

## Temperature Factors for Large Librations of Molecules. Expressions in a General Crystal Metric and for Any Site Symmetry

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With large librations of molecules, the anharmonic contributions to the temperature factors of the atoms are described by means of the cumulant expansion of the temperature factor. This is done for a general crystal metric and for any (no) site symmetry of the molecule. Two assumptions are made: (1) The librations of the molecule are harmonic. (2) There is one point  $-\mathbf{p}$  in the molecule which can be chosen as the coordinate origin, and for which the translations of the molecule are simultaneously harmonic. The cumulants are calculated up to and including the fourth moments of librations and translations, and are represented as functions of the translation tensor  $\mathbf{T}$ , the libration tensor  $\mathbf{L}$ , the correlation tensor  $\mathbf{S}$  and the coordinate origin  $-\mathbf{p}$ . The TLSp model of the rigid-body motions for large librations contains 24 parameters which can be determined from diffraction data.

### 1. Introduction

With large librations of molecules, the atoms do not move along a straight line through their equilibrium position, but rather along a circle. Hence, in this case, the harmonic approximation of the nuclear motions no longer holds, and the temperature factors must be formulated so as also to contain the anharmonic contributions of the nuclear motions. This was first done by Willis & Pawley (1970) and Pawley & Willis (1970) – hereinafter referred to as P & W. P & W derived the temperature factor by calculating the thermal average  $\langle \exp 2\pi i \mathbf{h} \cdot \mathbf{u} \rangle$ . This approach is cumbersome, and its use imposes the following limitations on their result: (1) The equations are only valid in that Cartesian coordinate system in which the libration tensor  $\mathbf{L}$  is diagonal. (2) The molecule must have site symmetry  $\bar{1}$ . (3) The translations  $\mathbf{t}$  and the librations  $\omega$  of the (rigid) molecule are harmonic, *i.e.* they are Gaussian distributed. (4) The atomic motions are expressed up to and including the fourth moments of the librations  $\omega$ .

The first limitation was eased by Johnson (1970*a*) who gave a formulation which is valid in any Cartesian coordinate system.

The limitations (1) and (2) are stringent in actual practice, and we shall eliminate them in this paper; *i.e.* we shall derive temperature factors of the atoms for large librations of molecules in a general crystal metric and for any (no) site symmetry. The limitation (3) can also be eliminated in principle, but not in practice, since then there are so many parameters that they cannot be determined in a refinement. The limitation (4) could also be weakened by employing the methods used in this paper, and the anharmonic contributions could be collected up to sixth moments of  $\mathbf{t}$

and  $\omega$ , but the expressions obtained would be very lengthy. In view of the present experimental accuracy, we do not consider the limitations (3) and (4) to be stringent and we shall retain them.

In this paper we make use of the cumulant expansion of the temperature factor (Johnson, 1969, 1970*a,b*). In an earlier work (Scheringer, 1977) we showed that lattice dynamical calculations suggest that the cumulant expansion is the formally correct means for taking into account anharmonic contributions to the temperature factor. Hence, in this paper, we have only to determine the cumulants of the nuclear displacements for large librations of molecules. Since the cumulants are tensors and, hence, their transformation properties known, they can be expressed in every coordinate system. For this reason we shall be able to formulate our equations in a general crystal metric.

### 2. Librations expressed in a general metric

The amplitude  $\mathbf{u}$  of an atom at a position  $\mathbf{x}$  with a large libration about a fixed origin is given by Schomaker & Trueblood (1968), Willis & Pawley (1970) and Johnson (1970*a*), for a Cartesian coordinate system. In matrix notation it is

$$\begin{aligned} \mathbf{u} &= (\alpha \mathbf{V}_{\text{Cart}} - \beta \mathbf{V}_{\text{Cart}} \mathbf{V}_{\text{Cart}}^T) \mathbf{x}_{\text{Cart}} \\ \alpha &= (\sin \omega) / \omega, \quad \beta = (1 - \cos \omega) / \omega^2, \\ \omega^2 &= \omega_x^2 + \omega_y^2 + \omega_z^2, \\ \mathbf{V}_{\text{Cart}} &= \begin{pmatrix} 0 & -\omega_z & \omega_y \\ \omega_z & 0 & -\omega_x \\ -\omega_y & \omega_x & 0 \end{pmatrix}. \end{aligned} \quad (2.1)$$

The origin of libration is defined by the atomic coordinates  $\mathbf{x}$ . We obtain (2.1) in a general metric if we transform from an orthonormal basis to a general basis. Let the transformation of the base vectors be defined by

$$\mathbf{a}_{\text{cell}} = \mathbf{G}^{T-1} \mathbf{a}_{\text{Cart}}. \quad (2.2)$$

Let  $\mathbf{E}$  be the unit matrix,  $\mathbf{g}$  the metric tensor of direct space,  $\mathbf{g}^*$  the metric tensor of reciprocal space,  $\mathbf{x}$  the contravariant components of the position vector in direct space, then we have  $\mathbf{g}_{\text{Cart}} = \mathbf{g}_{\text{Cart}}^* = \mathbf{E}$ , and

$$\begin{aligned} \mathbf{g}_{\text{cell}} &= \mathbf{G}^{T-1} \mathbf{G}^{-1}, & \mathbf{g}_{\text{cell}}^* &= \mathbf{g}_{\text{cell}}^{-1} = \mathbf{G} \mathbf{G}^T, \\ \mathbf{x}_{\text{cell}} &= \mathbf{G} \mathbf{x}_{\text{Cart}}, \end{aligned} \quad (2.3)$$

and

$$\boldsymbol{\omega}_{\text{cell}} = \mathbf{G}^{T-1} \boldsymbol{\omega}_{\text{Cart}} \text{sign}(\det \mathbf{G}), \quad (2.4a)$$

$$\mathbf{V}_{\text{cell}} = \mathbf{G} \mathbf{V}_{\text{Cart}} \mathbf{G}^T. \quad (2.4b)$$

$\mathbf{V}$  transforms doubly contravariant to the basis  $\mathbf{a}$ . By comparison of (2.4a) and (2.4b) we obtain the result that the components of  $\mathbf{V}_{\text{cell}}$  are equal to the components  $\boldsymbol{\omega}_{\text{cell}}$  ( $\det \mathbf{g}$ )<sup>-1/2</sup> (which are covariant to the basis  $\mathbf{a}$ ) (Hirshfeld & Rabinovich, 1966). In the following we omit the subscript 'cell', since we shall refer all equations to the crystal basis  $\mathbf{a}$ . With (2.1-4) we obtain for the contravariant components of the vibration amplitudes

$$\mathbf{u} = \alpha \mathbf{V} \mathbf{g} \mathbf{x} - \beta \mathbf{V} \mathbf{g} \mathbf{V}^T \mathbf{g} \mathbf{x}, \quad (2.5)$$

and

$$\omega^2 = \boldsymbol{\omega}^T \mathbf{g}^* \boldsymbol{\omega} = \text{trace}(\mathbf{g}^* \boldsymbol{\omega} \boldsymbol{\omega}^T). \quad (2.6)$$

An important auxiliary relation which we shall often use to evaluate the first term of (2.5), is given by

$$\mathbf{V} \mathbf{g} \mathbf{x} = -\mathbf{V}_x \boldsymbol{\omega}. \quad (2.7)$$

$\mathbf{V}_x$  is an antisymmetric tensor such as  $\mathbf{V}$ , and contains the components  $\mathbf{g} \mathbf{x}$  ( $\det \mathbf{g}$ )<sup>-1/2</sup>. A further relation, which we shall use to evaluate the second term in (2.5), is given by

$$\begin{aligned} \mathbf{V} \mathbf{g} \mathbf{V}^T &= \mathbf{g}^* \text{trace}(\mathbf{g}^* \boldsymbol{\omega} \boldsymbol{\omega}^T) - \mathbf{g}^* \boldsymbol{\omega} \boldsymbol{\omega}^T \mathbf{g}^* \\ &= \mathbf{g}^* \boldsymbol{\omega}^T \mathbf{g}^* \boldsymbol{\omega} - \mathbf{g}^* \boldsymbol{\omega} \boldsymbol{\omega}^T \mathbf{g}^*. \end{aligned} \quad (2.8)$$

The coefficients  $\alpha$  and  $\beta$  in (2.5) have to be expanded into a series in order to enable us to evaluate the moments of  $\mathbf{u}$ . Hence,

$$\begin{aligned} \alpha &= (\sin \omega) \omega = 1 - \frac{1}{3!} \omega^2 + \frac{1}{5!} \omega^4 - \dots, \\ \beta &= (1 - \cos \omega) / \omega^2 = \frac{1}{2!} - \frac{1}{4!} \omega^2 + \frac{1}{6!} \omega^4 - \dots \end{aligned} \quad (2.9)$$

### 3. The cumulant expansion of the temperature factor

With anharmonic motions the temperature factor should be represented by the cumulant expansion (Johnson, 1969, 1970a,b; Scheringer, 1977), *i.e.*

$$\begin{aligned} T(\mathbf{h}) &= \exp \left[ 2\pi i \sum_i {}^1\kappa^i h_i + \frac{(2\pi i)^2}{2!} \sum_{ij} {}^2\kappa^{ij} h_i h_j \right. \\ &\quad + \frac{(2\pi i)^3}{3!} \sum_{ijk} {}^3\kappa^{ijk} h_i h_j h_k \\ &\quad \left. + \frac{(2\pi i)^4}{4!} \sum_{ijkl} {}^4\kappa^{ijkl} h_i h_j h_k h_l + \dots \right]. \end{aligned} \quad (3.1)$$

The cumulants  $\kappa$  in (3.1) refer to the atomic displacements  $\mathbf{u}$  and are tensors. With reference to a crystal basis,  $h_i, h_j, h_k, h_l$  are the Miller indices,  $\mathbf{h}$  denotes an index-triple. The cumulants can be calculated from the moments of  $\mathbf{u}$ , which we denote by angle brackets. We have

$$\begin{aligned} {}^1\kappa^i &= \langle u^i \rangle, & {}^2\kappa^{ij} &= \langle u^i u^j \rangle - \langle u^i \rangle \langle u^j \rangle, \\ {}^3\kappa^{ijk} &= \langle u^i u^j u^k \rangle - \langle u^i \rangle \langle u^j u^k \rangle - \langle u^j \rangle \langle u^i u^k \rangle \\ &\quad - \langle u^k \rangle \langle u^i u^j \rangle + 2 \langle u^i \rangle \langle u^j \rangle \langle u^k \rangle; \quad i, j, k = 1, 2, 3; \end{aligned} \quad (3.2)$$

(Johnson, 1970a,b). The fourth cumulant is also given by Johnson; we do not include it here, since it is zero in the approximations (3) and (4) of § 1.

Before we attack our main problem, which consists of expressing the cumulants of  $\mathbf{u}$  by the moments of  $\boldsymbol{\omega}$  and  $\mathbf{t}$ , we list the moments of  $\boldsymbol{\omega}$  and  $\mathbf{t}$ . Here the approximation (3) of § 1 is an important help. With the Gaussian distribution of  $\boldsymbol{\omega}$  and  $\mathbf{t}$ , all odd moments of  $\boldsymbol{\omega}$  and  $\mathbf{t}$  vanish, and the even moments are the central moments. The second moments are the libration and translation tensors respectively

$$\langle \boldsymbol{\omega} \boldsymbol{\omega}^T \rangle = \mathbf{L}, \quad \langle \mathbf{t} \mathbf{t}^T \rangle = \mathbf{T}, \quad (3.3)$$

and the second mixed moment is the correlation tensor

$$\langle \boldsymbol{\omega} \mathbf{t}^T \rangle = \mathbf{S}, \quad \langle \omega_i t^j \rangle = S_i^j. \quad (3.4)$$

The fourth moments can be calculated from the second cumulants of  $\boldsymbol{\omega}$  and  $\mathbf{t}$ , *i.e.* from  $\mathbf{T}$ ,  $\mathbf{L}$  and  $\mathbf{S}$ . Generalizing the expressions given by Kendall & Stuart (1969) and Johnson (1970a), we find

$$\begin{aligned} \langle \omega_i \omega_j \omega_k \omega_l \rangle &= L_{ij} L_{kl} + L_{ik} L_{jl} + L_{il} L_{jk} \\ \langle t^i \omega_j \omega_k \omega_l \rangle &= S_j^i L_{kl} + S_k^i L_{jl} + S_l^i L_{jk} \\ \langle t^i t^j \omega_k \omega_l \rangle &= T^{ij} L_{kl} + S_k^i S_l^j + S_l^i S_k^j \\ \langle t^i t^j t^k \omega_l \rangle &= T^{ij} S_l^k + T^{ik} S_l^j + T^{jk} S_l^i, \end{aligned} \quad (3.5)$$

Since  $i, j, k, l = 1, 2, 3$ , at least two indices in (3.5) must be equal.

Our problem, expressing the cumulants of  $\mathbf{u}$  by the moments of  $\boldsymbol{\omega}$  and  $\mathbf{t}$ , will be solved in three steps. Firstly, we consider the simple case of site symmetry  $\bar{1}$ , for which librations and translations of the molecule are statistically independent (§ 4). In the second step, we set aside the site symmetry of the molecule, but assume a special origin for describing the librations (§ 5). Finally, we also remove this limitation (§ 6).

#### 4. Cumulants for site symmetry $\bar{1}$

Since the centre of symmetry defines the librational origin, we refer the atomic coordinates to it. Then  $\mathbf{S} = \mathbf{0}$ , and the translations are harmonic with our approximation (3) of § 1. The anharmonic contributions to the cumulants of  $\mathbf{u}$  thus arise only from the librations  $\boldsymbol{\omega}$ , and, hence, can be represented as functions of  $\mathbf{L}$ ,  $\mathbf{x}$  and  $\mathbf{V}_x$ . In the following, we do not write out expressions which lead to odd moments of  $\boldsymbol{\omega}$  and, hence, are zero.

For the first cumulant we obtain from (2.5–6) and (2.9)

$${}^1\boldsymbol{\kappa} = \langle \mathbf{u} \rangle = -\frac{1}{2} \langle \mathbf{VgV}^T \rangle \mathbf{gx} + \frac{1}{24} \langle \boldsymbol{\omega}^T \mathbf{g}^* \boldsymbol{\omega} \mathbf{VgV}^T \rangle \mathbf{gx}. \quad (4.1)$$

We use (2.6) and (2.8), calculate the moments with (3.3) and (3.5), and obtain after ordering of terms

$${}^1\boldsymbol{\kappa} = -\frac{1}{2} [\mathbf{E} \text{ trace } (\mathbf{g}^* \mathbf{L}) - \mathbf{g}^* \mathbf{L}] \mathbf{x} + \frac{1}{24} (\mathbf{E} \gamma - \mathbf{g}^* \mathbf{A}) \mathbf{x}, \quad (4.2)$$

$$\gamma = [\text{trace } (\mathbf{g}^* \mathbf{L})]^2 + 2 \text{ trace } (\mathbf{g}^* \mathbf{Lg}^* \mathbf{L}), \quad (4.3)$$

$$\mathbf{A} = \mathbf{L} \text{ trace } (\mathbf{g}^* \mathbf{L}) + 2 \mathbf{Lg}^* \mathbf{L}, \quad \mathbf{A} = \mathbf{A}^T. \quad (4.4)$$

The first cumulant term in (3.1) is  $2\pi i {}^1\boldsymbol{\kappa} \cdot \mathbf{h}$ .

For the second cumulant we obtain with (2.5–6), (2.9) and (3.2)

$${}^2\boldsymbol{\kappa} = \langle (1 - \frac{1}{3} \boldsymbol{\omega}^T \mathbf{g}^* \boldsymbol{\omega}) \mathbf{Vgxx}^T \mathbf{gV}^T \rangle + \frac{1}{4} \langle \mathbf{VgV}^T \mathbf{gxx}^T \mathbf{gVgV}^T \rangle - \langle \mathbf{u} \rangle \langle \mathbf{u}^T \rangle. \quad (4.5)$$

We use (2.6–8), calculate the moments with (3.3) and (3.5), and finally obtain with  $\mathbf{A}$  of (4.4)

$${}^2\boldsymbol{\kappa} = \mathbf{V}_x (\mathbf{L} - \frac{1}{3} \mathbf{A}) \mathbf{V}_x^T + \frac{1}{2} [\mathbf{xx}^T \text{ trace } (\mathbf{g}^* \mathbf{Lg}^* \mathbf{L}) - \mathbf{xx}^T \mathbf{Lg}^* \mathbf{Lg}^* - (\mathbf{xx}^T \mathbf{Lg}^* \mathbf{Lg}^*)^T + \frac{1}{2} \mathbf{g}^* (\mathbf{Lx}^T \mathbf{Lx} + \mathbf{Lxx}^T \mathbf{L}) \mathbf{g}^*]. \quad (4.6)$$

The term  $\mathbf{V}_x \mathbf{LV}_x^T$  in (4.6) is due to the harmonic approximation. The second cumulant term in (3.1) is  $-2\pi^2 \mathbf{h}^T {}^2\boldsymbol{\kappa} \mathbf{h}$ .

Since there are three indices with the third cumulant, we cannot here fully express our equations in matrix notation. However, we still use it as far as possible. With (2.5), (2.9) and (3.2) we obtain

$${}^3\boldsymbol{\kappa}^{ijk} = \{-\frac{1}{2} \langle (\mathbf{Vgx})^i (\mathbf{Vgx})^j (\mathbf{VgV}^T \mathbf{gx})^k \rangle - \langle u^i u^j \rangle \langle u^k \rangle + \{jki\} + \{kij}\}. \quad (4.7)$$

With  $\{jki\} + \{kij\}$  we denote the two equivalent terms with indices interchanged. We use (2.7–8), calculate the moments with (3.3) and (3.5), and obtain after re-ordering of terms

$${}^3\boldsymbol{\kappa}^{ijk} = \{-\mathbf{V}_x \mathbf{Lg}^* \mathbf{LV}_x^T\}^{ij} x^k + \frac{1}{2} (\mathbf{V}_x \mathbf{B}^k \mathbf{V}_x^T)^{ij} + \{jki\} + \{kij\}, \quad (4.8)$$

where the symmetric  $3 \times 3$  matrix  $\mathbf{B}^k$  means

$$\mathbf{B}^k = (\mathbf{Lg}^*)^k \mathbf{x}^T \mathbf{L} + [(\mathbf{Lg}^*)^k \mathbf{x}^T \mathbf{L}]^T. \quad (4.9)$$

The index  $k$  belongs to the metric tensor  $\mathbf{g}^*$ .  $(\mathbf{Lg}^*)^k$  is a  $3 \times 1$  column matrix, and  $\mathbf{x}^T \mathbf{L}$  a  $1 \times 3$  row matrix. Obviously  $\mathbf{L}$  appears only in the second power in (4.8–9). The threefold summation in the third cumulant term extends itself over 27 terms. Since the indices can be interchanged pairwise, *cf.* (3.2), the summation can be shortened according to the permutations of indices. For the index combination *iii* there is one permutation, for the combinations *ijj* there are three, and for the combinations *ijk* there are six permutations (Johnson, 1970*b*, Table 9.2). Our equations (4.7–8) are valid for *one* permutation of indices.

We shall show that the fourth cumulant is zero in the approximations (3) and (4) of § 1. In these approximations, only the terms  $\mathbf{u} = -\mathbf{V}_x \boldsymbol{\omega}$  make a contribution. Since the relation between  $\mathbf{u}$  and  $\boldsymbol{\omega}$  is linear and  $\boldsymbol{\omega}$  is Gaussian distributed,  $\mathbf{u}$  is also Gaussian distributed. Hence, the fourth cumulant of  $\mathbf{u}$  is zero. P & W and Johnson (1970*a*) also found this result, but by a more complicated term by term analysis of the explicit expression for the fourth cumulant.

In a Cartesian coordinate system ( $\mathbf{g} = \mathbf{g}^* = \mathbf{E}$ ) and  $\mathbf{L}$  being diagonal, our expressions reduce to those found by P & W. Note that in P & W's expressions, the multiplicity, *i.e.* the number of permutations, is accounted for, whereas in ours it is not.

Johnson (1970*a*) remarks that the third mixed moment  $\langle \boldsymbol{\omega} \mathbf{t} \mathbf{t} \rangle$  which represents a correlation term between translations and librations, can also contribute to the cumulants of  $\mathbf{u}$  in the case of the site symmetry  $\bar{1}$ . On the other hand, P & W found by a term analysis that there is no correlation between translations and librations.

We comment: because of the Gaussian distribution of  $\boldsymbol{\omega}$  and  $\mathbf{t}$  the 3rd moment  $\langle \boldsymbol{\omega} \mathbf{t} \mathbf{t} \rangle$  vanishes. Moreover, with site symmetry  $\bar{1}$ , the covariance matrix  $\langle \boldsymbol{\omega} \mathbf{t}^T \rangle = \mathbf{S}$  is zero. For Gaussian distributions, zero covariance means statistical independence. Thus, P & W's result is confirmed. Johnson's result, however, applies if the

translations and/or librations no longer satisfy the harmonic approximation.

P & W point out that the first cumulant, which affects the position of the atom, also contains the bond-length correction. Johnson (1970c) gave the bond-length correction in a general metric. Thus, Johnson's equation (A5) and our (4.2) should give the same result. At first glance, this is not obvious, and here we outline the steps for calculating one result from the other. Johnson lists the libration tensor in contravariant components, but in (4.2) we use covariant components of  $\mathbf{L}$ . Let us denote the vector between the mean atomic positions by  $\mathbf{d}$ , then we obtain from Johnson's (1970c) equations (A4) and (A5), and with  $\mathbf{L}$  covariant,

$$d_{\text{corr}} = d + (2d)^{-1} \mathbf{d}^T \mathbf{g} [\mathbf{E} \text{ trace } (\mathbf{g}^* \mathbf{L}) - \mathbf{g}^* \mathbf{L}] \mathbf{d}. \quad (4.10)$$

Comparison of (4.10) and (4.2) can only be made with the first term of (4.2), where  $\mathbf{L}$  appears in the first power. In (4.2)  $\mathbf{x}$  already denotes the thermally corrected coordinates. In (4.2) and (4.10), the square brackets are equal, and, hence, the two equations give the same result in the linear terms of the libration tensor  $\mathbf{L}$ .

### 5. Cumulants for any site symmetry

In the case of site symmetry  $\bar{1}$ , we have assumed, without further specification, that the translations of the molecule were harmonic. In doing so, it was self-evident that we had to assume  $\bar{1}$  as the coordinate (librational) origin. If  $\bar{1}$  is no longer given, the point is unknown which we have to use as origin and for which we simultaneously assume harmonic translations. Therefore, we reformulate the assumptions (3) and (4) of § 1 as follows: (3a) The librations  $\omega$  are harmonic (as before). (3b) There is one origin of libration (coordinate origin), usually unknown, for which the translations  $\mathbf{t}$  are harmonic. (4) The atomic motions are expressed up to and including the fourth moments of  $\omega$  and  $\mathbf{t}$ . In this section we choose the origin of (3b) as coordinate origin ( $\mathbf{x}$  system). The problems which arise with the choice of another origin will be discussed in § 6.

In the  $\mathbf{x}$  system,  $\omega$  and  $\mathbf{t}$  are Gaussian distributed and, hence, the first and third moments of  $\omega$  and  $\mathbf{t}$  are zero. The second and fourth moments are given in (3.3–5). We have to calculate the cumulants of  $\mathbf{u}$  from the moments (3.3–5). Since  $\langle \mathbf{t} \rangle = \mathbf{0}$ , there are no new contributions to the first cumulant and (4.2–4) are also valid in our more general case. The fourth cumulant of  $\mathbf{u}$  is zero as in the case of site symmetry  $\bar{1}$ : In the approximation (4) we only consider librational contributions  $\mathbf{u}_{\text{lib}} = -\mathbf{V}_x \omega$ . Since  $\omega$  is Gaussian distributed,  $\mathbf{u}_{\text{lib}}$  is also Gaussian distributed and, hence, the fourth cumulant of  $\mathbf{u}$  is zero. There are, however,

new contributions to the second and third cumulant. In order to evaluate them, it is expedient to divide  $\mathbf{u}$  with respect to translations and librations, *i.e.*  $\mathbf{u} = \mathbf{t} + \mathbf{l}$ , and to express the cumulants correspondingly. We use the fact that the second and third cumulants are equal to the central moments, and thus obtain

$${}^2\kappa^{ij} = {}^2\kappa(t^i t^j) + {}^2\kappa(t^i l^j) + {}^2\kappa(l^i t^j) + {}^2\kappa(l^i l^j), \quad (5.1a)$$

$$\begin{aligned} {}^3\kappa^{ijk} = & {}^3\kappa(t^i t^j t^k) + {}^3\kappa(t^i t^j l^k) + {}^3\kappa(t^i l^j t^k) + {}^3\kappa(l^i t^j t^k) \\ & + {}^3\kappa(t^i l^j l^k) + {}^3\kappa(l^i t^j l^k) + {}^3\kappa(l^i l^j t^k) + {}^3\kappa(l^i l^j l^k). \end{aligned} \quad (5.1b)$$

(5.1) is valid in every coordinate system. The pure librational cumulants  ${}^2\kappa(l^i l^j)$  and  ${}^3\kappa(l^i l^j l^k)$  are already known, and calculated from (4.6) and (4.8–9) respectively. Since  $\mathbf{t}$  is Gaussian distributed the pure translation cumulants are also known:  ${}^2\kappa(t^i t^j) = T^{ij}$  is the translation tensor (3.3), and  ${}^3\kappa(t^i t^j t^k) = 0$ . The mixed cumulants in (5.1) are new. Since they differ partially in the assignment of the indices, and since the sequence of the  $t$ 's and  $l$ 's is arbitrary there is only one new cumulant in (5.1a) and two in (5.1b). In matrix notation, we have  ${}^2\kappa(tl) = {}^2\kappa^T(tl)$ . The determination of the three new cumulants in (5.1) forms the remainder of this section.

With  $\langle \mathbf{t} \rangle = \mathbf{0}$ , we obtain with (2.5), (2.9) and (3.2)

$${}^2\kappa(tl) = \langle \mathbf{t} \mathbf{l}^T \rangle = \langle \mathbf{V} \mathbf{g} \mathbf{x} \mathbf{t}^T \rangle - \frac{1}{6} \langle \omega^2 \mathbf{V} \mathbf{g} \mathbf{x} \mathbf{t}^T \rangle. \quad (5.2)$$

We use (2.5–7), (3.4–5) and obtain after reordering of terms

$${}^2\kappa(tl) = -\mathbf{V}_x \mathbf{S} + \frac{1}{6} \mathbf{V}_x \mathbf{S} \text{ trace } (\mathbf{L} \mathbf{g}^*) + \frac{1}{3} \mathbf{V}_x \mathbf{L} \mathbf{g}^* \mathbf{S}. \quad (5.3)$$

The first term in (5.3),  $-\mathbf{V}_x \mathbf{S}$ , is known to be the harmonic contribution. The anharmonic contributions arise from the fourth moment  $\langle \omega_i \omega_j \omega_k t^l \rangle$ , and, hence,  $\mathbf{T}$  does not occur.

For the mixed cumulants in (5.1b) we obtain from (3.2) with  $\langle \mathbf{t} \rangle = \mathbf{0}$

$${}^3\kappa(t^i t^j l^k) = \langle t^i t^j l^k \rangle - \langle l^k \rangle \langle t^i t^j \rangle, \quad (5.4)$$

$${}^3\kappa(t^i l^j l^k) = \langle t^i l^j l^k \rangle - \langle l^j \rangle \langle t^i l^k \rangle - \langle l^k \rangle \langle t^i l^j \rangle. \quad (5.5)$$

With (2.5–6), (2.8–9) and (3.4–5), we obtain for the third moments

$$\begin{aligned} \langle t^i t^j l^k \rangle = & -\frac{1}{2} \langle t^i t^j (\mathbf{V} \mathbf{g} \mathbf{V}^T \mathbf{g} \mathbf{x})^k \rangle \\ = & -\frac{1}{2} \{ T^{ij} x^k \text{ trace } (\mathbf{g}^* \mathbf{L}) + 2(\mathbf{S}^T \mathbf{g}^* \mathbf{S})^{ij} x^k \\ & - T^{ij} (\mathbf{g}^* \mathbf{L} \mathbf{x})^k + (\mathbf{g}^* \mathbf{S})^{ki} (\mathbf{S} \mathbf{x})^j + (\mathbf{g}^* \mathbf{S})^{kj} (\mathbf{S} \mathbf{x})^i \}, \end{aligned} \quad (5.6)$$

$$\begin{aligned}
\langle t^i l^j l^k \rangle &= \frac{1}{2} \langle t^i (\mathbf{V}_x \boldsymbol{\omega})^j (\mathbf{V}_g \mathbf{V}^T \mathbf{g}_x)^k \rangle \\
&+ \frac{1}{2} \langle t^i (\mathbf{V}_x \boldsymbol{\omega})^k (\mathbf{V}_g \mathbf{V}^T \mathbf{g}_x)^j \rangle \\
&= \frac{1}{2} \{ [(\mathbf{V}_x \mathbf{S})^{ji} \text{trace}(\mathbf{g}^* \mathbf{L}) + 2(\mathbf{V}_x \mathbf{L} \mathbf{g}^* \mathbf{S})^{ji}] x^k \\
&- (\mathbf{V}_x \mathbf{S})^{ji} (\mathbf{g}^* \mathbf{L}_x)^k + (\mathbf{V}_x \mathbf{L} \mathbf{g}^*)^{jk} (\mathbf{S}_x)^i \\
&+ (\mathbf{V}_x \mathbf{L}_x)^j (\mathbf{g}^* \mathbf{S})^{ki} \} + \frac{1}{2} \{ kij \}. \quad (5.7)
\end{aligned}$$

The bracket  $\{kij\}$  is equivalent to the first bracket, but with indices  $j$  and  $k$  interchanged. In (5.4) and (5.5) we multiply out the first and second moments up to fourth-order terms, and finally obtain with (4.2–4) and (5.3–7):

$$\begin{aligned}
{}^3\kappa(t^i t^j l^k) &= -\frac{1}{2} \{ 2(\mathbf{S}^T \mathbf{g}^* \mathbf{S})^{ij} x^k \\
&+ (\mathbf{g}^* \mathbf{S})^{ki} (\mathbf{S}_x)^j + (\mathbf{g}^* \mathbf{S})^{kj} (\mathbf{S}_x)^i \}, \quad (5.8) \\
{}^3\kappa(t^i l^j l^k) &= \frac{1}{2} \{ 2[(\mathbf{V}_x \mathbf{L} \mathbf{g}^* \mathbf{S})^{ji} x^k + (\mathbf{V}_x \mathbf{L} \mathbf{g}^* \mathbf{S})^{ki} x^j] \\
&- \{ (\mathbf{V}_x \mathbf{L} \mathbf{g}^*)^{jk} + (\mathbf{V}_x \mathbf{L} \mathbf{g}^*)^{kj} \} (\mathbf{S}_x)^i \\
&+ (\mathbf{V}_x \mathbf{L}_x)^j (\mathbf{g}^* \mathbf{S})^{ki} + (\mathbf{V}_x \mathbf{L}_x)^k (\mathbf{g}^* \mathbf{S})^{ji} \}. \quad (5.9)
\end{aligned}$$

(5.8) is symmetric in  $i$  and  $j$ , and (5.9) in  $j$  and  $k$ .  ${}^3\kappa(ttl)$  depends only on  $\mathbf{S}$ , and  ${}^3\kappa(ill)$  on  $\mathbf{L}$  and  $\mathbf{S}$ . All the mixed cumulants vanish for  $\mathbf{S} = \mathbf{0}$  (site symmetry  $\bar{1}$ ), which is as it should be.

## 6. Arbitrary origin of libration

In § 5 the coordinate origin was fixed at the point for which we assume with (3b) that the translations of the molecule are harmonic ( $\mathbf{x}$  system). Since this point is generally unknown, one cannot work with the  $\mathbf{x}$  system in practice. Thus, we have to look for a more general description. For this purpose, we define another coordinate system, the  $\mathbf{y}$  system, and in this system we define the origin for which we assume harmonic translations by means of the vector  $\boldsymbol{\rho}$ . Then the coordinates of the  $\mathbf{x}$  and  $\mathbf{y}$  systems transform into each other by

$$\mathbf{x} - \boldsymbol{\rho} = \mathbf{y}, \quad \mathbf{y} + \boldsymbol{\rho} = \mathbf{x}. \quad (6.1)$$

The  $\mathbf{y}$  system can be chosen arbitrarily (e.g. the crystal system). The tensors  $\mathbf{T}$  and  $\mathbf{S}$  of § 5 now refer to the point  $-\boldsymbol{\rho}$ .† Our task consists of expressing the cumulants of  $\mathbf{u}$  as functions of  $\mathbf{T}$ ,  $\mathbf{S}$  and the vector  $\boldsymbol{\rho}$ . Here we make use of the invariance conditions which require the displacement vectors  $\mathbf{u}$  and the cumulants of  $\mathbf{u}$  to be equal in every coordinate system. We abbreviate (2.5) as  $\mathbf{u}(\text{lib}) = \mathbf{D}\mathbf{x}$ , and obtain the conditions

$$\mathbf{u} = \mathbf{t}_x + \mathbf{D}\mathbf{x} = \mathbf{t}_y + \mathbf{D}\mathbf{y}, \quad \boldsymbol{\kappa}_x = \boldsymbol{\kappa}_y, \quad (6.2)$$

† The transformation (6.1) of the origin is defined in accordance with that used by Schomaker & Trueblood (1968), Johnson (1970a) and Scheringer (1973). This definition implies that, in the  $\mathbf{y}$  system, the point for which we assume the translations to be harmonic, is given by  $-\boldsymbol{\rho}$ .

for all cumulants of  $\mathbf{u}$ . With (6.1–2), we obtain the further transformations

$$\mathbf{t}_y = \mathbf{t}_x + \mathbf{D}\boldsymbol{\rho}, \quad \boldsymbol{\omega}_y = \boldsymbol{\omega}_x = \boldsymbol{\omega}, \quad \mathbf{L}_y = \mathbf{L}_x = \mathbf{L}. \quad (6.3)$$

Hence,  $\boldsymbol{\omega}$  and  $\mathbf{L}$  are independent of the chosen origin, but  $\mathbf{t}$  is not. With our assumption (3b),  $\mathbf{t}_x$  is Gaussian distributed, but, because of the term  $\mathbf{D}\boldsymbol{\rho}$ ,  $\mathbf{t}_y$  is not. It is this fact that causes the complications of the description in the  $\mathbf{y}$  system. Thus, we expect that the third cumulant of the pure translations no longer vanishes. Since the fourth cumulant of  $\mathbf{u}$  is zero in the  $\mathbf{x}$  system, it is also zero in the  $\mathbf{y}$  system.

The cumulants of  $\mathbf{u}$  will also be derived from (5.1). But now we have to insert  $\mathbf{t}_y = \mathbf{t}_x + \mathbf{D}\boldsymbol{\rho}$  for the translations, and  $\mathbf{D}\mathbf{y}$  for the librations. Since the terms  $\mathbf{D}\boldsymbol{\rho}$  which occur in the translations are formally librations, which we have to distinguish from the librations  $\mathbf{D}\mathbf{y}$ , we use the notation

$$(\mathbf{D}\mathbf{y})^i = l^i(\mathbf{y}), \quad (\mathbf{D}\boldsymbol{\rho})^i = l^i(\boldsymbol{\rho}), \quad i = 1, 2, 3. \quad (6.4)$$

Moreover, we omit the subscript  $x$  for denoting the  $\mathbf{x}$  system, i.e. we put  $\mathbf{t}_x = \mathbf{t}$ . In order to evaluate the translational parts in the cumulants, we again use the fact that the second and third cumulants are equal to the respective central moments. Since with (6.2–3) there are only moments and cumulants of  $\mathbf{t}$ ,  $\mathbf{D}\boldsymbol{\rho}$  and  $\mathbf{D}\mathbf{y}$ , it will be possible to express the cumulants in the  $\mathbf{y}$  system by those of the  $\mathbf{x}$  system. Hence, we can use fully the equations of §§ 4 and 5, but we will have to replace  $\mathbf{x}$  by  $\mathbf{y}$  and  $\boldsymbol{\rho}$  respectively. The determination of the cumulants in the  $\mathbf{y}$  system forms the remainder of this section.

For the first cumulant we find with (6.2–3) and  $\langle \mathbf{t} \rangle = \mathbf{0}$

$${}^1\boldsymbol{\kappa} = \langle \mathbf{l}(\boldsymbol{\rho}) \rangle + \langle \mathbf{l}(\mathbf{y}) \rangle = {}^1\boldsymbol{\kappa}(\boldsymbol{\rho}) + {}^1\boldsymbol{\kappa}(\mathbf{y}), \quad (6.5)$$

where  ${}^1\boldsymbol{\kappa}$  is calculated from (4.2), with  $\boldsymbol{\rho}$  and  $\mathbf{y}$  in place of  $\mathbf{x}$ . (6.5) simply corresponds to (6.1).

For the first term in (5.1a) we find with (6.3–4)

$$\begin{aligned}
{}^2\kappa(t_y^i t_y^j) &= {}^2\kappa(t^i t^j) + {}^2\kappa[l^i l^j(\boldsymbol{\rho})] \\
&+ {}^2\kappa[l^i(\boldsymbol{\rho}) t^j] + {}^2\kappa[l^i(\boldsymbol{\rho}) l^j(\boldsymbol{\rho})]. \quad (6.6)
\end{aligned}$$

The first term in (6.6) is the tensor  $\mathbf{T}$ ; the following two terms are obtained from (5.3), and the final term from (4.6), with  $\boldsymbol{\rho}$  in place of  $\mathbf{x}$ .

For the mixed terms in (5.1a) we find with (6.2–4)

$${}^2\kappa(t_y^i l_y^j) = {}^2\kappa[t^i l^j(\mathbf{y})] + {}^2\kappa[l^i(\boldsymbol{\rho}) l^j(\mathbf{y})]. \quad (6.7)$$

The first term in (6.7) is obtained from (5.3), with  $\mathbf{y}$  in place of  $\mathbf{x}$ ; the second term from (4.6) with  $\boldsymbol{\rho}$  in the first and  $\mathbf{y}$  in the second position.

The fourth term in (5.1a) is

$${}^2\kappa(l_y^i l_y^j) = {}^2\kappa[l^i(\mathbf{y}) l^j(\mathbf{y})], \quad (6.8)$$

and is obtained from (4.6), with  $\mathbf{y}$  in place of  $\mathbf{x}$ .

For the third cumulant we obtain for the pure translation term [first term in (5.1b)] with (6.3–4)

$$\begin{aligned} {}^3\kappa(t_y^i, t_y^j, t_y^k) &= {}^3\kappa[l^i l^j l^k(\rho)] \\ &+ {}^3\kappa[l^i l^j(\rho) t^k] + {}^3\kappa[l^i(\rho) t^j t^k] \\ &+ {}^3\kappa[t^i l^j(\rho) l^k(\rho)] + {}^3\kappa[l^i(\rho) t^j l^k(\rho)] \\ &+ {}^3\kappa[l^i(\rho) l^j(\rho) t^k] + {}^3\kappa[l^i(\rho) l^j(\rho) l^k(\rho)]. \end{aligned} \quad (6.9)$$

The mixed terms in (6.9) are obtained from (5.8–9), the pure libration term from (4.8–9), with  $\rho$  in place of  $\mathbf{x}$ .

For the  $ttl$  terms in (5.1b), we find with (6.2–4)

$$\begin{aligned} {}^3\kappa(t_y^i, t_y^j, l_y^k) &= {}^3\kappa[l^i l^j l^k(\mathbf{y})] + {}^3\kappa[l^i l^j(\rho) l^k(\mathbf{y})] \\ &+ {}^3\kappa[l^i(\rho) l^j(\mathbf{y})] + {}^3\kappa[l^i(\rho) l^j(\rho) l^k(\mathbf{y})]. \end{aligned} \quad (6.10)$$

The first term in (6.10) is obtained from (5.8), with  $\mathbf{y}$  in place of  $\mathbf{x}$ ; the following two terms from (5.9), where  $\mathbf{y}$  is connected with the index  $k$ , and  $\rho$  with the index  $j$  or  $i$ . The final term in (6.10) is obtained from (4.8–9), where  $\mathbf{y}$  is connected with  $k$ , and  $\rho$  with  $i$  and  $j$ .

For the  $lll$  terms in (5.1b), we find with (6.2–4)

$$\begin{aligned} {}^3\kappa(l_y^i, l_y^j, l_y^k) &= {}^3\kappa[l^i l^j l^k(\mathbf{y})] \\ &+ {}^3\kappa[l^i(\rho) l^j(\mathbf{y}) l^k(\mathbf{y})]. \end{aligned} \quad (6.11)$$

The two terms in (6.11) are obtained from (5.9) and (4.8–9) respectively, with the corresponding substitutions for  $\mathbf{x}$ .

The pure librational contribution in (5.1b) is simply

$${}^3\kappa(l_y^i, l_y^j, l_y^k) = {}^3\kappa[l^i l^j l^k(\mathbf{y})], \quad (6.12)$$

and is obtained from (4.8–9) with  $\mathbf{y}$  in place of  $\mathbf{x}$ .

## 7. T and S in the y system

It has been shown that in the  $\mathbf{y}$  system the translations of the molecule are anharmonic, *cf.* (6.3). In this section we shall analyse the anharmonic contributions of  $\mathbf{T}$  and  $\mathbf{S}$  and see how much the centre of reaction (Schomaker & Trueblood, 1968; Johnson, 1970a) will become displaced by the anharmonic contributions to the  $\mathbf{S}$  tensor.

The translation tensor in the  $\mathbf{y}$  system is given by

$$\mathbf{T}_y = \langle \mathbf{t}_y, \mathbf{t}_y^T \rangle = {}^2\kappa(tl) + \langle l(\rho) \rangle \langle l^T(\rho) \rangle. \quad (7.1)$$

The harmonic contribution to  $\mathbf{T}_y$  is

$$\mathbf{T}_y^{\text{harm}} = \mathbf{T} - \mathbf{V}_\rho \mathbf{S} - (\mathbf{V}_\rho \mathbf{S})^T + \mathbf{V}_\rho \mathbf{L} \mathbf{V}_\rho^T, \quad (7.2)$$

in agreement with expressions derived previously (Schomaker & Trueblood, 1968; Scheringer, 1973). If

we also determine the purely anharmonic contribution in (7.1) we can write

$$\mathbf{T}_y = \mathbf{T}_y^{\text{harm}} + \mathbf{T}_y^{\text{anh}}, \quad (7.3)$$

with

$$\begin{aligned} \mathbf{T}_y^{\text{anh}} &= -\frac{1}{3} \mathbf{V}_\rho \mathbf{A} \mathbf{V}_\rho^T + \frac{1}{4} \{ \rho \rho^T \gamma - \rho \rho^T \mathbf{A} \mathbf{g}^* \\ &- (\rho \rho^T \mathbf{A} \mathbf{g}^*)^T + \mathbf{g}^* (\mathbf{L} \rho^T \mathbf{L} \rho + 2 \mathbf{L} \rho \rho^T \mathbf{L}) \mathbf{g}^* \} \\ &+ \frac{1}{6} \text{trace}(\mathbf{L} \mathbf{g}^*) [\mathbf{V}_\rho \mathbf{S} + (\mathbf{V}_\rho \mathbf{S})^T] \\ &+ \frac{1}{3} [\mathbf{V}_\rho \mathbf{L} \mathbf{g}^* \mathbf{S} + (\mathbf{V}_\rho \mathbf{L} \mathbf{g}^* \mathbf{S})^T], \end{aligned} \quad (7.4)$$

where  $\gamma$  and  $\mathbf{A}$  are obtained from (4.3–4). The transformation of  $\mathbf{T}$  from the  $\mathbf{x}$  into the  $\mathbf{y}$  system is contained in (7.3), if we insert (7.2) and (7.4). This transformation is no longer linear in  $\mathbf{L}$  and  $\mathbf{S}$  as in the harmonic case (7.2) but is quadratic in our approximation (4). The anharmonic contribution arises from the fourth moments of  $\omega$  and  $\mathbf{t}$ , and vanishes for  $\rho = \mathbf{0}$ .

The  $\mathbf{S}$  tensor in the  $\mathbf{y}$  system is given by

$$\mathbf{S}_y = \langle \omega \mathbf{t}_y^T \rangle = \langle \omega \mathbf{t}^T \rangle + \langle \omega l^T(\rho) \rangle. \quad (7.5)$$

Evaluation of the moments leads to

$$\mathbf{S}_y = \mathbf{S} + [\mathbf{E} - \frac{1}{6} \mathbf{E} \text{trace}(\mathbf{L} \mathbf{g}^*) - \frac{1}{3} \mathbf{L} \mathbf{g}^*] \mathbf{L} \mathbf{V}_\rho. \quad (7.6)$$

The harmonic contribution is given if we consider only  $\mathbf{E}$  in the square brackets. The anharmonic modification consists of the two negative terms and arises from the fourth moments of  $\omega$ ; it is quadratic in  $\mathbf{L}$  in our approximation (4).

(7.6) enables us to estimate the effect of large librations on the position of the centre of reaction. This is the point where the  $\mathbf{S}$  tensor becomes symmetric (Schomaker & Trueblood, 1968; Johnson, 1970a). Since  $[\ ] \mathbf{L} \equiv \mathbf{C}$  constitutes a symmetric matrix in (7.6), Johnson's (1970a) procedure for determining the point  $\rho(\mathbf{S} = \mathbf{S}^T)$  can also be applied to the anharmonic case. Instead of  $\mathbf{L}$ , we have to insert  $\mathbf{C}$  in Johnson's equation (48). The more  $\mathbf{C}$  deviates from  $\mathbf{L}$ , the more the centre of reaction will be displaced by the anharmonic contributions. Evaluation of (7.6) with  $L_{ii} = 40 \text{ deg}^2$ , yields  $0.99\mathbf{E}$  for the square bracket; *i.e.* the anharmonic contribution only makes up 1% of the whole in this case. Thus, we conclude that the centre of reaction will usually not be displaced much by the anharmonic contributions to  $\mathbf{S}$ .

One may suppose that a simpler description than that of § 6 will be obtained if one first calculates  $\mathbf{T}_y$  and  $\mathbf{S}_y$  and then uses these quantities in the equations of § 5. We have done this and found the results partially to differ from those of § 6. The reason is that  $\mathbf{t}_y$  is no longer Gaussian distributed and, hence, the third moments  $\langle t_y^i, t_y^j, t_y^k \rangle$ ,  $\langle t_y^i, t_y^j, \omega_k \rangle$  and  $\langle t_y^i, \omega_j, \omega_k \rangle$  do not vanish, but also contribute to the cumulants. Therefore, the calculation with  $\mathbf{T}_y$  and  $\mathbf{S}_y$  becomes more complicated than that of § 6.

### 8. Discussion of the TLS $\rho$ model

In the preceding sections we have shown how the cumulants, and, hence, the temperature factors of the atoms, can be calculated from the rigid-body vibration tensors **TLS** and the vector  $\rho$ . Our description of the anharmonic motions of the atoms (due to large librations of molecules) thus constitutes an anharmonic TLS $\rho$  model [within the limitations (3) and (4)] which contains 24 parameters. In contrast, the harmonic TLS model contains only 20 parameters. One additional parameter in the anharmonic model arises from nine (and no longer from eight) parameters of **S**. With the equations of § 5, the components  $S_i^i$  and, hence, also trace **S** are fully determined. The other three additional parameters are the coordinates of  $-\rho$ , since the coordinate origin for which we assume harmonic translations is generally unknown. In the harmonic TLS model, the three parameters for  $-\rho$  do not arise, because the translations are harmonic for every coordinate origin. This implies that, with a change of origin, **T** and **S** transform linearly in TLS. In the anharmonic TLS $\rho$  model, however, **T** and **S** do not transform linearly in **L** and **S**, cf. (7.3) and (7.5), and the translations are generally anharmonic cf. (6.3).

Two unique points offer themselves which, when chosen as origins, may give rise to translations that are harmonic: the centre of gravity and the centre of reaction. On the usefulness of the centre of reaction we are careful in our prediction, since there is too little evidence as to where it usually lies. From its definition, the centre of gravity appears to be suitable as a possible origin (3*b*), if the molecule is not anchored one-sidedly by external forces. In the special case of site symmetry  $\bar{1}$ , the centre of gravity coincides with  $\bar{1}$  and thus yields the correct value for  $-\rho$ .

We emphasize that the assumption (3*b*) of the translations being harmonic for one fixed origin has not been proven. This statement also holds for the TL model with site symmetry  $\bar{1}$ . The successful refinements with the TL model, however, seem to suggest that the assumption (3*b*) can well be made in most cases. Hence, we expect that anharmonic translations are in most cases due to large librations where the correct point  $-\rho$  has not been found, and are not due to the breakdown of our assumption (3*b*).

If we discard the assumption (3*b*) the simple description of §§ 5 and 6 will be lost. There would be higher cumulants for the pure translations (10 parameters for the third, 15 parameters for the fourth cumulant) and the third moments  $\langle t^i t^j \omega_k \rangle$  and  $\langle t^i \omega_j \omega_k \rangle$  would contribute to the mixed cumulants, with 18 parameters each. The fourth moments, which we have calculated from TLS, (3.5), would have to be treated as independent variables. The moments  $\langle t^i t^j t^k \omega_l \rangle$  and  $\langle t^i \omega_j \omega_k \omega_l \rangle$  yield 30 parameters each, and the moment  $\langle t^i t^j \omega_k \omega_l \rangle$  yields 36 parameters.

(More parameters arise for the mixed moments than for the pure moments, because one has to distinguish between directions of space and librations/translations.)

Needless to say, the components of TLS for large librations can only be determined in a structure factor calculation, and not from atomic vibration tensors that were determined in the standard harmonic approximation. Generally, the 24 parameters TLS $\rho$  have to be determined in the refinement. It is probably sufficient to calculate the derivatives for **T**, **L** and the off-diagonal components of **S** in the harmonic approximation, and to calculate correspondingly more cycles. For the components  $S_i^i$ , however, the full derivatives are needed, since in the harmonic approximation the normal matrix becomes singular for these parameters. If one does not wish to determine the single components  $S_i^i$ , trace **S** = 0 is a useful constraint, although not quite correct (Scheringer, 1973). For determining the coordinates of  $-\rho$ , the full derivatives are also needed, unless one is satisfied with keeping  $-\rho$  constant at the centre of gravity.

### 9. Conclusion

For large librations of molecules, a TLS $\rho$  model with 24 parameters has been described which, in view of the present experimental accuracy, will in most cases satisfy the requirements of actual practice. The point  $-\rho$ , for which we assume the translations of the molecule to be harmonic, is a unique origin in this model, and it is expected to lie in the vicinity of the centre of gravity as long as the molecule is not anchored one-sidedly by external forces. As a rule, the 24 parameters should be well-determined with good experimental data, as is suggested by the experience gained with the harmonic TLS model that already contains 20 parameters. However, it appears to be impossible in practice to eliminate the assumption (3*b*) since then too many parameters would arise which could no longer be determined. The formulation of the TLS $\rho$  model in a general crystal metric allows us to use the coordinates in lattice units and the Miller indices of the observed data, which makes programming easier.

With the determination of electron density distributions in molecular crystals by means of  $X - N$  or  $X - X$  (high-angle data) maps, small errors in the temperature factors give rise to large errors in the density distribution (Scheringer, Kutoglu & Mullen, 1978). Hence, a correct description of the nuclear motions in these maps is of primary importance. The anharmonic TLS $\rho$  model should here help us to proceed a step further.

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## Experimental Study of Disordered Mica Structures by High-Resolution Electron Microscopy

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Disorder in stacking sequences of mica minerals, predominantly 1M muscovite from York, Ontario and biotite from Mitchell Co., North Carolina, was observed using high-resolution electron microscopy. The specimens were prepared by sectioning the flakes of mica in the microtome with a diamond knife, so that crystals were viewed down the direction parallel to the Si–O layers. Disordered sequences of the layers, as well as ordered crystals, are best described by citing the positions of tunnels between alkali ions lying in the interlayers, since these individual sites are resolved in electron micrographs of micas. An evaluation of the usefulness of one-dimensional lattice fringe images for studying disordered states in crystals is also discussed by comparing them with structure images of corresponding crystals. Intimate intergrowths of different mica polytypes on a scale of tens of ångströms raise questions as to the definition of origins of unit cells and therefore polytypes.

### 1. Introduction

The structures of the mica minerals are complex and varied, although based on a relatively simple stacking arrangement. There is a sixfold multiplicity for the stacking of adjacent layers, resulting in a large number of possible stacking sequences and thus polytypes (Smith & Yoder, 1956; Ross, Takeda & Wones, 1966; Takeda, 1967; Baronnet, 1975). X-ray diffraction techniques have been a powerful means of determining average stacking sequences and have solved the problems of mica polytypes, but they are not suitable for studying heavily disordered stacking sequences and their variations within a given crystal.

Recently, high-resolution transmission electron microscopy has been recognized as a powerful means for studying structural irregularities in crystals, particularly linear or planar defects, occurring within one

or a few unit cells. We have utilized this technique for the study of crystal defects in various oxide crystals (Iijima, 1971). The basis of the technique is that images of crystals taken under critical experimental conditions (focusing, crystal orientation, *etc.*) directly represent an arrangement of relatively heavy atoms, or groups of atoms in a projection of the structure parallel to the direction of the incident electron beam. Such images are called 'structure images' hereinafter.

We previously reported structure images of some minerals (Iijima, Cowley & Donnay, 1973; Buseck & Iijima, 1974; Pierce & Buseck, 1976). One of the advantages of structure images over X-ray diffraction techniques, where observed quantities are averaged over vast numbers of unit cells, is that they allow us to examine local irregularities in crystals at the unit-cell level. This advantage was utilized to study defects and polytypism of enstatites (Iijima & Buseck, 1975; Buseck & Iijima, 1975).