equation (4.4) of Scheringer (1972*c*). But the coupling tensors are also only defined in terms of the dynamical matrices and cannot be determined by experiment either.

For our interpretation of **TLS** we need to know the trace of S, at least approximately. In the refinement of the components S_i^i an arbitrary condition is usually imposed on the trace of S. The most obvious one, which was also proposed by Schomaker & Trueblood, is

$$\text{trace}\ (\mathbf{S})=0. \qquad (4.1)$$

This condition is meaningful in that it usually keeps the magnitudes of the components S^i_i smaller than the magnitudes of the components T^{ii} and L_{ii}. But, in general, we may not expect that the condition (4.1) corresponds exactly to equation (2.18). We denote the components S^i_i of equation (4.1) by $S^i_i(0)$, and those of equation (2.18) by $S^i_i(\mathrm{dyn})$. Since the difference $S^i_i - S^k_k$ can be determined uniquely, only a constant K is unknown. We write

$$S^i_i(\mathrm{dyn}) = S^i_i(0) + K;\quad i = 1,2,3. \tag{4.2}$$

With equations (4.1) and (4.2) we have trace $[\mathbf{S}(\mathrm{dyn})] = 3K$.

Schomaker & Trueblood (1968) remarked that limits for the trace of **S** can be derived using Schwarz's inequality, and they obtain

$$|\mathrm{trace}\ (\mathbf{S})| \le \sqrt{\mathrm{trace}\ (\mathbf{T})\ \mathrm{trace}\ (\mathbf{L})}\,. \tag{4.3}$$

Somewhat narrower limits can be obtained if one applies Schwarz's inequality to the components T^{ii}, L_{ii}, and S^i_i; one then obtains

$$K_{\mathrm{lim}} = -S^i_i \pm \sqrt{T^{ii}L_{ii}};\quad i = 1,2,3. \tag{4.4}$$

The conditions (4.4) also follow from the condition that the respective 2×2 principal minors are positive; their zero values yield the limits K_{lim} of equation (4.4). Thus even narrower limits can be obtained if one postulates that all eigenvalues of the **TLS** matrix $\mathbf{C}_{66}$ are positive, *i.e.*

$$\lambda_j\{\mathbf{C}_{66}\} \ge 0;\quad j = 1\ldots 6. \tag{4.5}$$

The equal sign gives the limits for K. Equation (4.5) can be used numerically by varying the value of K and examining the signs of the eigenvalues. In practice all three conditions (4.3), (4.4) and (4.5) are not strong enough to determine the value of K with sufficient accuracy.

Hence we shall try to estimate the value of K from equations (2.1) and (2.18). Constraints on the elements of **L** follow from constraints which are valid for the intermolecular force constants. In order to derive them let us write the 6×6 intermolecular-force-constant matrix, referring to molecules $\binom{l}{k}$ and $\binom{l'}{k'}$ in the crystal, as

$$\boldsymbol{\varphi}_{66}\binom{l\,l'}{kk'} = \left(\begin{array}{c|c} \boldsymbol{\varphi}_t & \boldsymbol{\varphi}^1_{\mathrm{corr}} \\ \boldsymbol{\varphi}^2_{\mathrm{corr}} & \boldsymbol{\varphi}_{\mathrm{rot}} \end{array}\right), \tag{4.6}$$

where the subscripts t, rot, and corr refer to translation, rotation and correlation respectively. Now we have to express $\boldsymbol{\varphi}_{66}$ in terms of interatomic force constants. This was done by Hahn & Biem (1963), and by Powell (1969). Here we give a matrix representation which makes the structure of the terms more obvious. For this purpose we choose a fixed Cartesian coordinate system for all atoms and molecules and write the interatomic force constants as 3×3 matrices $\boldsymbol{\varphi}\binom{l\ \ l'}{krk'r'}$, where r and r' denote the respective atoms. Let the Cartesian coordinates of the atoms, referred to the origin of the molecule, be contained in the antisymmetric tensor

$$\mathbf{V}_r = \begin{pmatrix} 0 & -Z_r & Y_r \\ Z_r & 0 & -X_r \\ -Y_r & X_r & 0 \end{pmatrix}. \tag{4.7}$$

Then

$$\boldsymbol{\varphi}_t\binom{l\,l'}{kk'} = \sum_{rr'} \boldsymbol{\varphi}'\binom{l\ \ l'}{krk'r'}, \tag{4.8a}$$

$$\boldsymbol{\varphi}_{\mathrm{rot}}\binom{l\,l'}{kk'} = \sum_{rr'} \mathbf{V}_r\binom{l}{k}\boldsymbol{\varphi}'\binom{l\ \ l'}{krk'r'}\mathbf{V}^T_{r'}\binom{l'}{k'}, \tag{4.8b}$$

$$\boldsymbol{\varphi}^1_{\mathrm{corr}}\binom{l\,l'}{kk'} = \sum_{rr'} \boldsymbol{\varphi}'\binom{l\ \ l'}{krk'r'}\mathbf{V}^T_{r'}\binom{l'}{k'}, \tag{4.8c}$$

$$\boldsymbol{\varphi}^2_{\mathrm{corr}}\binom{l\,l'}{kk'} = \sum_{rr'} \mathbf{V}_r\binom{l}{k}\boldsymbol{\varphi}'\binom{l\ \ l'}{krk'r'}. \tag{4.8d}$$

The summations only refer to atoms r and r' which belong to the molecules lk and $l'k'$ respectively. Equations (4.8) hold only for the case $lk \ne l'k'$. The 'self terms', $lk = l'k'$, have essentially the same structure and can be derived from the invariance conditions of the force constants when the crystal undergoes rigid translations and rotations, *cf.* Hahn & Biem (1963), Powell (1969). In the rigid-molecule approximation we assume infinitely large forces between atoms of the same molecule; *i.e.* all $\boldsymbol{\varphi}'\binom{l\ l}{krkr'}$ are infinitely large for $r \ne r'$. In practice we eliminate these terms by putting them equal to zero. (This means that we do not calculate internal frequencies of the molecule.) From the symmetry condition of the interatomic force constants [Maradudin, Montroll & Weiss, 1963, equation (2.1.9)] we obtain the corresponding condition

$$\boldsymbol{\varphi}_{66}\binom{l\,l'}{kk'} = \boldsymbol{\varphi}^T_{66}\binom{l'\,l}{k'k} \tag{4.9}$$

for molecular crystals. In particular, we obtain

$$\boldsymbol{\varphi}^1_{\mathrm{corr}}\binom{l\,l'}{kk'} = \boldsymbol{\varphi}^{2T}_{\mathrm{corr}}\binom{l'\,l}{k'k}, \tag{4.10a}$$

$$\boldsymbol{\varphi}^2_{\mathrm{corr}}\binom{l\,l'}{kk'} = \boldsymbol{\varphi}^{1T}_{\mathrm{corr}}\binom{l'\,l}{k'k}. \tag{4.10b}$$

So far we have used a fixed Cartesian coordinate system. Now we have to investigate how the structure of equations (4.8) is altered if we refer to the various molecular coordinate systems. Let us express the transformation into the molecular systems by equations (3.10) and (3.12), where the rotation of coordinate axes is described by the 3×3 matrix $\mathbf{B}$ ($\mathbf{B}^T = \mathbf{B}^{-1}$). We then obtain for all 3×3 force-constant matrices $\boldsymbol{\varphi}_{rr'}$, $\boldsymbol{\varphi}_t$, $\boldsymbol{\varphi}_{\mathrm{rot}}$ and $\boldsymbol{\varphi}_{\mathrm{corr}}$ the same law of transformation, namely

$$\boldsymbol{\varphi}_B\binom{l\,l'}{kk'} = \mathbf{B}\boldsymbol{\varphi}\binom{l\,l'}{kk'}\mathbf{B}'^T.$$

B and **B**$'$ refer to the molecules k and k'. This law implies that, for $k \ne k'$, the structure of equations (4.8) is destroyed, since the molecules k and k' are usually differently oriented in the crystal, and hence $\mathbf{B} \ne \mathbf{B}'$. For $k = k'$ we have $\mathbf{B} = \mathbf{B}'$ and the structure of equations (4.8) remains unaltered. It also remains unaltered if the origin of the molecular system is shifted because only the values of the components X_r, Y_r, Z_r of equation (4.7) are altered. The force-constant matrices $\boldsymbol{\varphi}_{66}$ $(k=k')$ are on the diagonal of the $6n\times 6n$ intermolecular-force-constant matrix which refers to molecules in the cells l and l'. Only the diagonal blocks $\boldsymbol{\varphi}_{66}$ $(k=k')$ are important in what follows.

In order to benefit from equations (4.8) we now have to make the following assumption. The potential energy of the crystal is the sum of contributions from atom pairs r,r' and these contributions depend only on the distance between the atoms r and r'. This assumption does not appear to be very stringent and is usually made in lattice-dynamical calculations with the use of '6-exp' potential functions, *cf.* Harada & Shimanouchi (1966, 1967), Pawley (1967), Powell (1969). With this assumption the interatomic-force-constant matrices become symmetric,

$$\boldsymbol{\varphi}\binom{ll'}{rr'}=\boldsymbol{\varphi}^{T}\binom{ll'}{rr'}, \tag{4.11}$$

cf. Maradudin, Montroll & Weiss [1963, equation (2.1.20)].* With equation (4.11) we obtain for each term r,r' of equation (4.8*c*) trace $[\boldsymbol{\varphi}\binom{l\ \ l'}{krk'r'}\mathbf{V}^{T}_{r'}\binom{l'}{k'}]=0$, and the corresponding result for the terms r,r' of equation (4.8*d*). Thus we obtain the important result

$$\text{trace}\,(\boldsymbol{\varphi}^{1}_{\text{corr}})=\text{trace}\,(\boldsymbol{\varphi}^{2}_{\text{corr}})=0 \tag{4.12}$$

for the diagonal blocks, $k=k'$, of the $6n\times 6n$ force-constant matrix. Equation (4.12) is valid in any coordinate system, as discussed above.

Since the dynamical matrices $\mathbf{L}(\mathbf{q})$ are sums of force-constant matrices, each term being multiplied by a phase factor, *cf.* equation (2.1), a relation corresponding to (4.12) also holds for the dynamical matrices. Let $\mathbf{L}_{66}$ be a 6×6 diagonal block of $\mathbf{L}(\mathbf{q})$, then we obtain from (4.6) and (4.12)

$$\{\mathbf{L}_{66}\}_{1,4}+\{\mathbf{L}_{66}\}_{2,5}+\{\mathbf{L}_{66}\}_{3,6}=0, \tag{4.13}$$

for each wave vector $\mathbf{q}$. In order to make use of equation (4.13) we now introduce the high-temperature approximation of equation (2.18)

$$\mathbf{C}=\frac{k_{B}T}{N}\sum_{\mathbf{q}}\mathbf{L}^{-1}(\mathbf{q})\ . \tag{4.14}$$

Equations (4.13) and (4.14) form the basis of our estimation of the constant K. Generally we cannot expect that a corresponding relation holds for the 6×6 diagonal blocks of $\mathbf{L}^{-1}(\mathbf{q})$ because such a relation will be destroyed by the matrix inversion. In order to obtain a condition for K we now assume that the change in the sum of the elements $1,4+2,5+3,6$ of $\mathbf{L}_{66}(\mathbf{q})$, which occurs during the inversion $\mathbf{L}\rightarrow\mathbf{L}^{-1}$, is largely compensated for if we invert the sum of the inverse matrices; *i.e.* we assume that the sum of the elements $1,4+2,5+3,6$ in $[\sum\mathbf{L}^{-1}(\mathbf{q})]^{-1}$ is approximately zero. Since we know only the diagonal blocks $\mathbf{C}_{66}$ of $\mathbf{C}$, we can carry out the inversion only with these blocks. With the above assumptions we thus obtain

$$\{\mathbf{C}_{66}^{-1}\}_{1,4}+\{\mathbf{C}_{66}^{-1}\}_{2,5}+\{\mathbf{C}_{66}^{-1}\}_{3,6}=0. \tag{4.15}$$

Equation (4.15) can only be used numerically.

The following consideration seems to indicate that the constant K will generally not be zero but will remain small. Let the sum of the three elements $1,4+2,5+3,6$ in each diagonal block of $\mathbf{L}^{-1}(\mathbf{q})$ be $f(\mathbf{q})$. With equation (4.13) we generally expect $f(\mathbf{q})$ to be non-zero. Hence, in the high-temperature approximation,

$$\text{trace}\,[\mathbf{S}(\text{dyn})]=\frac{k_{B}T}{N}\sum_{\mathbf{q}}f(\mathbf{q})$$

will usually be non-zero. But we may expect that the $\sum f(\mathbf{q})$ remains small in magnitude because the single terms $f(\mathbf{q})$ may have different signs and thus tend to cancel each other to a large extent.

The value of trace $[\mathbf{S}(\text{dyn})]=3K$ is invariant with respect to the chosen coordinate system. From equation (3.15) we see that trace $(\mathbf{S})$ is invariant with respect to changes of axes [as long as inversion is excluded, whereby trace $(\mathbf{S})$ changes its sign], and from equation (3.18) we see that trace $(\mathbf{S})$ is invariant with respect to a shift of the molecular origin. The invariance of trace $(\mathbf{S})$ corresponds to the invariance of our result (4.12) which refers to the corresponding three elements in the 6×6 intermolecular-force-constant matrices.

In view of the assumptions made in deriving equation (4.15) it is obvious that the value of K cannot be determined very accurately. The assumed symmetry of the interatomic-force-constant matrices (4.11) and the high-temperature approximation (4.14) for $T=19\,^{\circ}\text{C}$ do not appear to be very stringent. Also the block-diagonal inversion of $\mathbf{C}$ does not seem to give rise to serious errors. However, we should point out that equation (4.15) does not strictly follow from equations (4.13) and (4.14) but represents the most probable consequence which we can derive from (4.13) and (4.14). We have examined this with some numerical calculations using 6×6 matrices. It turned out that equation (4.15) does not strictly hold; but on the average over all examples the right-hand side of equation (4.15) approaches zero. Thus we consider (4.15) to be the best possible condition that we can obtain in order to determine the constant K. The error limits for K seemed to be $K=0$ on the one side, and $2K$ on the other. These limits will probably be larger if the value of K is very small compared to the magnitude of the components S^{j}_{i}.

5. Principal motions

In order to derive the 'principal components' of the rigid-body motions as they are to be understood dynamically, we follow the standard procedures for multidimensional oscillators. These procedures have already been discussed in § 2, but now we have to

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* von Laue (1960) seems to assume that equation (4·11) holds without restrictions, *cf*, his equation (21·17*c*).

apply them to the mean-square-amplitude matrix $\mathbf{C}_{66}$ of the given molecule.

The first step is the mass normalization of $\mathbf{C}_{66}$, and from equation (3.8) we obtain

$$\mathbf{D}_{66}=\mathbf{G}_{66}^{-1}\mathbf{C}_{66}\mathbf{G}_{66}^{T-1}. \qquad (5.1)$$

$\mathbf{D}_{66}$ refers to the system of eigenvectors which is obtained by the specific form of the transformation matrix $\mathbf{G}_{66}$ which reduces the kinetic-energy matrix $\mathbf{A}_{66}$ to the unit matrix, *cf.* § 3. Only if the mass normalization has been performed is it meaningful to rotate the six-dimensional coordinate system in order to obtain the principal components. The rotation is described with the aid of the 6×6 orthogonal matrix $\mathbf{R}_{66}$, *i.e.* $\mathbf{R}_{66}^{T}=\mathbf{R}_{66}^{-1}$. $\mathbf{R}_{66}$ diagonalizes $\mathbf{D}_{66}$, and the principal components $D_{\Lambda j}$, $j=1\ldots6$, are given by

$$\mathbf{D}_{\Lambda 66}=\mathbf{R}_{66}^{T}\mathbf{D}_{66}\mathbf{R}_{66}. \qquad (5.2)$$

If one reduces $\mathbf{A}_{66}$ to unit masses then the elements of $\mathbf{D}_{66}$ and the principal components are obtained in squared unit lengths, where the unit length is given by 1 Å/m. If one reduces $\mathbf{A}_{66}$ to $m\mathbf{E}$ (instead of $\mathbf{E}$) the elements of $\mathbf{D}_{66}$ and the principal components are obtained in Å^2. This difference in dimension will become important for our interpretation of **TLS**, *cf.* § 7 below. The principal components represent linear combinations of translations and librations of the molecules, which generally cannot be visualized geometrically in three-dimensional space. Only if the correlation tensor $\mathbf{S}$ vanishes in the principal inertial system with origin at the centre of gravity, are $\mathbf{D}_{66}$ and $\mathbf{R}_{66}$ 3×3 block diagonal, the principal components representing pure translations and pure librations. Only in this case can the elements of the two 3×3 blocks of $\mathbf{R}_{66}$ be interpreted as direction cosines (with respect to the principal inertial system). [If $\mathbf{S}$ is zero in a system whose origin is not at the centre of gravity, then $\mathbf{S}$ will usually not be zero if referred to the centre of gravity as origin, because of the transformation (3.18).] The uncertainty in the trace of $\mathbf{S}$ usually does not affect the values of the principal components to a large extent, since, as a rule, the components S_i^i are small compared to the components T^{ii} and L_{ii} and so contribute only slightly to the principal components.

It is instructive to discuss the determination of the principal components in terms of the eigenvectors of the lattice modes. Then we can interpret the determination of the principal components as a transformation of a second-rank tensor into its system of principal axes. With equations (3.9), (5.1), and (5.2) we obtain

$$\mathbf{D}_{\Lambda 66}=\frac{1}{2N}\sum_{\mathbf{q}j}\frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})}\,\mathbf{R}_{66}^{T}\{\boldsymbol{\varepsilon}_{66}+\boldsymbol{\varepsilon}_{66}^{*}\}_{\mathbf{q}j}\mathbf{R}_{66}. \qquad (5.3)$$

The components of the eigenvectors, which are contained in $\boldsymbol{\varepsilon}_{66}$, are referred to the six-dimensional basis which has been obtained with the transformation matrix $\mathbf{G}_{66}$. This basis is orthonormal since all vibration coordinates are expressed in the same units, *cf.* § 3. Thus, for each mode $\mathbf{q}j$, $\boldsymbol{\varepsilon}_{66}+\boldsymbol{\varepsilon}_{66}^{*}$ is a real symmetric tensor of second rank. The expression $\mathbf{R}_{66}^{T}\{\boldsymbol{\varepsilon}_{66}+\boldsymbol{\varepsilon}_{66}^{*}\}_{\mathbf{q}j}\mathbf{R}_{66}$ in equation (5.3) can hence be interpreted as a tensor transformation with which the axes are rotated in six-dimensional space so that the tensor $\boldsymbol{\varepsilon}_{66}+\boldsymbol{\varepsilon}_{66}^{*}$ becomes diagonal on the average over all lattice modes. The corresponding transformations of the base vectors and the components of the eigenvectors are

$$\mathbf{a}_{\Lambda}=\mathbf{R}^{T}\mathbf{a},\quad \mathbf{e}_{\Lambda}=\mathbf{R}^{T}\mathbf{e} \qquad (5.4)$$

respectively. ($\mathbf{a},\mathbf{a}_{\Lambda}$ and $\mathbf{e},\mathbf{e}_{\Lambda}$ are 6×1 column matrices.) The set of base vectors $\mathbf{a}_{\Lambda}$ expresses the principal axes of the tensor $\boldsymbol{\varepsilon}_{66}+\boldsymbol{\varepsilon}_{66}^{*}$ (lattice average).

The total contribution of the mode $\mathbf{q}j$ to the mean-square amplitudes of the kth molecule is equal to

$$\frac{\bar{E}(\mathbf{q}j)}{N\omega_j^2(\mathbf{q})}\operatorname{trace}[\boldsymbol{\varepsilon}_{66}(\mathbf{q}j)]=\frac{\bar{E}(\mathbf{q}j)}{N\omega_j^2(\mathbf{q})}\sum_{t=1}^{6}|e_t(k|\mathbf{q}j)|^2. \qquad (5.5)$$

Thus this contribution is proportional to the square of the length (in six-dimensional space) of that part of the eigenvector that specifies the motions of the kth molecule in this mode. Obviously the square of this length in (5.5) is independent of the six-dimensional orthonormal basis selected.

The determination of the principal components described above is analogous to the determination of the principal components of the atomic vibrations. For the individual atoms, however, the 3×3 kinetic-energy matrix is already diagonal in any Cartesian coordinate system, namely $\mathbf{A}_{33}=m_r\mathbf{E}$. Hence the transformation with the matrix $\mathbf{G}$ is redundant. Therefore it is sufficient to diagonalize the vibration tensors $\mathbf{U}_r$ in a Cartesian coordinate system in order to determine the principal components. The rotation of the Cartesian axes corresponds to the transformation $\mathbf{R}^{T}(\boldsymbol{\varepsilon}+\boldsymbol{\varepsilon}^{*})\mathbf{R}$ (all matrices are of order 3×3). The principal components of the atomic vibrations can be visualized geometrically in the principal Cartesian system, whereas the principal components of the molecular motions cannot, since they formally refer to a six-dimensional basis which cannot, in general, be resolved into two three-dimensional bases.

6. Comments on Schomaker & Trueblood's interpretation of TLS

In 1968 Schomaker & Trueblood were the first to deduce the correlation tensor $\mathbf{S}$, and at the same time they gave a detailed interpretation of the tensors **TLS**. They found that, by introducing the $\mathbf{S}$ tensor, the three positional parameters of the centre of libration, which were introduced by Pawley (1963) and by Hirshfeld, Sandler & Schmidt (1963), became redundant. Hence the origin of the centre of libration was found to constitute an arbitrary element in the **TLS** description, and Schomaker & Trueblood proceeded to find a description in which this arbitrary element was removed. They achieved this by transforming the tensors **TLS** so that as many components as possible would become zero. There are several ways of doing this; in the description preferred by Schomaker & Trueblood, the tensor **L** is diagonalized, the three axes of the principal system of **L** are shifted so that **S** becomes diagonal, and finally **T** is referred to its own principal system. Hence only 9 components remain non-zero ($3L_{ii}$, $3S^i_i$, $3T^{ii}$), and the description obtained is unique in that reference to a particular molecular origin is no longer necessary.

However, Schomaker & Trueblood (1968) state that this set of components corresponds to 'six independently distributed instantaneous motions' (or 'six independent simple motions'); these are 'three screw librations about non-intersecting axes and three translations'. With the use of physical terms of this type Schomaker & Trueblood associate a certain physical reality with the description that was originally designed to remove some arbitrary elements. This poses the following question: are the physical statements, which are associated with the preferred description, 'true' in the sense that they express what really happens in nature? If this question can be answered positively then the physical statements made by Schomaker & Trueblood should, at least, not be in contradiction to the results of a different physical approach to the problem, or (even better) they should be confirmed by such an approach.

To examine the physical statements made by Schomaker & Trueblood from the point of view of the lattice-dynamical treatment which we have developed in this paper, we divide the problem into three questions.

(*a*) Are the six simple motions described by Schomaker & Trueblood statistically independent motions of the rigid molecule?

(*b*) Is it physically meaningful to regard certain vibrations of the molecule as 'screw motions' when the diagonal components of the **S** tensor are non-zero?

(*c*) Is a description of the molecular rigid-body motions with the aid of a system of non-intersecting axes physically reasonable?

(*a*) *'Independent simple motions'*

Schomaker & Trueblood (1968, p. 67) derive these concepts in the following way. They first establish the system of '... non-intersecting axes, each used for one of the principal directions of libration and chosen to eliminate the off-diagonal part of **S**. The diagonal components of **S** are then accounted for by regarding the eigenvalues of **L** as representing independent rotations, each with a screw component. Finally, **T** is appropriately reduced to keep **U** invariant and is referred to its own principal axes. The picture is thus one of six independent simple motions.'

We believe that the transformations of the tensors **TLS** described by Schomaker & Trueblood do not yield a set of components which describe six statistically independent motions. Since the components S^i_i remain non-zero the vibrations obtained by diagonalizing **L** and **S** always contain the correlation between translations and librations. We believe that it is not legitimate to interpret the components S^i_i only in relation to the components L_{ii} and to treat the translations separately. Such a procedure implies that the translations would form an independent set of motions and would not be affected by the components S^i_i. Thus, as long as the components S^i_i remain non-zero, the respective set of **TLS** components does not represent a set of statistically independent motions. These are obtained only if the 6×6 mean-square-amplitude matrix of **TLS** is transformed so that the S^i_i (and all other off-diagonal terms of the 6×6 matrix) become zero. The results of such a (linear) transformation are always six linear combinations of translations and librations. Formally, there is an infinite number of sets of such linear combinations depending on the type of six-dimensional basis chosen. The only set which appears to be physically meaningful is the set of principal components which is obtained with the choice of an orthonormal basis for the eigenvectors, *cf.* § 5. The six principal motions, however, have the disadvantage that they cannot be visualized in simple geometrical terms and in this sense we cannot give them the attribute 'simple.'

(*b*) *Screw motions*

The components S^i_i represent the time and lattice averages of the coupling of the translations along the axis i with the librations about the same axis. We share Schomaker & Trueblood's (1968) opinion that translations which are coupled with rotations about the same axis, can be visualized as (partial) screw motions of the molecule, and we wish to establish this view with the aid of a lattice-dynamical study. But we do not mean that the screw motions are the 'simple motions' about non-intersecting axes, *cf.* the preceding section. With a single pair of lattice modes $\mathbf{q}j$ and $-\mathbf{q}j$ we show how the components S^i_i are related to the phase differences of translations and rotations, and how the screw character of the motions can be understood in terms of the phase differences. The generalization for all lattice modes follows immediately.

We use the principal inertial system with the origin at the centre of gravity because in this system the components of **TLS** are directly related to the eigenvectors, *cf.* equations (3.7). For the modes $\mathbf{q}j$ and $-\mathbf{q}j$ we define a correlation coefficient

$$\mu_i=\{S^i_i/\sqrt{T^{ii}L_{ii}}\}_{\mathbf{q}j,\,-\mathbf{q}j} \qquad (6.1a)$$

which expresses the coupling of translations and rotations about the axis i. Its extreme values are $+1$ and -1. To express μ_i in terms of the phase difference of translation and rotation in the modes $\mathbf{q}j$ and $-\mathbf{q}j$, we introduce phase angles φ in the (complex) components $e_i(k|\mathbf{q}j)$ of the eigenvectors. For the mode $\mathbf{q}j$, let $a\exp(i\varphi_1)$ be a component of the eigenvector which refers to the translation of the molecule in the direction i, and let $b\exp(i\varphi_2)$ be a component which refers to a rotation about the axis i, then the phase difference of translation and rotation in this mode is $\varphi_1-\varphi_2$. If one calculates μ_i of equation (6.1*a*) with the aid of equations (3.7) most factors cancel each other. For the two lattice modes $\mathbf{q}j$ and $-\mathbf{q}j$ we obtain

$$\mu_i(\mathbf{q}j,-\mathbf{q}j)=\cos(\varphi_1-\varphi_2), \qquad (6.1b)$$

and thus we have expressed the correlation coefficient in terms of the phase difference between translation and rotation. The modes $\mathbf{q}j$ and $-\mathbf{q}j$ have the same frequency. Therefore we can discuss the 'partial screw motions' with the aid of equation (6.1*b*). Consider the extreme cases of maximum correlation, $\mu_i=\pm 1$, and of zero correlation, $\mu_i=0$. For $\mu_i=1$ we have $\varphi_1-\varphi_2=0°$, and thus complete in-phase motion of translation and rotation occurs. Therefore $\mu_i=1$ means pure screw motion about the axis *i*. For $\mu_i=-1$ we have $\varphi_1-\varphi_2=180°$ and complete out-of-phase motion, therefore $\mu_i=-1$ also means pure screw motion, but in the opposite sense. For $\mu_i=0$ we have $\varphi_1-\varphi_2=90°$. Hence during translation in one direction (half a period) rotation occurs half the time in one sense and half the time in the opposite sense. In those cases which lie between these extremes, $0<|\mu_i|<1$, rotation in one sense dominates during translation in one direction but will be partially compensated by rotation in the opposite sense. Thus a certain part of the screw motion remains for $|\mu_i|>0$.

In a similar manner we can define the correlation coefficient for all lattice modes in the crystal, thus

$$\mu_i=S^i_i/\sqrt{T^{ii}L_{ii}}\,. \qquad (6.2)$$

This average value of correlation corresponds to an average of phase differences between translations and rotations, taken over all modes. For the individual modes the phase differences may vary; they may be smaller or larger than 90°, which corresponds to positive or negative senses of the partial screw motions. On the average over all modes the senses of the various screw motions will frequently cancel each other, but a certain part may remain. This part is expressed by μ_i of equation (6.2). For the translation component of the average screw motion we obtain

$$\mu_i\sqrt{T^{ii}}=S^i_i/\sqrt{L_{ii}}\equiv\gamma_i\,, \qquad (6.3)$$

and for the rotation component

$$\mu_i\sqrt{L_{ii}}=S^i_i/\sqrt{T^{ii}}\equiv\delta_i\,. \qquad (6.4)$$

Equation (6.3) for the translation component is equal to Schomaker & Trueblood's (1968) result.

So far we have used the principal inertial system. Our results are also valid in any other coordinate system with intersecting axes (with a defined origin) because the physical motions remain the same whereas the tensor transformations (3.15) and (3.18) ensure that we have only used another (valid) description of these motions (which is less suited for treating our problem).

To conclude: if the components S^i_i are non-zero then there are lattice modes with which the molecules undergo partial screw motions, and we need not carry out a lattice-dynamical calculation in order to confirm this [Pawley, *cf.* Ahmed (1970), pp. 250–251]. The results of refinements of many structures have shown, however, that the components S^i_i are usually small in magnitude, and values of $|\mu_i|>0{\cdot}2$ rarely occur, *cf.* § 8 below. For this reason it will seldom be possible to relate the observed screw components to the packing of the molecules in a given structure. Such an attempt will be rendered even more difficult by the fact that the constant K and hence the values of the components S^i_i are not precisely known.

(*c*) *Non-intersecting axes*

The system of non-intersecting axes was originally introduced by Schomaker & Trueblood (1968) in order to discuss the six 'simple motions' of the molecule. If one does not consider this particular point of interpretation the question remains whether or not it is physically meaningful to describe the rigid-body motions in a system of non-intersecting axes. The position of the non-intersecting axes with respect to the geometry of the molecule was calculated for several structures [*cf.*, *e.g.*, Seff & Trueblood (1968); Goldstein, Seff & Trueblood (1968); Palenik, Donohue & Trueblood (1968); Long, Maddox & Trueblood (1969); Ellison, Johnson & Levy (1971)], and in some cases an attempt was made to relate the position of the displaced axes to some structural features. We do not consider such attempts appropriate because we believe that conclusions about motions 'which really happen in nature', can only be drawn in a coordinate system which, in principle, allows a dynamical (*i.e.* a physical in contrast to a geometrical) formulation of the motions of the molecules.

A dynamical treatment of the vibrational problem demands that positional and vibrational coordinates are all expressed in one and the same coordinate system. This, however, is not possible in a system with non-intersecting axes. In such a system the vibrational coordinates can be expressed whereas the positional ones cannot since an origin of the molecular system is not defined. This has the consequence that neither the potential nor the kinetic energy can be represented. In order to show this we use the description used in this paper. But this does not imply a restriction on our results since our description is convertible into any other.

Since no origin is defined (in a system with non-intersecting axes) the position of an atom *r* in the molecule cannot be described by a tensor $\mathbf{V}_r$ of equation (4.7). Hence the intermolecular correlation and couple constants can no longer be expressed as in equations (4.8). But our problem demands that such a description be possible.

In the expression $\mathbf{A}_{66}$ of equation (2.4) for the kinetic-energy matrix of a molecule, we have seen that cross terms for translation and rotation always exist unless all three coordinate axes pass through the centre of gravity. These cross terms contain the components of the vector $\boldsymbol{\varrho}$ from the molecular origin to the centre of gravity. With a system of non-intersecting axes only one axis can pass through the centre of gravity; hence there are cross terms for the two remaining axes. Let the z axis pass through the centre of gravity; then a cross term $-m\varrho_z$ exists, where $|\varrho_z|$ represents the distance of the x and y axes from the centre of gravity. Since the x and y axes do not intersect they have no common distance from the centre of gravity. Hence the component ϱ_z is not defined, nor is the matrix $\mathbf{A}_{66}$.

In the dynamical theory of rigid-body motions an attempt to use a system with non-intersecting axes does not appear to be necessary because the most general motion of a rigid body can always be described by translations, and by rotations about a fixed point, *cf.* Schäfer (1950).

7. Interpretation of TLS

We have seen that no geometrical interpretation of the six principal motions can be given (for $\mathbf{S}\neq\mathbf{0}$) because the principal motions represent linear combinations of the translations along and librations about all coordinate axes. Hence, in general, it will be impossible to interpret the principal motions with respect to the arrangement of the molecules in a given structure. But it is, of course, always possible to calculate **TLS** in any (Cartesian) coordinate system and to try to relate the corresponding translations, rotations, and screw motions to the packing of the molecules. Then the interpretation of the coupling terms in the mean-square-amplitude matrix $\mathbf{C}_{66}$ usually presents a difficult problem which we shall not attempt to solve.

Our interpretation consists of firstly reformulating the mean-square-amplitude data **TLS** into intermolecular-force data, and secondly of relating the force data to the packing of the molecules in the structure. The interpretation in terms of intermolecular forces rather than in terms of mean-square amplitudes offers several advantages. It allows the question of normalization to be tackled in a more rational manner and so facilitates the (numerical) comparison of translations and rotations. Also the question of a suitable coordinate system can be more clearly handled. Finally, it is a matter of convenience, to rediscuss the dynamically important intermolecular interactions in terms of (average) intermolecular forces rather than in terms of mean-square amplitudes.

Our basic equation is (2.18), but first we consider the simpler case of the high-temperature approximation (4.14). In (4.14) the summation is carried out over the inverse dynamical matrices. The dynamical matrices contain sums over the intermolecular-force-constant matrices, where each term is multiplied by a phase factor which depends on the wave vector $\mathbf{q}$, *cf.* equation (2.1). Thus in the dynamical matrices the force constants for the various intermolecular contacts are added. This means that the dynamical matrix $\mathbf{L}(\mathbf{q})$ describes the resultant intermolecular forces for the wave $\mathbf{q}$, and hence describes the resultant force field in which the molecules in a unit cell vibrate in the wave $\mathbf{q}$. The average motions of the molecules are obtained by adding up the mean-square amplitudes of the molecules (and not the dynamical matrices), as is stated by equation (4.14). This way of forming the average seems to be reasonable since the molecules vibrate independently in the various modes (in the harmonic approximation). In order to describe the average motions of the molecules in terms of a force field rather than in terms of mean-square amplitudes we invert the matrices in equation (4.14) and define a $6n\times 6n$ matrix $\mathbf{F}$ as follows

$$k_BT\mathbf{C}^{-1}=N[\sum_{\mathbf{q}}\mathbf{L}^{-1}(\mathbf{q})]^{-1}\equiv\mathbf{F}. \tag{7.1}$$

The elements of $\mathbf{F}$ have the dimensions of force, couple and of (translation–rotation) correlation constants respectively. We call $\mathbf{F}$ a 'pseudo-force-constant matrix' since the elements of $\mathbf{F}$ are not intermolecular-force constants as given by equations (4.8). $\mathbf{F}$ may be interpreted as follows. The molecules in the unit cell vibrate *as if* they were in a force field with the force-constant matrix $\mathbf{F}$; or alternatively, a force field described by the matrix $\mathbf{F}$ would produce exactly the same mean-square amplitudes as the molecules actually have in the crystal.

Unfortunately, we cannot calculate $\mathbf{F}$ from equation (7.1) because we can only determine the diagonal blocks of $\mathbf{C}$ which are occupied by the tensors **TLS**. Hence we have to make a further assumption which goes beyond the rigid-molecule assumption and the harmonic approximation used so far. We have to assume that $\mathbf{C}$ is 6×6 block diagonal. This assumption means 'uncorrelated motion' for the molecules in the unit cell, *cf.* Scheringer (1972*c*). Generally, it will not hold exactly for molecular crystals, but it will be fairly well fulfilled because in most molecular crystals only weak van der Waals forces occur which are independent of direction. If the assumption is valid, $\mathbf{C}$ and $\mathbf{F}$ are block diagonal and we obtain in the high-temperature approximation

$$\mathbf{F}_{66}=k_BT\mathbf{C}_{66}^{-1}, \tag{7.2}$$

which allows us to calculate $\mathbf{F}$ immediately from the vibration tensors **TLS**.

At room temperature the high-temperature approximations (7.1) and (7.2) are usually adequate for molecular crystals. But we want to show here how the matrix $\mathbf{F}_{66}$ can be calculated from the components of **TLS** at low temperatures. For this purpose we write

$$\mathbf{F}_{66}=\mathbf{\Omega}_{66}\mathbf{C}_{66}^{-1}=N\mathbf{\Omega}_{66}[\sum_{\mathbf{q}}\mathbf{L}^{-1}(\mathbf{q})\mathbf{\Omega}(\mathbf{q})]^{-1}, \tag{7.3}$$

again assuming $\mathbf{C}$ to be 6×6 block diagonal. In equation (7.3) $\mathbf{F}_{66}$ and $\mathbf{\Omega}_{66}$ are unknown, but $\mathbf{\Omega}_{66}$ is defined analogously to $\mathbf{\Omega}(\mathbf{q})$ of equation (2.16), *i.e.* $\mathbf{\Omega}_{66}=(\mathbf{G}_{66}\mathbf{R}_{66})^{T-1}\mathbf{\Gamma}_{66}(\mathbf{G}_{66}\mathbf{R}_{66})^{T}$. $\mathbf{F}_{66}$ can be evaluated by numerical procedures. One uses the diagonal form $\mathbf{F}_{A66} = (\mathbf{G}_{66}\mathbf{R}_{66})^T\mathbf{F}_{66}\mathbf{G}_{66}\mathbf{R}_{66}$ whose elements F_{Aj} are the squares of the pseudo frequencies ω_j, $j = 1 \ldots 6$. These frequencies can be determined from the principal components D_{Aj} of equation (5.2) with the aid of the equation

$$D_{Aj} = \frac{\hbar}{2\omega_j m} \coth\left(\frac{\hbar\omega_j}{2k_BT}\right). \tag{7.4}$$

With equation (7.4) the normalization is performed to the mass m, with the aid of $\mathbf{G}_{66}$. $\mathbf{F}_{66}$ is now obtained according to $\mathbf{F}_{66} = (\mathbf{G}_{66}\mathbf{R}_{66})^{T-1}\mathbf{F}_{A66}(\mathbf{G}_{66}\mathbf{R}_{66})^{-1}$, where $\mathbf{R}_{66}$ is determined from equation (5.2).

Equations (7.2) and (7.3) describe the relation between the tensors **TLS** and the pseudo force and couple constants, but, similarly to **T** and **L**, the force and couple constants do not have the same dimension. The pseudo force constants for the translations have the dimension of energy/Å^2, and the pseudo couple constants for the librations have the dimension of energy. Hence the values of all elements in $\mathbf{F}_{66}$ cannot be compared with one another, and, consequently, one has to express the couple constants as force constants, or, equally, the rotations of the molecule as translations. This is achieved by the mass-normalizing transformation. However, a further point has to be observed. If one wants to obtain the pseudo force constants on an absolute scale, *i.e.* in energy/Å^2 units, one has to normalize to the mass m of the molecule and not to the mass one, *cf.* § 5. This is important if one wants to compare the pseudo force constants of different molecules, which usually have different masses. Thus, with the mass-normalizing transformation

$$\mathbf{G}_{66}^T\mathbf{A}_{66}\mathbf{G}_{66} = m\mathbf{E} \tag{7.5}$$

the normalized pseudo-force-constant matrix

$$\mathbf{F}_{66}^{\text{norm}} = \mathbf{G}_{66}^T\mathbf{F}_{66}\mathbf{G}_{66} \tag{7.6}$$

is obtained, and all of its elements have the dimensions energy/Å^2. If the molecular origin is placed at the centre of gravity $\mathbf{F}_{66}^{\text{norm}}$ refers to the principal inertial system for the translations as well as for the librations. If, however, the molecular origin is not at the centre of gravity and the mass normalization is carried out with a matrix $\mathbf{G}_{66} = \mathbf{P}_{66}\mathbf{Q}_{66}$ as described in § 2, then $\mathbf{F}_{66}^{\text{norm}}$ refers to a six-dimensional orthonormal basis, *cf.* § 3. In this case the elements of $\mathbf{F}_{66}^{\text{norm}}$ cannot be interpreted in three-dimensional space of the actual structure since the six-dimensional basis cannot, in general, be resolved into two three-dimensional bases. Thus, for our interpretation, it is not only advantageous but necessary to use the centre of gravity as the molecular origin.

It is our aim to relate the values of the elements of $\mathbf{F}_{66}^{\text{norm}}$ of equation (7.6) to the packing of the molecules in the static structure. There are usually two properties of molecular crystals which make this possible.

(1) Molecules usually have a low symmetry (in contrast to atoms). The shape of the molecules largely determines the possible intermolecular interactions (contacts). Hence $\mathbf{F}_{66}$ is usually strongly influenced by the low symmetry of the molecular shape and will thus display a pronounced anisotropy. This facilitates relating the elements of $\mathbf{F}_{66}^{\text{norm}}$ to characteristic features of the structure.

(2) The important intermolecular forces usually occur only between adjacent molecules (nearest and next-nearest neighbours). This could be well confirmed by lattice-dynamical calculations with the aid of '6-exp' potential functions and by comparison with corresponding experimental data on some structures. We draw attention to the following investigations (MI stands for the range of molecular interactions which was used to obtain a good fit to the experimental results or, at least, to stabilize the calculation of the lattice frequencies): benzene and naphthalene, MI (H···H and C···H) 3·3 Å, calculations only for $\mathbf{q} = \mathbf{0}$, comparison with infrared and Raman data, Harada & Shimanouchi (1966, 1967); naphthalene and anthracene, MI 5·5 Å, calculations for all wave vectors, comparison with infrared and Raman data, Debye–Waller factors (**TL**), elastic constants, Pawley (1967); hexamethylenetetramine, MI 3·87 Å, calculations for all wave vectors, comparison with inelastic neutron scattering, Powell (1969); chrysene, MI not stated, calculations for all wave vectors, comparison with thermal diffuse scattering, Hogan & McMullan (1972). The fact that, with molecular crystals, only interactions among adjacent molecules occur (to a good approximation) means that the pseudo-force-constant matrix contains only interactions of this type.

The interpretation of the mean-square amplitudes in terms of the pseudo force constants, which we have outlined for molecular crystals, could formally be carried out for atomic crystals as well. In particular, the low-temperature equivalent to (7.1), reduced to a $3n \times 3n$ atomic pseudo-force-constant matrix, provides a correct description for atomic crystals. However, a corresponding interpretation usually cannot be applied successfully since the inherent assumptions do not hold for atomic crystals. For ionic crystals and metals the assumption of uncorrelated motion may be nearly fulfilled, but the interatomic interactions are usually not restricted to adjacent atoms, as could be shown in many cases by comparison between observed and calculated dispersion curves, *cf.*, *e.g.*, Cochran & Cowley (1967). Furthermore, in ionic crystals and metals the atomic motions are often not markedly anisotropic, even in cases where this would be allowed by low site symmetry, In covalent crystals. on the other hand, the interactions are usually of the short-range type and anisotropic motions may easily occur when the atoms are strongly bound in certain directions. But then the assumption of uncorrelated motion is not appropriate and the diagonal block $\mathbf{F}_{33}$, which is obtained merely from the vibration tensor of the respective atom, does not represent the elements of the proper pseudo-force-constant matrix.

We see that the interpretation of **TLS** described above is possible mainly because the interatomic interactions in molecular crystals are of a distinct type (uncorrelated motion, molecular shape, short-range interactions) which usually cannot be found in atomic crystals.

8. Interpretation of two structures

(*a*) *Details of programs*

In order to be able to apply the treatment discussed in the preceding sections we have written two programs. With the first program scale factors, positional parameters of the individual atoms, and the parameters **TLS** (or alternatively the parameters **TLX**, **X** denoting the origin for the molecular librations) can be refined from diffraction data, whereby **TLS** (and **TLX**) are referred to crystal axes. During the refinement the condition trace $(\mathbf{S})=0$ is imposed, which reduces the order of the matrix of the normal equations by one.

With the second program the coordinates of the atoms and the parameters **TLS** are first transformed into a Cartesian reference system and then into the principal inertial system of the molecule with origin at the centre of gravity. The constant K is determined from equation (4.15) by a cyclic interpolation procedure. The various limits of K are calculated from equations (4.3), (4.4) and (4.5). The following quantities are also calculated: the principal components of equation (5.2), the screw components of equations (6.2), (6.3) and (6.4), and the pseudo force constants of equations (7.2) and (7.6) for $T=292$°K.

(*b*) *Values of the constant K*

The two structures selected are maleic anhydride (MAL) and 5-chloro-1,4-naphthoquinone (5ClN). The respective values for K were computed to be $-0·00026$ and $-0·00052$ rad Å, *cf.* Table 1. The uncertainty for these values is about $\pm 0·00030$ rad Å. It is interesting to compare the values of K, determined from equation (4.15), with the central values between the limits of K, *cf.* Table 1. K(II) is the central value between the narrowest limits that follow from equations (4.4); K(III) is the central value which is obtained from the singularities of $\mathbf{C}_{66}$, equation (4.5). K(II) is negative for MAL and 5ClN, as is K. But for MAL $K(\mathrm{II})=-0·000293$ rad Å deviates strongly from the value of K, whereas for 5ClN $K(\mathrm{II})=-0·00087$ rad Å comes much closer. The central values K(III) of the narrower limits (4.5) are, however, in good agreement with the value of K, particularly for 5ClN. This agreement seems to indicate that the values of K are determined to a fair approximation from equation (4.15). Moreover, the values for the limits of K show that these are not narrow enough to determine the value of K with sufficient accuracy. The narrowing of the limits due to the use of equation (4.5) instead of equation (4.4) is slight for MAL but considerable for 5ClN, *cf.* Table 1.

For MAL the value of K ($-0·00026$ rad Å) is small compared to the values of the components S_i^i (average 0·00210 rad Å). Therefore the use of $K=0$ would lead to essentially the same values for the screw components and pseudo force constants. For 5ClN, however, the value of K ($-0·00052$ rad Å) is significant compared to the values of the components S_i^i (average 0·00126 rad Å), and the use of $K=0$ would lead to markedly different values for the screw components, whereas the values for the pseudo force constants would hardly be affected.

(*c*) *Maleic anhydride*

The structure of MAL was determined by Marsh, Ubell & Wilcox (1962) (MUW). Refinements of thermal rigid-body parameters **TLX** were carried out by Pawley (1963). The space group is $P2_12_12_1$, with one molecule in the asymmetric unit. MAL is essentially planar. The planes of different molecules in the crystal are not parallel to one another, which results in a loose packing of the molecules, *cf.* Figs. 3, 4, 5 of MUW. All intermolecular contacts are of the van der Waals type. The molecules are arranged in zigzag chains.

We have refined MAL from the MUW diffraction data by using the rigid-body thermal parameters **TLS** and **TLX**. With **TLX** we confirm Pawley's (1963) results. The **S** tensor proved to be highly significant compared to the origin parameters **X**. The two respective R values were 6·36 and 6·77% so that the parameters **X** could be rejected below the 0·005 level of significance. The R value of 6·36% for **TLS** is even smaller then that reported by MUW (6·5%). The parameters **TLS** [trace $(\mathbf{S})=0$] referred to the principal inertial system with the origin at the centre of gravity, the total mass of the molecule, the principal inertial moments, and the principal components D_{Ai} are given in Table 2. Since the molecule is essentially planar two principal axes are located in the plane of the molecule; their position is indicated in Fig. 1.

Table 1. *Values of the constant K and its limits* (rad Å) *for MAL and 5ClN*

K is determined from equation (4·15). K_{lim}(I) refers to equation (4·3), K_{lim}(II) to equation (4·4), K_{lim}(III) to equation (4·5). K(I), K(II), and K(III) are the respective central values between the limits.

	MAL	5ClN		MAL	5ClN
K	−0·00026	−0·00052	$K^{\pm}_{\mathrm{lim}}$(I)	±0·02628	±0·01012
K(I)	0·0	0·0	K^{+}_{lim}(II)	0·01961	0·00494
K(II)	−0·00293	−0·00087	K^{-}_{lim}(II)	−0·02547	−0·00669
K(III)	−0·00047	−0·00050	K^{+}_{lim}(III)	0·01941	0·00229
			K^{-}_{lim}(III)	−0·02035	−0·00330

Table 2. *Parameters* **TLS** [trace (**S**) = 0] *referred to the principal inertial system with origin at the centre of gravity, for MAL and 5ClN*

T^{ik} in Å^2, L_{ik} in rad^2, S_i^k in rad Å. m is the mass of the molecule in mole, I_i are the principal moments of inertia in mole Å^2. D_{Ai} are the principal components of the rigid-body motions in Å^2.

	MAL	5ClN		MAL	5ClN
T^{11}	0·04857	0·01598	S_2^2	−0·00097	0·00102
T^{22}	0·05642	0·03537	S_2^3	0·00110	−0·00302
T^{33}	0·06878	0·03373	S_3^1	−0·00277	−0·00278
T^{12}	0·00611	0·01001	S_3^2	0·00263	0·00152
T^{13}	−0·00046	−0·00680	S_3^3	−0·00213	−0·00189
T^{23}	−0·00709	0·00573	m	98·06	192·60
L_{11}	0·01063	0·00212	I_1	273·87	1187·97
L_{22}	0·01239	0·00258	I_2	200·77	747·01
L_{33}	0·01277	0·00615	I_3	73·17	443·69
L_{12}	0·00107	0·00022	D_{A1}	0·0727	0·0417
L_{13}	−0·00113	−0·00058	D_{A2}	0·0585	0·0367
L_{23}	−0·00027	0·00257	D_{A3}	0·0457	0·0222
S_1^1	0·00310	0·00087	D_{A4}	0·0285	0·0128
S_1^2	0·00222	−0·00143	D_{A5}	0·0238	0·0058
S_1^3	0·00287	−0·00047	D_{A6}	0·0091	0·0032
S_2^1	0·00220	−0·00032			

The correlation coefficients, μ_i of equation (6.2), the screw translations γ_i of equation (6.3), and the screw rotations δ_i of equation (6.4) are given in Table 3. The magnitudes of the correlation coefficients are small, all of them less than 0·13. For this reason and because of the uncertainty in the value of K, we have not tried to relate the screw components to the geometrical arrangement of the molecules in the crystal.

Table 3. *Correlation coefficients* μ_i, *screw translations* γ_i (Å), *and screw rotations* δ_i (rad) (i = 1,2,3) *for MAL and 5ClN*

	MAL	5ClN		MAL	5ClN
μ_1	0·125	0·061	γ_3	−0·0212	−0·0308
μ_2	−0·046	0·052	δ_1	0·0129	0·0028
μ_3	−0·081	−0·168	δ_2	−0·0052	0·0026
γ_1	0·0276	0·0077	δ_3	−0·0091	−0·0132
γ_2	−0·0110	0·0097			

Our main concern is the interpretation of the molecular motions of MAL in terms of the pseudo force constants. We have used the high-temperature approximation and found it convenient to express the constants in units of Å^{-2} as computed from the equation

$$\mathbf{D}_{66}^{-1}\ (\text{Å}^{-2}) = \mathbf{F}_{66}^{\text{norm}}/k_BT. \qquad (8.1)$$

The diagonal components of **L** have similar magnitudes ranging from 34·9 to 41·9 deg^2. When the components are normalized to the mass m of the molecule they are markedly different (0·0297, 0·0254, 0·0095 Å^2) because the inertial moment about the Z axis is particularly small (73·17 mole Å^2). This demands that the respective pseudo force constants also display pronounced differences, *cf.* Table 4.

One interesting result for MAL is that the pseudo-force-constant matrix is diagonal to a fair approximation; the off-diagonal terms are rarely larger than 10% of the corresponding diagonal elements. This means that the translations in the direction of and the rotations about the principal inertial axes are, to a fair approximation, the principal motions of the molecule. This was also observed to hold for naphthalene (Cruickshank, 1957*a*) and anthracene (Cruickshank, 1956, 1957*b*), but it does not represent a general phenomenon, *cf.* 5ClN below.

Since for MAL the off-diagonal elements of the pseudo-force-constant matrix are small we restrict the following discussion to the diagonal elements. The diagonal elements which refer to rotations are all larger than those which refer to translations of the molecule. The largest element refers to the rotations about the Z axis (108·9 Å^{-1}), the smallest one to the translations in the direction of the Z axis (15·0 Å^{-2}).

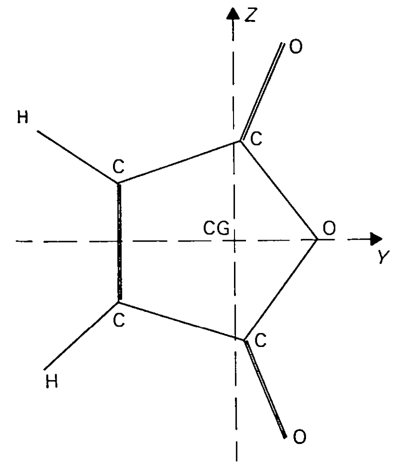

Fig. 1. Position of principal inertial axes in the molecule of maleic anhydride. The positive X axis points upwards from the molecular plane. CG = centre of gravity.

Table 4. *Normalized pseudo-force-constant matrices* $\mathbf{F}_{66}^{\text{norm}}/k_BT = \mathbf{D}_{66}^{-1}$ (Å^{-2}) *for MAL and 5ClN*

The high-temperature approximation with T = 292°K has been used.

MAL						5ClN					
21·6	−2·4	0·3	−2·7	−2·5	5·5	120·2	−43·9	35·9	−6·7	−9·4	56·4
	18·7	1·9	−2·7	1·7	−5·0		46·4	−19·3	10·3	−2·3	−22·8
		15·0	−2·5	−0·5	2·4			45·2	−3·0	20·7	13·8
			35·4	−3·2	5·3				86·8	−33·2	27·0
symmetric				40·2	−0·3	symmetric				201·3	−111·6
					108·9						159·4

Thus the translations are less hindered than the rotations of the molecule. Moreover, vibrations which take place in the plane of the molecule are less hindered and require smaller forces (translations in the Y and Z directions, rotations about the X axis, with pseudo force constants of 18·7, 15·0 and 35·4 Å^{-2} respectively). The greatest forces are required for the rotation about the Z axis. This may, perhaps, be ascribed to the fact that the molecules are arranged in zigzag chains where they may possibly be 'connected' to one another to some extent.

(*d*) 5-*Chloro*-1,4-*naphthoquinone*

This structure is described by Scheringer (1973). The space group is $P2_1/b$, with one molecule in the asymmetric unit. 5ClN is essentially planar. The molecules are packed parallel to one another, the mean perpendicular interplanar distance being 3·51 Å. All intermolecular contacts are of the van der Waals type. The arrangement of the molecules in the crystal is shown in Figs. 2 and 3 of Scheringer (1973). The normal to the molecular planes is inclined by 26° to **a**. In the **a** direction the crystals grow as needles.

With 5ClN the **S** tensor also proved to be highly significant compared to the origin parameters **X**. The corresponding refinement yielded R values of 8·45 and 9·04% respectively so that the parameters **X** could be rejected below the 0·005 level of significance. The numerical data for the description of the rigid-body thermal motions are listed in Tables 2, 3, and 4. Two of the principal axes, referred to the centre of gravity, are located in the plane of the molecule; their position is indicated in Fig. 2.

The magnitudes of the correlation coefficients μ_i are all smaller than 0·17, *cf.* Table 3, and thus we have not tried to relate the resulting screw translations and rotations to the geometrical arrangement of the molecules in the crystal.

For 5ClN L_{33} is particularly large (20·2 deg^2), but I_3 is particularly small (443·69 mole Å^2) because the Z axis is close to the chlorine atom, *cf.* Fig. 2. Hence the mass-normalized components L_{ii} are rather similar. The pseudo force constants are computed in the high-temperature approximation, *cf.* Table 4. As for MAL, for 5ClN the diagonal pseudo force constants referring to rotations are, with one exception, larger than those referring to translations. But for 5ClN the pseudo-force-constant matrix is not even approximately diagonal. The pseudo force constants for the translations in the plane of the molecule are the smallest ones (46·4 and 45·2 Å^{-2}). The constants, which refer to vibrations which would loosen the packing of the molecules (translations along the X axis, librations about the Y and Z axes), are much larger (120·2, 201·3, and 159·4 Å^{-2} respectively); these motions are hindered most. The large values of the pseudo force constants are in agreement with the following structural features.

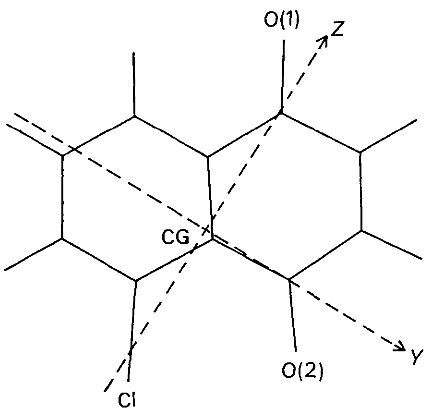

Fig. 2. Position of principal inertial axes in the molecule of 5-chloro-1,4-napthoquinone. The positive X axis points upwards from the molecular plane. CG = centre of gravity.

(1) In the X direction the molecules are packed parallel, with the short perpendicular interplanar distance of 3·51 Å,

(2) In the **a** direction the crystals grow as needles. Considering the off-diagonal terms of the pseudo-force-constant matrix we see that the translations are coupled to each other as well as the rotations. However the motions of the molecule cannot be separated into translations and rotations as is shown by the large coupling constant of 56·4 Å^{-2} for the translations along the X axis and the rotations about the Z axis. Thus the principal motions of the molecule cannot be attributed to any of the motions with respect to a principal inertial axis. The pseudo force constants for the principal motions are 24·0, 27·3, 45·1, 78·2, 171·4, and 313·3 Å^{-2} respectively. Obviously the librations about the Y and Z axes contribute mainly to the principal motions with the two largest constants. Thus, to a rough approximation, the six principal motions of the molecule consist of two librations, which loosen the stacks of the molecules perpendicular to the molecular plane, of two translations within the plane of the molecule, and of two mixed translation–rotational types of motions, which cannot be specified with respect to the geometrical arrangement of the molecules in the structure.

(*e*) *Comparison of MAL and 5ClN*

For both MAL and 5ClN the pseudo force constants for the translations are smaller than those for the librations. This seems to be a fairly general phenomenon in molecular crystals, at least for non-spherical molecules, *cf.* Scheringer (1972*d*). Also Davydov (1962, p. 12) states that the translation frequencies in a crystal are usually smaller than the rotational ones. The reason probably is that the molecules almost exclusively execute translations in the low-frequency acoustic modes, in which the molecules largely vibrate in phase thus employing the intermolecular forces only to a minor extent [*cf.*, *e.g.*, Pawley's (1967) dispersion curves for naphthalene and anthracene].

For 5ClN the diagonal pseudo force constants are markedly larger than those for MAL. In particular, the constant referring to the translations along the X axis (perpendicular to the molecular planes) is even larger ($120{\cdot}2$ Å^{-2}) than the largest rotational pseudo force constant of MAL ($108{\cdot}9$ Å^{-2}); and the largest constant referring to a principal motion of the 5ClN molecule ($313{\cdot}3$ Å^{-2}) is almost three times as large as the largest constant of MAL. These thermal data reflect the fact that the arrangement of the molecules in the two structures is fundamentally different. In the MAL structure the molecular planes are inclined at an angle to one another, in the 5ClN structure the molecules are aligned parallel. The MAL structure is built up more loosely than the 5ClN structure. Thus our interpretation of the rigid-body thermal motions with the aid of the pseudo-forceconstant matrices not only seems to give reasonable results for each structure but also when we compare the two structures.

I am indebted to Dr N. Brodherr and Dr J. Gassmann, München, for pointing out to me the coupling terms in the kinetic-energy matrix.

APPENDIX

Proof that the mean-square-amplitude matrix C is positive definite

We refer to equation (2.19) in which the matrices $\{\mathbf{R}\boldsymbol{\Lambda}^{-1}\boldsymbol{\Gamma}\tilde{\mathbf{R}}\}_{\mathbf{q}}$ are Hermitian and positive definite because they have the eigenvalues $\{\boldsymbol{\Lambda}^{-1}\boldsymbol{\Gamma}\}_{\mathbf{q}}$. The sum of two Hermitian and positive definite matrices is also positive definite, see below. Hence $\sum_{\mathbf{q}}\{\mathbf{R}\boldsymbol{\Lambda}^{-1}\boldsymbol{\Gamma}\tilde{\mathbf{R}}\}_{\mathbf{q}}$ is positive definite. The congruence transformation with the matrix $\mathbf{G}$ does not change the signature of the matrix. Hence $\mathbf{C}$ has positive eigenvalues only.

Let $\mathbf{A}_1$ and $\mathbf{A}_2$ be Hermitian and positive definite, then the sum matrix

$$\mathbf{A}_1+\mathbf{A}_2=\mathbf{A}_3 \qquad (A1)$$

is also Hermitian. Hence a unitary matrix $\mathbf{B}$ exists which diagonalizes $\mathbf{A}_3$. From equation ($A1$) we obtain

$$\tilde{\mathbf{B}}\mathbf{A}_1\mathbf{B}+\tilde{\mathbf{B}}\mathbf{A}_2\mathbf{B}=\tilde{\mathbf{B}}\mathbf{A}_3\mathbf{B}=\boldsymbol{\Lambda}\ \text{(diagonal)}. \qquad (A2)$$

Since $\mathbf{B}$ is unitary and $\mathbf{A}_1$ and $\mathbf{A}_2$ are positive definite, the transformed matrices on the left-hand side of equation ($A2$) have positive diagonal elements only. Hence each eigenvalue of $\mathbf{A}_3$ is the sum of two positive elements and is thus positive.

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