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A General Procedure for the Calculation of Theoretical Nuclear Magnetic Resonance Second Moments in Dipolar Solids; Application to Oxalic Acid Dihydrate

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It is shown that the second moment of a dipolar solid can be written as a sum of products of real second-order spherical harmonic functions. This sum can be contracted to a quadratic form, $\tilde{\mathbf{q}}\mathbf{S}\mathbf{q}$, where $\mathbf{q}$ depends only on the direction of the magnetic field and $\mathbf{S}$, the second moment tensor, only on the crystal structure and the assumptions made concerning the molecular motions. The effects on $\mathbf{S}$ of symmetry, rigid-body reorientations, and librational motion are investigated quantitatively. A formula for the second moment of a powder is also given. The procedure is illustrated by refinements of the relative hydrogen positions in oxalic acid dihydrate from experimental second moments.

GENERAL INTRODUCTION

In 1953 Andrew and Eades (*1*) concluded from NMR data that the molecules in solid benzene reorient around their sixfold pseudosymmetry axes. Since then, numerous investigations using continuous-wave and pulse NMR have determined different types of motion in solids: free and hindered rotation, conformational motion (*2*), collective reorientational processes (*3*), diffusional motion, and lattice vibrations. The NMR technique is well suited for such studies which provide valuable information about the dynamic properties of solids.

It is the purpose of this and the subsequent (*4*) paper to illustrate, using second moment tensors, that second moments from a wide-line study are actually closely related to the relaxation constants obtained from measurements of T_1 and $T_{1\rho}$. It is also the author's purpose to demonstrate that second moment tensors may readily be calculated theoretically from the known crystal structure and from assumptions about the reorientational and vibrational motions taking place. A summary of some of the results obtained is given in (*5*).

In Part I expressions are derived for the second moment tensor in the presence of reorientational motion including rigid-body reorientations. Symmetry constraints are investigated and an expression is derived for the second moment of a powder. The procedure is illustrated by calculations on oxalic acid dihydrate. The topic "Vibrational Motion" requires a special introduction and is therefore treated separately in Part II.

I. THE SECOND MOMENT TENSOR

Introduction

The lineshape of an NMR spectrum of a dipolar solid is, in general, difficult to calculate theoretically (*6*); the Van Vleck formula (*7–10*) for the second moment is therefore usually used. The direct application of this formula has, however, several

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disadvantages: The tedious calculations must be carried out for each of the orientations of a single crystal and for a number of evenly distributed orientations sufficiently large to enable an estimate to be made of the average over a powder. (The latter procedure is necessary only when molecular motions occur.) Furthermore, it is not clear from the formula how the situation is affected by symmetry, how many independent parameters one may determine from a set of experimental data, or how averaging over lattice vibrations may be carried out. In 1959 McCall and Hamming (*11*, *12*) proposed a method which allowed the separate evaluation of the orientational and structural dependencies of the second moment in rigid solids, and found that, in general, fifteen quantities are sufficient to describe the structural dependence of the second moment. This method was never used by the authors themselves, but has been applied by others (*13–15*), as described in a review article by Gorskaya and Fedin (*16*). O'Reilly and Tsang published a more comprehensive study using more suitable functions for the structural dependence of the second moment, namely, the even complex spherical harmonics up to and including fourth order (*17*). Making extensive use of group theory, they derived somewhat cumbersome expressions for the symmetry-adapted functions and tabulated the number of independent structural parameters for the different crystal symmetries. Dereppe (*18*) recently extended the procedure to include molecular motion, and also derived a convenient formula for the average over a powder. In 1969, Falaleev, Falaleeva, and Lundin (*19*) introduced a tensor approach which was later supplemented by symmetry considerations (*20*). Their method is more convenient than the others referred to but does not include cases involving molecular reorientations. This seriously limits the applicability since relaxation times for rigid solids are usually very long.

Mathematical Derivations

The second moment tensor. The second moment, M_2, of an NMR line broadened by dipolar interactions may be calculated according to the well-known Van Vleck formula (*7–9*)

$$M_2 = M_{2l} + M_{2u},$$

where

$$M_{2l} = \tfrac{3}{4}\cdot(1/N) \sum_{i=1}^{N} \sum_{j=1}^{\infty} \gamma_j^4 \hbar^2 I_j(I_j+1) \langle\langle b_{ij}\rangle^2\rangle,$$

$$M_{2u} = \tfrac{1}{3}\cdot(1/N) \sum_{i=1}^{N} \sum_{k=1}^{\infty} \gamma_i^2 \gamma_k^2 \hbar^2 I_k(I_k+1) \langle\langle b_{ik}\rangle^2\rangle, \qquad [1]$$

and

$$b_{ij} = (3\cos^2\theta_{ij} - 1)/r_{ij}^3.$$

The quantities M_{2l} and M_{2u} are the contributions from interactions between spins of the same and of different kinds, respectively, r_{ij} is the distance between atoms i and j and θ_{ij} is the angle between the external magnetic field and the vector connecting two atoms. The quantity N is the number of atoms at resonance per unit cell, and γ and I are the gyromagnetic ratio and spin for a nucleus.

Two averaging symbols are included in formula [1]. The inner average of b_{ij} is taken over all motions characterized by a correlation time sufficiently short to cause the maximum possible reduction of the second moment. The outer average takes account of static disorder, or of molecular motion which is too slow to affect the second moment.

To simplify what follows, the indices i and j will be dropped, and the summation over i and j will be included in the outer average. Only spins at resonance will be treated since the extension required to include the term M_{2u} is trivial. We can now write

$$M_2 = \alpha\langle\langle b\rangle^2\rangle, \qquad [2]$$

where α is the proper constant as apparent from formula [1].

It is convenient to express the second moment tensor, to be introduced shortly, as a function of atom coordinates in an orthonormal system. It is convenient to specify the relations between the basis vectors in the orthonormal system **i**, **j**, and **k** and the crystallographic axes **a**, **b**, and **c** since the components of a tensor depend on the basis. The symmetry considerations later in this paper become particularly simple for the following choice: The vector **i** is parallel to **a**, **j** is perpendicular to **a** and lies in the plane defined by **a** and **b** and $\mathbf{k} = \mathbf{i} \times \mathbf{j}$.

Formula [1] can now be rewritten in terms of the interatomic vector $\tilde{\mathbf{r}} = (r_1, r_2, r_3)$ and the unit vector $\tilde{\mathbf{h}} = (h_1, h_2, h_3)$ which is parallel to the external magnetic field.

$$\begin{aligned} b &= \frac{3(\tilde{\mathbf{h}}\mathbf{r})^2 - r^2}{r^5} = \frac{3\tilde{\mathbf{h}}(\mathbf{r}\tilde{\mathbf{r}})\mathbf{h} - r^2}{r^5} \\ &= \frac{3}{r^5}(h_1, h_2, h_3)\begin{pmatrix} r_1{}^2 - \frac{r^2}{3} & r_1 r_2 & r_1 r_3 \\ r_1 r_2 & r_2{}^2 - \frac{r^2}{3} & r_2 r_3 \\ r_1 r_3 & r_2 r_3 & r_3{}^2 - \frac{r^2}{3} \end{pmatrix}\begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix} \\ &= (1/r^5)\tilde{\mathbf{h}}(3\mathbf{R} - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R})\mathbf{h}, \qquad \text{where } \mathbf{R} = \mathbf{r}\tilde{\mathbf{r}}. \end{aligned} \qquad [3]$$

Here **I** is the identity matrix. This expression may be expanded in the matrices $\mathbf{B}_k$ shown in Table 1.

$$\begin{aligned} b &= (1/r^5)\tilde{\mathbf{h}}(3\mathbf{R} - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R})\mathbf{h} = \tilde{\mathbf{h}} \sum_{k=1}^{5} a_k \mathbf{B}_k \mathbf{h} \\ &= \sum_{k=1}^{5} a_k(\tilde{\mathbf{h}}\mathbf{B}_k\mathbf{h}) = \sum_{k=1}^{5} a_k q_k, \end{aligned} \qquad [4]$$

TABLE 1

THE MATRICES $\mathbf{B}_k$[a]

$\mathbf{B}_1 = \frac{(5)^{1/2}}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$	$\mathbf{B}_4 = \frac{(15)^{1/2}}{2}\begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}$
$\mathbf{B}_2 = \frac{(15)^{1/2}}{2}\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\mathbf{B}_5 = \frac{(15)^{1/2}}{2}\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}$
$\mathbf{B}_3 = \frac{(15)^{1/2}}{2}\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$	$\mathbf{B}_6 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

[a] See text.

where

$$a_k = (4\pi^{1/2}/5r^3)\,\phi_k(\mathbf{r}) \qquad \text{and} \qquad q_k = 2\pi^{1/2}\,\phi_k(\mathbf{h}). \tag{5}$$

The functions ϕ_k are the second-order spherical harmonic functions shown in Table 2. There is no contribution $a_6 q_6$ since $(3\mathbf{R} - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R})$ has zero trace.

TABLE 2

THE REAL SECOND-ORDER SPHERICAL HARMONICS ILLUSTRATED AS FUNCTIONS OF THE VECTOR $\mathbf{p} = (x, y, z)$[a]

$\phi_1 = (5/16\pi)^{1/2}\,[(x^2 + y^2 - 2z^2)/p^2]$
$\phi_2 = (15/16\pi)^{1/2}\,[(x^2 - y^2)/p^2]$
$\phi_3 = (15/4\pi)^{1/2}\,(xy/p^2)$
$\phi_4 = (15/4\pi)^{1/2}\,(xz/p^2)$
$\phi_5 = (15/4\pi)^{1/2}\,(yz/p^2)$

[a] The definition of the basis vectors is given in the text.

Using [4] we may now rewrite [2].

$$\begin{aligned} M_2 = \alpha\langle\langle b\rangle^2\rangle &= \alpha\left\langle\left\langle \sum_{i=1}^{5} a_i q_i\right\rangle^2\right\rangle \\ &= \alpha\left\langle\left(\sum_{i=1}^{5} \langle a_i\rangle q_i\right)^2\right\rangle \\ &= \alpha\left\langle \sum_{i=1}^{5}\sum_{j=1}^{5} \bar{a}_i \bar{a}_j q_i q_j\right\rangle \\ &= \sum_{i=1}^{5}\sum_{j=1}^{5} \langle \alpha \bar{a}_i \bar{a}_j\rangle q_i q_j \\ &= \sum_{i=1}^{5}\sum_{j=1}^{5} S_{ij} q_i q_j = \tilde{\mathbf{q}}\mathbf{S}\mathbf{q}. \end{aligned} \tag{6}$$

This is a quadratic form in $\mathbf{q}$ and the symmetric tensor S, where S may be called the second moment tensor.

Reorientational rigid-body motion. Let us assume that the reorientations of a rigid body take place at a rate much faster than that corresponding to the linewidth, that there are n equally probable configurations, and that each such configuration i is described by a real and unitary transformation $\mathbf{U}_i$. Such a transformation contains only the rotational part (centered at the origin) of the actual reorientation, since the intra-rigid-body second moment is not affected by translations. The matrices $\mathbf{B}_k$ shown in Table 1 and the $\mathbf{U}_i$ may be used in the definition of $\mathbf{T}$:

$$(1/n) \sum_{i=1}^{n} \mathbf{U}_i \mathbf{B}_k \tilde{\mathbf{U}}_i = \sum_{m=1}^{5} T_{km} \mathbf{B}_m, \qquad k = 1, \ldots, 5. \tag{7}$$

The coefficient for the term $\mathbf{B}_6$ is zero since the trace is invariant under a unitary transformation.

The vector $\mathbf{U}_i\mathbf{r}$ is inserted into [3], [4], and [5] and the proper average is taken over the motion:

$$\begin{aligned} b &= \frac{1}{n}\sum_{i=1}^{n}\frac{3(\tilde{\mathbf{h}}(\mathbf{U}_i\mathbf{r}))^2 - r^2}{r^5} = \frac{1}{n}\frac{1}{r^5}\tilde{\mathbf{h}}\sum_{i=1}^{n}\mathbf{U}_i(3\mathbf{R} - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R})\tilde{\mathbf{U}}\mathbf{h} \\ &= (1/n)\tilde{\mathbf{h}}\sum_{i=1}^{n}\sum_{k=1}^{5} a_k\mathbf{U}_i\mathbf{B}_k\tilde{\mathbf{U}}_i\mathbf{h} \qquad [8] \\ &= \tilde{\mathbf{h}}\sum_{k=1}^{5} a_k\sum_{m=1}^{5} T_{km}\mathbf{B}_m\mathbf{h} = \sum_{k=1}^{5} a_k\sum_{n=1}^{5} T_{km}q_m. \end{aligned}$$

Using the relation

$$q_k' = \sum_{m=1}^{5} T_{km}q_m,$$

we can now insert the result from [8] into [6] and obtain

$$M_2' = \tilde{\mathbf{q}}'\mathsf{S}\mathbf{q}' = \tilde{\mathbf{q}}\tilde{\mathbf{T}}\mathsf{S}\mathbf{T}\mathbf{q}; \qquad [9]$$

thus, $\mathsf{S}^{(r)} = \tilde{\mathbf{T}}\mathsf{S}\mathbf{T}$. The quantity S is the second moment tensor for the rigid body at rest, and $\mathsf{S}^{(r)}$ is the second moment tensor for the body when it is reorienting. Equation [9] holds also in cases where S is already narrowed by internal motions.

For example, a rigid body reorients around the $\mathbf{k}$ axis in such a way that the $\mathbf{U}_i$ transformations correspond to rotations by 0, 90, 180, and 270 degrees. If the $\mathbf{U}_i$ are inserted into [7], one obtains $T_{11} = 1$, and $T_{ij} = 0$ for all other values of i and j. The term $\mathbf{T}$ may now be inserted in [9], which gives $S_{11}^{(r)} = S_{11}$ and $S_{ij}^{(r)} = 0$ otherwise. Thus, the reduced second moment is $S_{11}q_1^2$.

The second moment for a powder. An expression for the average of the second moment over the orientations of the crystallites in a powder can readily be derived if we write [6] in terms of the orthogonal and normalized spherical harmonic functions shown in Table 2:

$$M_2 = \tilde{\mathbf{q}}\mathsf{S}\mathbf{q} = \sum_{i=1}^{5}\sum_{j=1}^{5} S_{ij}q_iq_j = 4\pi\sum_{i=1}^{5}\sum_{j=1}^{5} S_{ij}\phi_i(\mathbf{h})\cdot\phi_j(\mathbf{h}).$$

The average is

$$\bar{M}_2 = \frac{4\pi\sum_{i=1}^{5}\sum_{j=1}^{5} S_{ij}\int_{\text{sphere}}\phi_i\phi_j\,d\tau}{\int_{\text{sphere}} d\tau} = \mathrm{Tr}\,\mathsf{S}. \qquad [10]$$

Results

The second moment tensor. The second moment, M_2, of an NMR line broadened by dipolar interactions may be calculated according to the well-known Van Vleck formula (*7–10*). This formula was rewritten in the preceding section in the form

$$M_2 = \tilde{\mathbf{q}}\mathsf{S}\mathbf{q}. \qquad [11]$$

The right-hand side of the formula is a quadratic form in $\mathbf{q}$ and S where $\mathbf{q}$ depends only on the direction of the external magnetic field relative to the crystal (cf. Table 2), and S, which may be called the second moment tensor, depends only on the crystal structure and the motions present. Since S is a symmetric 5×5 tensor there are at most 15 elements to be determined, which also means that at most 15 structural parameters may be determined from comparisons between experimental and calculated second moment tensors. This is consistent with earlier results (cf. Introduction).

Reorientational rigid-body motion. In many cases encountered in practice a molecule or a segment of a molecule reorients as a rigid body. It was shown in the preceding section that the intra-rigid-body second moment tensor averaged over the reorientational motion, $\mathrm{S}^{(r)}$, is given by the formula

$$\mathrm{S}^{(r)} = \tilde{\mathbf{T}}\mathbf{S}\mathbf{T}. \qquad [12]$$

Here S is the second moment tensor for the rigid body at rest and $\mathbf{T}$ depends only on the reorientations. Equation [12] holds also in cases where S is already reduced by any internal motions.

The second moment of a powder. The second moment averaged over the crystallites in a powder is simply the trace (the sum of the diagonal elements) of the second moment tensor (cf. preceding section).

Symmetry considerations. If symmetry is present, it is possible to find a transformation of the functions $q_i q_j$ such that each new function transforms according to one of the symmetry species of the group (*21*). Since the second moment is totally symmetric with respect to all symmetry operations, all the coefficients of functions which do not belong to the totally symmetric species must vanish. This means that the coefficients of the untransformed functions are related to each other in such a way that the total symmetry is preserved.

The symmetry of a periodic solid may be described by one of the 230 space groups (*22*). The NMR spectrum is, however, independent of the translation symmetry, and this restricts our considerations to the corresponding 32 point groups. In addition, the Hamiltonian for the dipole–dipole interaction has inversion symmetry and thus also has the second moment. We need therefore only consider the point group of highest symmetry for each of the 11 Laue groups. Such an analysis has been made using group theory and the result is shown in Table 3. The number of independent parameters which completely describe the second moment for different symmetries agrees with those in (*5*, *17*, *20*).

It is important that the symmetry elements considered so far are those of the crystal structure or have been derived from it. If, instead, the symmetry of the second moment itself were to be investigated, one might find that it was higher. Thus, a tetragonal crystal structure whose Laue symmetry is $4/m$ has a second moment tensor whose Laue symmetry is $4/mmm$. The trigonal point groups $\bar{3}$ and $\bar{3}m$ are similarly related. These relations together with the results listed in Table 3 imply that it is only possible to determine the *crystal class* of a substance if only its experimental second moment tensor is known. This conclusion has been drawn earlier (cf. Refs. *5*, *20*).

Refinement of the relative hydrogen positions in oxalic acid dihydrate using second moment tensors. The crystal structures of normal and deuterated oxalic acid dihydrate have been determined in several diffraction studies (*23–29*). The structure of the normal compound, which is only known to crystallize in the α-phase, was obtained from neutron diffraction by Garrett (*25*) and is illustrated in Fig. 1. In addition, the relative positions of the hydrogens have been determined from NMR data by several authors (*14*, *30–32*). Dereppe *et al.* (*14*) applied the procedure proposed by McCall and

Hamming (*11*, *12*) using 350 experimentally obtained second moments of a single crystal. Håland and Pedersen (*32*) compared experimental and calculated lineshapes and obtained results in good agreement with those from the neutron diffraction study (*25*). They also critically discussed the results of Dereppe *et al.*, making the criticism that they had not taken the flippings of the water molecules into account. The purpose of this section is twofold: to illustrate the use of the second moment tensor and to redetermine the relative hydrogen positions from the data of Dereppe *et al.* according to a more realistic model for the molecular motion.

TABLE 3

THE POSSIBLE SYMMETRIES OF THE SECOND MOMENT AND THEIR RESTRICTIONS ON THE ELEMENTS OF THE SECOND MOMENT TENSOR

Crystal class	Laue symmetry		No. of independent parameters	The nonzero elements of S ($S_{ij} = S_{ji}$) and their symmetry relations
Triclinic	$\bar{1}$	$S_2(C_i)$	15	all 15
Monoclinic[a]	$2/m$	C_{2h}	9	$S_{11}\, S_{12}\, S_{14}\, S_{22}\, S_{24}\, S_{33}\, S_{35}\, S_{44}\, S_{55}$
Orthorombic	mmm	$D_{2h}(V_h)$	6	$S_{11}\, S_{12}\, S_{22}\, S_{33}\, S_{44}\, S_{55}$
Tetragonal	$4/m$	C_{4h}	5	$S_{11}\, S_{22}\, S_{23}\, S_{33}\, S_{44} = S_{55}$
Tetragonal	$4/mmm$	D_{4h}	4	$S_{11}\, S_{22}\, S_{33}\, S_{44} = S_{55}$
Trigonal[b]	$\bar{3}$	$S_6(C_{3i})$	5	$S_{11}\, S_{22} = S_{33}\, S_{44} = S_{55}\, S_{24} = -S_{35}\, S_{34} = S_{25}$
Trigonal[b]	$\bar{3}m$	D_{3d}	4	$S_{11}\, S_{22} = S_{33}\, S_{44} = S_{55}\, S_{34} = S_{25}$
Hexagonal	$6/mmm$	D_{6h}	3	$S_{11}\, S_{22} = S_{33}\, S_{44} = S_{55}$
Cubic	$m3m$	T_d	2	$S_{11} = S_{22}\, S_{33} = S_{44} = S_{55}$

[a] The symmetry axis is **b**.

[b] The symmetry axis is **c** in the corresponding hexagonal cell given in Ref. (*22*).

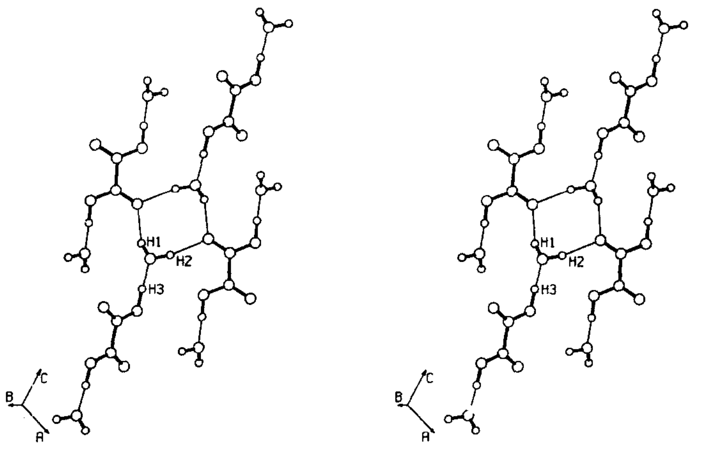

FIG. 1. The crystal structure of oxalic acid dihydrate as given in Ref. (*25*).

The experimental second moment tensor given in Table 4 was determined in a least-squares procedure using the data in (*14*). Two orientation angles, around the c^* and *a* axes, could also be included in the refinement since the symmetry is monoclinic. The total shifts in these angles were only about one degree in both cases, however, which thus partly confirms the orientation given in (*14*). The quantity minimized was the root mean square value of $(M_2(\text{obs}) - M_2(\text{calc}))/M_2(\text{calc})$ and its final value became 0.049. The computer program (ESM) used for these calculations is described in (*33*).

The theoretical second moment tensors for the interactions from within an asymmetric unit (the two water hydrogens and the acid hydrogen) and between this unit and its 33 nearest neighboring asymmetric units were calculated from the structural data in (*25*). The water molecules are known to reorient around their twofold pseudosymmetry axes (*32*). This motion was taken into account in the calculations which were performed as described earlier (*34*, *35*) using the general program PSM (*33*, *35*), which is based on the procedure described above. The result is shown in Table 4.

TABLE 4

Experimental and Calculated Second Moment Tensors in G^2 for Oxalic Acid Dihydrate[a]

	S_{11}	$2S_{12}$	$2S_{14}$	S_{22}	$2S_{24}$	S_{33}	$2S_{35}$	S_{44}	S_{55}
Experimental	2.053	−0.396	5.130	1.460	0.087	6.254	7.116	5.612	3.141
Theoretical intraunit	4.724	1.866	8.746	0.854	1.790	11.437	8.406	4.050	1.689
Theoretical interunit	0.781	−0.125	0.225	0.665	0.059	0.841	0.342	0.448	0.491
Intraunit tensors in refinements of the structure[b]									
observed	1.272	−0.271	4.905	0.795	0.028	5.413	6.774	5.164	2.650
calculated	1.237	−0.256	5.043	0.637	0.043	5.479	6.662	5.227	2.422

[a] $S_{ij} = S_{ji}$; the elements not listed are zero.

[b] See text.

It was assumed that the detailed geometry has little effect on the theoretical interasymmetric unit second moment. The difference between the experimental and the theoretical interasymmetric unit second moment tensors was therefore used in the subsequent least-squares refinements of the relative hydrogen positions in the asymmetric unit. The interatomic distances and angles between the interatomic vectors and the crystallographic axes are shown in Table 5, together with the results from earlier studies. The intra-asymmetric unit tensor calculated from the final positional parameters is given in Table 4.

The agreement obtained in this study between the interatomic vectors and those obtained by diffraction methods or lineshape analysis is reasonable in view of the systematic errors involved in a second moment study. It is, for instance, well known that the second moment is very sensitive to the shape of the wings of the wide-line spectrum, and that part of these often have to be excluded because of signal-to-noise difficulties. Furthermore, it is well known that the vibrational motion of a water

TABLE 5

STRUCTURAL DATA FOR THE HYDROGEN ATOMS IN OXALIC ACID DIHYDRATE LABELED IN FIGURE 1, COMPARED WITH RESULTS FROM EARLIER STUDIES[a]

	i	j	r_{ij}	χ_1	χ_2	χ_3
Garrett (*25*) (neutron diffraction)	1	2	1.524	40.7	53.8	86.8
	1	3	2.108	47.7	82.3	27.5
	2	3	2.068	82.7	72.5	19.7
Itoh *et al.* (*30, 31*)[b] (NMR lineshape)	1	2	1.65	40.2	57.6	82.5
	1	3	2.31	43.1	90.0	41.6
	2	3	1.96	77.2	67.6	3.5
Dereppe *et al.* (*14*)[b] (NMR second moment)	1	2	1.563	45.2	52.0	81.9
	1	3	2.071	47.6	83.3	27.3
	2	3	2.203	82.3	71.0	20.7
Håland and Pedersen (*32*) (NMR lineshape)	1	2	1.595	38.9	55.5	87.5
	1	3	2.131	46.6	81.4	29.1
	2	3	2.046	83.7	73.5	19.4
This study (NMR second moment)	1	2	1.66	45.4	55.5	77.4
	1	3	2.03	37.2	87.3	36.7
	2	3	2.16	77.9	67.1	23.1

[a] The interatomic distances, r_{ij}, between atoms i and j are shown together with the angles χ_1, χ_2, and χ_3 between the interatomic vectors and the crystallographic axes **a**, **b**, and **c**, respectively.

[b] An incorrect model has been used in this study as discussed in Ref. (*32*).

molecule causes an increase of the apparent intramolecular NMR distance (*36*), while it decreases the distance observed by diffraction techniques (*36*, *37*).

Discussion

One advantage of using procedures in which the structural and orientational dependencies of the second moment are separated is that the summations in Van Vleck's formula only have to be performed once. However, additional features are often desired. Real functions are much easier to use than complex ones for computer calculations. The use of symmetry-adapted functions not only allows the determination of a minimal number of parameters, but also in many cases the orientation of the crystal. It is important that molecular motion is considered since the relaxation times can be forbiddingly long in rigid solids. Furthermore, it is often desirable to be able to calculate the average over a powder conveniently, since it is a tedious and sometimes almost impossible task to grow large single crystals. Finally, it is well known, particularly for weakly bonded molecules with small moments of inertia, that the librational motions cause a nonnegligible decrease of the second moment (cf. Part II). The applicability of the present procedure is compared in Table 6 with those of the procedures described in the Introduction. The method has been used in experimental studies of molecular motion in dimethylammonium (*38*) and trimethylammonium salts (*38*, *39*).

TABLE 6

A COMPARISON OF THE APPLICABILITY OF THE DIFFERENT PROCEDURES FOR CALCULATIONS OF SECOND MOMENTS[a]

	McCall and Hamming (*11, 12*)	O'Reilly and Tsang (*17*)	Falaleev *et al.* (*19, 20*)	Dereppe (*18*)	Present study
Real functions	yes	no	yes	no	yes
Symmetry	no	yes	yes	no	yes
Molecular motion	no	no	no	yes	yes
Dynamical average for a powder	no	no	no	yes	yes
Librational motion (cf. Part II)	no	no	no	no	yes
Relaxation constants (cf. Ref. (*4*))	no	no	no	no	yes

[a] See text.

II. VIBRATIONAL MOTION

Introduction

A general description of the vibrational motion in a solid is very complicated (*40, 41*), usually involving several approximations. Such approximations include harmonic motion and "low temperature" (most oscillators are in their ground states). The problem is still rather complex, however, and one often makes the additional assumption that the vibrational motions of the atoms are completely uncorrelated. For such motions the mean square amplitude of vibration along a direction **p** is equal to **pTp**, where **T** here is the translation tensor of the atom.

A great number of temperature factors (which are closely related to the translation tensor above) and atomic positions are normally determined in diffraction studies (*42*).

The approximation assuming uncorrelated atomic motions is probably at its worst for molecular solids in which the amplitudes of the intramolecular oscillations may be expected to be small compared to the motions of the molecules as a whole. Accordingly, several authors have derived methods for making rigid-body motion analysis (*43–47*). The rigid-body motion is described to second order by the tensors **T**, **L**, and **S**, where **T** is the translational tensor, **L** the librational tensor (torsional oscillation), and **S** the screw tensor, which may be interpreted as the tensor which describes the coupling between **T** and **L** (the TLS model; an alternative formulation is the somewhat related TLX model (*45*)).

It has been shown (*48–50*) that the second moment is unaltered by isotropic and uncorrelated atomic vibrations. It would therefore be tempting to conclude that the vibrational alteration of the second moment can in general be neglected. However, anisotropy as well as correlations of the vibrations do affect the second moment, as indicated by the results of several experimental studies (*51, 52*).

The alteration of the second moment due to vibrational motion has been investigated by Ibers and Stevenson (*53*), and the effect on the line splittings in hydrates (which are closely related to the second moments) has been studied comprehensively by Pedersen (*54–56*). Recently, Polak *et al.* have analyzed the alteration of the second moment caused by intramolecular (*57*) and intermolecular (*58*) rigid-body vibrations.

Approximations

Some approximations are now made in the light of the results given in the Introduction. The alterations of the second moments due to intermolecular vibrations are neglected for the following reasons. (a) They are zero if the motions are isotropic and uncorrelated, (b) they may vary in sign, (c) the relative reduction becomes small at large atom–atom distances, and (d) the intermolecular second moment can be comparatively small anyway.

The rigid-body approximation is used for the intramolecular vibrations. However, this approximation is not always a very good one since segments of a molecule (such as methyl groups) may have considerable vibrational mobility relative to the rest of the molecule. However, as is illustrated below, such problems cause very little difficulty, since the calculations can be performed in steps: first on the segments and then on the molecule as a whole. (The vibrational alteration caused by interactions between such groups or any such group and the rest of the molecule are then partially neglected.)

The assumptions made imply that the interatomic distances to be used in the calculations are constant. Furthermore, only the librational parts of the molecular vibrations need to be considered since only the *relative* positions of two atoms affect the second moment.

Mathematical Derivations

The approach used by Shmueli *et al.* (*57*) is applied here in the initial stages of a more general derivation of expressions for the librationally reduced second moment tensors.

As illustrated in Fig. 2, the vector $\mathbf{r}$ is transformed to $\mathbf{r}_c$ by a rotation c radians around the axis $\mathbf{c}$. We obtain

$$\begin{aligned}
\mathbf{r}_{\parallel} &= (\mathbf{c}/c^2)(\tilde{\mathbf{r}}\cdot\mathbf{c}),\\
\mathbf{r}_{\perp} &= \mathbf{r} - (\mathbf{c}/c^2)(\tilde{\mathbf{r}}\cdot\mathbf{c}),\\
\mathbf{r}_{c_{\parallel}} &= \mathbf{r}_{\parallel},\\
\mathbf{r}_{c_{\perp}} &= \mathbf{r}_{\perp}\cos(c) + [(\mathbf{c}\times\mathbf{r}_{\perp})/c]\sin(c),\\
\mathbf{r}_c &= \mathbf{r} + (\mathbf{r}_c - \mathbf{r})\\
&= \mathbf{r} + \frac{(1-\cos(c))}{c^2}(\mathbf{C}\mathbf{r} - c^2\mathbf{r}) + \frac{\sin(c)}{c}(\mathbf{c}\times\mathbf{r}),
\end{aligned}$$

where $\mathbf{C} = \mathbf{c}\tilde{\mathbf{c}}$. For small angles:

$$\begin{aligned}
\mathbf{r}_c &= \mathbf{r} + \tfrac{1}{2}(\mathbf{C}\mathbf{r} - c^2\mathbf{r}) + \mathbf{c}\times\mathbf{r}\\
&= \mathbf{r} + \mathbf{C}_{\parallel}\mathbf{r} + \mathbf{C}_{\perp}\mathbf{r},
\end{aligned}$$

where $\mathbf{C}_{\parallel} = \tfrac{1}{2}(\mathbf{C} - c^2\mathbf{I})$ and

$$\mathbf{C}_{\perp} = \begin{pmatrix} 0 & -c_3 & c_2\\ c_3 & 0 & -c_1\\ -c_2 & c_1 & 0 \end{pmatrix}, \qquad \text{where } (c_1, c_2, c_3) = \tilde{\mathbf{c}}.$$

Furthermore,

$$\begin{aligned}
\langle \mathbf{r}_c\tilde{\mathbf{r}}_c\rangle = \langle \mathbf{R}_c\rangle &= \langle(\mathbf{r} + \mathbf{C}_{\parallel}\mathbf{r} + \mathbf{C}_{\perp}\mathbf{r})\widetilde{(\mathbf{r} + \mathbf{C}_{\parallel}\mathbf{r} + \mathbf{C}_{\perp}\mathbf{r})}\rangle\\
&= \langle(\mathbf{r} + \mathbf{C}_{\parallel}\mathbf{r} + \mathbf{C}_{\perp}\mathbf{r})(\tilde{\mathbf{r}} + \tilde{\mathbf{r}}\mathbf{C}_{\parallel} - \tilde{\mathbf{r}}\mathbf{C}_{\perp})\rangle\\
&= \langle\mathbf{R}\rangle + \langle\mathbf{R}\mathbf{C}_{\parallel}\rangle - \langle\mathbf{R}\mathbf{C}_{\perp}\rangle + \langle\mathbf{C}_{\parallel}\mathbf{R}\rangle + \langle\mathbf{C}_{\parallel}\mathbf{R}\mathbf{C}_{\parallel}\rangle\\
&\quad - \langle\mathbf{C}_{\parallel}\mathbf{R}\mathbf{C}_{\perp}\rangle + \langle\mathbf{C}_{\perp}\mathbf{R}\rangle + \langle\mathbf{C}_{\perp}\mathbf{R}\mathbf{C}_{\parallel}\rangle - \langle\mathbf{C}_{\perp}\mathbf{R}\mathbf{C}_{\perp}\rangle.
\end{aligned}$$

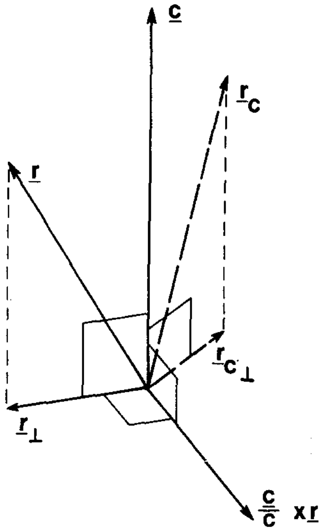

FIG. 2. The vector r is rotated through an angle c around an axis $\mathbf{c}$ so that it coincides with $\mathbf{r}_c$.

The third- and higher-order terms may be neglected:

$$\langle \mathbf{R}_c \rangle = \mathbf{R} + \langle \mathbf{R}\mathbf{C}_\parallel + \mathbf{C}_\parallel \mathbf{R} \rangle - \langle \mathbf{C}_\perp \mathbf{R}\mathbf{C}_\perp \rangle. \qquad [13]$$

However,

$$\begin{aligned} \langle \tilde{\mathbf{C}}_\perp \mathbf{R}\mathbf{C}_\perp \rangle &= \langle \tilde{\mathbf{R}}_\perp \mathbf{C}\mathbf{R}_\perp \rangle = \tilde{\mathbf{R}}_\perp \langle \mathbf{C} \rangle \mathbf{R}_\perp \\ &= \tilde{\mathbf{R}}_\perp \mathbf{L}\mathbf{R}_\perp = \sum_{i=1}^{3} \lambda_i \tilde{\mathbf{R}}_\perp (\mathbf{l}_i \tilde{\mathbf{l}}_i) \mathbf{R}_\perp \\ &= \sum_{i=1}^{3} \lambda_i \tilde{\mathbf{L}}_{i_\perp} \mathbf{R}\mathbf{L}_{i_\perp}, \end{aligned}$$

where

$$\mathbf{R}_\perp = \begin{pmatrix} 0 & -r_3 & r_2 \\ r_3 & 0 & -r_1 \\ -r_2 & r_1 & 0 \end{pmatrix}, \qquad \mathbf{L}_{i_\perp} = \begin{pmatrix} 0 & l_{i3} & -l_{i2} \\ -l_{i3} & 0 & l_{i1} \\ l_{i2} & -l_{i1} & 0 \end{pmatrix},$$

and $\langle \mathbf{C} \rangle = \mathbf{L}$, the libration tensor, which can be split up into its eigenvalues λ_i and eigenvectors $\mathbf{l}_i$.

Equation [13] can now be written

$$\langle \mathbf{R}_c \rangle = (1 - \mathrm{Tr}\,\mathbf{L})\mathbf{R} + \tfrac{1}{2}(\mathbf{L}\mathbf{R} + \mathbf{R}\mathbf{L}) + \sum_{i=1}^{3} \lambda_i \tilde{\mathbf{L}}_{i_\perp} \mathbf{R}\mathbf{L}_{i_\perp} = \mathbf{E}\mathbf{R}. \qquad [14]$$

The operator $\mathbf{E}$ in Eq. [14] is a linear operator (although not a simple matrix). It can be shown by explicit evaluations that the trace of a symmetric matrix is invariant under operations by $\mathbf{E}$.

The librational reduction matrix, $\mathbf{T}^{(l)}$, is defined by the formula

$$\mathbf{E}\mathbf{B}_k = \sum_{m=1}^{5} T_{km}{}^{(l)} \mathbf{B}_m, \qquad \text{where } k = 1, \ldots, 5. \qquad [15]$$

The rest of the derivation is very similar to that for reorientational rigid-body motion. The product $(1/r^5)(3\mathbf{R} - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R})$ in formula [3] should be substituted for

$$(1/r^5)(3\langle \mathbf{R}_c \rangle - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R}_c) = (1/r^5)(3\mathbf{E}\mathbf{R} - \mathbf{I}\,\mathrm{Tr}\,\mathbf{R}) = \sum_{k=1}^{5} a_k \sum_{m=1}^{5} T_{km} \mathbf{B}_m.$$

The result is

$$\mathsf{S}^{(l)} = \tilde{\mathbf{T}}^{(l)}\mathsf{S}\mathbf{T}^{(l)} \qquad [16]$$

Again S is the rigid second moment tensor, and $\mathsf{S}^{(l)}$ is the second moment tensor reduced by the librational motion. The formula is clearly also valid in cases where S is already reduced by *any* internal motion.

The second moment tensor for isotropic librations is evaluated as an example: $\mathsf{L} = \langle c^2\rangle \mathbf{I} = \frac{1}{3}\mathbf{I}\,\mathrm{Tr}\,\mathsf{L}$, since the librations are isotropic. The diagonal elements of $\mathbf{T}^{(l)}$ then become $1 - 3\langle c^2\rangle$ and the others zero, which implies that

$$\mathsf{S}^{(l)} = (1 - 3\langle c^2\rangle)^2\,\mathsf{S} \approx (1 - 6\langle c^2\rangle)\,\mathsf{S}$$

or

$$\langle c^2\rangle \approx (M_2 - M_2{}^{(l)})/6M_2 \qquad [17]$$

for any orientation. This result is consistent with that obtained for less general cases in (*57*).

Results and Discussion

It is shown in formulas [14, 15, 16] that a reasonable estimate of the vibrational average of the second moment tensor may be obtained if the librational tensors are known. The method has the important property that all the summations in Van Vleck's formula can be performed before the vibrational average is taken. The librational reduction matrix **T** depends namely only on the corresponding libration tensor. Conversely, components of the libration tensor may be evaluated if **T** has been determined experimentally; the symmetry involved has to be carefully considered since it may not be possible to determine the librational tensor uniquely. The reduction of the second moment due to isotropic librations is given by [17].

The effect of vibrational motion on the relaxation times in the laboratory and rotating frames of reference are discussed in the subsequent article (*4*).

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