Abschätzung der Fehler

Die Fehler der Strukturamplituden (Tabelle 4) liegen bei den starken Reflexen unter 1 % und bei den schwachen Reflexen zwischen 2 und 5 %. Auf Grund der Fehlerfortpflanzung ergibt sich ein Fehler der Elektronendichte von etwa 0,05 e Å^{-3} in allgemeinen und 0,1 e Å^{-3} in speziellen Lagen.

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On the Use of Thermal Parameters in N.m.r. Second-Moment Calculations

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A relationship between average small-amplitude molecular motion in a crystal and the mean-squared half width of an n.m.r. absorption line, *i.e.* the second moment, is rederived, extended and discussed. The average motion is represented by rigid-body tensors **T**, **L** and **S** of the atom groups considered and anisotropic vibration tensors of the atoms composing these groups. Thus, the geometrical part of the second moment is expressed in terms of conventional positional and thermal parameters. Three kinds of dipolar interactions, between nuclear spins, are considered: (*a*) nuclei belonging to the same group, (*b*) nuclei belonging to different non-bonded groups and (*c*) interactions between rigid segments of a non-rigid molecule. Equations applicable to the second moment of both single crystals and powder specimens are presented, and the simplified versions resulting from the assumption of isotropic motion are also derived. A discussion of possible limitations of the method and some programming considerations concerning its application are given.

Introduction

Average atomic and molecular motions in a crystal affect a number of physical properties but such effects appear to have been treated satisfactorily only in connexion with techniques in which the concept of mean-squared displacement is associated with a measurable quantity, such as diffraction by crystals or the Mössbauer effect. However, any property depending on interatomic distances should, at least in principle, depend on their variation with time and therefore a unified approach to the effect of motion on the measurable quantity seems to be of interest. The thermal parameters used by crystallographers are of considerable importance in this context, for two reasons. Firstly, the average-motion formalism in crystallography has been extensively developed and is, within the underlying restrictions, quite general, and secondly, the wealth of detail on average motion, accumulated so far by crystallographers, could well be applied to other properties with advantage. Such considerations motivated our study of the effect of lattice vibrations on the nuclear magnetic resonance of crystals (Shmueli, Polak & Sheinblatt, 1973; Polak, Sheinblatt & Shmueli, 1974). In the present article, we wish to outline our approach to the problem and to extend the results derived previously.

Among the physical properties of crystals which can be predicted from the knowledge of a crystal structure, the nuclear magnetic resonance (n.m.r.) parameters are of the most extensively investigated. In particular, the mean-squared half width of an absorption line, known as the 'second moment', has been given much attention. A useful expression for the second moment of an n.m.r absorption line, broadened by the dipolar interactions between nuclear spins, was derived by van Vleck (1948),

$$\langle \Delta H^2 \rangle = \tfrac{3}{2} I(I+1)\gamma^2 \hbar^2 N^{-1} \sum_{i>j} \left(\frac{1-3\cos^2\theta_{ij}}{r_{ij}^3} \right)^2 , \qquad (1)$$

where I is the quantum number of the nuclear spin, γ is the gyromagnetic ratio [equation (1) is valid only for the case of nuclei having the same γ], $\hbar$ is Planck's constant, and N is the number of nuclei involved in the summation; r_{ij} is the separation of nuclei i and j, and θ_{ij} is the angle between the internuclear vector $\mathbf{r}_{ij}$ and the external magnetic field.

Thus, van Vleck's expression gives a simple relationship between the macroscopic measured second moment and the geometrical arrangement of atomic nuclei. The theoretical basis of (1), as well as its applications and experimental aspects of second-moment measurements, have been reviewed in detail (Andrew, 1958; Slichter, 1963; Kitaigorodskii, 1973).

The double summation in (1) can be regarded as the 'structure factor' of the second moment $\langle \Delta H^2 \rangle$ and can be computed in a straightforward manner once the atomic positional parameters are known. Such a calculation, however, refers to a structure at rest. It has been shown both theoretically and experimentally, that motions occurring in the solid affect the measurable second moment, provided their frequencies exceed the rigid-lattice line width (Abragam, 1961). These effects are expressed by averaging the spatial factor of the dipolar interaction term, $(1-3\cos^2\theta)/r^3$, over all displacements caused by such motions. This permits an investigation of motions in solids by n.m.r spectroscopy, and, indeed, various types of motions such as reorientation of a methyl group about its C_3 axis (Gutowsky & Pake, 1950), rotation of benzene about its sixfold axis (Andrew & Eades, 1953) and isotropic 'tumbling' of a molecule (*e.g.* Smith, 1962), have been characterized by their effect on the second moment.

In this paper, we wish to concentrate on the commonly occurring restricted motions in crystals – the lattice vibrations, or more accurately, their average effect on the second moment. The frequencies of these motions exceed by about seven orders of magnitude the rigid-lattice line width, which warrants their effect on the second moment. Furthermore, lattice vibrations hardly affect the spin-lattice relaxation times, because their frequencies greatly exceed the Larmor resonance frequency of the spins, and hence their effects on line-shape parameters are left to be considered. Early attempts to treat such effects were confined to simple systems and applications were restricted to crystals such as hydrates (Pedersen, 1964), ammonium salts (Gutowsky, Pake & Bersohn, 1954; Ibers & Stevenson, 1958) and other simple examples. No attempt was made in these studies to account for the effect of motion on interactions between nuclei which belong to different molecules.

A general solution of this problem must clearly be a rather complicated one, since $\langle \Delta H^2 \rangle$ is affected by the change of orientations as well as separations of all the nuclear pairs in the crystal. Since the same types of motion also affect the intensities of diffracted radiation and their effect on the latter can be conveniently expressed by atomic and molecular vibration tensors, it occurred to us, some time ago, that an attempt to derive what might be called a 'temperature factor' of $\langle \Delta H^2 \rangle$, in terms of the crystallographic average-motion formalism, should be worthwhile. We have followed the conventional subdivision of the second moment into its intramolecular and intermolecular parts and restricted the validity of our derivations to crystals composed of rigid molecules. We found that the motional correction of the intramolecular part could be expressed using the molecular libration tensor only (Shmueli *et al.*, 1973) while the effect of motion on the intermolecular contribution to the second moment was expressed in terms of molecular libration tensors, atomic anisotropic vibration tensors and interatomic correlated-displacement tensors (Polak, Sheinblatt & Shmueli, 1974). Thus, assuming independent vibration of rigid molecules, it was possible to evaluate the effect of lattice vibrations on the second moment, and compare the result with experiment.

We intend, in the present paper, to rederive the equations obtained so far and to examine their modifications which may be appropriate for dealing with the more general case of non-rigid molecules composed of rigid segments. A preliminary consideration of this problem has been reported elsewhere (Polak, Shmueli & Sheinblatt, 1974).

Second moment and molecular vibrations

We shall consider the general case of two nuclei belonging to different (coupled) rigid groups of atoms in a crystal. Since a displacement of either group is likely to change the orientation and, in general, also the length of the internuclear vector $\mathbf{r}_{ij}$, we must average the dipolar interaction term over all possible types of motion, including the coupled motion of the two groups in question. We assume that the average motion of each of these groups is described in terms of rigid-body tensors and that for each of the nuclei the anisotropic vibration tensor is also given. Approximations regarding the usually unknown parameters of coupled motion will be made in the applications of the general result, to be derived, to several important special cases. The motion is assumed to be harmonic and thus only quadratic average displacements will be retained.

The geometry of the problem is specified as follows. Nuclei i and j, belonging to rigid groups A and B respectively, undergo instantaneous displacements $\mathbf{u}_i^A$ and $\mathbf{u}_j^B$ from their equilibrium positions $\mathbf{r}_i^A$ and $\mathbf{r}_j^B$. The instantaneous internuclear vector is given by

$$\mathbf{r}'_{ij} = (\mathbf{r}_i^A + \mathbf{u}_i^A) - (\mathbf{r}_j^B + \mathbf{u}_j^B) \equiv \mathbf{r}_{ij} + \mathbf{d}$$

where $\mathbf{r}_{ij}$ is the equilibrium internuclear vector and $\mathbf{d}$ is a small relative displacement. The external magnetic field vector $\hat{\mathbf{H}}_0$, taken here as a unit vector, forms angles θ and θ' with $\mathbf{r}_{ij}$ and $\mathbf{r}'_{ij}$ respectively. All vectors and tensors are assumed to be referred to a Cartesian coordinate system. A schematic representation of this situation is given in Fig. 1.

The quantity to be evaluated is

$$\langle D_{ij}(\mathbf{r}'_{ij})\rangle = \left\langle \frac{1-3\cos^2\theta_{ij}}{r'^3_{ij}} \right\rangle = \left\langle \frac{1}{r'^3_{ij}} - \frac{3(H_k X'_k)^2}{r'^5_{ij}} \right\rangle \tag{2}$$

where H_k and X'_k are components of $\hat{\mathbf{H}}_0$ and $\mathbf{r}'_{ij}$ respectively, and the brackets denote averaging over all nuclear displacements from equilibrium. This can be accomplished by expanding D_{ij} in a Taylor series about the equilibrium internuclear vector $\mathbf{r}_{ij}$

$$\begin{aligned} D_{ij}(\mathbf{r}'_{ij}) &= D_{ij}(\mathbf{r}_{ij}+\mathbf{d}) \\ &= D_{ij}(\mathbf{r}_{ij}) + \frac{\partial D_{ij}(\mathbf{r}_{ij})}{\partial X_k} d_k + \tfrac{1}{2}\frac{\partial^2 D_{ij}(\mathbf{r}_{ij})}{\partial X_k \partial X_l} d_k d_l + \dots \end{aligned} \tag{3}$$

where X_k and d_k are components of $\mathbf{r}_{ij}$ and $\mathbf{d}$ respectively. Only the first three terms of the series are taken, since the displacements are assumed to be small (harmonic approximation). The required result is then obtained by evaluating the averages $\langle\mathbf{d}\rangle$ and $\langle\mathbf{dd}^T\rangle$.

The first average, $\langle\mathbf{d}\rangle$, is the difference between the average displacements of nuclei i and j. As shown by Schomaker & Trueblood (1968), the average small displacement of an atom is given by

$$\langle\mathbf{u}\rangle = \tfrac{1}{2}[\mathbf{L}-\mathrm{Tr}(\mathbf{L})\mathbf{I}]\boldsymbol{\varrho} + \langle\boldsymbol{\lambda}\rangle \times \boldsymbol{\varrho} + \langle\mathbf{t}\rangle \tag{4}$$

where $\boldsymbol{\lambda}$ and $\mathbf{t}$ are instantaneous angular and translational displacements of the rigid group to which the atom belongs, $\mathbf{L}$ is the libration tensor of the group, $\mathbf{I}$ is a unit matrix and $\boldsymbol{\varrho}$ is the atomic position vector, referred to the centre of libration of the rigid group (see Fig. 1). Assuming that average linear displacements vanish (Schomaker & Trueblood, 1968; Scheringer, 1972), we obtain

$$\langle\mathbf{d}\rangle = \tfrac{1}{2}\{[\mathbf{L}^A - \mathrm{Tr}\,(\mathbf{L}^A)\mathbf{I}]\boldsymbol{\varrho}_i^A - [\mathbf{L}^B - \mathrm{Tr}\,(\mathbf{L}^B)\mathbf{I}]\boldsymbol{\varrho}_j^B\}\,. \tag{5}$$

The components of the position vectors $\boldsymbol{\varrho}_i^A$ and $\boldsymbol{\varrho}_j^B$ are, of course, assumed to be corrected for libration.

The second average, $\langle\mathbf{dd}^T\rangle$, hereafter defined by $\mathbf{V}$, is given by

$$\begin{aligned} \langle\mathbf{dd}^T\rangle &= \langle(\mathbf{u}_i^A - \mathbf{u}_j^B)\,(\mathbf{u}_i^A - \mathbf{u}_j^B)^T\rangle \\ &= \langle\mathbf{u}_i^A(\mathbf{u}_i^A)^T\rangle + \langle\mathbf{u}_j^B(\mathbf{u}_j^B)^T\rangle - \langle\mathbf{u}_i^A(\mathbf{u}_j^B)^T\rangle - \langle\mathbf{u}_j^B(\mathbf{u}_i^A)^T\rangle \\ &\equiv \mathbf{U}_i^A + \mathbf{U}_j^B - \mathbf{U}_{i\,j}^{AB} - (\mathbf{U}_{i\,j}^{AB})^T \\ &\equiv \mathbf{V}\,. \end{aligned} \tag{6}$$

The first two averages in the right-hand side of (6) are the anisotropic vibration tensors of nuclei i and j, while the other two describe the average correlated motion of these nuclei [*cf.* equation (3·2) of Scheringer, (1972)].

Carrying out the differentiation indicated in (3) and substituting the averages from (5) and (6), we obtain

$$\begin{aligned} \left\langle \frac{1-3\cos^2\theta'_{ij}}{r'^3_{ij}} \right\rangle &= \frac{1-3\cos^2\theta_{ij}}{r^3_{ij}} \\ &+ \frac{3}{r^4_{ij}}\,[(5\cos^2\theta_{ij}-1)\hat{\mathbf{r}}^T\langle\mathbf{d}\rangle - 2\hat{\mathbf{H}}_0^T\langle\mathbf{d}\rangle\cos\theta_{ij}] \\ &+ \frac{3}{2r^5_{ij}}\,[(5\cos^2\theta_{ij}-1)\,\mathrm{Tr}\,(\mathbf{V}) \\ &+ 5(1-7\cos^2\theta_{ij})\hat{\mathbf{r}}^T\mathbf{V}\hat{\mathbf{r}} \\ &+ 20\hat{\mathbf{H}}_0^T\mathbf{V}\hat{\mathbf{r}}\cos\theta_{ij} - 2\hat{\mathbf{H}}_0\mathbf{V}\hat{\mathbf{H}}_0] \end{aligned} \tag{7}$$

where $\hat{\mathbf{r}} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$.

The effect of motion on the correction terms is thus described in terms of libration of the rigid groups A and B, the anisotropic vibration tensors of nuclei i and j and the coupling tensors of these nuclei. Specifically, the term $[\mathbf{L}-\mathrm{Tr}\,(\mathbf{L})\mathbf{I}]$ appearing in $\langle\mathbf{d}\rangle$ corresponds to the apparent foreshortening of the vector, $\mathrm{Tr}\,(\mathbf{V})$ is the sum of mean-squared relative displacements along the coordinate axes, $\hat{\mathbf{r}}^T\mathbf{V}\hat{\mathbf{r}}$ and $\hat{\mathbf{H}}_0^T\mathbf{V}\hat{\mathbf{H}}_0$ are mean-squared relative displacements along $\hat{\mathbf{r}}$ and $\hat{\mathbf{H}}_0$ respectively (Scheringer, 1972). The remaining term, $\hat{\mathbf{H}}_0^T\mathbf{V}\hat{\mathbf{r}} = \langle(\hat{\mathbf{H}}_0^T\mathbf{d})\,(\mathbf{d}^T\hat{\mathbf{r}})\rangle$, is the mean product of relative displacement projections on the vectors $\hat{\mathbf{H}}_0$ and $\hat{\mathbf{r}}$. Hence, the motional correction depends on the directions of the internuclear vector and the external magnetic-field vector as well as on their relative orientation.

The largest contributions to the second moment are due to close-lying nuclei, because of the r^{-6} dependence, and it is therefore convenient to treat separately inter-

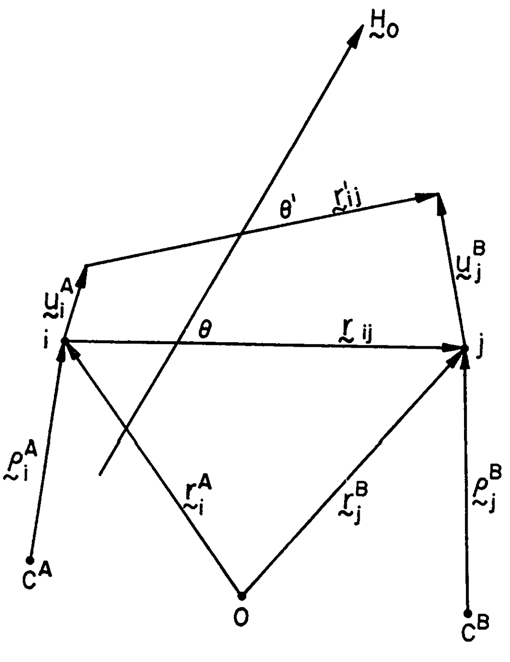

Fig. 1. Geometry of the problem (schematic). All vectors and angles appearing in the figure are defined in the text. The points O, C^A and C^B denote the origin of the Cartesian working system and the centres of libration (Pawley, 1968) of the rigid groups A and B respectively.

molecular and intramolecular pairs of nuclei. We shall also consider the case of two nuclei belonging to rigid parts of the same non-rigid molecule. These three cases differ only in the extent of correlated motion and hence in the form of the tensor **V** given by (6). We shall now express **V** in terms of the displacements of groups *A* and *B* and turn later to the evaluation of the above mentioned special cases.

Since an atomic instantaneous displacement can be written as

$$\mathbf{u} \cong \boldsymbol{\lambda} \times \boldsymbol{\varrho} + \mathbf{t} \equiv \mathbf{B}\boldsymbol{\lambda} + \mathbf{t}\,,$$

where the matrix **B** is given by

$$\mathbf{B} = \begin{pmatrix} 0 & \varrho_3 & -\varrho_2 \\ -\varrho_3 & 0 & \varrho_1 \\ \varrho_2 & -\varrho_1 & 0 \end{pmatrix}$$

we can express the coupling tensor $\mathbf{U}_{ij}^{AB}$ [equation (6)] as

$$\begin{aligned} \mathbf{U}_{ij}^{AB} &= \langle(\mathbf{B}^{iA}\boldsymbol{\lambda}^A + \mathbf{t}^A)\,(\mathbf{B}^{jB}\boldsymbol{\lambda}^B + \mathbf{t}^B)^T\rangle \\ &= \mathbf{B}^{iA}\mathbf{L}^{AB}(\mathbf{B}^{jB})^T + \mathbf{B}^{iA}\mathbf{S}^{AB} + (\mathbf{B}^{jB}\mathbf{S}^{BA})^T + \mathbf{T}^{AB} \qquad (8) \end{aligned}$$

where $\mathbf{L}^{AB} = \langle\boldsymbol{\lambda}^A(\boldsymbol{\lambda}^B)^T\rangle$, $\mathbf{S}^{AB} = \langle\boldsymbol{\lambda}^A(\mathbf{t}^B)\rangle$ and $\mathbf{T}^{AB} = \langle\mathbf{t}^A(\mathbf{t}^B)^T\rangle$ are tensors describing the coupled motion of the rigid groups *A* and *B*.

We also use the conventional representation of atomic vibration tensors, *e.g.*,

$$\mathbf{U}_i^A = \mathbf{B}^{iA}\mathbf{L}^A(\mathbf{B}^{iA})^T + \mathbf{B}^{iA}\mathbf{S}^A + (\mathbf{B}^{iA}\mathbf{S}^A)^T + \mathbf{T}^A\,. \qquad (9)$$

Equation (9) is the same as that given by Pawley (1968) except for the sign of the matrix **B**, due to which the products **BS** and $(\mathbf{BS})^T$ are now added rather than subtracted. Using (8) and (9), we can rewrite (6) as

$$\mathbf{V} = \mathbf{V}_L + \mathbf{V}_S + \mathbf{V}_T \qquad (10)$$

where

$$\begin{aligned} \mathbf{V}_L = \mathbf{B}^{iA}\mathbf{L}^A(\mathbf{B}^{iA})^T &+ \mathbf{B}^{jB}\mathbf{L}^B(\mathbf{B}^{jB})^T \\ &- \mathbf{B}^{iA}\mathbf{L}^{AB}(\mathbf{B}^{jB})^T - \mathbf{B}^{jB}\mathbf{L}^{BA}(\mathbf{B}^{iA})^T \qquad (11) \end{aligned}$$

$$\begin{aligned} \mathbf{V}_S = \mathbf{B}^{iA}(\mathbf{S}^A - \mathbf{S}^{AB}) + \mathbf{B}^{jB}(\mathbf{S}^B - \mathbf{S}^{BA}) &- [\mathbf{B}^{iA}(\mathbf{S}^A - \mathbf{S}^{AB})]^T \\ &- [\mathbf{B}^{jB}(\mathbf{S}^B - \mathbf{S}^{BA})]^T \qquad (12) \end{aligned}$$

and

$$\mathbf{V}_T = \mathbf{T}^A + \mathbf{T}^B - \mathbf{T}^{AB} - \mathbf{T}^{BA}\,. \qquad (13)$$

The condition $\mathbf{U}_{ji}^{BA} = (\mathbf{U}_{ij}^{AB})^T$ [*cf.* (6) and Scheringer (1972)] has not been used, since it would make (12) less obvious for the present purpose. Equations (10)–(13) represent the tensor **V** in terms of second-order tensors describing the independent and coupled motions of the rigid groups *A* and *B* to which the nuclei *i* and *j* respectively belong.

The intramolecular contribution

Suppose that nuclei *i* and *j* belong to the same rigid group of atoms. This amounts to saying, in terms of the above, that the rigid groups *A* and *B* are now parts of the same rigid body. Since, in this case, $\boldsymbol{\lambda}^A = \boldsymbol{\lambda}^B \equiv \boldsymbol{\lambda}$ and $\mathbf{t}^A = \mathbf{t}^B \equiv \mathbf{t}$ all the tensors in equations (11), (12) and (13) reduce to the rigid-body tensors **L**, **S** and **T** respectively, of the group containing both nuclei. It is seen that $\mathbf{V}_S$ and $\mathbf{V}_T$ vanish identically and $\mathbf{V}_L$ becomes

$$\mathbf{V}_L = (\mathbf{B}^{iA} - \mathbf{B}^{jB})\mathbf{L}(\mathbf{B}^{iA} - \mathbf{B}^{jB})^T\,. \qquad (14)$$

Equation (14), derived here by standard methods of rigid-body motion analysis, was also deduced by Scheringer (1972) *via* comparison of lattice-dynamical representations of atomic vibration tensors and interatomic coupling tensors.

Since the internuclear vector is now given by $\mathbf{r}_{ij} = \boldsymbol{\varrho}_i^A - \boldsymbol{\varrho}_j^B$, we can write

$$\mathbf{V}_L = r_{ij}^2\ \mathbf{QLQ}^T \qquad (15)$$

where

$$\mathbf{Q} = \begin{pmatrix} 0 & r_3 & -r_2 \\ -r_3 & 0 & r_1 \\ r_2 & -r_1 & 0 \end{pmatrix},$$

r_k being the Cartesian components of the unit vector $\hat{\mathbf{r}}$.

Substituting $\mathbf{V}_L$ from (15) for **V** into (7), we see that the second and fourth terms cancel each other while the fifth and sixth terms vanish identically. This happens because, as can be shown using standard tensor algebra,

$$\mathrm{Tr}\,(\mathbf{V}_L) = r_{ij}^2\hat{\mathbf{r}}^T[\mathrm{Tr}\,(\mathbf{L})\mathbf{I} - \mathbf{L}]\hat{\mathbf{r}}$$

and

$$\hat{\mathbf{H}}_0^T\mathbf{V}_L\hat{\mathbf{r}} = r_{ij}^2\hat{\mathbf{H}}_0^T\mathbf{QLQ}^T\hat{\mathbf{r}} = 0$$

because $\mathbf{Q}^T\hat{\mathbf{r}} = \hat{\mathbf{r}} \times \hat{\mathbf{r}} = 0$.

The quadratic form $\hat{\mathbf{r}}^T\mathbf{V}_L\hat{\mathbf{r}}$ vanishes for the same reason.

Equation (7) thus becomes

$$\begin{aligned} \left\langle\frac{1 - 3\cos^2\theta'_{ij}}{r'^3_{ij}}\right\rangle_{\text{intra}} &= \frac{1}{r_{ij}^3}\{1 - 3[\cos^2\theta_{ij}(1 - \mathrm{Tr}\,(\mathbf{L})) \\ &+ \hat{\mathbf{H}}_0\mathbf{L}\hat{\mathbf{r}}\cos\theta_{ij} + (\hat{\mathbf{H}}_0^T\mathbf{Q})\mathbf{L}(\hat{\mathbf{H}}_0^T\mathbf{Q})^T]\}\,. \qquad (16) \end{aligned}$$

The same result was obtained by Shmueli *et al.* (1973) by a direct averaging of $\cos^2\theta$, which is clearly the only quantity affected by motion in the present case. Equation (16) can be conveniently employed in the evaluation of the intramolecular contribution to the second moment of a single crystal (Shmueli *et al.*, 1973).

In the case of isotropic libration, the right-hand side of (16) reduces to

$$\begin{aligned} &\left\langle\frac{1 - 3\cos^2\theta'_{ij}}{r'^3_{ij}}\right\rangle_{\substack{\text{intra} \\ \text{isotropic}}} \\ &= \frac{1}{r_{ij}^3}\ \{1 - 3\cos^2\theta[1 - \mathrm{Tr}\,(\mathbf{L})]\ - \mathrm{Tr}\,(\mathbf{L})\} \qquad (17) \end{aligned}$$

with $\mathrm{Tr}\,(\mathbf{L}) = 3L_0$, where L_0 is the (scalar) isotropic mean-squared libration amplitude (Shmueli *et al.*, 1973). Equation (17) can be shown to be equivalent to the result obtained by Pedersen (1964) for the case of isotropic librations of a water molecule in hydrates.

The intermolecular contribution

We now turn to reconsider the case of nuclei i and j belonging to different molecules A and B respectively (Polak, Sheinblatt & Shmueli 1974). A glance at equations (6) and (10) through (13) shows that, in principle, the vibration tensors as well as the coupling tensors ought to be known in order to evaluate $\mathbf{V}$. Unfortunately, the coupling tensors are not available experimentally nor can they be calculated without recourse to lattice dynamics in the harmonic approximation (Scheringer, 1972). However, when a large number of such intermolecular contributions to the second moment are summed, it is not unreasonable to assume that the contribution of average intermolecular coupling is very small and to neglect it as a first approximation (the Einstein model of a crystal). Under such an assumption, the last two tensors on the right-hand side of (6) vanish and equation (7) with $\mathbf{V}$ given by

$$\mathbf{V} \simeq \mathbf{U}_i^A + \mathbf{U}_j^B \qquad (18)$$

can be used for the calculation of the intermolecular contribution of nuclei i and j to the second moment. It is of interest to recall that the second correction term on the right-hand side of equation (7) vanishes in the case of isotropic and uncorrelated vibration of the nuclei (Polak, Sheinblatt & Shmueli, 1974). This result suggests that the effect of motion on the second moment of ionic cubic crystals, in which the nuclei are located at certain special positions, should be very small. For such crystals, the first correction term also vanishes because the ions are located on their centres of libration. Hence only terms of order higher than the second might be of some small possible significance. This is in apparent agreement with Engelsberg & Lowe's (1974) derivations of motional correction to the second moment of the calcium fluoride crystal.

The intersegment contribution

Let us now suppose that the nuclei i and j belong to two rigid parts of the same molecule and that these parts are connected by bonds about which they can librate. There are a large number of examples which correspond to this situation, such as organic molecules with bulky phenyl substituents, and hence this case is of a considerable importance. Formally, the whole $\mathbf{V}$ tensor should again be evaluated in order to find the required contribution. However, whereas in the case of the intermolecular contribution the neglect of coupled motion is equivalent to the assumption of the often successful Einstein model, such a neglect in the case of, say, two bonded benzene rings would certainly be wrong. The most important part of the coupled motion, in this case, is probably the translation of the molecule as a whole and it appears reasonable to assume that the instantaneous translations of the segments A and B are always identical. This is, of course, an approximation because internal stretching and bending vibrations are neglected. We shall also assume that the librations of the two segments are uncorrelated.

Considering equations (11), (12) and (13), we see that in view of the above assumptions $\mathbf{V}_T$ vanishes and the same happens to $\mathbf{V}_S$ since $\mathbf{S}^A=\mathbf{S}^{AB}$ for $\mathbf{t}^A=\mathbf{t}^B$ *etc.* Thus, the $\mathbf{V}$ tensor reduces to

$$\mathbf{V}=\mathbf{B}^{iA}\mathbf{L}^A(\mathbf{B}^{iA})^T+\mathbf{B}^{jB}\mathbf{L}^B(\mathbf{B}^{jB})^T\,. \qquad (19)$$

An alternative approach, which also assumes uncorrelated librations of segments A and B, can be proposed. Assuming, as above, that the translations of the segments are identical, it follows that $\mathbf{T}^A+\mathbf{T}^B=\mathbf{T}^{AB}+\mathbf{T}^{BA}\equiv 2\mathbf{T}'$. If we further neglect the coupling 'screw' tensors $\mathbf{S}^{AB}$ and $\mathbf{S}^{BA}$, $\mathbf{V}$ can be written as*

$$\mathbf{V} \cong \mathbf{U}_i^A + \mathbf{U}_j^B - 2\mathbf{T}'\,, \qquad (20)$$

where $\mathbf{T}'$ is the mean translation tensor of segments A and B. This may have the advantage that internal vibrations are taken into account *via* the observed anisotropic vibration tensors $\mathbf{U}_i^A$ and $\mathbf{U}_j^B$. It is, however, difficult to say which of the two approximations is the better one. A complete calculation of the motion-affected second moment for a flexible molecule consisting of rigid segments can thus be outlined. The intrasegment contributions are evaluated from equation (16), the intersegment contributions are found using equation (7) with $\mathbf{V}$ defined by (19) or (20) and the intermolecular contributions follow from equation (7) with $\mathbf{V}$ given by (18). The individual contributions are squared and summed as indicated by equation (1). The above method of calculation is applicable to second moments of single-crystal spectra.

Second moment of a polycrystalline substance

In order to obtain the second moment of a powder sample we have, in principle, to calculate the second moment of each individual crystallite and sum all these contributions. The resulting procedure for the derivation of the relevant expression is therefore to average the corrected-for-motion and squared dipolar interaction term over all orientations of the internuclear vector or, what amounts to the same, of the external magnetic field. In what follows we present the results for the intramolecular (Shmueli *et al.*, 1973) and intermolecular (Polak, Sheinblatt & Shumeli, 1974) contributions, for the derivation of which equations (16) and (7) respectively were employed. Prior to the orientational averaging, terms containing atomic or molecular displacements of order higher than the second have been deleted. The integrations were performed by referring $\hat{\mathbf{H}}_0$ to spherical coordinates and making use of Cartesian tensor algebra. Examples of such integrations are given in the Appendix to the article by Polak, Sheinblatt & Shmueli (1974).

The quantity averaged is

$$M_{ij}=\left\langle\left\langle\frac{1-3\cos^2\theta'_{ij}}{r'^3_{ij}}\right\rangle^2_{\text{motion}}\right\rangle_{\text{orientation}} \qquad (21)$$

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* The translation tensors of two segments of the same molecule usually turn out to be somewhat different (*e.g.* Rietveld, Maslen & Clews, 1970).

and the results are

$$M_{ij}=\frac{4}{5}\frac{1}{r_{ij}^6}\{1-3[\mathrm{Tr}\,(\mathbf{L})-\hat{\mathbf{r}}^T\mathbf{L}\hat{\mathbf{r}}]\} \tag{22}$$

for the intramolecular contribution and

$$M_{ij}=\frac{4}{5}\frac{1}{r_{ij}^6}\left(1-\frac{6C}{r_{ij}}+\frac{6D}{r_{ij}^2}\right) \tag{23}$$

where $C=\hat{\mathbf{r}}^T\langle\mathbf{d}\rangle$ and $D=3\hat{\mathbf{r}}^T\mathbf{V}\hat{\mathbf{r}}-\mathrm{Tr}\,(\mathbf{V})$, for the intermolecular contribution.

It can be readily shown that (23) reduces to (22) if the tensor $\mathbf{V}$, given by equation (15), is substituted into (23). Although equation (23) is, in fact, applicable to all three cases outlined above, it is convenient to treat the significant intramolecular contribution separately.

The expression for the second moment of a polycrystalline substance thus becomes

$$\langle \varDelta H^2\rangle=K\left[\frac{4}{5}\sum_{i>j}^{\text{all}}\frac{1}{r_{ij}^6}-\frac{12}{5}\left(\sum_{i>j}^{\text{intra}}\frac{G}{r_{ij}^6}\right.\right.$$
$$\left.\left.+2\sum_{i>j}^{\text{inter}}\frac{C}{r_{ij}^7}-2\sum_{i>j}^{\text{inter}}\frac{D}{r_{ij}^8}\right], \tag{24}$$

where $K=\frac{3}{2}I(I+1)\gamma^2\hbar^2/N$, as in (1), and $G=\mathrm{Tr}(\mathbf{L})-\hat{\mathbf{r}}^T\mathbf{L}\hat{\mathbf{r}}$. The first term is also obtained by an orientational averaging of equation (1) and thus refers to the case of nuclei at rest. It is known, and is always referred to, as the second moment of the rigid lattice.

Molecular motion usually leads to a reduction of the second moment from its rigid-lattice value. It is often convenient to be able to estimate this reduction and for this purpose the reduction factor defined as

$$\varrho=\langle \varDelta H^2\rangle/\langle \varDelta H^2\rangle_{\text{rigid}} \tag{25}$$

(Gutowsky & Pake, 1950) is usually calculated. For example, the reduction factor for the intramolecular contribution of a single crystal [see (17)] as well as of a polycrystalline substance, [see (22)], under the assumption of isotropic libration, is given by

$$\varrho=1-2\,\mathrm{Tr}\,(\mathbf{L})=1-6L_0\,. \tag{26}$$

This is a crude but rapid way of estimating the magnitude of the effect of motion on the intramolecular contribution to the second moment.

Discussion

Within some limitations, to be discussed below, the above method constitutes a link between the manifestations of lattice vibrations in two different phenomena: diffraction by crystals and their nuclear magnetic resonance. Thus, a direct application of the above expressions would be a confrontation of experimental second-moment data with theoretical values of the vibration-affected second moment, calculated using crystallographic positional and thermal parameters. Several such examples, concerning powder specimens, have been reported elsewhere (Polak, Sheinblatt & Shmueli, 1974). Undoubtedly, experiments with single-crystal specimens are called for, if an extraction of meaningful information about motion, from second-moment measurements, is to be attempted.

Assuming that the crystallographic thermal parameters are sufficiently accurate for the purpose of these calculations, we are still faced with a difficulty – the necessity of neglecting correlated motion. For a given crystal, a comparison with reliable second-moment experimental results is likely to indicate whether such an approximation (in fact, the assumption of an Einstein model of a crystal) is a valid one. In the case of segmented molecules, one may assume the model of 'riding' motion (Busing & Levy, 1964; Johnson, 1970) and represent thereby some degree of correlated motion of neighbouring segments. The composite vibration tensor $\mathbf{V}$ [equation (6)] reduces, in the case of the riding-motion model, to a simple expression, *viz.* $\mathbf{V}_{\text{riding}}=\mathbf{U}_i^A-\mathbf{U}_j^B$ (*cf.* Scheringer, 1972), calculable from available anisotropic vibration tensors. Thus, rough estimates of the effect of correlated motion can sometimes be obtained. It should be pointed out that the missing coupling tensors [equation (6)] can be calculated in the harmonic approximation, using semiempirical potential functions (Scheringer, 1972; Pawley, 1972), by well defined, yet rather cumbersome procedures. It is possible that advances in the application of lattice dynamics may contribute to the solution of this problem in the present context as well as in others.

Another possible source of discrepancy is the fact that the second moment is not affected by motions with frequencies smaller than the rigid-lattice line width (about 10^3–10^4 c.p.s. for typical hydrogen spectra). Actually, the density of states for such low-frequency vibration modes is usually very small (Kittel, 1971) and this does not appear to be a serious limitation, especially where librational motion is concerned.

An important practical aspect is the availability of anisotropic vibration tensors of hydrogen atoms. They are usually available from neutron diffraction studies but only very rarely from X-ray work. Neutron data are therefore definitely preferable, but in the case of X-ray results, the anisotropic vibration tensors of hydrogens can be approximately calculated from the rigid-body tensors of the heavy-atom skeleton.

Second-moment calculations for anthracene (Shmueli *et al.*, 1973) *trans,trans*-muconodinitrile (Polak, Sheinblatt & Shmueli, 1974) and *p*-terphenyl (Polak, Sheinblatt & Shmueli, 1975) indicate that, at least at present, the applicability of the method is restricted to large libration amplitudes (translational motion is less important, mainly because it does not affect the intramolecular motional correction). Thus, the calculated reduction factors of the second moments of polycrystalline anthracene, *trans,trans*-muconodinitrile and *p*-terphenyl are 98·1, 88 and 81 % respectively. Calculated reduction factors for the last two substances, in a single-crystal state, are significantly smaller for some orientation ranges of the crystal with respect to the external magnetic field (Polak, Sheinblatt & Shumeli, 1974, 1975). A typical error in second-moment determinations using computerized conventional experimental setups is 3 to 5%, which obviously limits the detectability of the effect to cases of large libration. However, very accurate techniques of second-moment measurements are being developed and the accuracies claimed are of the order of 1% (Engelsberg & Lowe, 1974). It follows that conventional second-moment measurements may provide, with the present method, useful indications about the genuineness of large librational motions indicated by diffraction methods. More sophisticated experimental approaches may lead to an independent application of the second moment to the study of average vibrational motion of nuclei, of spin $I=\frac{1}{2}$, in crystals.

Programming considerations

The equations summarized above have been applied (Shmueli *et al.*, 1973; Polak, Sheinblatt & Shmueli, 1974) to several examples with the aid of computer programs written in Fortran. Prior to the calculation, a rigid-body-motion analysis is required, which provides, apart from the rigid-body tensors of the group(s) considered, transformation matrices for coordinates and vibration tensors from the crystal system to the system to which the libration tensor is referred. These transformations are also applied to the space-group operations, so that standard structural data may be used as input, and the whole calculation is conveniently referred to a working Cartesian system. Some care must be exercised in evaluating the first correction term in equation (7) because the atomic position vectors $\boldsymbol{\varrho}_i^A$ say, are there referred to the effective centre of libration of group A (Pawley, 1968). If this group happens to be related to the reference molecule by a space-group operation, only the rotational part of this operation needs to be employed in order to generate the vector $\boldsymbol{\varrho}_i^A$.

The lattice sum in (1) was in some cases evaluated out to $r=8$ Å, although mostly smaller cut-off distances appear to be sufficient.

In second-moment calculations for single-crystal specimens, the magnetic-field vector must also be specified and transformed to the working system. Since the goniometer axis is usually perpendicular to the magnetic field lines, a theoretical curve for comparison with the experiment is easily obtained by taking $\hat{\mathbf{H}}_0$ as normal to the lattice vector about which the crystal is being rotated, and by rotating $\hat{\mathbf{H}}_0$ about this direction in preset steps throughout the required range. Examples of such curves are presented elsewhere (Polak, Sheinblatt & Shmueli, 1974).

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