The Effect of Rigid-Body Vibrations on the Nuclear Magnetic Resonance Signal for Quadrupole, Chemical Shift, and Dipole–Dipole Interactions in Solids

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In molecular solids, the rigid-body vibrational motions usually affect the quadrupole, the chemical shift, and the dipole–dipole interactions as well as the second moment much more strongly than other vibrations. It is shown here that the changes in these couplings and second moments due to librational motions are given by simple expressions linear in the elements of the librational tensor.

In a previous paper (*1*) a general procedure was described for the evaluation of NMR second moments in dipolar solids. This procedure included the effects of librational and reorientational motion and is applicable to single crystals and powders. The purpose of the present paper is to provide more convenient formulas for the librational averaging of the second moments, and also to demonstrate the application of this formalism to quadrupole, chemical shift, and dipole–dipole interactions.

VIBRATIONAL MOTIONS

A brief background and some references relating to vibrational motion may be found in Ref. (*1*). The mathematical derivations made later in this paper are based on the following approximations: (1) the molecules in a solid vibrate as rigid bodies, and (2) the amplitudes of librations are small. The justification for (1) is that the amplitudes of intermolecular vibrations are often much larger than those of the intramolecular vibrations. Within this approximation, the vibrational properties required in the following treatment of vibrational averaging are conveniently summarized in the 3×3 matrix $\mathbf{L}$ containing the components of the librational tensor. $\mathbf{L}$ may be defined for a librating molecule as

$$\mathbf{L} = \langle \mathbf{c}\tilde{\mathbf{c}} \rangle, \tag{1}$$

where $\mathbf{c}$ is parallel to the instantaneous rotation axis and $|\mathbf{c}|$ is the angle of displacement (in radians) from equilibrium about this axis.

The symmetry restrictions on $\mathbf{L}$ depend on the symmetry about the center of libration and may be derived by applying the approach used in Ref. (*1*):

(1) One mirror plane perpendicular to the z axis implies that $L_{13} = L_{23} = 0$.

(2) Three mirror planes perpendicular to the x, y, and z axes imply that $L_{12} = L_{13} = L_{23} = 0$.

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(3) A threefold, fourfold, or sixfold symmetry axis parallel to the z axis implies that $L_{12} = L_{13} = L_{23} = 0$ and $L_{11} = L_{22}$.

(4) For cubic site symmetries L is isotropic: $L_{11} = L_{22} = L_{33}$ and $L_{12} = L_{13} = L_{23} = 0$.

MATHEMATICAL DERIVATIONS

Let us assume that, in the presence of librations about an axis c, the instantaneous value of a measurable quantity, v_c, associated with a molecule may be written

$$v_c = \tilde{\mathbf{p}} \mathbf{U}_c \mathbf{p} \tag{2}$$

where $\mathbf{p}$ is a laboratory-fixed unit vector and $\mathbf{U}_c$ is a real, symmetric and traceless 3×3 matrix. Furthermore, let $\mathbf{U}$ be the equilibrium matrix equal to $\mathbf{U}_c$ in the absence of librations. In the following the elements of $\mathbf{p}$ and $\mathbf{U}_c$ are defined with respect to an ortho-normal basis. Assume, furthermore, that the elements of $\mathbf{U}_c$ are stationary in a frame fixed in the molecule and therefore, in general, time dependent in the laboratory system. We then have $\mathbf{U}_c = \mathbf{R}_c \mathbf{U} \tilde{\mathbf{R}}_c$, where $\mathbf{R}_c$ is a rotation matrix representing a rotation, relative to the equilibrium orientation of the molecule, about an instantaneous axis c. The average $\langle \mathbf{U}_c \rangle$ over the librational motion will then be $\langle \mathbf{R}_c \mathbf{U} \tilde{\mathbf{R}}_c \rangle$. The average of the observable v_c becomes

$$\langle v_c \rangle = \tilde{\mathbf{p}} \langle \mathbf{U}_c \rangle \mathbf{p}. \tag{3}$$

The expression $\langle \mathbf{U}_c \rangle = \langle \mathbf{R}_c \mathbf{U} \tilde{\mathbf{R}}_c \rangle$ may be rewritten in terms of the librational matrix L and it has been shown in Ref. (1) that

$$\langle \mathbf{U}_c \rangle = (1 - \operatorname{Tr} \mathbf{L})\mathbf{U} + \tfrac{1}{2}(\mathbf{L}\mathbf{U} + \mathbf{U}\mathbf{L}) + \sum_{i=1}^{3} \lambda_i \tilde{\mathbf{L}}_{i_\perp} \mathbf{U} \mathbf{L}_{i_\perp}. \tag{4}$$

Here

$$\mathbf{L}_{i_\perp} = \begin{pmatrix} 0 & l_{i3} & -l_{i2} \\ -l_{i3} & 0 & l_{i1} \\ l_{i2} & -l_{i1} & 0 \end{pmatrix}$$

and λ_i is the eigenvalue corresponding to the ith eigenvector, $\mathbf{l}_i$, of L. Thus $L = \sum_{i=1}^{3} \lambda_i \mathbf{l}_i \tilde{\mathbf{l}}_i$. In a similar way U may be written in terms of its eigenvectors and eigenvalues: $\mathbf{U} = \sum_{i=1}^{3} \mu_i \mathbf{u}_i \tilde{\mathbf{u}}_i$.

The last term in [4] may be written

$$\mathbf{F} = \sum_{i=1}^{3} \lambda_i \tilde{\mathbf{L}}_{i_\perp} \mathbf{U} \mathbf{L}_{i_\perp}$$

$$= \sum_{i=1}^{3} \lambda_i \tilde{\mathbf{L}}_{i_\perp} \left(\sum_{j=1}^{3} \mu_j \mathbf{u}_j \tilde{\mathbf{u}}_j \right) \mathbf{L}_{i_\perp}$$

$$= \sum_{i=1}^{3} \sum_{j=1}^{3} \lambda_i \mu_j \tilde{\mathbf{L}}_{i_\perp} \mathbf{u}_j \tilde{\mathbf{u}}_j \mathbf{L}_{i_\perp}.$$

The elements of **F** can now readily be evaluated. For example

$$F_{11} = \sum_{i=1}^{3} \sum_{j=1}^{3} \lambda_i \mu_j (-l_{i3} u_{j2} + l_{i2} u_{j3})^2$$

$$= \left(\sum_{i=1}^{3} \lambda_i l_{i3}^2 \right) \left(\sum_{j=1}^{3} \mu_j u_{j2}^2 \right) - 2 \left(\sum_{i=1}^{3} \lambda_i l_{i2} l_{i3} \right) \left(\sum_{j=1}^{3} \mu_j u_{j2} u_{j3} \right) + \left(\sum_{i=1}^{3} \lambda_i l_{i2}^2 \right) \left(\sum_{j=1}^{3} \mu_j u_{j3}^2 \right)$$

$$= L_{33} U_{22} - 2 L_{23} U_{23} + L_{22} U_{33}.$$

TABLE 1

THE MATRIX **B** IN THE RELATION $\langle \mathbf{u} \rangle = \mathbf{Bu}$

$1-L_{22}-L_{33}$	L_{12}	L_{13}	L_{33}	$-2L_{23}$	L_{22}
$\frac{1}{2}L_{12}$	$1-\frac{1}{2}L_{11}-\frac{1}{2}L_{22}-2L_{33}$	$\frac{3}{2}L_{23}$	$\frac{1}{2}L_{12}$	$\frac{3}{2}L_{13}$	$-L_{12}$
$\frac{1}{2}L_{13}$	$\frac{3}{2}L_{23}$	$1-\frac{1}{2}L_{11}-2L_{22}-\frac{1}{2}L_{33}$	$-L_{13}$	$\frac{3}{2}L_{12}$	$\frac{1}{2}L_{13}$
L_{33}	L_{12}	$-2L_{13}$	$1-L_{11}-L_{33}$	L_{23}	L_{11}
$-L_{23}$	$\frac{3}{2}L_{13}$	$\frac{3}{2}L_{12}$	$\frac{1}{2}L_{23}$	$1-2L_{11}-\frac{1}{2}L_{22}-\frac{1}{2}L_{33}$	$\frac{1}{2}L_{23}$
L_{22}	$-2L_{12}$	L_{13}	L_{11}	L_{23}	$1-L_{11}-L_{22}$

TABLE 2

THE FUNCTIONS RELATED TO THE
REAL SECOND-ORDER SPHERICAL
HARMONICS

$$f_1(\mathbf{A}) = (A_{11} + A_{22} - 2A_{33})/3^{1/2}$$
$$f_2(\mathbf{A}) = A_{11} - A_{22}$$
$$f_3(\mathbf{A}) = 2A_{12}$$
$$f_4(\mathbf{A}) = 2A_{13}$$
$$f_5(\mathbf{A}) = 2A_{23}$$

The other terms in [4] also give sums of simple products of the elements of **U** and **L**. The elements of $\langle \mathbf{U}_c \rangle$ have been evaluated as outlined above, and the result may be summarized as

$$\langle \mathbf{u} \rangle = \mathbf{Bu}$$

with $\tilde{\mathbf{u}} = (U_{11} U_{12} U_{13} U_{22} U_{23} U_{33})$. The 6 × 6 matrix **B** is given in Table 1.

Equation [2] may be rewritten using functions related to the real second-order spherical harmonics (cf. Table 2) as described in Ref. (1):

$$v_c = \tilde{\mathbf{p}} \mathbf{U} \mathbf{p} = \sum_{i=1}^{5} d_{ci} q_i = \tilde{\mathbf{d}} \mathbf{q}. \tag{5}$$

Here $q_i = 2\pi^{1/2} \phi_i(\mathbf{p})$, where the ϕ_i are the real second-order spherical harmonics. These may be written $(15/16\pi)^{1/2} f_i(\mathbf{X})$ in terms of the functions f_i in Table 2. The matrix **X** has elements $x_i x_j$ formed from the components $(x_1 x_2 x_3)$ of the unit vector **p**. Similarly, Eq. [3] can be written

$$\langle v_c \rangle = \langle \mathbf{d}_c \rangle \mathbf{q}. \tag{6}$$

In a similar fashion a set of *six* functions g_i may be defined in terms of L; the first five of these are $g_i = f_i(L)/2$. The sixth function, $g_6 = L_{11} + L_{22} + L_{33}$, arises since the trace of L is nonzero. The relations between $\langle d_c \rangle$, g, and d can be obtained from the various

TABLE 3

THE MATRIX T IN THE RELATION $\langle d_c \rangle = \mathbf{T}\mathbf{d}^a$

$1-g_6-\varepsilon g_1$	εg_2	εg_3	$-\frac{1}{2}\varepsilon g_4$	$-\frac{1}{2}\varepsilon g_5$
εg_2	$1-g_6+\varepsilon g_1$	0	$\frac{3}{2}g_4$	$-\frac{3}{2}g_5$
εg_3	0	$1-g_6+\varepsilon g_1$	$\frac{3}{2}g_5$	$\frac{3}{2}g_4$
$-\frac{1}{2}\varepsilon g_4$	$\frac{3}{2}g_4$	$\frac{3}{2}g_5$	$1-g_6-\frac{1}{2}\varepsilon g_1+\frac{3}{2}g_2$	$\frac{3}{2}g_3$
$-\frac{1}{2}\varepsilon g_5$	$-\frac{3}{2}g_5$	$\frac{3}{2}g_4$	$\frac{3}{2}g_3$	$1-g_6-\frac{1}{2}\varepsilon g_1-\frac{3}{2}g_2$

$^a \varepsilon = 3^{1/2}$.

relations involving $\langle U_c \rangle$, L, U, d, and g, given above and shown in Table 1. The algebraic manipulations required are straightforward and the result may be written

$$\langle \mathbf{d}_c \rangle = \mathbf{T}\mathbf{d}. \qquad [7]$$

The 5×5 matrix T is given in Table 3. Matrix T is symmetric and its elements are linear in g_i. Finally, Eqs. [6] and [7] give the bilinear form

$$\langle v_c \rangle = \tilde{\mathbf{q}}\mathbf{T}\mathbf{d}. \qquad [8]$$

APPLICATIONS

In the following sections the applicability of the formalism outlined above is demonstrated for a number of second-rank tensorial quantities encountered in NMR and NQR experiments.

Quadrupole Interactions

The quadrupole interaction for a nucleus with a quadrupole moment is proportional to the electric field gradient, V, with elements $V_{ij} = \partial^2 V/\partial p_i \partial p_j$ evaluated at the site of the nucleus. The observable splittings in NMR due to this interaction may be written in form [2] and are proportional to

$$V_{pp} = \tilde{\mathbf{p}}\mathbf{V}\mathbf{p}, \qquad [9]$$

where p is a unit vector along the magnetic field. Similarly the NQR frequency in an NQR experiment will be a linear function of the elements of V. The field gradient tensor is affected by vibrations and, as a result, one observes a temperature dependence of the NQR frequencies or the quadrupole splittings in NMR: in most cases a decrease of the coupling with increasing temperature. The first attempt to account for this behavior was made by Bayer (2). He proposed an expression for the NQR frequency for an axially symmetric field gradient and a single librational motion about an axis normal to the symmetry axis of the field gradient. The theory was extended by Kushida (3) to include a general field gradient and general molecular vibrations, and by Kushida et al. (4) to include the effect of pressure. Contributions from acoustic branches of the phonon spectrum to the librational averaging were discussed by McEnnan and Schempp (5).

We limit ourselves here to the case where the electric field gradient is intramolecular in origin. Furthermore, the effect of intramolecular vibrations is not dealt with explicitly

but is considered to be included in $\mathbf{V}$, the field gradient in the absence of librations. Under these conditions only the instantaneous directions of the eigenvectors of $\mathbf{V}$, but not the eigenvalues, will be affected by librations, and $\mathbf{V}$ will behave in exactly the same way as $\mathbf{U}_c$ in the previous section.

As an example, let us select the coordinate system to be the principal axis system of the field gradient in the absence of librations and write $eq = V_{33}$ and $\eta = (V_{11} - V_{22})/V_{33}$. Then

$$d_1 = -\tfrac{1}{2}eq,$$
$$d_2 = \tfrac{1}{2}eq\eta,$$

and

$$d_3 = d_4 = d_5 = 0.$$

From Table 3,

$$\langle V_{33} \rangle = (1 - 3g_1 - 3g_6)eq - g_2 eq\eta$$
$$= eq\{1 - \tfrac{3}{2}(L_{11} + L_{22}) - \tfrac{1}{2}\eta(L_{11} - L_{22})\}.$$

Note that the quantity $\langle V_{33} \rangle$ will not, for an arbitrary $\mathbf{L}$, be an eigenvalue of the average field gradient tensor. Only if the eigenvectors of $\mathbf{L}$ and of the equilibrium $\mathbf{V}$ coincide will the average $\langle \mathbf{V} \rangle$ have the same eigenvectors as the equilibrium quantity. Our relation is therefore more general than the similar relation given, for example, by McEnnan and Schempp (Eq. [2] in Ref. (5)).

Chemical Shielding Tensors

With the appearance in recent years of multiple pulse and double-resonance high-resolution techniques applied to solids, the determination of chemical shielding tensors has become possible. From the chemical shielding tensor, $\boldsymbol{\sigma}$, the chemical shift σ may be evaluated for an arbitrary direction of the magnetic field

$$\sigma = \tilde{\mathbf{p}}\boldsymbol{\sigma}\mathbf{p},$$

where $\mathbf{p}$ is a unit vector along the field. Provided the shielding tensor is intramolecular in origin, and provided we treat the influence of intramolecular vibrations as in the case of the field gradient in the preceding section, $\boldsymbol{\sigma}$ will behave as $\mathbf{U}_c$ under librations.

In general, however, $\text{Tr }\boldsymbol{\sigma} \neq 0$ since the chemical shift is always given with respect to an arbitrary reference and the trace will depend on the choice of this reference. Since, however, $\text{Tr }\boldsymbol{\sigma}$ is invariant under rotations, the librations will have no effect on this trace. Therefore, without loss of generality, one can define a traceless tensor $\boldsymbol{\sigma}'$ with components

$$\sigma'_{ij} = \sigma_{ij} - \tfrac{1}{3}\delta_{ij}\text{ Tr }\boldsymbol{\sigma},$$

for which formulas [6] to [8] and the relations in Table 3 may be used.

Dipole–Dipole Interactions

The dipole–dipole interactions between two nuclei of spin $\tfrac{1}{2}$ give rise to a splitting of the resonance line. This splitting, β, can be written

$$\beta = \tfrac{1}{2}\gamma^2 \hbar \tilde{\mathbf{a}}\mathbf{q}, \qquad [10]$$

where

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

r is the internuclear vector, h is a unit vector parallel to the external magnetic field, and the ϕ_k are the real second-order spherical harmonic functions defined above. If r is rapidly reorienting, the average of $\phi_k(r)$ over the reorientations should be used (1).

It can be shown that isotropic and uncorrelated vibrations of the two nuclei do not affect the dipolar interactions (6–8). Consequently, the rigid-body approximation should be particularly good for dipolar interactions. See Ref. (1) for a more detailed discussion. The librationally averaged splitting can be written

$$\beta = \tfrac{3}{2}\gamma^2 \hbar \tilde{a} Tq, \qquad [11]$$

where T(L) is given in Table 3.

Second Moments in Dipolar Solids

The second moment in dipolar solids is closely related to the dipolar splitting. For the case studied in the preceding section (Eq. [11]), one obtains from the definition of the second moment

$$M_2 = (\beta^2/4) = (9/16)\gamma^4\hbar^2\,\tilde{q}Ta\tilde{a}Tq.$$

Here $(9/16)\gamma^4\hbar^2 a\tilde{a}$ is equal to the second moment tensor S (1). The resulting relation

$$M_2 = \tilde{q}TSTq \qquad [12]$$

is here derived for a special case, a two-spin system. The relation is general, however, and valid for an n-spin system, as can be seen by combining formula [8] (and Table 3) with Eqs. [14], [15], and [16] in Ref. (1).

Equation [12] is equivalent to stating that the second moment tensor averaged over the librations, $S^{(l)}$, is equal to TST. It should be noted that this relation is actually *linear* to the first nonvanishing order in the elements of L. This follows since T can be written $T = I + E$, where $I_{ij} = \delta_{ij}$, and where the elements of E are linear combinations of the elements of L. Then

$$TST = (I + E)S(I + E) = S + ES + SE + ESE \approx S + ES + \check{S}\tilde{E} = S + ES + \widetilde{ES} \qquad [13]$$

One example of a calculation which can be simplified by the use of Eq. [12] is the evaluation of the librationally averaged second moment for a powder. The result obtained for this quantity is Tr(TST), in agreement with previous results for less general cases (9).

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