

Effect of tunneling on the frequency dependence and time evolution of nuclear magnetization in the rotating frame

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(Received 27 June 1978)

The proton spin-lattice relaxation time in the rotating frame of a NH_4 group embedded in a crystal lattice is calculated. The effect of the NH_4 -group tunneling is incorporated on the basis of a phenomenological model introduced by Clough and Punkkinen. It is shown that, in general, the magnetization decays with five time constants. If tunneling is very large, $\omega_T \gg \gamma H_0$, the magnetization decays in the rotating frame with one time constant. Search for large tunneling frequencies by varying the Larmor frequency at a constant spin-locking field H_1 is thus easier in the rotating frame than at high fields. If tunneling splitting is small, $\omega_T \sim \gamma H_1$, the relaxation rate shows maxima whenever $\omega_T = 2\gamma H_1$, in good accord with experiment.

I. INTRODUCTION

It has been known for a long time that at low temperatures the tunneling of the NH_4 ion affects the spin-lattice relaxation, particularly in lattices with low hindering potential for NH_4 reorientation. It has been pointed out before, and is also supported by the present calculations, that the tunneling splittings in the energy spectrum of the NH_4 ion embedded in a crystal lattice, in general, cause multiple minima in the temperature dependence of the spin-lattice relaxation. However, to study the temperature dependence of the spin-lattice relaxation in detail the torsional-phonon interaction would have to be included explicitly and its effect on the transitions between the Zeeman-torsional levels of the NH_4 ion calculated. Since the corresponding correlation functions in the present work are assumed rather than calculated, the temperature dependence of the spin-lattice relaxation will not be studied.

Our calculation was motivated by the experimental results reported in Refs. 1–3. In that work, very small splittings of the torsional ground state of the NH_4 ion^{4–6} were measured in solid lattices by matching the precooled nuclear Zeeman states to the torsional states at lattice temperature. Since the Zeeman system and the torsional system are coupled by the dipole-dipole interaction, there is a flow of energy between these two energy reservoirs. The rate with which the energy is being transferred between the two systems depends on the relative magnitude of the tunneling splittings with respect to the magnitude of the Zeeman splitting of nuclear-spin levels. As a result, measuring $M_x(t)$ as a function of H_1 , it is possible to observe the effects of the crystal field on the spin-lattice relaxation in the rotating frame. It was found,^{1–3} that for certain values of H_1 , the frequency dependence of M_x shows a local minimum,

and it was concluded that for those values of H_1 the Zeeman and torsional splittings are matched.

The present calculation is based on the model discussed by several authors.^{7–9} The same model was also applied previously in a study of the proton spin-lattice relaxation of NH_4 compounds in the laboratory frame.¹⁰ In the present paper, this model is used to calculate the spin-lattice relaxation of the four-spin- $\frac{1}{2}$ system in the rotating frame. Our results show that in an asymmetric crystal field the proton magnetization in the rotating frame will, in general, decay with five separate time constants, and that the frequency dependence of the spin-lattice relaxation will show minima for those values of H_1 which satisfy the condition $2\gamma H_1 = \omega_T$. The tunneling splitting of those energy levels, which are coupled by the intraionic part of the dipole-dipole interaction, is $\hbar\omega_T$.

The most interesting result of the present calculation is that the magnetization in the rotating frame recovers with a single exponential in the case of large tunneling splittings. This makes a high-field dispersion study (by varying ω_0) much more convenient in the rotating frame (at constant ω_1). In addition, the results for small F splittings are in qualitative agreement with the observations reported in Refs. 1–3.

In the calculation it is assumed that the torsional system is at the lattice temperature at all times. Also the experimentally determined torsional relaxation time³ T_{1T} is considered to be the correlation time for the relaxation. The first assumption limits the applicability of the presented calculation to larger than very low temperatures since at very low temperatures the torsional system becomes practically isolated from the lattice ($T_{1T} \sim 1$ sec) on the scale of a typical experiment (1 msec). The technique of spin thermodynamics is then applicable. Such a calculation is compared with the experimental data as given in Ref.

11. The method is extended also into the nonequilibrium time domain.^{12,13}

II. HAMILTONIAN OF THE SYSTEM

In what follows, we will consider an isolated NH₄ ion placed in a crystal field and an externally applied magnetic field. The Hamiltonian of the system can be written in the form

$$H(t) = H_Z + H_T + H_P + H_{TP} + H_D + H_{rf}(t) , \quad (1)$$

where the various terms are defined as follows. The proton Zeeman operator is

$$H_Z = -\hbar\omega_0 I_z , \quad (2)$$

where I_z is the z component of the total spin for the four-spin- $\frac{1}{2}$ system of the NH₄ ion and ω_0 is the Larmor frequency of the proton spin in the external dc magnetic field \vec{H}_0 . The torsional operator is

$$H_T = \vec{L}^2/2J + V(\alpha, \beta, \gamma) , \quad (3)$$

with J representing the moment of inertia. \vec{L}^2 is the square of the orbital angular momentum of the NH₄ tetrahedron. $V(\alpha, \beta, \gamma)$ is the potential energy of the ion embedded in the crystal lattice, while α, β, γ are the Euler angles determining the orientation of the NH₄ ion with respect to some spatially fixed coordinate system. H_P is the phonon Hamiltonian and H_{TP} represents the interaction between the torsional degrees of freedom and phonons. At present we do not need their explicit forms.

The intraionic dipole-dipole interaction is

$$H_D = K_D \sum_{k=-2}^2 \sum_{i < j} (-1)^k U_{ij}^{-k} V_{ij}^k , \quad (4)$$

where $K_D \equiv \gamma^2 \hbar^2 / r_0^3$. The proton-proton distance is r_0 , and γ is the gyro-magnetic ratio for protons. The spatial part is

$$U_{ij}^{-k} = \left(\frac{6}{5}\pi\right)^{1/2} Y_2^{-k}(\theta_{ij}, \phi_{ij}) ,$$

with (θ_{ij}, ϕ_{ij}) representing the spherical coordinates of the proton-proton vector \vec{r}_{ij} . The spherical harmonics $Y_2^k(\theta, \phi)$ are defined with respect to the coordinate system (x, y, z) which is oriented so that the z axis is parallel to the external dc magnetic field \vec{H}_0 .

The spin operators V_{ij}^k are given by

$$\begin{aligned} V_{ij}^0 &= -\left(\frac{8}{3}\right)^{1/2} [I_i^0 I_j^0 - \frac{1}{4} (I_i^+ I_j^- + I_i^- I_j^+)] , \\ V_{ij}^{\pm 1} &= \pm (I_i^0 I_j^{\pm 1} + I_i^{\pm 1} I_j^0) , \\ V_{ij}^{\pm 2} &= -I_i^{\pm 1} I_j^{\pm 1} , \end{aligned}$$

also

$$I_j^{\pm 1} \equiv I_{jx} \pm i I_{jy} , \quad I_j^0 \equiv I_{jz} .$$

Finally, the rf interaction term has the form

$$H_{rf}(t) = -\hbar\omega_1 I_x (e^{i\omega t} + e^{-i\omega t}) , \quad (5)$$

where $\omega_1 = \gamma H_1$.

III. SCHRÖDINGER EQUATION IN THE LABORATORY AND IN THE ROTATING COORDINATE FRAME

The Schrödinger equation corresponding to the system under consideration is

$$i \hbar \frac{\partial \psi(t)}{\partial t} = H(t) \psi(t) , \quad (6)$$

with $H(t)$ given by Eq. (1). The transformation to a rotating coordinate frame is introduced by

$$\psi(t) = e^{i\omega I_z t} \psi_r(t) ,$$

where $\psi_r(t)$ is the wave function of the system as seen in the rotating coordinate frame. The Schrödinger equation in the rotating frame is

$$i \hbar \frac{\partial \psi_r(t)}{\partial t} = H_r(t) \psi_r(t) , \quad (7)$$

where the Hamiltonian in the rotating frame $H_r(t)$ is given at exact resonance ($\omega = \omega_0$) by

$$\begin{aligned} H_r(t) &= H_T + H_P - \hbar\omega_1 I_x + H_{TP} \\ &+ K_D \sum_{k=-2}^2 \sum_{i < j} (-1)^k e^{-ik\omega_0 t} U_{ij}^{-k} V_{ij}^k . \end{aligned} \quad (8)$$

In the above expression we have omitted the term

$$-\frac{1}{2} \hbar\omega_1 (I^+ e^{-i2\omega_0 t} + I^- e^{i2\omega_0 t}) ,$$

since its effect in the rotating frame is negligible because $\omega_1/\omega_0 \ll 1$.

In the laboratory frame usually the following set of spin operators is used

$$I_z, I_x \pm i I_y \equiv I^{\pm} ,$$

and the spin-states are chosen to be the eigenstates of $I^2 = I_x^2 + I_y^2 + I_z^2$ and I_z . In the rotating frame, however, it is more convenient to choose the spin states as eigenstates of I^2 and I_x , that is,

$$I_x |M\rangle = M |M\rangle .$$

Correspondingly we have to define raising and lowering operators as

$$I^{\pm} = I_y \pm i I_z .$$

Using these new operators, the rotating-frame Hamiltonian can be written

$$\begin{aligned} H_r(t) &= H_T + H_P - \hbar\omega_1 I_x + H_{TP} \\ &+ K_D \sum_{k, k'=-2}^2 \sum_{i < j} (-1)^k e^{-ik\omega_0 t} U_{ij}^{-k} C_{k, k'} S_{ij}^{k'} , \end{aligned} \quad (9)$$

where the spin operators S_{ij}^k are obtained from the expressions for the V_{ij}^k upon replacing in the expressions for the latter

$$I_j^0 \rightarrow I_{jx} \text{ and } I_{jx} \pm iI_{jy} \rightarrow I_{jy} \pm iI_{jx} .$$

The matrix $C_{k,k'}$ is given in Appendix A.

IV. CALCULATION OF THE TRANSITION PROBABILITIES PER UNIT TIME IN THE ROTATING FRAME

We define a Hilbert space spanned by the eigenstates of the unperturbed Hamiltonian in the rotating frame,

$$H_r^0 = H_T + H_P - \hbar\omega_1 I_x . \quad (10)$$

An eigenstate of this Hamiltonian is written in the form

$$\psi_{\xi n, M, p} = \psi_{T, \xi n} \phi_{\sigma, \xi M} \chi_p \equiv |\xi n M p\rangle .$$

The subscripts have the following meaning: T stands for the torsional degrees of freedom, σ stands for the spin degrees of freedom, p stands for the phonon degrees of freedom, $n=0, 1, 2, \dots$, denotes the ground, first excited torsional oscillator states, ξ denotes the symmetry type (A, E, F), M denotes the magnetic quantum number ($-2, \dots, +2$). The eigenequation for H_r^0 reads

$$H_r^0 |\xi n M p\rangle = (E_{\xi n}^T + E_p - M \hbar\omega_1) |\xi n M p\rangle . \quad (11)$$

Writing $\psi_r(t) = U(t)\psi_r(0)$, we obtain from Eq. (7) the equation of motion for the evolution operator

$$i \hbar \frac{\partial U}{\partial t} = H_r(t) U . \quad (12)$$

Up to first order in dipolar interaction, the solution of the above equation is

$$U(t, 0) = e^{-i(i/\hbar)H_r^0 t} \left[U'(t, 0) + \left(\frac{-i}{\hbar} \right) \int_0^t U'(t, t') e^{(i/\hbar)H_r^0 t'} H_D(t') e^{-(i/\hbar)H_r^0 t'} U'(t', 0) dt' \right] , \quad (13)$$

$$U'(t) = T \left[\exp \left[\frac{-i}{\hbar} \int_0^t H_{TP}(t') dt' \right] \right] ,$$

where T is the time-ordering operator and

$$H_{TP}(t) = e^{(i/\hbar)H_r^0 t} H_{TP} e^{-(i/\hbar)H_r^0 t} .$$

The operator $H_D(t')$ is given in Eq. (9).

Now we wish to calculate the matrix element

$$\begin{aligned} \langle \alpha | U(t, 0) | \beta \rangle &= e^{-i(i/\hbar)E_\alpha t} \langle \alpha | U'(t, 0) | \beta \rangle + \left(\frac{-i}{\hbar} \right) e^{-i(i/\hbar)E_\alpha t} \int_0^t dt' \langle \alpha | U'(t, t') | \nu \rangle \langle \nu | H_D(t') | \lambda \rangle \\ &\quad \times \langle \lambda | U'(t', 0) | \beta \rangle e^{-i(i/\hbar)(E_\lambda - E_\nu)t'} . \end{aligned} \quad (14)$$

In the above expression $|\alpha\rangle, |\beta\rangle, \dots$, are eigenstates of H_r^0 :

$$H_r^0 |\alpha\rangle = E_\alpha |\alpha\rangle .$$

The subscript α stands for $\xi n M p$:

$$E_\alpha \equiv E_{\xi n M p} = E_{\xi n}^T + E_p - M \hbar\omega_1 .$$

In what follows we will consider only such transitions, for which $\langle \alpha | U'(t) | \beta \rangle = 0$, and therefore the absolute square of the above amplitude can be written

$$\begin{aligned} |\langle \alpha | U(t, 0) | \beta \rangle|^2 &= \frac{1}{\hbar^2} \int_0^t \int_0^t dt_1 dt_2 \langle \alpha | U'(t, t_1) | \nu \rangle \\ &\quad \times \langle \alpha | U'(t, t_2) | \lambda \rangle^* \langle \nu | H_D(t_1) | \nu' \rangle \langle \lambda | H_D(t_2) | \lambda' \rangle^* \\ &\quad \times e^{-i(i/\hbar)(E_\nu - E_{\nu'})t_1} e^{i(i/\hbar)(E_{\lambda'} - E_\lambda)t_2} \langle \nu' | U'(t_1, 0) | \beta \rangle \langle \lambda' | U'(t_2, 0) | \beta \rangle^* . \end{aligned} \quad (15)$$

In Eqs. (14) and (15) the summation over repeated indices has to be taken.

The above result for the transition amplitude is not immediately applicable because we do not know the explicit form of the evolution operator $U'(t)$, generated by the torsional-phonon interaction. We shall assume however that $U'(t)$ is a stationary random operator. We have to calculate therefore the ensemble average of the transition amplitude. However, instead of calculating this ensemble average, we simply assume the following result:

$$\sum_{p,p'} P_p^B \langle |\langle \xi_0' M' p' | U(t) | \xi_0 M p \rangle|^2 \rangle = \frac{1}{\hbar^2} \int_0^t \int_0^t dt_1 dt_2 \langle \xi_0' M' | H_D(t_1) | \xi_0 M \rangle \langle \xi_0' M' | H_D(t_2) | \xi_0 M \rangle^* \times \exp(-|t_1 - t_2|/\tau_c) \exp[-(i/\hbar)(E_{\xi_0 M} - E_{\xi_0' M'})(t_1 - t_2)] \quad (16)$$

In the above expression we made the simplest possible assumption, namely, that the effect of the interaction between torsional degrees of freedom and phonons can be approximated by a single exponential correlation function. Of course, one could make more specific assumptions concerning the effect of $U'(t)$ which would also enable one to calculate the correlation times, but we will not go into such details here. We have also assumed that at low temperatures most of the NH_4 ions are in the ground torsional manifold (consisting of several states), and we need to consider only the transitions among these states. Furthermore we introduced the following notation in Eq. (16):

$$E_{\xi_0 M} \equiv E_{\xi_0}^T - M \hbar \omega_1$$

and

$$|\xi_0 M\rangle \equiv \psi_{T, \xi_0} \phi_{\sigma, \xi_0 M}$$

If the dipolar interaction is written in the form

$$H_D(t) = \sum_{k=-2}^2 e^{-ik\omega_0 t} H_D^k, \quad (17)$$

where

$$H_D^k = K_D \sum_{k'=-2}^2 \sum_{i < j} (-1)^k U_{ij}^{-k} C_{k,k'} S_{ij}^{k'}, \quad (18)$$

and if we define the transition probability per unit time among the lowest lying states of the ammonium ion as

$$W_{\xi_0 M \rightarrow \xi_0' M'} = \lim_{t \rightarrow \infty} \left(\frac{\sum_{p,p'} P_p^B \langle |\langle \xi_0' M' p' | U(t) | \xi_0 M p \rangle|^2 \rangle}{t} \right),$$

we obtain from Eq. (16),

$$W_{\xi_0 M \rightarrow \xi_0' M'} = \frac{1}{\hbar^2} \sum_k |\langle \xi_0' M' | H_D^k | \xi_0 M \rangle|^2 \times \frac{2\tau_c}{1 + [\omega_{\xi_0' \xi_0}^T + (M' - M)\omega_1 + k\omega_0]^2 \tau_c^2} \quad (19)$$

where $\omega_{\xi_0' \xi_0}^T \equiv (E_{\xi_0'}^T - E_{\xi_0}^T)/\hbar$ are the tunneling splittings of the ground torsional state.

V. RATE EQUATIONS FOR THE POPULATION DEVIATIONS

The calculation in this section is based on a model discussed previously.^{7,10} The energy-level scheme for the ground torsional state of the NH_4 ion is shown in Fig. 1, where the following tunneling frequencies are introduced

$$\omega_{F_i}^T = (1/\hbar)(E_{F_i}^T - E_A^T),$$

$$\omega_E^T = (1/\hbar)(E_E^T - E_A^T),$$

and

$$\Delta_{ij} = (1/\hbar)(E_{F_j}^T - E_{F_i}^T), \quad i=1, 2, 3.$$

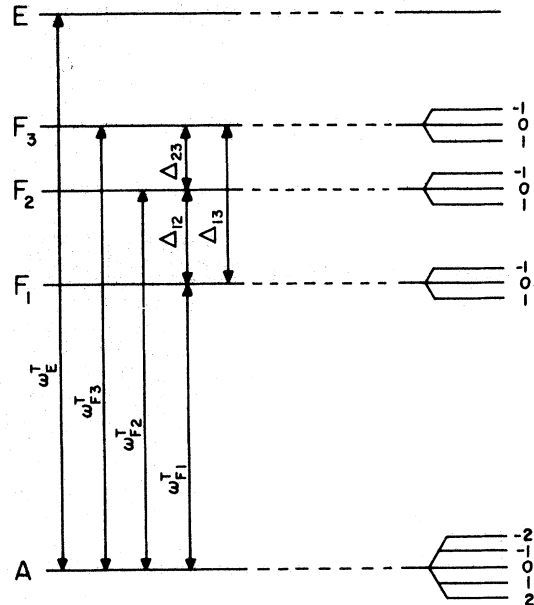


FIG. 1. Energy-level scheme for the ground torsional state of the NH_4 ion in an asymmetric crystal field.

The spin-lattice relaxation can be described^{7,14} in terms of the deviations of the populations of various states $N_{\xi n M}$ from their thermal equilibrium values

$$\Delta N_{\xi n M} = N_{\xi n M} - N_{\xi n M}^0 \quad (20)$$

It will be assumed that this holds true also for the spin-lattice relaxation in the rotating frame. In other words, the torsional-Zeeman system can be described in terms of the populations of various eigenstates of the Hamiltonian H^0 . The combined effect of the torsional-phonon and of the dipole-dipole interaction are transitions among these eigenstates. This causes the relaxation of the Zeeman system. All the nonzero transition probabilities per unit time among the energy levels shown in Fig. 1, are given in Appendix B. We also neglect the Boltzmann factors $p_{\xi_0}^B$, which discriminate between the downward and the corresponding upward transition rates. As pointed out in Refs. 7 and 10, this is admissible, as long as one is dealing only with the deviations of the populations from their thermal-equilibrium values.

Using the transition rates listed in Appendix B, the time variation of the $\Delta N_{\xi_0 M}$ is governed by the following set of coupled differential equations:

$$\frac{d}{dt}(\Delta N_{\xi_0 M}) = \sum_{\xi_0' M'} H_{\xi_0 M; \xi_0' M'} \Delta N_{\xi_0' M'} \quad (21)$$

where we have introduced the notation

$$H_{\xi_0 M; \xi_0' M'} = H_{\xi_0' M'; \xi_0 M} = W_{\xi_0 M - \xi_0' M'} \quad ,$$

$$\xi_0 M \neq \xi_0' M'$$

and

$$H_{\xi_0 M; \xi_0 M} = - \sum_{\substack{\xi_0' M' \\ \xi_0' M' \neq \xi_0 M}} H_{\xi_0 M; \xi_0' M'} \quad .$$

In terms of the populations of the energy levels the deviation of the magnetization from its thermal equilibrium value is given by

$$\Delta M_x = \gamma \hbar \left\{ 2(\Delta N_{A_2} - \Delta N_{A_{-2}}) + (\Delta N_{A_1} - \Delta N_{A_{-1}}) + \sum_{i=1}^3 (\Delta N_{F_{i,1}} - \Delta N_{F_{i,-1}}) \right\} \quad (22)$$

Introducing the notation

$$\Delta N_{\xi} \equiv \sum_M \Delta N_{\xi M} \quad (23)$$

and assuming the existence of a common spin temperature for A , E_i , and F_i spin species,^{7,10} we obtain

$$\frac{d}{dt} \begin{pmatrix} \Delta M_x \\ \gamma \hbar \Delta N_A \\ \gamma \hbar \Delta N_{F_1} \\ \gamma \hbar \Delta N_{F_2} \\ \gamma \hbar \Delta N_{F_3} \end{pmatrix} = K \begin{pmatrix} \Delta M_x \\ \gamma \hbar \Delta N_A \\ \gamma \hbar \Delta N_{F_1} \\ \gamma \hbar \Delta N_{F_2} \\ \gamma \hbar \Delta N_{F_3} \end{pmatrix} \quad (24)$$

where K is a 5×5 matrix, the elements of which are given in Appendix C. If we introduce

$$\begin{pmatrix} \Delta M_x \\ \gamma \hbar \Delta N_A \\ \gamma \hbar \Delta N_{F_1} \\ \gamma \hbar \Delta N_{F_2} \\ \gamma \hbar \Delta N_{F_3} \end{pmatrix} \equiv \begin{pmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \\ x_5 \end{pmatrix} \quad ,$$

then the solution of Eq. (24) can be written in the form

$$x_i(t) = \sum_{j=1}^5 \alpha_{ij} e^{\lambda_j t} \quad (25)$$

where λ_j 's are the eigenvalues of the matrix K and the coefficients α_{ij} are determined by the equations

$$\sum_{j=1}^5 (K_{ij} - \lambda_l S_{ij}) \alpha_{jl} = 0 \quad ,$$

$$i, l = 1, 2, 3, 4, 5 \quad (26)$$

and the initial conditions

$$x_i(0) = \sum_{j=1}^5 \alpha_{ij} \quad .$$

From Eq. (25), it follows that the time evolution of the magnetization in the rotating frame is given, in general, as a sum of five decaying exponentials. The constants α_{ij} are given in terms of the matrix coefficients K_{ij} , and they also depend linearly on the initial values of ΔM_x , ΔN_A , and ΔN_{F_i} . The dependence of the α_{ij} 's on the initial values implies that the decay of the magnetization towards thermal equilibrium will depend, in general, on the preparation of the system; i.e., on the pulse sequence being used in the experiment.¹⁵

VI. RELAXATION IN THE ROTATING FRAME

The spin-lattice relaxation in the rotating frame, under the condition that the spin system is initially in thermal equilibrium with the lattice, is measured by applying a 90° pulse, which is immediately followed by a spin-locking rf-field pulse. The rf pulse is phase shifted by 90° with respect to the 90° pulse. If the duration of the 90° pulse is short compared to the shortest of the time constants $-1/\lambda_j$ ($j = 1, 2, 3, 4, 5$),

then the appropriate initial conditions for the system of differential equations (24) are

$$\begin{pmatrix} x_{1(0)} \\ x_{2(0)} \\ x_{3(0)} \\ x_{4(0)} \\ x_{5(0)} \end{pmatrix} = \begin{pmatrix} \Delta M_{x_0} \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \quad (27)$$

In the following we will consider some special cases of Eq. (24).

(a) All splittings vanish.

$$\omega_F^I, \omega_E^I, \Delta_{ij} = 0 \quad (i, j = 1, 2, 3), \quad (28)$$

here one obtains

$$K_{1j} = K_{j1} = 0, \quad j = 2, 3, 4, 5$$

and the decay of the magnetization is exponential

$$\Delta M_x(t) = \Delta M_{x_0} e^{-t/T_{1\rho}}, \quad (29)$$

and the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ is given by

$$\frac{1}{T_{1\rho}} = \frac{K_D^2}{\hbar^2} \frac{9}{10} \left(\frac{3}{2} \frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} + \frac{5}{2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right). \quad (30)$$

This result is the same as the one obtained by the semiclassical Bloembergen-Purcell-Pound (BPP) theory.¹⁶

(b) Large splittings in a crystal field of tetrahedral symmetry.

$$\omega_F^I, \omega_E^I \gg \omega_0, \quad \Delta_{ij} = 0 \quad (i, j = 1, 2, 3). \quad (31)$$

In this case again $K_{1j} = K_{j1} = 0$ ($j = 2, 3, 4, 5$). This can be seen from the results presented in Appendix C. In this case the magnetization in the rotating frame again decays with a single time constant; which is given by Eq. (30) multiplied by $\frac{5}{16}$. It was also assumed that $\omega_F^I \tau_c, \omega_E^I \tau_c \gg 1$. We see that the presence of large tunneling splittings (large compared to ω_0) slows down the relaxation by a factor of $\frac{5}{16}$. This reduction of the spin-lattice relaxation rate occurs because for large tunneling splitting only the transitions within the F manifold are effective in relaxing the spin system. Note that there are no transitions within the A manifold because $\langle AM' | H_D | AM \rangle \equiv 0$ (H_D is assumed to include only the intraionic dipole-dipole interaction). As already mentioned in Appendix B, the matrix elements of the intraionic dipolar interaction were calculated by assuming that the torsional oscillations of the NH_4 ion about its equilibrium orientations are of small amplitude, and could be neglected. This is a good approximation in the case of large hindering potential [case (a)], but is not so good when tunneling splittings are large. In this case one would expect additional reduction of the spin-lattice relaxation, due to large torsional oscillations of the NH_4 ion.^{10,17}

(c) Moderate splittings in a crystal field of tetrahedral symmetry.

$$\Delta_{ij} = 0; \quad \omega_F^I, \omega_E^I \gg \omega_1 \quad (i, j = 1, 2, 3) \quad (32)$$

(ω_F^I, ω_E^I are of the order of Zeeman splitting in the laboratory frame.) In this case the decay of the magnetization is again exponential. $T_{1\rho}$ is given by

$$\begin{aligned} \frac{1}{T_{1\rho}} = & \frac{K_D^2}{\hbar^2} \frac{9}{160} \left\{ 5 \left(\frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} + \frac{5}{2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) + \left(\frac{27}{2} \frac{\tau_c}{1 + (\omega_F^I)^2 \tau_c^2} + 3 \frac{\tau_c}{1 + (\omega_E^I)^2 \tau_c^2} \right) \right. \\ & + \left[\frac{9}{2} \left(\frac{\tau_c}{1 + (\omega_F^I - 2\omega_0)^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_F^I + 2\omega_0)^2 \tau_c^2} \right) + \frac{45}{4} \left(\frac{\tau_c}{1 + (\omega_F^I - \omega_0)^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_F^I + \omega_0)^2 \tau_c^2} \right) \right] \\ & \left. + \left[\left(\frac{\tau_c}{1 + (\omega_E^I - 2\omega_0)^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_E^I + 2\omega_0)^2 \tau_c^2} \right) + \frac{5}{2} \left(\frac{\tau_c}{1 + (\omega_E^I - \omega_0)^2 \tau_c^2} + \frac{\tau_c}{1 + (\omega_E^I + \omega_0)^2 \tau_c^2} \right) \right] \right\}. \quad (33) \end{aligned}$$

For the sake of simplicity we assumed in the above expression that the frequency ω_0 is such that none of the terms with $\omega_\xi^I - 2\omega_0, \omega_\xi^I - \omega_0, (\xi = F, E)$ is close to zero.

The fact that the magnetization in the rotating frame decays with a single time constant is an important advantage. According to the calculation in Ref. 10, the magnetization in the laboratory frame in gen-

eral decays with three time constants whenever ω_F^T and ω_E^T are of the order of ω_0 . In the rotating frame, however, if ω_F^T and ω_E^T are in the neighborhood of ω_0 (assuming of course $\omega_0 \gg \omega_1$) the magnetization M_x still decays with a single time constant. Consequently, it is easier to study the tunneling splittings which are of the order of ω_0 , by measuring the H_0 dependence of $T_{1\rho}$ rather than by measuring the H_0 dependence of the spin-lattice relaxation in the laboratory frame.

(d) Small splittings in the tetrahedral crystal field. In such field it holds that

$$\Delta_{ij} = 0 \quad (i, j = 1, 2, 3) . \quad (34)$$

It is also considered that ω_F^T, ω_E^T are of the order of ω_1 . From the results given in Appendix C, one obtains by imposing the conditions (34) that the 5×5 matrix K which appears in Eq. (24) reduces to a block diagonal form which consists of one 3×3 matrix and two 1×1 matrices. The evolution of the magnetization $M_x(t)$ is given by the following set of equations:

$$\frac{d}{dt} \begin{pmatrix} \Delta M_x \\ \gamma \hbar \Delta N_A \\ \gamma \hbar \Delta N_F \end{pmatrix} = \begin{pmatrix} K_{11} & K_{12} & K_{13} \\ K_{21} & K_{22} & K_{23} \\ 3K_{31} & 3K_{32} & -\frac{5}{3}K_{32} \end{pmatrix} \begin{pmatrix} \Delta M_x \\ \gamma \hbar \Delta N_A \\ \gamma \hbar \Delta N_F \end{pmatrix} , \quad (35)$$

where we have defined

$$\Delta N_F \equiv \Delta N_{F_1} + \Delta N_{F_2} + \Delta N_{F_3} ,$$

and the matrix coefficients K_{ij} appearing in Eq. (35) are obtained by using the results given in Appendix C and making use of the conditions (34). We were not able to obtain an analytical solution for this case. We did however obtain some approximate expressions for the time evolution of the magnetization for the two limiting situations: (i) $\omega_E^T \approx \omega_F^T \approx \omega_1$ and (ii) $\omega_E^T \gg \omega_F^T, \omega_1 \leq \omega_F^T$. In both cases the magnetization decays with two time constants. Since qualitatively very similar behavior results in some other examples where the analytical solutions exist, we will not discuss the present case in any more details.

(e) Large A -to- E and A -to- F splitting but small F splitting. Here we consider the crystal field where

$$\omega_E^T, \omega_F^T \gg \omega_0, \quad (i = 1, 2, 3) , \quad (36)$$

but the splitting of the F states is of the order of ω_1 ,

$$\Delta_{ij} \approx \omega_1 \quad (i, j = 1, 2, 3) . \quad (37)$$

We also assume ($\omega_E^T \tau_c \gg 1, \xi = E, F_i$). We will consider three special cases of F splitting.

(i) *upper-level doubly degenerate:*

$$\Delta_{12} = \Delta_{13} = \Delta, \quad \Delta_{23} = 0 ; \quad (38a)$$

(ii) *triplet with equal spacings:*

$$\Delta_{12} = \Delta_{23} = \Delta, \quad \Delta_{13} = 2\Delta ; \quad (38b)$$

(iii) *triplet with unequal spacings:*

$$\Delta_{23} = \Delta, \quad \Delta_{12} = \Delta_{13} = \Delta' \gg \omega_1, \quad \Delta' \gg \Delta . \quad (38c)$$

The time evolution of the magnetization in the rotating frame is coupled only to the time evolution of the ΔN_{F_i} ($i = 1, 2, 3$), which is a consequence of the assumption $\omega_{F_i}^T \gg \omega_0$ ($i = 1, 2, 3$). By solving the matrix equation (24) we obtain for all cases (i)–(iii) the following result:

$$\Delta M_x(t) = \frac{1}{2} \Delta M_{x_0} [(1+A)e^{\lambda^{(+)}t} + (1-A)e^{\lambda^{(-)}t}] . \quad (39)$$

The constants $A, \lambda^{(+)}$, and $\lambda^{(-)}$ for the three situations considered, respectively, are given by

$$\lambda^{(\pm)} = \frac{1}{2} [(K_{11} - 3K_{34}) \pm [(K_{11} + 3K_{34})^2 + \frac{9}{8}K_{13}^2]^{1/2}] , \quad (40a)$$

$$A = \frac{K_{11} + 3K_{34}}{[(K_{11} + 3K_{34})^2 + \frac{9}{8}K_{13}^2]^{1/2}} ;$$

$$\lambda^{(\pm)} = \frac{1}{2} [-(K_{34} + 2K_{35} - K_{11}) \pm [(K_{11} + K_{34} + 2K_{35})^2 + \frac{3}{2}K_{13}^2]^{1/2}] , \quad (40b)$$

$$A = \frac{K_{11} + K_{34} + 2K_{35}}{[(K_{11} + K_{34} + 2K_{35})^2 + \frac{3}{2}K_{13}^2]^{1/2}} ;$$

$$\lambda^{(\pm)} = \frac{1}{2} [(K_{11} - K_{34} - 2K_{45}) \pm [(K_{11} + K_{34} + 2K_{45})^2 + \frac{3}{2}K_{14}^2]^{1/2}] ; \quad (40c)$$

$$A = \frac{K_{11} + K_{34} + 2K_{45}}{[(K_{11} + K_{34} + 2K_{45})^2 + \frac{3}{2}K_{14}^2]^{1/2}} .$$

The matrix elements K_{ij} are given in Appendix C but also satisfy the conditions (36)–(38c).

Since the value of the magnetization in the rotating frame in thermal equilibrium with the lattice is small

compared with the thermal-equilibrium value in the laboratory frame, we may replace ΔM_x and ΔM_{x_0} by M_x and M_{x_0} in all the formulas given above. Whenever the splitting between A and F states is large compared to the K_D/\hbar ($\omega_{F_i}^T \gg K_D/\hbar$), M_{x_0} is given by

$$M_{x_0} = M_0 \left(\frac{5}{8} \frac{\omega_1^2}{\omega_1^2 + \omega_{LA}^2} + \frac{3}{8} \frac{\omega_1^2}{\omega_1^2 + \omega_{LF}^2} \right), \quad (41)$$

M_0 is the thermal equilibrium value of the magnetization in the laboratory frame and ω_{LA} , ω_{LF} are the local fields in the rotating frame for the A and F species, respectively. If $\omega_{F_i}^T \approx K_D/\hbar$, the appropriate expression for M_{x_0} becomes

$$M_{x_0} = M_0 [\omega_1^2 / (\omega_1^2 + \omega_L^2)] \quad (42)$$

with ω_L representing the local field in the rotating frame of all species.

VII. DISCUSSION

In general, the presence of the tunneling splitting of the torsional ground state of the NH_4 ion causes the magnetization in the rotating frame to decay with several different time constants. Specifically, Eq. (24) shows that under the assumption of the common Zeeman spin temperature the magnetization will have, in general, decay with five time constants. Furthermore, Eqs. (25) and (26) also show that the evolution of the spin system towards the thermal equilibrium will depend on the preparation of the system, i.e., on the particular pulse sequence applied.

The details of the time evolution of the magnetization depend on the relative magnitudes of the tunneling splittings as compared with the magnitude of the Larmor frequencies: $\omega_0 \equiv \gamma H_1$ and $\omega_1 \equiv \gamma H_1$, where $\omega_0 \gg \omega_1$. In the limit of vanishing tunneling splittings, Eq. (29) tells us that the magnetization in the rotating frame decays with a single time constant, which is identical to the semiclassical expression obtained previously.¹⁶ Similar situation results also in the case when the tunneling splittings are large compared to ω_0 , except that the strength of the relaxation is reduced by a constant factor with respect to the result obtained in the case of zero splittings. Moreover, from Eq. (33) and the above discussion, it follows that the decay of the magnetization in the rotating frame is exponential provided that the tunneling splittings are either large or small compared with ω_1 .

If we were to study the temperature dependence of the spin-lattice relaxation in the rotating frame, Eq. (33) also shows that several minima would occur in the temperature dependence of $T_{1\rho}$, in addition to the

classical minimum which is given by the condition that $\omega_1 \tau_c \approx 1$. However, one should keep in mind that the applicability of expression (33) is restricted to the temperature range consistent with the assumption that most of the NH_4 ions are in the ground torsional state. Identical conclusions hold true also for the remaining examples discussed in Sec. VI. Because a rather crude approximation of a single exponential correlation function was employed in our calculation, a study of the temperature dependence of the magnetization was not attempted. On the other hand, for the analysis of the frequency dependence and the time evolution of the nuclear magnetization, the assumption of a single exponential correlation function is quite reasonable.

The remainder of this discussion is restricted to the case of large A -to- F and large A -to- E splittings, and small intra- F splittings, as presented in case (e) of Sec. VI. The characteristic feature of this type of splitting is that the magnetization decays with two time constants as shown in Eq. (39).

In Fig. 2 the H_1 dependence of the magnetization $M_x(H_1, t)$ as given by Eq. (39) is shown. The corresponding crystal-field splitting is given in (38a). The upper graph in Fig. 2 corresponds to a 100- μsec rf pulse and the lower graph corresponds to a 4-msec rf pulse. The splitting Δ of F states was chosen to be 24 G. In order to take into account the finite linewidth of the transitions under consideration, the $j(\tau_c, \omega)$, which are given in Appendix C, were replaced by $\bar{j}(\tau_c, \omega)$ defined by Eq. (C5). The distribution function $\rho(\delta)$ was assumed to have a Lorentzian shape,

$$\rho(\delta) = (1/2\pi) \sigma / (\delta^2 + \sigma^2),$$

where σ , the broadening parameter, was chosen to be 2 G. The correlation time τ_c appearing in the expressions for $j(\tau_c, \omega)$ is equal to the torsional relaxation time T_{1T} , determined from the experimental data for NH_4I at 20 °K.¹⁻³ From the expressions for $j(\tau_c, \omega)$ it follows that the resonance condition is fulfilled when $\Delta = 2H_1$. This is manifested by a drastic loss of magnetization as seen on the upper graph of Fig. 2. Since Δ was chosen to be 24 G, the maximum loss occurs for $H_1 \approx 12$ G. The lower graph in Fig. 2 which corresponds to $t = 4$ msec, does not show such a pronounced resonance effect because for longer times also those levels, for which the resonance condition is not exactly fulfilled, become important for the relaxation. This broadens the resonances. It was also established that the characteristic features of the graphs in Fig. 2 do not change significantly when the temperature is varied between 10 and 67 K.^{2,12,13} The results for the crystal-field splitting corresponding to example (38c) are almost identical to the results for (38a) and need not be discussed. On the other hand, Fig. 3 shows the H_1

dependence of $M_x(H_1, t)$ corresponding to example (38b). The parameters characterizing these graphs were taken to be the same as those in Fig. 2. Here again a significant loss of magnetization occurs at two values of H_1 . The two values of H_1 are Δ and $\frac{1}{2}\Delta$, respectively, where $\Delta = 24$ G. It should be noted, that the results presented in Figs. 2 and 3 are valid only for values of H_1 large compared to the local field in the rotating frame.

The magnetization losses due to the resonant matching of Zeeman and torsional levels were observed experimentally in NH_4I in the temperature range between 4 and 67 K.¹⁻³ The relative loss of the magnetization for the upper graph in Fig. 2, at $H_1 \approx 12$ G is approximately 29%, while the example presented in Fig. 3, gives for $H_1 \approx 12$ G, the relative loss of 57%. The measured loss of magnetization in NH_4I at 10 °K and $H_1 \approx 12$ G is $(32 \pm 4)\%$.³ The maximum losses of the magnetization as given by our calculation are somewhat larger than the corresponding spin-temperature estimates.¹¹ This results from the assumption that the temperature of the torsional system is equal to the lattice temperature at all times. Similar results were obtained also for $\text{CH}_3\text{CD}_2\text{I}$.^{12, 13}

From the above results it can be concluded that the values of H_1 , where the maximum losses of the magnetization occur, are related to the tunneling splittings of the torsional ground state of the system

through the relation of $2\gamma H_1 = \omega^T$, where ω^T is the tunneling splitting. This is true for rf pulses which are a few T_2 long. On the other hand, the determination of the type of the crystal-field splitting from the magnetization losses alone is not unique. This result should be compared to the data from neutron scattering, and NMR line-shape experiments. The magnetization evolution spectra are significantly better resolved.^{12, 13}

In Figs. 4 and 5 the time dependence of $M_x(H_1, t)$ was plotted on a semilog scale for a fixed value of $H_1 = 16$ G. Since all three examples [(38a)–(38c)] show the same behavior only case (38b) is presented. The values of the parameters appearing in expression (39) are the same as those on the H_1 graphs. The two graphs in Figs. 4 and 5 differ only in time scales, which were chosen to be 100 and 10 msec, respectively. The characteristic feature of both graphs is the rapid drop of the magnetization at the origin and the subsequent exponential decay of the magnetization. This is typical of the situation where the time evolution of the magnetization is governed by two time constants. If the slope corresponding to the longer time constants is extrapolated back to the origin, the semilog axis is intercepted at a given point. The ratio of the lengths of the divided sections is given by $(1 - A)/(1 + A)$, where A is defined by Eq. (40b). This was observed in NH_4I in the temperature range between 4 and 60 K.¹¹

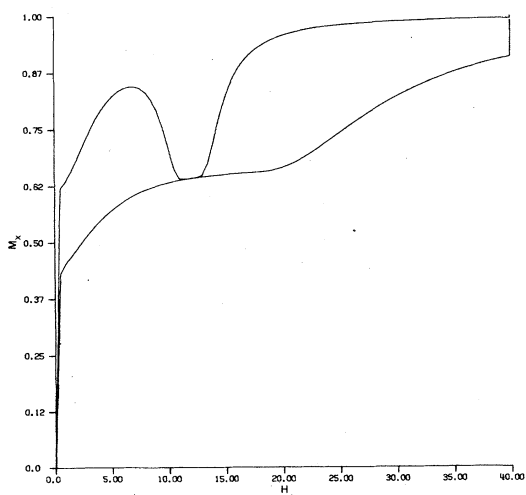


FIG. 2. H_1 dependence of the magnetization M_x in the rotating frame. The crystal field is such that $\omega_E^T, \omega_F^T \gg \omega_0$ ($i = 1, 2, 3$) and $\Delta_{12} = \Delta_{13} = \Delta = 24$ G, $\Delta_{23} = 0$. Temperature is $T = 20$ K, the broadening parameter $\sigma = 2$ G, and time $t = 100$ μsec for the upper graph and $t = 4$ msec for the lower graph.

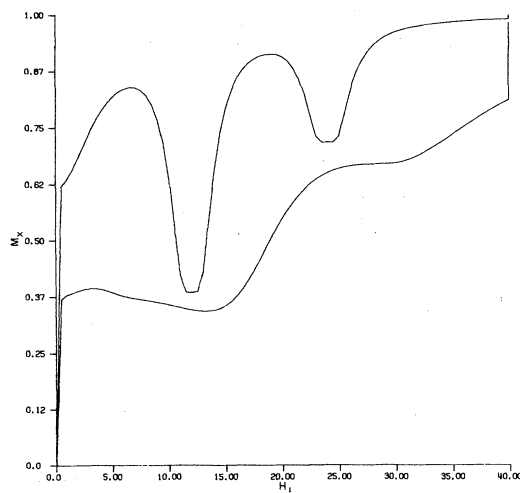


FIG. 3. H_1 dependence of the magnetization M_x in the rotating frame. The crystal field is such that $\omega_E^T, \omega_F^T \gg \omega_0$ ($i = 1, 2, 3$) and $\Delta_{13} = 2\Delta$, $\Delta_{12} = \Delta_{23} = \Delta = 24$ G. Temperature is $T = 20$ K, the broadening parameter $\sigma = 2$ G, and time $t = 100$ μsec for the upper graph and $t = 4$ msec for the lower graph.

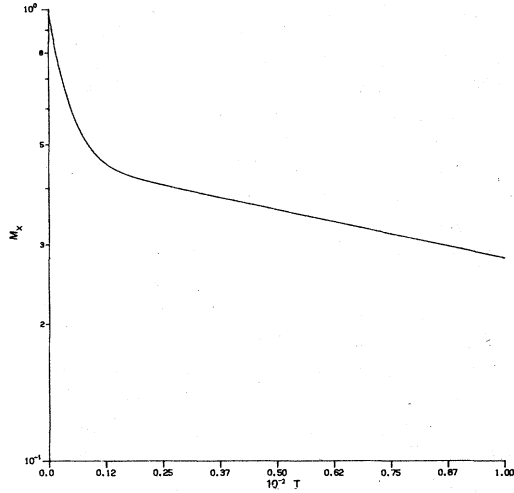


FIG. 4. Time dependence of the magnetization M_x in the rotating frame. The crystal field is such that $\omega_E^T, \omega_{F_i}^T \gg \omega_0$ ($i=1, 2, 3$) and $\Delta_{13}=2\Delta$, $\Delta_{12}=\Delta_{23}=\Delta=24$ G. Temperature is $T=20$ K, the broadening parameter $\sigma=2$ G, and $H_1=16$ G. Time varies from 0 to 10 msec.

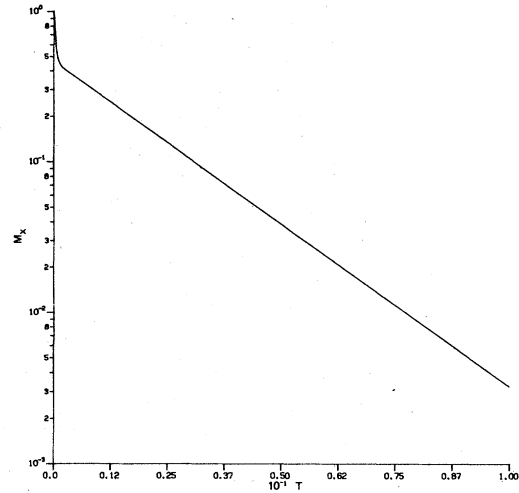


FIG. 5. Time dependence of the magnetization M_x in the rotating frame. The crystal field is such that $\omega_E^T, \omega_{F_i}^T \gg \omega_0$ ($i=1, 2, 3$) and $\Delta_{13}=2\Delta$, $\Delta_{12}=\Delta_{23}=\Delta=24$ G. Temperature is $T=20$ K, the broadening parameter $\sigma=2$ G, and $H_1=16$ G. Time varies from 0 to 100 msec.

ACKNOWLEDGMENTS

Very helpful assistance of Dr. R. S. Hallsworth with the computer programs for Figs. 2-5 is acknowledged. This research was supported by the National Research Council, Ottawa.

APPENDIX A

The matrix $C_{k,k'}$ is given by

$$k/k' \begin{pmatrix} 2 & 1 & 0 & -1 & -2 \\ 2 & \begin{pmatrix} -\frac{1}{4} & -\frac{1}{2}i & (\frac{3}{8})^{1/2} & \frac{1}{2}i & -\frac{1}{4} \end{pmatrix} \\ 1 & \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}i & 0 & -\frac{1}{2}i & \frac{1}{2} \end{pmatrix} \\ 0 & \begin{pmatrix} -(\frac{3}{8})^{1/2} & 0 & -\frac{1}{2} & 0 & -(\frac{3}{8})^{1/2} \end{pmatrix} \\ -1 & \begin{pmatrix} -\frac{1}{2} & \frac{1}{2}i & 0 & \frac{1}{2}i & \frac{1}{2} \end{pmatrix} \\ -2 & \begin{pmatrix} -\frac{1}{4} & \frac{1}{2}i & (\frac{3}{8})^{1/2} & -\frac{1}{2}i & -\frac{1}{4} \end{pmatrix} \end{pmatrix}$$

APPENDIX B

For powder samples Eq. (19) yields the following results for the transition probabilities per unit time:

$$W_{AM' \rightarrow F_i M}$$

$$= \frac{K_B^2}{\hbar^2} B_{M',M} \sum_{k=-2}^2 \frac{9}{20} |C_{k,M'-M}|^2 D_k^{(M'-M)}(\omega_{F_i}^T) \quad (i=1, 2, 3) \quad (B1)$$

$$W_{AM' \rightarrow E_i 0} = \frac{K_B^2}{\hbar^2} \sum_k \frac{9}{40} |C_{k,M'}|^2 D_k^{(M')}(\omega_E^T) \quad (i=a, b) \quad (B2)$$

$$W_{F_i M' \rightarrow F_j M}$$

$$= \frac{K_B^2}{\hbar^2} \frac{|M'-M|}{18} \sum_k \frac{27}{10} |C_{k,M'-M}|^2 D_k^{(M'-M)}(0) \quad (i=1, 2, 3) \quad (B3)$$

$$W_{F_i M \rightarrow F_j M} = \frac{K_B^2}{\hbar^2} \frac{1}{3(1+M^2)^2} \sum_k \frac{9}{20} |C_{k,0}|^2 D_k^{(0)}(\Delta_{ij}) \quad (i \neq j, i, j=1, 2, 3) \quad (B4)$$

$$W_{F_i M' \rightarrow F_j M}$$

$$= \frac{K_B^2}{\hbar^2} \frac{|M'-M|}{4} \sum_k \frac{9}{20} |C_{k,M'-M}|^2 D_k^{(M'-M)}(\Delta_{ij}) \quad (i \neq j, i, j=1, 2, 3) \quad (B5)$$

Here the matrix $C_{k,k'}$ is given in Appendix A, while the matrix $B_{M',M}$ is as follows:

$$B_{M',M} = \begin{matrix} M'/M & 1 & 0 & -1 \\ 2 & \left(\begin{array}{ccc} \frac{1}{2} & 1 & 0 \\ \frac{3}{4} & \frac{1}{4} & \frac{1}{2} \\ \frac{3}{4} & 0 & \frac{3}{4} \\ \frac{1}{2} & \frac{1}{4} & \frac{3}{4} \\ 0 & 1 & \frac{1}{2} \end{array} \right) \\ 1 & \\ 0 & \\ -1 & \\ -2 & \end{matrix}$$

We have also defined

$$D_k^{(M'-M)}(\omega^T) \equiv \frac{2\tau_c}{1 + [\omega^T + (M' - M)\omega_1 + k\omega_0]^2 \tau_c^2} \quad (\text{B6})$$

In calculating the above results we made the following approximations; the states $|\xi_0 M\rangle$ have the form of a product $\psi_T \xi_0 \phi_{\sigma, \xi M}$, where the torsional part of the wave function is given by¹⁸

$$\psi_{T, \xi_0} = \sum_R C_{\xi_0}(R) \psi(R)$$

The sum in the above expression runs over the 12 symmetry operations of the point group T , and

$$\psi(R) = O_R \psi(E)$$

where $\psi(E)$ stands for the normalized torsional ground state belonging to a certain orientation of the NH_4 ion, and O_R is the operator representing the effect of the symmetry operation R on $\psi(E)$. In calculating the matrix elements $\langle \xi_0 M' | H_B^k | \xi_0 M \rangle$ we make the approximation

$$\langle \psi(R') | U_{ij}^{-k} | \psi(R) \rangle \cong \delta_{R,R'} \langle \psi(R) | U_{ij}^{-k} | \psi(R) \rangle,$$

and we also assume that the angular variables appearing in $\psi(R)$, enter only as arguments of the δ functions corresponding to a given orientation of the NH_4 ion relative to the crystal lattice. The states $\psi_{T, \xi_0} \phi_{\sigma, \xi M}$ used in this calculation are given in Ref. 18, except the spin states, formally the same as those in Ref. 18, are chosen to be the eigenstates of \bar{I}^2 and I_x .

APPENDIX C

In order to write the matrix coefficients K_{ij} in a compact form, we first define

$$j(\tau_c, \omega) \equiv 2\tau_c / (1 + \omega^2 \tau_c^2), \quad (\text{C1})$$

$$j(\tau_c, \omega \pm \omega')_{(+)} \equiv j(\tau_c, \omega - \omega') + j(\tau_c, \omega + \omega'), \quad (\text{C2})$$

$$j(\tau_c, \omega \pm \omega')_{(-)} \equiv j(\tau_c, \omega - \omega') - j(\tau_c, \omega + \omega'). \quad (\text{C3})$$

Using the above definitions we can write the elements K_{ij} for a powder sample, as follows:

$$K_{11} = -\frac{K_B^2}{\hbar^2} \frac{9}{160} \left[\sum_{i=1}^3 \left[\frac{3}{4} j(\tau_c, \omega_{F_i}^T \pm 2\omega_0)_{(+)} + \frac{15}{8} j(\tau_c, \omega_{F_i}^T \pm \omega_0)_{(+)} + \frac{9}{8} j(\tau_c, \omega_{F_i}^T \pm 2\omega_1)_{(+)} \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \omega_E^T \pm 2\omega_0)_{(+)} + \frac{5}{4} j(\tau_c, \omega_E^T \pm \omega_0)_{(+)} + \frac{3}{4} j(\tau_c, \omega_E^T \pm 2\omega_1)_{(+)} \right] \right. \\ \left. + [j(\tau_c, 2\omega_0) + \frac{5}{2} j(\tau_c, \omega_0) + \frac{3}{2} j(\tau_c, 2\omega_1)] \right. \\ \left. + \frac{1}{4} [j(\tau_c, \Delta_{12} \pm 2\omega_0)_{(+)} + j(\tau_c, \Delta_{13} \pm 2\omega_0)_{(+)} + j(\tau_c, \Delta_{23} \pm 2\omega_0)_{(+)}] \right. \\ \left. + \frac{5}{8} [j(\tau_c, \Delta_{12} \pm \omega_0)_{(+)} + j(\tau_c, \Delta_{13} \pm \omega_0)_{(+)} + j(\tau_c, \Delta_{23} \pm \omega_0)_{(+)}] \right. \\ \left. + \frac{3}{8} [j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(+)} + j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(+)} + j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(+)}] \right],$$

$$K_{12} = \frac{K_B^2}{\hbar^2} \frac{9}{100} \left[\sum_{i=1}^3 \frac{9}{8} j(\tau_c, \omega_{F_i}^T \pm 2\omega_1)_{(-)} + \frac{21}{8} j(\tau_c, \omega_E^T \pm 2\omega_1)_{(-)} \right],$$

$$K_{13} = (K_B^2 / \hbar^2) \frac{9}{160} [j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(-)} + j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(-)} - 3j(\tau_c, \omega_{F_1}^T \pm 2\omega_1)_{(-)} + 3j(\tau_c, \omega_E^T \pm 2\omega_1)_{(-)}],$$

$$K_{14} = (K_B^2 / \hbar^2) \frac{9}{160} [-3j(\tau_c, \omega_{F_2}^T \pm 2\omega_1)_{(-)} + 3j(\tau_c, \omega_E^T \pm 2\omega_1)_{(-)} - j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(-)} + j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(-)}],$$

$$K_{15} = (K_B^2/\hbar^2) \frac{9}{160} [-3j(\tau_c, \omega_{F_3}^T \pm 2\omega_1)_{(-)} + 3j(\tau_c, \omega_E^T \pm 2\omega_1)_{(-)} - j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(-)} - j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(-)}] ,$$

$$K_{21} = \frac{K_B^2}{\hbar^2} \frac{27}{320} \left[\frac{3}{8} \sum_{i=1}^3 j(\tau_c, \omega_{F_i}^T \pm 2\omega_1)_{(-)} + \frac{1}{8} j(\tau_c, \omega_E^T \pm 2\omega_1)_{(-)} \right] ,$$

$$K_{22} = -\frac{K_B^2}{\hbar^2} \frac{9}{100} \left[\sum_l \left[\frac{3}{2} j(\tau_c, \omega_{F_l}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_l}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_l}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_l}^T) \right] \right. \\ \left. + \left[\frac{7}{2} j(\tau_c, \omega_E^T \pm 2\omega_0)_{(+)} + \frac{7}{2} j(\tau_c, \omega_E^T \pm \omega_0)_{(+)} + \frac{21}{16} j(\tau_c, \omega_E^T \pm 2\omega_1)_{(+)} + \frac{7}{8} j(\tau_c, \omega_E^T) \right] \right] ,$$

$$K_{23} = (K_B^2/\hbar^2) \frac{9}{60} \left\{ \left[\frac{3}{2} j(\tau_c, \omega_{F_1}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_1}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_1}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_1}^T) \right] \right. \\ \left. - \left[\frac{3}{2} j(\tau_c, \omega_E^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_E^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_E^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_E^T) \right] \right\} \equiv K_{23}(\omega_{F_1}^T) ,$$

$$K_{24} = K_{23}(\omega_{F_2}^T) ,$$

$$K_{25} = K_{23}(\omega_{F_3}^T) ,$$

$$K_{31} = (K_B^2/\hbar^2) \frac{27}{160} \left[\frac{1}{16} j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(-)} + \frac{1}{16} j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(-)} - \frac{3}{16} j(\tau_c, \omega_{F_1}^T \pm 2\omega_1)_{(-)} \right] ,$$

$$K_{32} = (K_B^2/\hbar^2) \frac{9}{100} \left[\frac{3}{2} j(\tau_c, \omega_{F_1}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_1}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_1}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_1}^T) \right] ,$$

$$K_{33} = -(K_B^2/\hbar^2) \frac{3}{20} \left\{ \left[\frac{3}{2} j(\tau_c, \omega_{F_1}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_1}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_1}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_1}^T) \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \Delta_{12} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{12} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{12}) \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \Delta_{13} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{13} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{13}) \right] \right\} ,$$

$$K_{34} = (K_B^2/\hbar^2) \frac{3}{20} \left[\frac{1}{2} j(\tau_c, \Delta_{12} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{12} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{12}) \right] ,$$

$$K_{35} = (K_B^2/\hbar^2) \frac{3}{20} \left[\frac{1}{2} j(\tau_c, \Delta_{13} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{13} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{13}) \right] ,$$

$$K_{41} = (K_B^2/\hbar^2) \frac{27}{160} \left[-\frac{3}{16} j(\tau_c, \omega_{F_2}^T \pm 2\omega_1)_{(-)} - \frac{1}{16} j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(-)} + \frac{1}{16} j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(-)} \right] ,$$

$$K_{42} = (K_B^2/\hbar^2) \frac{9}{100} \left[\frac{3}{2} j(\tau_c, \omega_{F_2}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_2}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_3}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_2}^T) \right] ,$$

$$K_{43} = K_{34} ,$$

$$K_{44} = -(K_B^2/\hbar^2) \frac{3}{20} \left\{ \left[\frac{3}{2} j(\tau_c, \omega_{F_2}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_2}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_2}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_2}^T) \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \Delta_{12} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{12} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{12} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{12}) \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \Delta_{23} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{23} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{23}) \right] \right\} ,$$

$$K_{45} = (K_B^2/\hbar^2) \frac{3}{20} \left[\frac{1}{2} j(\tau_c, \Delta_{23} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{23} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{23}) \right] ,$$

$$K_{51} = (K_B^2/\hbar^2) \frac{27}{160} \left[-\frac{3}{16} j(\tau_c, \omega_{F_3}^T \pm 2\omega_1)_{(-)} - \frac{1}{16} j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(-)} - \frac{1}{16} j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(-)} \right] ,$$

$$K_{52} = (K_B^2/\hbar^2) \frac{9}{100} \left[\frac{3}{2} j(\tau_c, \omega_{F_3}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_3}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_3}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_3}^T) \right] ,$$

$$K_{53} = K_{35} ,$$

$$K_{54} = K_{45} ,$$

$$K_{55} = -(K_B^2/\hbar^2) \frac{3}{20} \left\{ \left[\frac{3}{2} j(\tau_c, \omega_{F_3}^T \pm 2\omega_0)_{(+)} + \frac{3}{2} j(\tau_c, \omega_{F_3}^T \pm \omega_0)_{(+)} + \frac{9}{16} j(\tau_c, \omega_{F_3}^T \pm 2\omega_1)_{(+)} + \frac{3}{8} j(\tau_c, \omega_{F_3}^T) \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \Delta_{13} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{13} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{13} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{13}) \right] \right. \\ \left. + \left[\frac{1}{2} j(\tau_c, \Delta_{23} \pm 2\omega_0)_{(+)} + \frac{1}{2} j(\tau_c, \Delta_{23} \pm \omega_0)_{(+)} + \frac{3}{16} j(\tau_c, \Delta_{23} \pm 2\omega_1)_{(+)} + \frac{1}{8} j(\tau_c, \Delta_{23}) \right] \right\} .$$

The tunneling frequencies that appear in the above expressions for K_{ij} represent the average values of the tunneling splitting in the sense that each transition has a certain linewidth characterized by a distribution function $\rho(\delta)$, normalized to unity, i.e.,

$$\int_{-\infty}^{\infty} \rho(\delta) d\delta = 1 .$$

So in order to incorporate the effect of the finite

linewidth of the distribution function $\rho(\delta)$, one should use instead of $j(\tau_c, \omega)$ a new quantity $\bar{j}(\tau_c, \omega)$ defined by

$$\bar{j}(\tau_c, \omega) \equiv \int_{-\infty}^{\infty} \rho(\delta) j(\tau_c, \omega + \delta) d\delta , \quad (C4)$$

which is

$$\bar{j}(\tau_c, \omega) = 2 \int_{-\infty}^{\infty} d\delta \rho(\delta) \frac{1/\tau_c}{(1/\tau_c)^2 + (\omega + \delta)^2} . \quad (C5)$$

¹R. S. Hallsworth and M. M. Pintar, in *British Radiofrequency Spectroscopy Meeting*, Bristol, 1975 (unpublished); D. W. Nicoll *et al.*, 19th Ampere Conference, Heidelberg, 1976, edited by H. Brunner *et al.*, (unpublished), p. 570; and R. S. Hallsworth *et al.*, *Bull. Am. Phys. Soc.* **22**, 550 (1977).

²R. S. Hallsworth, Ph.D. Thesis (University of Waterloo, 1977) (unpublished).

³R. S. Hallsworth, D. W. Nicoll, J. Peternelj, and M. M. Pintar, *Phys. Rev. Lett.* **39**, 1493 (1977).

⁴The effect of torsional symmetry on NMR was studied first by K. Tomita [*Phys. Rev. B* **89**, (1953)].

⁵Earlier papers are listed in A. Watton, H. Petch, A. Sharp, and M. M. Pintar, *Phys. Rev. B* **5**, 4281 (1972).

⁶Latest literature can be found in *NMR Introductory Essays*, edited by M. M. Pintar (Springer-Verlag, Berlin, 1976).

⁷M. Punkkinen and S. Clough, *J. Phys. C* **7**, 3403 (1974).

⁸S. Emid, R. A. Wind, and S. Clough, *Phys. Rev. Lett.* **33**, 769 (1974).

⁹S. Clough and J. R. Hill, *Phys. Lett.* **49A**, 461 (1974).

¹⁰M. Punkkinen, *J. Magn. Res.* **19**, 222 (1975).

¹¹R. S. Hallsworth, D. W. Nicoll, and M. M. Pintar (unpublished).

¹²D. W. Nicoll, Ph.D. thesis (University of Waterloo, 1978) (unpublished).

¹³D. W. Nicoll and M. M. Pintar, *Phys. Rev. Lett.* **41**, 496 (1978).

¹⁴S. Emid, *Physica* **70**, 616 (1973); *Phys. Rev. Lett.* **33**, 1422 (1974).

¹⁵M. Punkkinen, L. P. Ingman, D. G. Taylor, and P. S. Allen, *J. Phys. C* **8**, 2159 (1975), R. A. Wind, S. Emid, J. F. J. M. Pourquie, and J. Smidt, *ibid.* **9**, 139 (1976).

¹⁶G. P. Jones, *Phys. Rev.* **148**, 332 (1966).

¹⁷G. A. DeWitt and M. Bloom, *Can. J. Phys.* **47**, 1195 (1969).

¹⁸A. Watton and H. E. Petch, *Phys. Rev. B* **7**, 12 (1973).

¹⁹D. W. Nicoll, R. S. Hallsworth, J. Peternelj and M. M. Pintar, *J. Magn. Reson.* (to be published).