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# A General Procedure for the Calculation of Theoretical Nuclear Magnetic Relaxation Times in Dipolar Solids; Applications to the Trimethylammonium Ion

ROLF SJÖBLOM

*Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden*

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It is shown that the relaxation time of a dipolar solid can be calculated from second moment tensors if the correlation times of the motional processes are known. Expressions are derived for the relaxation times in the laboratory and in the rotating frames of mono- and polycrystalline samples in the presence of one or several motional processes. The procedure is illustrated by calculations of theoretical relaxation constants for the trimethylammonium ion.

## INTRODUCTION

Fundamental equations for the relaxation caused by molecular motion in dipolar solids have been derived by Bloembergen, Purcell, and Pound (*1*) and by Kubo and Tomita (*2*). Much of the further development is described in (*3–14*). General methods for the calculation of relaxation constants and their rates have been developed by Runnels (*15*), Onsager and Runnels (*16*), and Punkkinen (*17*). Such calculations are considerably more complicated than those of second moments. For a polycrystalline sample, however, they may be greatly simplified, as shown recently by Soda and Chihara (*18*), since the relaxation constant in this case is proportional to the difference between the rigid second moment and the second moment averaged over the thermal motion.

It was shown in the preceding article (*19*) that theoretical second moments can readily be evaluated from the second moment tensor, which depends only on the crystal structure and the motions present. It is shown below using second moment tensors that the relaxation constant and the second moment of a mono- or polycrystalline sample are related in a simple way. Cases in which there are several different motions are also treated on the assumption that the various motions are completely uncorrelated.

## MATHEMATICAL DERIVATIONS

*Expressions for the relaxation times in the presence of one reorientational process.* Second moment tensors can be used for calculations of relaxation times, or rather the relaxation constants, since the reorientation rates (the inverse to the correlation times) usually have to be determined experimentally. Let us assume that there are *n* configurations of equal probability and that the jumping rate between any two of them is $\mu/n$. For a pair of atoms originally in configuration 1, we get:

$$\begin{aligned} &P_1(0) = 1, \\ &P_i(0) = 0, \qquad \mathrm{i} \neq 1, \\ &P_i(\infty) = 1/n. \end{aligned} \qquad [1]$$

and

$$\begin{aligned} &n \cdot \dot{p}_1 = -p_1 \mu(n-1) + p_i \mu(n-1), \qquad &i \neq 1, \\ &n \cdot \dot{p}_i = p_1 \mu - p_i \mu, \qquad &i \neq 1. \end{aligned} \qquad [2]$$

The differential equation [2] together with the initial conditions [1] has the solution

$$\begin{aligned} p_1(t) &= (1/n) + [(n-1)/n] e^{-\mu t}, \\ p_2(t) &= (1/n) - (1/n) e^{-\mu t}, \end{aligned}$$

where, by symmetry, $p_2 = p_3, \ldots$.

In general, if a pair of atoms at time $t = 0$ has the configuration $i$, then the probability that at a later time $t$ it has the configuration $j$ is given by

$$\begin{aligned} p_{ij}(t) &= (1/n) + [(n-1)/n] e^{-\mu t}, \qquad &i = j, \\ p_{ij}(t) &= (1/n) - (1/n) e^{-\mu t}, \qquad &i \neq j. \end{aligned}$$

The definitions of $F^{(m)}$ and $G(t)^{(m)}$ in (*4*) are used in the following derviation.

$$\begin{aligned} G(t)^{(m)} &= \frac{1}{n} \sum_{i=1}^{n} \langle F_i^{(m)}(0) F_i^{(m)}(t)^* \rangle \\ &= \frac{1}{n} \sum_{i=1}^{n} \sum_{j=1}^{n} F_i^{(m)}(0) F_j^{(m)}(0)^* p_{ij}(t) \\ &= \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} F_i^{(m)} F_j^{(m)*} + \left[ \frac{1}{n} \sum_{i=1}^{n} F_i^{(m)} F_i^{(m)*} - \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n} F_i^{(m)} F_j^{(m)*} \right] e^{-\mu t} \\ &= \langle F^{(m)} \rangle \langle F^{(m)} \rangle + [\langle F^{(m)} F^{(m)*} \rangle - \langle F^{(m)} \rangle \langle F^{(m)*} \rangle] e^{-\mu t} \end{aligned}$$

The Fourier transform is

$$J^{(m)}(m\omega) = 2[\langle F^{(m)} F^{(m)*} \rangle - \langle F^{(m)} \rangle \langle F^{(m)*} \rangle] \frac{\mu}{\mu^2 + m^2 \omega^2}. \qquad [3]$$

The functions $F^{(m)}$ are related to **a** (cf. [*4*] in the preceding article (*19*)) by the relation

$$F^{(m)} = f_m \tilde{\mathbf{v}}^{(m)} \tilde{\mathbf{T}} \mathbf{a}, \qquad [4]$$

where $f_0 = 1$, $f_{\pm 1} = 1/6^{1/2}$, and $f_{\pm 2} = (\frac{2}{3})^{1/2}$. The term **a** is proportional to the real second-order spherical harmonic functions defined in (*19*, Eqs. [4] and [5]). The matrix $\tilde{\mathbf{T}}$ transforms the functions **a** in the three-dimensional space, and is given by the relation

$$\mathbf{U} \mathbf{B}_k \tilde{\mathbf{U}} = \sum_{m=1}^{5} \mathbf{T}_{km} \mathbf{B}_m$$

(*19*, Eq. [7]). The term **U** is a matrix which transforms the vector $\mathbf{h} = (h_1, h_2, h_3)$ (that is, an arbitrary direction of the magnetic field) to $\mathbf{h} = (0, 0, 1)$. This condition does not define **U** uniquely. It can easily be shown, however, that this choice is immaterial since we are actually only interested in the rotationally symmetric part of $\mathbf{a}\tilde{\mathbf{a}}$ around the

TABLE 1

THE ORTHOGONAL MATRIX V[a] NORMALIZED IN THE SAME WAY AS q[b]

$$\sqrt{5}\begin{pmatrix} 0 & \varepsilon & i\varepsilon & 0 & 0 \\ 0 & 0 & 0 & \varepsilon & i\varepsilon \\ 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \varepsilon & -i\varepsilon \\ 0 & \varepsilon & -i\varepsilon & 0 & 0 \end{pmatrix}$$

[a] See text.

[b] $\varepsilon = 2^{-1/2}$, $i = (-1)^{1/2}$.

magnetic field direction. The vectors $\mathbf{v}^{(m)}$ are the rows of the matrix **V** shown in Table 1 ($\mathbf{v}^{(-2)}$ is the first row, $\mathbf{v}^{(-1)}$ the second, etc.). The matrix **V** transforms the real second-order spherical harmonic functions to the corresponding complex ones and is normalized similarly to **q**.

Formula [4] may be used for the evaluations of the averages in [3]:

$$\begin{aligned}\langle F^{(m)}F^{(m)*}\rangle &= f_m^{\,2}\,\langle(\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\mathbf{a})(\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\mathbf{a})^{*} \\ &= f_m^{\,2}\,\langle(\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\mathbf{a})(\tilde{\mathbf{a}}\mathbf{T}\mathbf{v}^{(m)*})\rangle \\ &= \mathrm{f}_m^{\,2}\,\langle\mathbf{v}^{(m)}\,\tilde{\mathbf{T}}(\mathbf{a}\tilde{\mathbf{a}})\,\mathbf{T}\mathbf{v}^{(m)*}\rangle = f_m^{\,2}\,\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\langle\mathbf{a}\tilde{\mathbf{a}}\rangle\,\mathbf{T}\mathbf{v}^{(m)*} \\ &= (f_m^{\,2}/\alpha)\,\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\,\mathrm{S}_{\mathrm{rigid}}\,\mathbf{T}\mathbf{v}^{(m)*}\end{aligned}$$

and

$$\begin{aligned}\langle F^{(m)}\rangle\langle F^{(m)*}\rangle &= f_m^{\,2}\,\langle\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\mathbf{a}\rangle\langle\tilde{\mathbf{a}}\mathbf{T}\mathbf{v}^{(m)*}\rangle \\ &= f_m^{\,2}\,\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}(\langle\mathbf{a}\rangle\langle\tilde{\mathbf{a}}\rangle)\,\mathbf{T}\mathbf{v}^{(m)*} \\ &= (f_m^{\,2}/\alpha)\,\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\,\mathrm{S}_{\mathrm{motion}}\,\mathbf{T}\mathbf{v}^{(m)*},\end{aligned}$$

where S is the second moment tensor derived in (*19*).

Formula [3] may now be rewritten

$$J^{(m)}(m\omega) = \frac{2f_m^{\,2}}{\alpha}(\tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\Delta\mathrm{S}\mathbf{T}\mathbf{v}^{(m)*})\frac{\mu}{\mu^2 + m^2\omega^2}, \qquad [5]$$

where

$$\Delta\mathrm{S} = \mathrm{S}_{\mathrm{rigid}} - \mathrm{S}_{\mathrm{motion}}$$

The quantity $K^{(m)}$ is defined by the relation

$$K^{(m)} = \tilde{\mathbf{v}}^{(m)}\,\tilde{\mathbf{T}}\Delta\mathrm{S}\mathbf{T}\mathbf{v}^{(m)*}. \qquad [6]$$

It may easily be seen from the formula that $K^{(m)}$ is always a real quantity. Furthermore, the orientational dependence of $K^{(m)}$ can always be described by any complete set of functions which are fourth order in the components of $\mathbf{h} = (h_1, h_2, h_3)$. This can be shown by evaluation of $F^{(m)}F^{(m)*}$ for an arbitrary direction of an internuclear vector and the magnetic field. The functions $q_i q_j$, which form such a set, will be used here since they form the basis for the second moment tensor, and since they make the symmetry considerations particularly convenient. Thus, the aim is to find tensors $\Delta\mathrm{S}^{(m)}$ such that formula [6] may be written

$$K^{(m)} = \tilde{\mathbf{q}}\Delta\mathrm{S}^{(m)}\mathbf{q}. \qquad [7]$$

An algebraic evaluation of $\Delta \mathrm{S}^{(m)}$ as a function of $(\mathrm{S}_{\mathrm{rigid}} - \mathrm{S}_{\mathrm{motion}})$ is straightforward but discouragingly tedious. Instead, a computer program was written which calculated $K^{(m)}$ for 45 evenly distributed points on a hemisphere using 15 linearly independent second moment tensors. The corresponding tensors $\Delta \mathrm{S}^{(m)}$ were then evaluated from the values of $K^{(m)}$ by a least-squares procedure. As expected, $\Delta \mathrm{S}^{(0)}$ turned out to be equal to $(\mathrm{S}_{\mathrm{rigid}} - \mathrm{S}_{\mathrm{motion}})$. The relations between $\Delta \mathrm{S}^{(0)}$ and $\Delta \mathrm{S}^{(1)}$ are given in Table 2a and those between $\Delta \mathrm{S}^{(0)}$ and $\Delta \mathrm{S}^{(2)}$ in Table 2b. The relations between $\Delta \mathrm{S}^{(1)}$ and $\Delta \mathrm{S}^{(2)}$ can easily be evaluated from those given in Table 2.

TABLE 2

THE RELATIONS BETWEEN THE RELAXATION TENSORS $\mathrm{S}^{(0)}$ AND $\mathrm{S}^{(1)}$ (2a), AND $\mathrm{S}^{(0)}$ AND $\mathrm{S}^{(2)}$ (2b)[a]

2a

$S_{11}{}^{(1)} = \frac{1}{6}\,(3S_{44}{}^{(0)} + 3S_{55}{}^{(0)})$
$S_{12}{}^{(1)} = \frac{1}{6}\,(2dS_{44}{}^{(0)} - 2dS_{55}{}^{(0)})$
$S_{13}{}^{(1)} = \frac{1}{6}\,(2dS_{45}{}^{(0)})$
$S_{14}{}^{(1)} = \frac{1}{6}\,(-3S_{14}{}^{(0)} - dS_{24}{}^{(0)} - dS_{35}{}^{(0)})$
$S_{15}{}^{(1)} = \frac{1}{6}\,(-3S_{15}{}^{(0)} + dS_{25}{}^{(0)} - dS_{34}{}^{(0)})$
$S_{22}{}^{(1)} = \frac{1}{6}\,(4S_{33}{}^{(0)} + S_{44}{}^{(0)} + S_{55}{}^{(0)})$
$S_{23}{}^{(1)} = \frac{1}{6}\,(-4S_{23}{}^{(0)})$
$S_{24}{}^{(1)} = \frac{1}{6}\,(-dS_{14}{}^{(0)} - S_{24}{}^{(0)} + 3S_{35}{}^{(0)})$
$S_{25}{}^{(1)} = \frac{1}{6}\,(dS_{15}{}^{(0)} - S_{25}{}^{(0)} - 3S_{34}{}^{(0)})$
$S_{33}{}^{(1)} = \frac{1}{6}\,(4S_{22}{}^{(0)} + S_{44}{}^{(0)} + S_{55}{}^{(0)})$
$S_{34}{}^{(1)} = \frac{1}{6}\,(-dS_{15}{}^{(0)} - 3S_{25}{}^{(0)} - S_{34}{}^{(0)})$
$S_{35}{}^{(1)} = \frac{1}{6}\,(-dS_{14}{}^{(0)} + 3S_{24}{}^{(0)} - S_{35}{}^{(0)})$
$S_{44}{}^{(1)} = \frac{1}{6}\,(3S_{11}{}^{(0)} + dS_{12}{}^{(0)} + S_{22}{}^{(0)} + S_{33}{}^{(0)} + S_{55}{}^{(0)})$
$S_{45}{}^{(1)} = \frac{1}{6}\,(2dS_{13}{}^{(0)} - S_{45}{}^{(0)})$
$S_{55}{}^{(1)} = \frac{1}{6}\,(3S_{11}{}^{(0)} - dS_{12}{}^{(0)} + S_{22}{}^{(0)} + S_{33}{}^{(0)} + S_{44}{}^{(0)})$

$S_{11}{}^{(0)} = \frac{1}{2}\,(-S_{22}{}^{(1)} - S_{33}{}^{(1)} + 2S_{44}{}^{(1)} + 2S_{55}{}^{(1)})$
$S_{12}{}^{(0)} = \frac{1}{2}\,(S_{12}{}^{(1)} + 2dS_{44}{}^{(1)} - 2dS_{55}{}^{(1)})$
$S_{13}{}^{(0)} = \frac{1}{2}\,(S_{13}{}^{(1)} + 2dS_{45}{}^{(1)})$
$S_{14}{}^{(0)} = \frac{1}{2}\,(-2S_{14}{}^{(1)} - dS_{24}{}^{(1)} - dS_{35}{}^{(1)})$
$S_{15}{}^{(0)} = \frac{1}{2}\,(-2S_{15}{}^{(1)} + dS_{25}{}^{(1)} - dS_{34}{}^{(1)})$
$S_{22}{}^{(0)} = \frac{1}{2}\,(-S_{11}{}^{(1)} + 3S_{33}{}^{(1)})$
$S_{23}{}^{(0)} = \frac{1}{2}\,(-3S_{23}{}^{(1)})$
$S_{24}{}^{(0)} = \frac{1}{2}\,(-dS_{14}{}^{(1)} + 3S_{35}{}^{(1)})$
$S_{25}{}^{(0)} = \frac{1}{2}\,(dS_{15}{}^{(1)} - 3S_{34}{}^{(1)})$
$S_{33}{}^{(0)} = \frac{1}{2}\,(-S_{11}{}^{(1)} + 3S_{22}{}^{(1)})$
$S_{34}{}^{(0)} = \frac{1}{2}\,(-dS_{15}{}^{(1)} - 3S_{25}{}^{(1)})$
$S_{35}{}^{(0)} = \frac{1}{2}\,(-dS_{14}{}^{(1)} + 3S_{24}{}^{(1)})$
$S_{44}{}^{(0)} = \frac{1}{2}\,(2S_{11}{}^{(1)} + dS_{12}{}^{(1)})$
$S_{45}{}^{(0)} = \frac{1}{2}\,(2dS_{13}{}^{(1)})$
$S_{55}{}^{(0)} = \frac{1}{2}\,(2S_{11}{}^{(1)} - dS_{12}{}^{(1)})$

2b

$S_{11}{}^{(2)} = \frac{1}{6}\,(3S_{22}{}^{(0)} + 3S_{33}{}^{(0)})$
$S_{12}{}^{(2)} = \frac{1}{6}\,(-3\mathrm{S}_{12}{}^{(0)} - 2dS_{44}{}^{(0)} + 2dS_{55}{}^{(0)})$
$S_{13}{}^{(2)} = \frac{1}{6}\,(-3S_{13}{}^{(0)} - 2dS_{45}{}^{(0)})$
$S_{14}{}^{(2)} = \frac{1}{6}\,(-dS_{24}{}^{(0)} + dS_{35}{}^{(0)})$

[a] $d = 3^{1/2}$.

TABLE 2—*Continued*

$S_{15}^{(2)} = \frac{1}{6}(-dS_{25}^{(0)} + dS_{34}^{(0)})$
$S_{22}^{(2)} = \frac{1}{6}(3S_{11}^{(0)} - S_{33}^{(0)} + 2S_{44}^{(0)} + 2S_{55}^{(0)})$
$S_{23}^{(2)} = \frac{1}{6}(S_{23}^{(0)})$
$S_{24}^{(2)} = \frac{1}{6}(dS_{14}^{(0)} - 2S_{24}^{(0)} - 3S_{35}^{(0)})$
$S_{25}^{(2)} = \frac{1}{6}(-dS_{15}^{(0)} - 2S_{25}^{(0)} - 3S_{34}^{(0)})$
$S_{33}^{(2)} = \frac{1}{6}(3S_{11}^{(0)} - S_{22}^{(0)} + 2S_{44}^{(0)} + 2S_{55}^{(0)})$
$S_{34}^{(2)} = \frac{1}{6}(dS_{15}^{(0)} + 3S_{25}^{(0)} - 2S_{34}^{(0)})$
$S_{35}^{(2)} = \frac{1}{6}(dS_{14}^{(0)} - 3S_{24}^{(0)} - 2S_{35}^{(0)})$
$S_{44}^{(2)} = \frac{1}{6}(-dS_{12}^{(0)} + 2S_{22}^{(0)} + 2S_{33}^{(0)} + 2S_{55}^{(0)})$
$S_{45}^{(2)} = \frac{1}{6}(-2dS_{13}^{(0)} - 2S_{45}^{(0)})$
$S_{55}^{(2)} = \frac{1}{6}(dS_{12}^{(0)} + 2S_{22}^{(0)} + 2S_{33}^{(0)} + 2S_{44}^{(0)})$

$S_{11}^{(0)} = 3S_{11}^{(2)} + S_{22}^{(2)} + S_{33}^{(2)} - 2S_{44}^{(2)} - 2S_{55}^{(2)}$
$S_{12}^{(0)} = 2S_{12} - 2dS_{44}^{(2)} + 2dS_{55}^{(2)}$
$S_{13}^{(0)} = 2S_{13}^{(2)} - 2dS_{45}^{(2)}$
$S_{14}^{(0)} = 5S_{14}^{(2)} + dS_{24}^{(2)} + dS_{35}^{(2)}$
$S_{15}^{(0)} = 5S_{15}^{(2)} - dS_{25}^{(2)} + dS_{34}^{(2)}$
$S_{22}^{(0)} = S_{11}^{(2)} + 3S_{22}^{(2)} - 3S_{33}^{(2)}$
$S_{23}^{(0)} = 6S_{23}^{(2)}$
$S_{24}^{(0)} = dS_{14}^{(2)} + 3S_{24}^{(2)} - 3S_{35}^{(2)}$
$S_{25}^{(0)} = -dS_{15}^{(2)} + 3S_{25}^{(2)} + 3S_{34}^{(2)}$
$S_{33}^{(0)} = S_{11}^{(2)} - 3S_{22}^{(2)} + 3S_{33}^{(2)}$
$S_{34}^{(0)} = dS_{15}^{(2)} + 3S_{25}^{(2)} + 3S_{34}^{(2)}$
$S_{35}^{(0)} = dS_{14}^{(2)} - 3S_{24} + 3S_{35}^{(2)}$
$S_{44}^{(0)} = -2S_{11}^{(2)} - dS_{12}^{(2)} + 3S_{44}^{(2)}$
$S_{45}^{(0)} = -2dS_{13}^{(2)} + 3S_{45}^{(2)}$
$S_{55}^{(0)} = -2S_{11}^{(2)} + dS_{12}^{(2)} + 3S_{55}^{(2)}$

The same results as those listed in Table 2 were also obtained in a similar but independent analysis using a second moment tensor based on the complex second-order spherical harmonics and their transformation matrix which is given in (*16*).

Equations [5], [6], and [7] may be inserted in the formulas for the relaxation time in the laboratory (*4*) and rotating (*8*, *11–13*) frames:

$$T_1^{-1} = \tfrac{3}{2}\gamma^4 \hbar^2 I(I+1)[J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)],$$

$$T_{1\rho}^{-1} = \tfrac{3}{2}\gamma^4 \hbar^4 I(I+1)\,[\tfrac{1}{4}J^{(0)}(2\omega_1) + \tfrac{5}{2}J^{(1)}(\omega_0) + \tfrac{1}{4}J^{(2)}(2\omega_0)]$$

The result is

$$T_1^{-1} = \tfrac{2}{3}K^{(1)}\frac{\tau}{1+\omega_0^2\tau^2} + \tfrac{8}{3}K^{(2)}\frac{\tau}{1+4\omega_0^2\tau^2}, \qquad [8]$$

$$T_{1\rho}^{-1} = K^{(0)}\frac{\tau}{1+4\omega_1^2\tau^2} + \tfrac{5}{3}K^{(1)}\frac{\tau}{1+\omega_0^2\tau^2} + \tfrac{2}{3}K^{(2)}\frac{\tau}{1+4\omega_0^2\tau^2}, \qquad [9]$$

where $\tau = \mu^{-1}$. The derivations of formulas [8] and [9] are made for a pair of atoms only, but it may be shown that they are valid also for systems containing many spins (see also (*20*, *21*)).

*The relaxation times in the presence of several processes.* In experimental studies of relaxation one often comes across cases where more than one relaxation process is present, and where one type of motion affects the others. Methods of coping with this type of problem have been developed (*15–17*) and initially we shall follow the one demonstrated by Punkkinen (*17*) (see also (*22*)) for the derivation of a procedure which permits the use of the second moment tensor.

Let us assume that there are two processes where the reorientation of one species occurs at a rate $\mu_1$ among $m_1$ different configurations (the probability for one particuar jump is then $\mu_1/m_1$), that the other reorients at a rate $\mu_2$ among $m_2$ different configurations, and that the probability is the same for all configurations within a certain reorientational species.

Assume, furthermore, that the processes are completely independent, i.e., a reorientation of one species does not effect the reorientation probability of the other. (This is, for instance, not the case for the threefold reorientations of an ammonium ion.) The differential equations can now be written in the same way as in [*2*], using matrix notation.

$$\begin{pmatrix} \dot{p}(00) \\ \dot{p}(10) \\ \dot{p}(01) \\ \dot{p}(11) \end{pmatrix} = \begin{pmatrix} -\frac{m_1-1}{m_1}\mu_1 - \frac{m_2-1}{m_2}\mu_2 & \frac{m_1-1}{m_1}\mu_1 & \frac{m_2-1}{m_2}\mu_2 & 0 \\ \frac{\mu_1}{m_1} & -\frac{\mu_1}{m_2} - \frac{m_2-1}{m_2}\mu_2 & 0 & \frac{m_2-1}{m_2}\mu_2 \\ \frac{\mu_2}{m_2} & 0 & -\frac{\mu_2}{m_2} - \frac{m_1-1}{m_1} & \frac{m_1-1}{m_1}\mu_1 \\ 0 & \frac{\mu_2}{m_2} & \frac{\mu_1}{m_1} & -\frac{\mu_1}{m_1} - \frac{\mu_2}{m_2} \end{pmatrix} \times \begin{pmatrix} p(00) \\ p(10) \\ p(01) \\ p(11) \end{pmatrix}$$

where $p(00)$ is the probability that the system has the initial configuration, $p(10)$ is the probability for each of the configurations which are different from the original configuration, but which can be reached from it by a single jump according to process 1, $p(01)$ is the corresponding probability for process 2, and $p(11)$ is the probability for each of the remaining configurations. Using the initial condition (at $t = 0$) that $p(00) = 1$ and $p(10) = p(01) = p(11) = 0$, the solution becomes

$$\begin{pmatrix} p(00) \\ p(10) \\ p(01) \\ p(11) \end{pmatrix} = \frac{1}{m_1 m_2} \begin{pmatrix} 1 & m_1 - 1 & m_2 - 1 & (m_1 - 1)(m_2 - 1) \\ 1 & -1 & m_2 - 1 & 1 - m_2 \\ 1 & m_1 - 1 & -1 & 1 - m_1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \begin{pmatrix} e^{-0.t} \\ e^{-\mu_1 t} \\ e^{-\mu_2 t} \\ e^{-(\mu_1+\mu_2)t} \end{pmatrix}$$

It can be shown that similar result would, under the initial conditions, be obtained for any number of processes. The general solution is given by

$$\begin{aligned} p(000\ldots 0) = \frac{1}{m_1 m_2 m_3 \ldots m_n} & (1 + (m_1 - 1)e^{-\mu_1 t} + (m_1 - 1)(m_2 - 1)e^{-(\mu_1+\mu_2)t} \\ & + (m_1 - 1)(m_2 - 1)(m_3 - 1)e^{-(\mu_1+\mu_2+\mu_3)t} + \ldots \\ & + (m_1 - 1)(m_2 - 1)(m_3 - 1)\ldots(m_n - 1)e^{-(\mu_1+\mu_2+\mu_3+\cdots+\mu_n)t} \\ & \text{plus other terms given by the symmetry of the problem}). \end{aligned}$$

To obtain the other functions $p$, one need only omit the values of $m_i$ in the expression in parentheses which do not correspond to zeros in the argument for $p$.

The solution for $p$ can be used in a more general derivation similar to the one leading to Eq. [3]. The full derivation will not be given here, but results in expressions of the type given in the next section.

## RESULTS

*Expressions for the relaxation times.* Derivations in the above section resulted in the following formulas for the relaxation times in the presence of one reorientational process:

$$T_1^{-1} = \tfrac{2}{3}K^{(1)}\frac{\tau}{1 + \omega_0^2\tau^2} + \tfrac{8}{3}K^{(2)}\frac{\tau}{1 + 4\omega_0^2\tau^2}, \qquad [10]$$

$$T_{1\rho}^{-1} = K^{(0)}\frac{\tau}{1 + 4\omega_1^2\tau^2} + \tfrac{5}{3}K^{(1)}\frac{\tau}{1 + \omega_0^2\tau^2} + \tfrac{2}{3}K^{(2)}\frac{\tau}{1 + 4\omega_0^2\tau^2} \qquad [11]$$

where

$$K^{(m)} = \tilde{\mathbf{q}}\Delta \mathrm{S}^{(m)}\mathbf{q}. \qquad [12]$$

The functions $q_i$ depend on the direction of the external magnetic field relative to the crystal and are given in [5] of the preceding article (*19*). $\Delta \mathrm{S}^{(0)}$ is equal to $\mathrm{S}_{\mathrm{rigid}} - \mathrm{S}_{\mathrm{motion}}$, where S is the second moment tensor which depends only on the crystal structure and the motions present as described in (*19*). $\Delta \mathrm{S}^{(0)}$, $\Delta \mathrm{S}^{(1)}$, and $\Delta \mathrm{S}^{(2)}$ are interrelated by simple transformations given in Table 2.

The derivations of the corresponding expressions for more than one motional process are briefly outlined in the above section and the results are the following.

For two processes:

$$\begin{array}{ll} 0, & K^{(m)}(00) = \tilde{\mathbf{q}}[\mathrm{S}^{(m)}(11)]\mathbf{q}, \\ \mu_1, & K^{(m)}(10) = \tilde{\mathbf{q}}[\mathrm{S}^{(m)}(01) - \mathrm{S}^{(m)}(11)]\mathbf{q}, \\ \mu_2, & K^{(m)}(01) = \tilde{\mathbf{q}}[\mathrm{S}^{(m)}(10) - \mathrm{S}^{(m)}(11)]\mathbf{q}, \\ \mu_1 + \mu_2, & K^{(m)}(11) = \tilde{\mathbf{q}}[\mathrm{S}^{(m)}(00) - \mathrm{S}^{(m)}(10) - \mathrm{S}^{(m)}(01) + \mathrm{S}^{(m)}(11)]\mathbf{q}, \end{array} \qquad [13]$$

where $\mathrm{S}^{(m)}(11)$ refers to the second moment tensor whose elements are reduced by both motions, and are transformed according to Table 2, $\mathrm{S}^{(m)}(01)$ refers to the second moment tensor whose elements are reduced by motion number 2. The corresponding rates ($\mu_i = \tau_i^{-1}$) are given to the left of the equations. These equations may now be used in the expressions for the relaxation time. For example,

$$\begin{aligned} T_1^{-1} = \tfrac{2}{3} & \sum_{m=1}^{2} \\ & \times \left[K^{(m)}(10)\frac{m^2\mu_1}{\mu_1^2 + m^2\omega_0^2} + K^{(m)}(01)\frac{m^2\mu_2}{\mu_2^2 + m^2\omega_0^2} + K^{(m)}(11)\frac{m^2(\mu_1 + \mu_2)}{(\mu_1 + \mu_2)^2 + m^2\omega_0^2}\right]. \end{aligned} \qquad [14]$$

Dropping the index $m$, we obtain for three processes:

$$\begin{array}{ll}
0, & K(000) = \tilde{\mathbf{q}}[\mathrm{S}(111)]\mathbf{q}, \\
\mu_1, & K(100) = \tilde{\mathbf{q}}[\mathrm{S}(011) - \mathrm{S}(111)]\mathbf{q}, \\
\mu_2, & K(010) = \tilde{\mathbf{q}}[\mathrm{S}(101) - \mathrm{S}(111)]\mathbf{q}, \\
\mu_3, & K(001) = \tilde{\mathbf{q}}[\mathrm{S}(110) - \mathrm{S}(111)]\mathbf{q}, \\
\mu_1 + \mu_2. & K(110) = \tilde{\mathbf{q}}[\mathrm{S}(001) - \mathrm{S}(011) - \mathrm{S}(101) + \mathrm{S}(111)]\mathbf{q}, \\
\mu_1 + \mu_3, & K(101) = \tilde{\mathbf{q}}[\mathrm{S}(010) - \mathrm{S}(110) - \mathrm{S}(011) + \mathrm{S}(111)]\mathbf{q}, \\
\mu_2 + \mu_3, & K(011) = \tilde{\mathbf{q}}[\mathrm{S}(100) - \mathrm{S}(110) - \mathrm{S}(101) + \mathrm{S}(111)]\mathbf{q}, \\
\mu_1 + \mu_2 + \mu_3, & K(111) = \tilde{\mathbf{q}}[\mathrm{S}(000) - \mathrm{S}(100) - \mathrm{S}(010) - \mathrm{S}(001) \\
 & \qquad + \mathrm{S}(110) + \mathrm{S}(101) + \mathrm{S}(011) - \mathrm{S}(111)]\mathbf{q}.
\end{array} \tag{15}$$

For four processes:

$$\begin{array}{ll}
0, & K(0000) = \tilde{\mathbf{q}}[\mathrm{S}(1111)]\mathbf{q}, \\
\mu_1, & K(1000) = \tilde{\mathbf{q}}[\mathrm{S}(0111) - \mathrm{S}(1111)]\mathbf{q}, \\
\mu_1 + \mu_2, & K(1100) = \tilde{\mathbf{q}}[\mathrm{S}(0011) - \mathrm{S}(1011) - \mathrm{S}(0111) + \mathrm{S}(1111)]\mathbf{q}, \\
\mu_1 + \mu_2 + \mu_3, & K(1110) = \tilde{\mathbf{q}}[\mathrm{S}(0001) - \mathrm{S}(1001) - \mathrm{S}(0101) - \mathrm{S}(0011) \\
 & \qquad + \mathrm{S}(1101) + \mathrm{S}(1011) + \mathrm{S}(0111) - \mathrm{S}(1111)]\mathbf{q}, \\
\mu_1 + \mu_2 + \mu_3 + \mu_4, & K(1111) = \tilde{\mathbf{q}}[\mathrm{S}(0000) - \mathrm{S}(1000) - \mathrm{S}(0100) - \mathrm{S}(0010) \\
 & \qquad - \mathrm{S}(0001) + \mathrm{S}(1100) + \mathrm{S}(1010) + \mathrm{S}(1001) \\
 & \qquad + \mathrm{S}(0110) + \mathrm{S}(0101) + \mathrm{S}(0011) - \mathrm{S}(1110) \\
 & \qquad - \mathrm{S}(1101) - \mathrm{S}(1011) - \mathrm{S}(0111) + \mathrm{S}(1111)]\mathbf{q}.
\end{array} \tag{16}$$

The other relations are given by symmetry. Similar results would be obtained for any number of processes.

*The relaxation times for a powder.* Although the $T_1$ and $T_{1\rho}$ relaxation for a single crystal is usually exponential (but see (*20*, *21*)), this is not generally so for a powder. The spin diffusion process is often not fast enough to give a spin temperature which is common to all crystallites of different orientations. The experimentally observed relaxation is, however, frequently exponential, and we shall make the approximation that the inverse relaxation time for a powder is just the average of the inverse relaxation times of the crystallites. This implies that the above formulas are valid also for polycrystalline samples if the powder average over $K^{(m)}$ $(=\bar{K}^{(m)})$ is substituted for $K^{(m)}$. Furthermore, $\bar{K}^{(m)} = \overline{\tilde{\mathbf{q}}\Delta\mathrm{S}^{(m)}\mathbf{q}} = Tr\ \Delta\mathrm{S}^{(m)}$ (cf. the preceding paper (*19*)) and $Tr\ \Delta\mathrm{S}^{(0)} = Tr\ \mathrm{S}^{(1)} = Tr\ \Delta\mathrm{S}^{(2)} = \Delta\bar{M}_2$ (cf. Table 2 and (*19*)). The relaxation times for one reorientational process in a polycrystalline sample are thus:

$$\bar{T}_1^{-1} = \tfrac{2}{3}[\bar{M}_{2\mathrm{rigid}} - \bar{M}_{2\mathrm{motion}}]\left[\frac{\tau}{1 + \omega_0^2\tau^2} + \frac{4\tau}{1 + 4\omega_0^2\tau^2}\right], \tag{17}$$

$$\bar{T}_{1\rho}^{-1} = \tfrac{2}{3}[\bar{M}_{2\mathrm{rigid}} - \bar{M}_{2\mathrm{motion}}]\left[\tfrac{3}{2}\frac{\tau}{1 + 4\omega_1^2\tau^2} + \tfrac{5}{2}\frac{\tau}{1 + \omega_0^2\tau^2} + \frac{\tau}{1 + 4\omega_0^2\tau^2}\right]. \tag{18}$$

These results are consistent with those obtained in (*18*).

*Symmetry.* It can readily be seen from Table 3 in the preceding paper (*19*) and Table 2 that $\Delta\mathrm{S}^{(0)}$, $\Delta\mathrm{S}^{(1)}$, and $\Delta\mathrm{S}^{(2)}$ in general have the same symmetry. Formulas [10]–[16] indicate that this restriction also applies to $T_1$, $T_{1\rho}$, and $M_2$.

*Vibrational motion.* It follows directly from the results in this section that, in order to calculate the relaxation constants in the presence of librational motion, one need only use the librationally averaged second moment tensors instead of the usual ones (cf. the preceding article (*19*)).

*Simplifications.* Some simplifications of practical importance arise in cases where the reorientation rates are sufficiently different in magnitude. For example, assume that there are two processes, and that $\mu_1 \ll \mu_2$. Then $\mu_1 + \mu_2 \approx \mu_2$ and Eq. [14] reduces to

$$T_1^{-1} = \frac{2}{3}\sum_{m=1}^{2}\left[K^{(m)}(10)\frac{m^2\mu_1}{\mu_1^2 + m^2\omega_0^2} + (K^{(m)}(01) + K^{(m)}(11))\frac{m^2\mu_2}{\mu_2^2 + m^2\omega_0^2}\right].$$

This explains why expressions of this type can be used successfully in many experimental studies of the relaxation time vs temperature (see, for example, (*23–25*)).

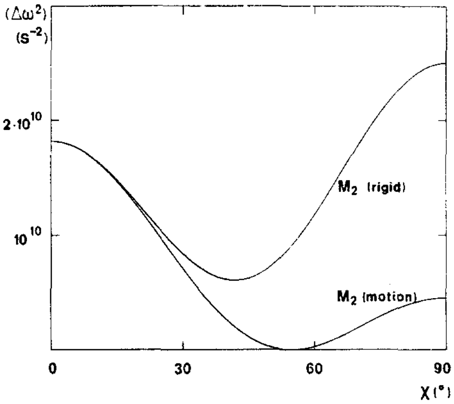

FIG. 1a. The second moment for a rigid and a reorienting methyl group as a function of the angle between the symmetry axis and the external magnetic field.

Another important explanation is, of course, that $K^{(m)}(11)$ may be small. The computational problem is reduced if some of the $\mu_i$ are equal; this is illustrated for the trimethylammonium ion later in this section.

*The second moment and relaxation constant as a function of orientation for a methyl group.* Let us assume that the threefold symmetry axis is parallel to the vector **k**, (cf. the preceding article (*19*)) and that the jumps consist of rotations by 0, 120, and 240 degrees around this axis. The second moment tensor for the rigid case has the following elements $S_{11} = 2\alpha/(5r^6)$, $S_{22} = S_{33} = 3\alpha/(5r^6)$ and the others are zero, with $\alpha$, as in (*19*), the constant in Van Vleck's formula. The tensor for the case of the molecule in motion has the elements $S_{11} = 2\alpha/(5r^6)$ and the others are zero. The orientational dependence of the second moment is of the form $M_{2\,\mathrm{rigid}} = \alpha r^{-6}[0.5(1 - 3h_3^2)^2 + 2.25(1 - h_3^2)^2]$ and $M_{2\,\mathrm{motion}} = 0.5\,\alpha r^{-6}(1 - 3h_3^2)^2$, where $h_3 = \cos\chi$ and $\chi$ is the angle between the magnetic field and the symmetry axis. These results are illustrated in Fig. 1a. The quantities $K^{(m)}$ may be obtained using Table 2 and formula [7]:

$$K^{(0)} = 2.25\alpha r^{-6}(1 - h_3^2)^2,$$
$$K^{(1)} = 1.5\alpha r^{-6}(1 - h_3^4),$$
$$K^{(2)} = 0.375\alpha r^{-6}(1 + 6h_3^2 + h_3^4).$$

The orientational dependence of $K^{(m)}$ is illustrated in Fig. 1b. Formula [8] shows that $T_1^{-1}$ is proportional to $K^{(1)} + K^{(2)}$ for $1 \ll \omega_0^2\tau^2$ and to $K^{(1)} + 4K^{(2)}$ for $1 \gg \omega_0^2\tau^2$.

*The relaxation rates and constants for molecular motion of the trimethylammonium ion.* Expressions for the relaxation rates and constants for the molecular motion of the cation in trimethylammonium hydrogen oxalate have recently been derived (*22*) according to a method developed by Punkkinen (*17*). These quantitities have been reevaluated in this study in order to test the present method by a comparison of the results from the two investigations. The assumptions used here will therefore be the same as those for the $R' = R'' = 0$ model in (*22*). Four reorientational processes take place in this trimethylammonium ion: Each of the three methyl groups reorient (at rates $\mu_2 = \mu_3 = \mu_4$) together with reorientations of the cation as a whole (at a rate $\mu_1$).

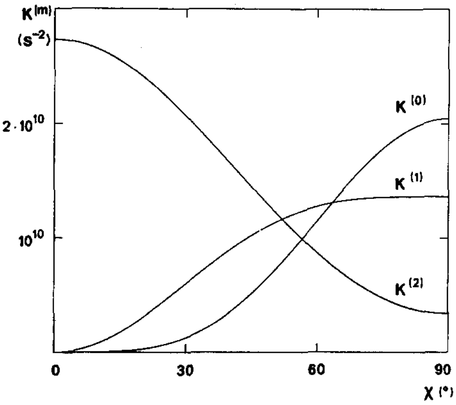

FIG. 1b. The constants $K^{(m)}$ which appear in expressions for the relaxation time (cf. text) for a reorienting methyl group as a function of the angle between the symmetry axis and the external magnetic field.

The combined rates are then $\mu_1$, $\mu_1 + \mu_2$,$\mu_1 + 2\mu_2$, $\mu_1 + 3\mu_2$, $\mu_2$, $2\mu_2$; and $3\mu_2$ as implied from the section above. However, no internuclear vector is affected by the combined motion of all three methyl groups. The relaxation constants for the rates $3\mu_2$ and $\mu_1 + 3\mu_2$ thus vanish.

The expressions relating the constants $K^{(m)}$ and the second moment tensors for four processes (cf. [16]) then reduce to (dropping the index $m$ as before):

$$K(\mu_1) = \tilde{\mathbf{q}}[\mathsf{S}(3\mu_2) - \mathsf{S}(\mu_1 + 3\mu_2)]\mathbf{q},$$

$$K(\mu_2) = 3\tilde{\mathbf{q}}[\mathsf{S}(\mu_1 + 2\mu_2) - \mathsf{S}(\mu_1 + 3\mu_2)]\mathbf{q},$$

$$K(\mu_1 + \mu_2) = 3\tilde{\mathbf{q}}[\mathsf{S}(2\mu_2) - \mathsf{S}(3\mu_2) - \mathsf{S}(\mu_1 + 2\mu_2) + \mathsf{S}(\mu_1 + 3\mu_2)]\mathbf{q},$$

$$K(2\mu_2) = 3\tilde{\mathbf{q}}[\mathsf{S}(\mu_1 + \mu_2) - 2\mathsf{S}(\mu_1 + 2\mu_2) + \mathsf{S}(\mu_1 + 3\mu_2)]\mathbf{q},$$

$$K(\mu_1 + 2\mu_2) = 3\tilde{\mathbf{q}}[\mathsf{S}(\mu_2) - \mathsf{S}(\mu_1 + \mu_2) - 2\mathsf{S}(2\mu_2) + 2\mathsf{S}(\mu_1 + 2\mu_2) + \mathsf{S}(3\mu_2) - \mathsf{S}(\mu_1 + 3\mu_2)]\mathbf{q}.$$

The argument for $K$ is the corresponding rate, and the argument for $\mathsf{S}$ indicates the motion over which the average should be taken. Thus, $\mathsf{S}(\mu_1 + 2\mu_2)$ means the second moment tensor averaged over the motion of the whole cation ($\mu_1$) and two of the methyl groups ($2\mu_2$). In addition, the rigid average (or outer in formula [1] in the preceding article (*19*)) over the three orientations of the cation is assumed. The powder average

TABLE 3

THE POWDER AVERAGES OF THE SECOND MOMENTS (IN $G^2$) FOR A TRIMETHYLAMMONIUM ION FOR DIFFERENT HYPOTHETICAL MOTIONS[a]

| | Contribution to $M_2$ from: | | |
|---|---|---|---|
| Type of reorientation | Intramethyl | Lone proton | Intermethyl |
| Rigid structure | 20.336 | 4.354 | 3.658 |
| One methyl group | 15.256 | 3.722 | 2.813 |
| Two methyl groups | 10.176 | 3.090 | 2.218 |
| Three methyl groups | 5.096 | 2.458 | 1.873 |
| Whole ion only | 5.932 | 0.373 | 0.708 |
| Ion + one methyl group | 4.243 | 0.252 | 0.541 |
| Ion + two methyl groups | 2.553 | 0.130 | 0.446 |
| Ion + three methyl groups | 0.864 | 0.009 | 0.422 |

[a] It is assumed that the reorientations of the methyl groups and the ions as a whole take place around the threefold pseudosymmetry axes.

TABLE 4

THE CONTRIBUTIONS TO THE RELAXATION CONSTANTS ($\frac{2}{3}\bar{K}^{(0)}$) FOR A TRIMETHYLAMMONIUM ION[a] CALCULATED FROM THE SECOND MOMENTS IN TABLE 3[b]

| | Rate of relaxing process[c] | Intramethyl | Lone proton | Intermethyl |
|---|---|---|---|---|
| This study | $\mu_2$ | 24.18 | 1.73 | 0.35 |
| | $\mu_1 + \mu_2$ | 48.53 | 7.31 | 4.60 |
| | $\mu_1$ | 20.19 | 11.69 | 6.92 |
| | $2\mu_2$ | | | 1.02 |
| | $\mu_1 + 2\mu_2$ | | | 2.55 |
| Sjöblom and Punkkinen (*22*)[d] | $\mu_2$ | 24.22 | 1.74 | 0.63 |
| | $\mu_1 + \mu_2$ | 48.45 | 7.28 | 4.30 |
| | $\mu_1$ | 19.99 | 11.68 | 6.86 |
| | $2\mu_2$ | | | 1.16 |
| | $\mu_1 + 2\mu_2$ | | | 2.39 |

[a] In units of $10^8$ sec$^{-2}$.

[b] See text.

[c] The reorientation rates are $\mu_1$ and $\mu_2$ for the ion and a methyl group, respectively.

[d] The relaxation constants from Sjöblom and Punkkinen (*22*) (which were calculated using the same assumptions) are also shown for comparison.

of $K$ is (as shown above) obtained by omitting $\mathbf{q}$ and using the traces of the second moment tensors in the relations above.

The second moments for powder were calculated using the computer program PSM (*26*, *27*) and the results are given in Table 3. The corresponding relaxation constants are listed in Table 4 together with those reported in (*22*) for comparison. The agreement is good, and the small differences may well be explained by the errors introduced by the averaging procedure used in (*22*).

## DISCUSSION

It has been shown above that relaxation constants and second moments are closely related. To the author's knowledge, this has only previously been reported for the case of a powder (*18*). Furthermore, the rates for the combined reorientations may readily he found if one assumes that the different processes are uncorrelated. This problem has been treated in (*22*), where it was found that essentially the same results were obtained using any reasonable assumption about the correlation, which suggests that this approximation is probably a good one.

The calculations of parameters for relaxation times have in the present approach been reduced to essentially calculations of second moments (cf. (19, Discussion, Part I)). Other methods (cf. Introduction) require that coupled differential equations be solved to give the rates, and that expressions be derived for the generally rather cumbersome summations of complex functions.

It has sometimes been assumed that the relaxation time varies only slightly with orientation. This is certainly true in many cases if one compares it with the temperature dependence, which is often determined by an Arrhenius equation for the correlation time: $\tau = \tau_0 \exp(E_A/kT)$. It is evident from Table 2 and formula [8], however, that the relative changes in relaxation time as the orientation is altered may, on average, be of approximately the same magnitude as that of the second moment. Second moments and relaxation times also have the same symmetry, in general. Thus, studies of the relaxation time as a function of orientation, although rarely performed, may be expected to provide information similar to that of a corresponding second moment study.

A second moment tensor may be obtained experimentally from measurements of second moments for each plateau in the second moment vs temperature curve. Intermediate values may actually also be used as shown by Andrew and Lipofsky (*28*). A common experimental procedure is to mount the crystal on a device such that any vector in the plane of a crystal can be brought into coincidence with the external magnetic field. More than one such mounting may be required in each case since one mounting allows the determination of at most five parameters.

Only differences between second moment tensors may be determined in an experimental study of the relaxation time vs orientation. For simplicity, we shall only discuss the relaxation time in the laboratory frame at constant temperature and for only one dynamical process. Under these conditions, at most ten parameters (including the correlation time) may be determined for one mounting if measurements are made at two frequencies, where one frequency is larger and the other smaller than the inverse of the correlation time. The number of different mountings required may thus be reduced considerably. Another aspect is that relaxation times are easier to measure and evaluate than second moments.

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