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Nuclear spin-lattice relaxation from hindered rotations in dipolar solids*

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A semiclassical theory is developed for the nuclear spin-lattice relaxation in dipolar solids resulting from hindered rotations of a general class of molecules in which the separations of the resonant nuclei in a molecule are equal. Within the weak-collision framework of nuclear spin-lattice relaxation the nuclear-spin coordinates are treated quantum mechanically while the spatial rotations are treated classically as simultaneous, independent Poisson processes constituting a Markov chain. Threefold rotations of CH_3 and multiple hindered rotations of $NH_4{}^+$ and $PF_6{}^-$ ions are used as illustrations of the theory.

I. INTRODUCTION

An important application of nuclear magnetic resonance (NMR) in both the physics and chemistry of the solid state is the identification of thermally activated molecular motions in solids along with the determination of such associated parameters as activation energies E_a and correlation times τ^0. In this respect, the main technique employed is the measurement of the temperature dependence of the spin-lattice relaxation time, either in the laboratory or rotating frame, of some nucleus belonging to the molecular group of interest. The plot of logarithmic relaxation time versus inverse temperature then yields information on the motional parameters.

In liquids and gases the best model for molecular reorientation is that of a rotational diffusion[1,2] in which the molecular orientation takes on a continuous range of values. This model is perfectly reasonable where, as in liquids and gases, the intermolecular bonding, and hence the barrier to rotation is low compared to the available thermal energy. However, in most solids, where the intermolecular bonding can be quite strong, a hindered rotational model is usually deemed more appropriate.[3-8] In this case, the molecular group is considered to jump discontinuously from one orientation to one of a discrete set of equivalent orientations.

Among the materials studied by NMR techniques a large class is comprised of what may be called "dipolar solids." These are the solids in which the predominant internuclear interaction between resonant nuclei is dipole-dipole. As a result of the interest in such molecular systems as the methyl group (CH_3) and ammonium ion ($NH_4{}^+$) a number of calculations have been made of the spin-lattice relaxation resulting from hindered rotations of such molecular groups in dipolar solids. The mechanisms investigated include threefold rotations of the methyl group[3] and combinations of twofold, threefold, and fourfold rotations of the ammonium ion.[4-8]

For example, the tetrahedral ammonium ion has three twofold and four threefold axes about which hindered rotations are possible. In a tetrahedral or higher symmetry crystal environment the twofold rotations would be equivalent, as would the threefold rotations.[7] However, in a lower symmetry environment some axial rotations will be preferred (less hindered) than others, necessitating a consideration of other combinations of axial rotations in these solids. The only theoretical derivations of the spin-lattice relaxation resulting from such low-symmetry mechanisms are for the cases of one threefold[3] and one twofold plus one threefold[8] rotation. Clearly, other possibilities, such as two threefold rotations, are numerous.

As has been observed previously[7] the interpretation of NMR relaxation-time data requires some care when more than one degree of molecular rotational freedom (i.e., more than one axis of rotation) is involved. The correlation times derivable from the data are not simply the correlation times for the individual rotations.

When the correlation times for the individual rotations are very different, the various contributions are easy to separate. However, when the correlation times are of the same order, producing relaxation time minima in the same temperature region, the various contributions to the relaxation are not easily separable. In these cases, specific expressions for the temperature dependence of the relaxation time must be developed for each individual rotational mechanism. Comparison with the data should then allow the rotational mechanism to be identified and the parameters estimated, for example, by least squares.

Many molecular systems of interest, for example CH_3, $NH_4{}^+$, $BF_4{}^-$, $PF_6{}^-$, and $SiF_6{}^{2-}$, and their associated hindered rotations are of the same general type when viewed from the point of view of magnetic resonance. The internuclear vectors of the resonant nuclei (H-H or F-F) in a given group all have the same length, if we neglect the usually small molecular distortion in the solid. Furthermore, the result of the molecular rotations is to cause each internuclear vector to be permuted among a finite number of orientations.

The purpose of this paper is to develop a general technique by which the relaxation times in dipolar solids resulting from any combination of hindered rotations of molecular groups of the above general type may be derived. The technique is illustrated by applications to CH_3, NH_4^+, and PF_6^-.

II. THEORY

A. Relaxation formalism

We consider a collection of N nuclei of spin I and gyromagnetic ratio γ, whose spin-lattice relaxation is determined by thermally induced modulation of their mutual dipolar coupling. In the weak collision theory of Bloembergen, Purcell, and Pound (BPP theory)[9] the spin-lattice relaxation times along the static magnetic field $\vec{H}_0$ and rotating magnetic field $\vec{H}_1$ for a pair of nuclei separated by a distance r have been shown to be[9-12]

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

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

Here $\omega_1=\gamma H_1$, $\omega_0=\gamma H_0$, and $J^{(q)}(\omega)$ are the spectral densities of the fluctuating dipolar interaction, given by

$$J^{(q)}(\omega)=\int_{-\infty}^{\infty} g^{(q)}(t)e^{-i\omega t}\,dt\ , \tag{2}$$

where $g^{(q)}(t)$ are the covariance functions

$$g^{(q)}(t)=\langle F^{(-q)}(t_0+t)F^{(q)}(t_0)\rangle - |\langle F^{(q)}(t_0)\rangle|^2\ , \tag{3}$$

the brackets $\langle\ \rangle$ denoting an ensemble average. The geometrical factors $F^{(q)}$ for the dipolar interaction are given by

$$\begin{aligned} F^{(0)}[\vec{R}(t)] &= (1-3\cos^2\theta)r^{-3}\ ,\\ F^{(1)}[\vec{R}(t)] &= \sin\theta\cos\theta e^{-i\phi}r^{-3}\ ,\\ F^{(2)}[\vec{R}(t)] &= \sin^2\theta e^{-2i\phi}r^{-3}\ , \end{aligned} \tag{4}$$

r, θ, ϕ being the polar coordinates of the internuclear vector $\vec{R}(t)$ at time t in a coordinate system in which $\vec{H}_0$ lies along the z axis. In Eq. (3), $F^{(-q)}=F^{(q)*}$.

In a collection of interacting nuclei, the cross correlations between nuclear pairs introduce a nonexponentiality into the spin-lattice relaxation.[1,13,14] However, it has been shown that this departure from exponentiality is a small effect and can be neglected for most practical purposes.[6,8,15] The spin-lattice relaxation rates for the collection of N equivalent nuclei are then given by[10-12]

$$T_1^{-1}=\tfrac{3}{2}\gamma^4\hbar^2 I(I+1)\sum_{j\neq i}^{N}[J_{ij}^{(1)}(\omega_0)+J_{ij}^{(2)}(2\omega_0)]\ ,$$

$$T_{1\rho}^{-1}=\tfrac{3}{2}\gamma^4\hbar^2 I(I+1)\sum_{j\neq i}^{N}[\tfrac{1}{4}J_{ij}^{(0)}(2\omega_1)+\tfrac{5}{2}J_{ij}^{(1)}(\omega_0)+\tfrac{1}{4}J_{ij}^{(2)}(2\omega_0)]\ .$$

For molecular groups of the general type considered in this paper, the nuclear pairs are equivalent so that the spectral densities for the (ij)th pair $J_{ij}^{(q)}(\omega)$ are independent of i and j and so can be written $J^{(q)}(\omega)$.

The relaxation rates for molecular groups of this type can be written

$$T_1^{-1}=\tfrac{3}{2}\gamma^4\hbar^2 I(I+1)(N-1)[J^{(1)}(\omega_0)+J^{(2)}(2\omega_0)]\ , \tag{5a}$$

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

the spectral densities for any nuclear pair $J(\omega)$ still being given by Eq. (2).

Note that since the geometrical factors at greatly different times are essentially uncorrelated, the covariance functions $g^{(q)}(t)\to 0$ as $t\to\infty$. This fact is essential for the existence of the spectral densities in Eq. (2). The existence of the spectral densities is a crucial property which will be utilized later.

B. Stochastic description of the rotation

We suppose that as a result of the hindered thermal rotations of the molecular group to which the nuclear pair belongs, the internuclear vector $\vec{R}(t)$ stochastically occupies the n internuclear positions $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_n$, e.g., for the methyl group CH_3 there are $n=3$, while for the ammonium ion NH_4^+ there are $n=6$ vector positions available for each proton pair.

At any time t_0 the probability that the internuclear vector occupies the position $\vec{r}_i$, $P(\vec{R}(t_0)=\vec{r}_i)$, is n^{-1} since any of the n positions is equally likely to be occupied. We can then write Eq. (3) as

$$g^{(q)}(t)=n^{-1}\sum_{i=1}^{n}\sum_{j=1}^{n}F_i^{(q)}F_j^{(-q)}\,[P_{ij}(t)-n^{-1}]\ ,$$

where $P_{ij}(t)=P(\vec{R}(t_0+t)=\vec{r}_j\ |\vec{R}(t_0)=\vec{r}_i)$ is the conditional probability that the internuclear vector is $\vec{r}_j$ at time t_0+t, given that it was $\vec{r}_i$ at time t_0. For notational convenience we have written $F^{(q)}(\vec{r}_i)$ as $F_i^{(q)}$.

We make the fundamental assumption that $P_{ij}(t)$, the probability of transition from $\vec{r}_i$ to $\vec{r}_j$ over the time interval (t_0, t_0+t), does not depend on the vector positions occupied prior to t_0, i.e., the stochastic reorientation process has the Markov property.[16] Furthermore, it is implicit in our notation that the process is stationary in that the transition probabilities $P_{ij}(t)$ depend only on the length of the time interval (t_0, t_0+t) and not on t_0, its location in time. In the language of the theory of stochastic processes we have assumed that the collection of random variables $\{\vec{R}(t); -\infty<t<\infty\}$ forms a homogeneous Markov chain over the states $\{\vec{r}_i; i=1,2,\ldots,n\}$. The stationary transition probability matrix with elements $P_{ij}(t)$ we denote by $P(t)$.

We now model the molecular reorientations as a number of simultaneous, independent Poisson processes in which (i) disjoint time intervals are independent, and (ii) the transition probability between distinct states is proportional to the time interval t for small t, i.e.,

$$P_{ij}(t)=\lambda_{ij}t+o(t), \quad i\neq j \ ,$$

where $o(t)/t\to 0$ as $t\to 0$. Of course this then means that

$$P_{ii}(t)=1-\sum_{j\neq i}^{n}\lambda_{ij}t+o(t) \ .$$

The parameters λ_{ij} for $i\neq j$, the transition probabilities per unit time from $\vec{r}_i$ to $\vec{r}_j$, are referred to as the intensities of transition from $\vec{r}_i$ to $\vec{r}_j$.

Now, considering the transitions over the time interval (t_0, t_0+t+h), which can be broken up into the disjoint intervals (t_0, t_0+t) and (t_0+t, t_0+t+h), and conditioning on events in the first interval allows us to write the Kolmogorov equations for the transition probabilities[16]

$$P_{ij}(t+h)=\sum_{k=1}^{n}P_{ik}(t)P_{kj}(h)$$

as

$$P_{ij}(t+h)=\sum_{k\neq j}P_{ik}(t)\lambda_{kj}h + P_{ij}(t)\Big(1-\sum_{k\neq j}\lambda_{jk}h\Big)+o(h) \ .$$

This then leads to the forward Kolmogorov differential equation for the Markov chain[16]

$$\frac{d}{dt}P_{ij}(t)=\sum_{k}[P_{ik}(t)\lambda_{kj}-P_{ij}(t)\lambda_{jk}], \quad t>0 \tag{6}$$

for any choice of λ_{jj}.

A convenient choice is

$$\lambda_{jj}=-\sum_{k\neq j}\lambda_{jk} \ , \tag{7}$$

since Eq. (6) can then be written

$$\frac{d}{dt}P_{ij}(t)=\sum_{k}P_{ik}(t)\lambda_{kj} \ . \tag{8}$$

Now, as mentioned previously, $g^{(q)}(t)\to 0$ as $t\to\infty$ and since its Fourier transform exists we know that

$$\begin{aligned}J^{(q)}(\omega)&=\lim_{T\to\infty}\int_{-T}^{T}g^{(q)}(t)e^{-i\omega t}\,dt\\&=n^{-1}\lim_{T\to\infty}\sum_i\sum_j F_i^{(q)}F_j^{(-q)}\\&\qquad\times[\mathcal{P}_{ij}^{T}(\omega)+\mathcal{P}_{ij}^{T}(-\omega)\\&\qquad\quad-2(\omega n)^{-1}\sin\omega T] \ ,\end{aligned} \tag{9}$$

exists, where

$$\mathcal{P}_{ij}^{T}(\omega)=\int_0^T P_{ij}(t)e^{-i\omega t}\,dt \ .$$

Multiplying Eq. (8) by $e^{-i\omega t}$, integrating over $(0,T)$, and using the initial condition $P_{ij}(0)=\delta_{ij}$, we find

$$e^{-i\omega T}P_{ij}(T)-\delta_{ij}+i\omega\mathcal{P}_{ij}^{T}(\omega)=\sum_k\mathcal{P}_{ik}^{T}(\omega)\lambda_{kj} \ ,$$

which reduces in matrix notation to

$$\mathcal{P}^{T}(\omega)=[e^{-i\omega T}P(T)-I](\Lambda-i\omega I)^{-1} \ ,$$

where $\mathcal{P}^T$ and Λ are the matrices with elements $\mathcal{P}_{ij}^T$ and λ_{ij}, respectively, and I is the identity matrix with elements δ_{ij}.

Hence,

$$\begin{aligned}\mathcal{P}^{T}(\omega)+\mathcal{P}^{T}(-\omega)&=-2\Lambda(\Lambda^2+\omega^2 I)^{-1}+2P(T)\\&\quad\times(\Lambda\cos\omega T+\omega I\sin\omega T)(\Lambda^2+\omega^2 I)^{-1} \ .\end{aligned}$$

Since the limit in Eq. (9) exists, the terms oscillating in T must cancel giving

$$\begin{aligned}J^{(q)}(\omega)&=-2n^{-1}\sum_i\sum_j F_i^{(q)}F_j^{(-q)}[\Lambda(\Lambda^2+\omega^2 I)^{-1}]_{ij}\\&=-2n^{-1}\mathrm{Tr}[\Lambda(\Lambda^2+\omega^2 I)^{-1}\tilde{\mathcal{F}}^{(q)}] \ ,\end{aligned} \tag{10}$$

where the matrices $\mathcal{F}^{(q)}$ have elements $\mathcal{F}_{ij}^{(q)}=F_i^{(q)}F_j^{(-q)}$ which depend only on the geometry of the molecular group and its orientation relative to $\vec{H}_0$.

Equations (5) and (10) then constitute general expressions for the spin-lattice relaxation times of a collection of N resonant spins undergoing hindered rotations in a dipolar solid. Since the process is thermally activated, the intensities of transition (λ_{ij}) will be given by the Arrhenius expression

$$\lambda_{ij}=\lambda_{ij}^{0}\exp(-E_{ij}/kT) \ ,$$

where E_{ij} is the activation energy for the hindered rotation which takes $\vec{R}(t)$ from $\vec{r}_i$ to $\vec{r}_j$, the preexponential factor λ_{ij}^0 is the transition intensity from

$\vec{r}_i$ to $\vec{r}_j$ "at infinite temperature" and k is the usual Boltzman constant.

C. Relaxation in a powder

The preceding derivation describes the rate at which the magnetization in a single crystal decays to its thermal equilibrium value. The magnetization observed in a powder sample composed of a large number of randomly oriented crystallites will be the polycrystalline average of the magnetization for a single crystal, e.g.,

$$\langle M(t)\rangle_a = M(0)(1-\langle e^{-Qt}\rangle_a) \ , \tag{11}$$

Q being the relaxation rate for a single-crystal orientation and $\langle\ \rangle_a$ denoting a polycrystalline average. In this expression $M(t)$ is the magnetization for a single crystal orientation and Q depends on the orientation.

It has been shown[8] that for the case of the ammonium ion, Eq. (11) can be written to an excellent approximation as

$$\langle M(t)\rangle_a = M(0)[1-\exp(-\langle Q\rangle_a t)] \ ,$$

so that the departure from exponential decay of the magnetization resulting from the anisotropy of Q is negligibly small. This, together with the fact that exponential relaxation is usually observed experimentally in powder samples, leads us to adopt the procedure of taking the polycrystalline average of the relaxation rates in Eq. (5). We then find that Eqs. (5) and (10) still hold except that $\mathfrak{F}^{(q)}$ is replaced by $\mathfrak{F}_a^{(q)}$, the polycrystalline average of $\mathfrak{F}^{(q)}$ with elements given by

$$(\mathfrak{F}_a^{(q)})_{ij} = \langle F_i^{(q)} F_j^{(-q)}\rangle_a \ .$$

If α_{ij} is the angle between the vectors $\vec{r}_i$ and $\vec{r}_j$ it is easy to show that[7]

$$(\mathfrak{F}_a^{(0)})_{ij} : (\mathfrak{F}_a^{(1)})_{ij} : (\mathfrak{F}_a^{(2)})_{ij} = 6:1:4$$

and

$$(\mathfrak{F}_a^{(1)})_{ij} = (3\cos^2\alpha_{ij} - 1)/15r^6 \ .$$

Combining these results with Eqs. (10) and (11) gives for the intramolecular contribution to the spin-lattice relaxation rates in a powder sample

$$T_1^{-1} = \frac{\gamma^4\hbar^2 I(I+1)(N-1)}{5r^6\omega_0 n}[M(\omega_0)+2M(2\omega_0)] \ , \tag{12a}$$

$$T_{1\rho}^{-1} = \frac{\gamma^4\hbar^2 I(I+1)(N-1)}{5r^6\omega_0 n} \times\left(\frac{3\omega_0}{4\omega_1}M(2\omega_1)+\tfrac{5}{2}M(\omega_0)+\tfrac{1}{2}M(2\omega_0)\right) \ , \tag{12b}$$

where

$$M(\omega) = Tr[X(I+X^2)^{-1}\tilde{A}] \tag{13}$$

and X, A are the dimensionless matrices defined by

$$X = \Lambda/\omega \ , \quad A_{ij} = 1-3\cos^2\alpha_{ij} \ .$$

Note that A is determined by the geometry of the molecule while X is determined by the particular reorientation mechanism under consideration. The spin-lattice relaxation times in a powder are given by Eq. (12) on computation of $M(\omega)$ from Eq. (13).

Since Λ and, hence, X is defined so that the rows sum to zero, then X and X^2 are singular matrices. Therefore, at high temperatures where some of the λ_{ij}'s are large enough for I to be negligible compared to X^2, $(X^2+I)^{-1}$ is the inverse of an almost singular matrix and so subject to large errors in computation.

A generally more satisfactory procedure for the evaluation of $M(\omega)$ is to find the matrix T which diagonalizes X,

$$TXT^{-1} = X_T \ ,$$

where $(X_T)_{ij} = x_i\delta_{ij}$, the $\{x_i\}$ being the eigenvalues of X. Of course, since X is singular one of these eigenvalues is always zero.

Then defining TAT^{-1} as A_T we can write Eq. (13) as

$$M(\omega) = \sum_{i=1}^{n}\frac{x_i}{1+x_i^2}(\tilde{A}_T)_{ii} \ . \tag{14}$$

This procedure can either be carried out by hand to produce an analytic expression for $M(\omega)$ or, in the more complicated cases, computed numerically by any one of a number of algorithms for the diagonalization of matrices.

III. EXAMPLES

A. CH$_3$ group in threefold rotation

For the methyl group we have $N=3$, $n=3$, and

$$\alpha_{ij} = \begin{cases} \frac{1}{3}\pi, & i\neq j \ , \\ 0, & i=j \ . \end{cases}$$

The dimensionless-transition matrix X can be written $X=xB$, where $x=\lambda/\omega$, λ being the intensity of transition for threefold rotations. The matrix B has elements given by

$$B_{ij} = \begin{cases} 1, & i\neq j \ , \\ -2, & i=j \ . \end{cases}$$

Evaluation of Eq. (14) then gives

$$M(\omega) = \tfrac{9}{2}f(\omega\tau) \ ,$$

where the correlation time τ is defined to be $(3\lambda)^{-1}$ and $f(z)$ is given by

$$f(z) = z/(1+z^2) \ . \tag{15}$$

Substitution of this $M(\omega)$ into Eq. (12) yields the

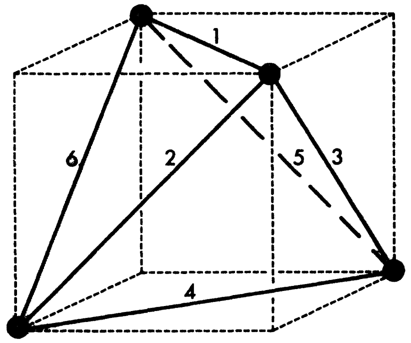

FIG. 1. Tetrahedral configuration of protons on the NH_4^+ ion. One possible numbering scheme for the interproton vectors is shown.

spin-lattice relaxation times for threefold hindered rotations of the methyl group.[3]

B. Ammonium ion

For the tetrahedral NH_4^+ ion, $N=4$ and $n=6$. The scheme chosen for numbering the internuclear vectors is shown in Fig. 1. With this choice we have

$$\alpha_{ii}=0,\quad \alpha_{i,i+3}=\tfrac{1}{2}\pi,\quad \alpha_{i,j}=\tfrac{1}{3}\pi,\quad j\neq i,\quad i+3\ .$$

However, for the NH_4^+ ion there are a number of reorientational mechanisms possible involving the three twofold and four threefold axes. A mechanism involving rotations about p twofold and q threefold axes will be denoted by $p\times C_2+q\times C_3$. We will consider just three of the many examples of this type.

1. $3\times C_2+4\times C_3$ mechanism

An ammonium ion in a tetrahedral crystal environment would be expected to undergo three equivalent twofold and four equivalent threefold rotations. The dimensionless transition matrix X, in this case, can be written

$$X=x_2B_2+x_3B_3\ , \tag{16}$$

where $x_m=\lambda_m/\omega$, λ_2, and λ_3 being the intensities of transition for twofold and threefold rotations, respectively. The matrices B_m have components

$$(B_m)_{ij}=\begin{cases}1 & \text{if } \vec{r}_i \text{ is related to } \vec{r}_j \text{ by the } m\text{-fold rotation, } i\neq j\\ 0 & \text{if } \vec{r}_i \text{ is not related to } \vec{r}_j \text{ by the } m\text{-fold rotation, } i\neq j\ ,\end{cases} \tag{17}$$

$$(B_m)_{ii}=-\sum_{j\neq i}(B_m)_{ij}\ .$$

In this case, the matrices B_2 and B_3 commute with each other and so can be simultaneously diagonalized by the same unitary transformation matrix T.

Evaluation of $M(\omega)$ from Eq. (14) then gives

$$M(\omega)=3[f(\omega\tau_3)+3f(\omega\tau)]\ ,$$

where the correlation times τ_3 and τ are defined by

$$\tau_3=(6\lambda_3)^{-1},\quad \tau_2=(3\lambda_2)^{-1}\ ,$$

$$\tau=1.5(\tau_2^{-1}+\tau_3^{-1})^{-1}\ ,$$

and $f(z)$ is given by Eq. (15).

Substituting this expression for $M(\omega)$ into Eq. (12) yields the spin-lattice relaxation times for the NH_4^+ ion undergoing hindered twofold and threefold rotations in a tetrahedral or higher-symmetry environment.[7,8]

2. $1\times C_2+1\times C_3$ mechanism

In a crystal environment of less than tetrahedral symmetry some twofold and threefold rotations may be energetically more favorable than others. Here we consider the case where only one twofold and one threefold rotation are effective.

The dimensionless transition matrix X is still given by Eq. (16) with the B_m matrices specified as in Eq. (17). However, B_2 and B_3 no longer commute and can no longer be simultaneously diagonalized. As a consequence, the diagonalizing transformation matrix T depends on x_2 and x_3, a fact which only serves to make the computations a little more laborious. The resulting $M(\omega)$ is given by

$$M(\omega)=3[f(\omega\tau_3)+f(\omega\tau)+f(\omega\tau_+)+f(\omega\tau_-)]\ ,$$

where the correlation times $\tau_3, \tau, \tau_\pm$ are defined by

$$\tau_2=(2\lambda_2)^{-1}\ ,\quad \tau_3=(3\lambda_3)^{-1}\ ,\quad \tau=\tau_2^{-1}+\tau_3^{-1}$$

and

$$\tau_\pm=\tfrac{1}{4}[3(\tau_2+\tau_3)\pm(9\tau_2^2-6\tau_2\tau_3+9\tau_3^2)^{1/2}]\ ,$$

and $f(z)$ is given by Eq. (15).

Substitution into Eq. (12) then yields the spin lattice relaxation times for the $1\times C_2+1\times C_3$ hindered rotation of the NH_4^+ ion.[8]

3. C_3+C_3' mechanism

In materials where the ammonium ion protons are involved in hydrogen bonds, threefold rotations seem more likely to occur than twofold rotations since, in the former case, only three hydrogen bonds need to be broken to allow the rotation, whereas, in the latter case, all four hydrogen bonds need to be broken.

In the case where only two threefold rotations are effective, the dimensionless transition matrix is given by

$$X=x_3B_3+x_3'B_3'\ ,$$

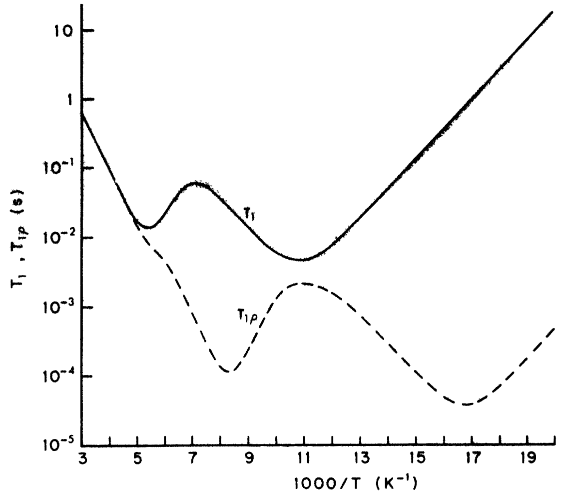

FIG. 2. Temperature dependence of the spin-lattice relaxation times for the C_3+C_3' hindered rotation of NH_4^+. The relevant parameters are given in the text.

where $x_3(x_3')=\lambda_3(\lambda_3')/\omega$, λ_3, and λ_3' being the intensities of transition for the two threefold rotations. The elements of the matrices B_3, B_3' are defined by an obvious extension to Eq. (17).

Since this particular mechanism has apparently not been investigated theoretically before we show the temperature dependence of the spin-lattice relaxation times computed from Eqs. (12) and (14) in Fig. 2. The calculation performed is for a Larmor frequency of 20 MHz, a spin-locking field H_1 of 10 G and a proton-proton separation of 1.68 Å. The activation energies chosen for the threefold rotations were 2.0 and 4.0 kcal/mole, with both pre-exponential factors 3.33×10^{12} sec^{-1}.

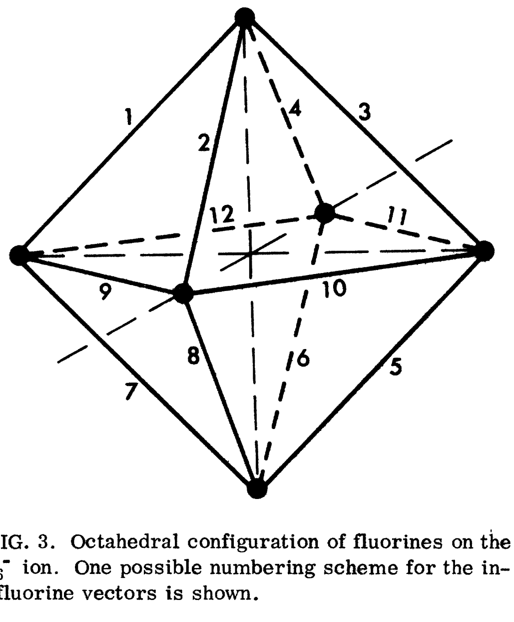

FIG. 3. Octahedral configuration of fluorines on the PF_6^- ion. One possible numbering scheme for the interfluorine vectors is shown.

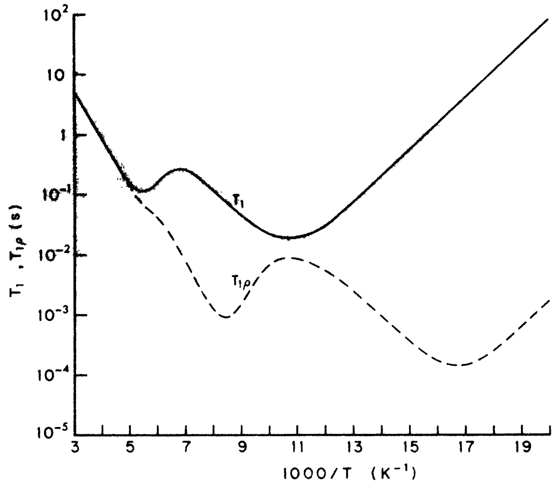

FIG. 4. Temperature dependence of the spin-lattice relaxation times for the C_4+C_4' hindered rotation of PF_6^-. The relevant parameters are given in the text.

C. $C_4 + C_4'$ mechanism of PF_6 group

This example is included because it illustrates very well the ease with which quite complex systems can be handled by the formalism contained in Eq. (14).

The scheme chosen for numbering the interfluorine vectors in the octahedral PF_6^- group is shown in Fig. 3. In this case, $N=6$ and for hindered rotations which simply permute fluorine nuclei $n=12$.

For the hindered rotational model in which only two inequivalent fourfold rotations are effective (C_4+C_4') we can write the dimensionless transition matrix as

$$X=x_4B_4+x_4'B_4' \ ,$$

where $x_4(x_4')=\lambda_4(\lambda_4')/\omega$, λ_4, and λ_4' being the intensities of transition for the two fourfold rotations. The matrices B_4 and B_4' are defined as in Eq. (17).

Figure 4 shows the computed temperature dependence of the spin-lattice relaxation times for this particular mechanism. The Larmor frequency, spin-locking field H_1, activation energies, and pre-exponential factors chosen were as in case B3 above. The fluorine-fluorine separation was taken as 2.23 Å, which is typical for PF_6^- groups.

IV. CONCLUSION

A semiclassical theory has been developed for the spin-lattice relaxation times resulting from hindered rotations of a broad class of molecular groups in dipolar solids. The nuclear-spin system has been treated quantum mechanically whereas the molecular rotation has been modeled classically as a stochastic process describable in terms of a Markov chain.

The theory allows computations to be made of the spin-lattice relaxation times for quite complex molecular systems involving many degrees of motional freedom. Illustrative examples are given for the CH_3, NH_4^+, and PF_6^- groups.

The convenient computation of the temperature dependence of the spin-lattice relaxation times, as outlined in this paper, could be a very valuable tool for the identification of molecular motions, and constitutes a vital first step in the least squares estimation of the associated motional parameters.

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