

Zero-Field Nuclear Quadrupole Spin-Lattice Relaxation in the Rotating Frame*

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Nuclear quadrupole spin-lattice relaxation rates in different frames of reference for pure electric quadrupole coupling are evaluated in terms of spectral density functions of lattice vibrations. The rate is determined in each of three important reference frames defined with respect to (1) the axial crystalline field in the laboratory, (2) a strong rotating radiofrequency field, and (3) internal dipolar fields following adiabatic demagnetization in the rotating frame. For spin states established by pure quadrupole coupling, modification of the relaxation behavior in the different frames does not conform to the behavior obtained from spins bound in pure magnetic Zeeman states. The density-matrix perturbation formalism is applied. In order to transform the total Hamiltonian into the interaction representation of the main quadrupole interaction, a convenient representation is devised for quadratic exponential unitary operators which do not directly carry out simple rotations. The transformation permits an approach to the rigorous analysis of dynamic nuclear quadrupole resonance phenomena which usually have been qualitatively described by comparison with analogous phenomena in pure magnetic resonance. The new representation is presented explicitly for spin $I = \frac{3}{2}$. Experimental measurements of Cl^{35} pure quadrupole spin-lattice relaxation times in chlorate salts in the three reference frames are compared with the theoretically determined relaxation rates.

INTRODUCTION

THE concept of spin temperature^{1,2} is especially helpful in experiments where spin-lattice relaxation times in solids are to be analyzed. If the spin levels by themselves happen to remain populated in ratios determined by the Boltzmann factor during the relaxation process, a spin temperature can be defined. If the perturbing lattice alone should cause the spin populations to deviate from their Boltzmann ratios, a larger perturbing nuclear dipole-dipole interaction can provide the mechanism for maintaining internal-spin thermal equilibrium, signified by a spin temperature, while the spin-lattice relaxation takes place. The spin-temperature concept applies not only in the laboratory frame of reference, but also in other frames of reference where the interacting nuclear spins are defined as magnetic energy reservoirs (a) with respect to strong rotating radiofrequency (rf) magnetic fields,³ or (b) with respect to internal dipolar magnetic fields.⁴ The lattice degrees of freedom constitute a separate energy reservoir at a constant lattice temperature, and the lattice heat capacity is taken to be exceedingly larger compared with that of the nuclear-spin energy reservoir. Coupling of spins to lattice therefore causes the spin temperature to approach the lattice temperature in a characteristic spin-lattice relaxation time T_1 , if the two temperatures are initially different upon coupling the two systems together.

Spin-lattice relaxation times in most experiments are measured in the laboratory frame of reference. The type and number of matrix elements which describe the perturbing interactions can depend very much upon the representation or measuring axis chosen for the Hamiltonians of the interacting reservoirs. If experimental means are available for preparing the spin system so that it is in thermal equilibrium in frames of reference different from the laboratory frame, it is possible for T_1 to acquire a value which is different from its value in the laboratory frame, and is unique for the reference frame chosen. The altered relaxation times in some cases are related to the laboratory spin-lattice relaxation time by a functional relationship^{5,2} which is independent of the particular spin sample being studied. This is shown not to be the case in this investigation, particularly for pure nuclear quadrupole coupled spins, although the lack of such a relationship is not excluded for magnetically coupled spins. Measurements of relaxation times in the rotating frame would be particularly valuable in determining components of spin relaxation which direct laboratory-frame measurements do not yield. Although it would appear that in nuclear magnetic resonance (NMR), the pure magnetic relaxation of systems with spin $I = \frac{1}{2}$ in dc magnetic fields are fundamental cases for studying transformed spin-lattice relaxation, we confine our attention here to cases where electric nuclear quadrupole relaxation in pure nuclear quadrupole resonance (NQR) is dominant in solids. Therefore, the influence of paramagnetic impurities is avoided, which is too often a controlling factor for pure magnetic relaxation in solids. Lowe and Look⁶ have

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¹ A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961).

² L. C. Hebel, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 15, p. 409.

³ A. G. Redfield, *Phys. Rev.* **98**, 1787 (1955).

⁴ A. G. Anderson and S. R. Hartmann, *Phys. Rev.* **128**, 2023 (1962).

⁵ Reference 1, p. 560. In work by W. I. Goldberg and B. C. Johnson in an unpublished thesis by Barent C. Johnson, The Pennsylvania State University, 1965, this is shown specifically to be the case for pure nuclear quadrupole relaxation in cubic crystals. In Ref. 1, p. 560, this relaxation property is shown for pure magnetic relaxation only.

⁶ David C. Look, thesis, University of Minnesota, 1962 (unpublished).

carried out unpublished initial NMR studies of changes in T_1 for pure magnetic relaxation in the rotating frame, where the relaxation is determined by localized molecular random motions.

The specific cases of concern are the pure nuclear quadrupole relaxation times of Cl^{35} nuclei in KClO_3 , $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$, and NaClO_3 . The Cl^{35} ($I = \frac{3}{2}$) site structure is noncubic, and the axially symmetric electric field gradient at these sites produces an NQR frequency in the range of 30 Mc/sec. No external dc fields are applied. The laboratory-frame relaxation establishes a thermal distribution of population among the quadrupole levels, in equilibrium with the lattice, as determined by internal crystalline fields. The laboratory-frame quadrupole spin-lattice relaxation time will be referred to hereafter as T_{1L} .

The definition of two other frames of reference should now be introduced briefly. For a variety of spin systems it is possible to take a nuclear magnetization M_0 , which is first oriented along an applied dc magnetic H_0 , and reorient or "spin lock"⁷ M_0 along a rotating rf field H_1 . A quadrupole system can be similarly processed. It has been shown⁸ that a spin $I = \frac{3}{2}$ system, with the two $m = \pm \frac{3}{2} \leftrightarrow m = \pm \frac{1}{2}$ degenerate quantum-level transitions identical in frequency, is equivalent to two rotating magnetization vectors, one precessing clockwise, and the other precessing counterclockwise. If two rotating rf fields H_1 are manipulated by proper 90° pulses and phase shifts, the two rotating magnetization vectors can be oriented parallel to these fields and reach thermal equilibrium with respect to each H_1 field in its respective rotating frame. This equilibrium corresponds to a very low spin temperature which is subsequently raised by spin-lattice relaxation toward the lattice temperature. This is the first type of spin-lattice relaxation in a transformed frame of reference, denoted by T_{1SL} , where SL denotes "spin-locked."

If the spin-temperature hypothesis is correct, then one should be able to reduce the nuclear quadrupole magnetization to zero in the rotating frame⁴ (ADRF), i.e., by slowly turning off the applied rf field H_1 . The spin order, which is initially in the rotating magnetizations, is now transferred to the dipole-dipole interaction reservoir, where individual spins of the ensemble are now oriented along internal local fields. The energy of the system resides completely in the magnetic dipolar reservoir, prescribed as being in internal thermal equilibrium at a low spin temperature. This temperature is subsequently also raised because of spin-lattice relaxation, and the time constant for this process is denoted by T_{1AD} , where AD refers to "adiabatic demagnetization (in the rotating frame)."

In the case of pure magnetic or quadrupole relaxation for nuclei oriented in a large dc field, a spin-temperature

TABLE I. Nuclear quadrupole spin-lattice relaxation times for Cl^{35} in alkali chlorates at 20°K and 77°K .

Chlorate	Relaxation times (sec)	
KClO_3 (at 77°K)	T_{1L}	0.42 ± 0.02
	T_{1SL}	0.65 ± 0.02
	T_{1AD}	0.43 ± 0.02
KClO_3 (at 20°K)	T_{1L}	39.5 ± 0.5
	T_{1SL}	56.0 ± 0.5
	T_{1AD}	40.5 ± 0.5
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ (at 77°K)	T_{1L}	1.65 ± 0.02
	T_{1SL}	≈ 0.3
	T_{1AD}	≈ 0.1
$\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$ (at 77°K)	T_{1L}	1.65 ± 0.02
	T_{1SL}	1.97 ± 0.06
	T_{1AD}	1.00 ± 0.08
NaClO_3 (at 77°K)	T_{1L}	1.87 ± 0.02
	T_{1SL}	4.8 ± 0.2
	T_{1AD}	13.0 ± 1.0

assumption applied to these relaxation processes would argue that the spin-locked magnetization should relax like a magnetization would⁵ if directed along a dc laboratory field H_0 . In other words, $T_{1L} = T_{1SL}$. Of course in the case of conventional adiabatic demagnetization in the laboratory frame, the relaxation rate in the demagnetized state is essentially twice that in the polarized state, because not only are the spins themselves flipping at the rate T_{1L}^{-1} , but the local fields along which they are oriented are also flipping at the same rate. By analogy, therefore, the theory of rotating frame relaxation would maintain that $T_{1AD} \approx \frac{1}{2} T_{1SL}$. That this is definitely not the case for pure nuclear-quadrupole-coupled nuclei is shown by the data in Table I, and by the theory which is presented in the next section.

The data for values of T_{1L} in Table I are obtained by first saturating the Cl^{35} NQR resonance with a series of 90° rf pulses. After a time t a single 90° rf pulse is applied and the height of the ensuing free-induction signal is measured. This signal is proportional to the population difference between the two degenerate m levels, $\pm \frac{3}{2}$ and $\pm \frac{1}{2}$. The T_{1SL} data were obtained by first applying a 90° pulse of rf field H_1 to the sample, and then suddenly shifting the phase of H_1 by $\frac{1}{2}\pi$ in a time short compared to the nuclear Larmor period about H_1 in the rotating frame. With H_1 chosen large compared to the local dipolar fields, the Cl^{35} magnetization M is locked along the direction of H_1 for a time t , but relaxes according to the expression $M(t) = M(0) \exp(-t/T_{1SL})$. When H_1 is suddenly turned off at time t , a free precession signal proportional to $M(t)$ is measured. In order to measure T_{1AD} , the procedure for spin locking is first carried out as described above. The Zeeman interaction energy reservoir ($-\mathbf{M}_0 \cdot \mathbf{H}_1$) is adiabatically converted into a dipolar interaction reservoir of lower energy by turning off H_1 slowly, but in a time much less than T_{1AD} . After a time t the field H_1 is turned on, and adiabatic remagnetization of $M(t)$ along the direction of H_1 is accom-

⁷ S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2041 (1962).

⁸ M. Bloom, B. Herzog, and E. L. Hahn, Phys. Rev. **103**, 148 (1956).

plished. The magnitude of $M(t) = M(0) \exp(-t/T_{1AD})$ is then measured in terms of the free induction signal which appears after H_1 is abruptly turned off.

It is significant that the values of relaxation times in Table I show, with one exception, that $T_{1SL} > T_{1L}$, and that $T_{1AD} \approx \frac{1}{2} T_{1SL}$. The one exception, $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$, gives anomalous results for special reasons to be discussed later. In general the rotating-frame relaxation times for pure NQR prove to be longer than those times predicted from general arguments used in pure NMR.^{2,5}

The detailed analysis which follows in the next section reveals why the three relaxation rates T_{1L} , T_{1SL} , and T_{1AD} should differ. In our study there appears to be no predominance of spectral components of lattice noise which peak near or at the rotating-frame frequency ($\sim \gamma H_1$) during spin-locking, or at the local field frequency ($\sim \gamma H_L$) during ADRF, where γ is the gyromagnetic ratio of the relaxing nuclei, and H_L is the local field. Although this may be an important relaxation effect, dependent upon the temperature,⁶ where particular atomic groups such as H_2O or CH_3 undergo rotations in solids, such effects do not appear to affect the quadrupole relaxation data here because the temperature is low enough in our experiments to suppress such rotations, i.e., of D_2O and H_2O . The reason for changes in relaxation times, which is very much connected with systems involving pure nuclear quadrupole coupling, arises from the anisotropic effect of lattice vibrations. A given component of lattice vibration in the laboratory frame of reference can be ineffective or effective, depending upon whether it, respectively, does or does not commute with the laboratory-frame interaction Hamiltonian. The roles of commutation of some terms of these perturbations are reversed or their magnitudes are altered upon making a physical transformation to a new representation or reference frame, and different relaxation times are therefore evaluated. The change is found to be in the direction toward longer relaxation times. Possibly a similar study of pure magnetic relaxation in systems of sufficient asymmetry in magnetic lattice perturbation might show a similar behavior of transformed relaxation times. We do not deal with such cases here, and restrict ourselves to pure quadrupole relaxation.

I. THEORY

The total Hamiltonian⁹ of the spin system is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{rf}} + \mathcal{H}_{\text{dd}} + \mathcal{H}_1, \quad (1)$$

where

$$\mathcal{H}_0 = \sum_j h_{Qj}, \quad (2a)$$

$$h_{Qj} = K[3I_{zj}^2 - I(I+1)], \quad (2b)$$

$$\mathcal{H}_{\text{rf}} = \sum_j h_{\text{rt}j}, \quad (3)$$

$K = e^2qQ/4I(2I-1)$, and the sum is over all spins j of a given species. \mathcal{H}_{rf} defines the interaction between the spins and the radiofrequency (rf) magnetic field, summed over all spins j ; \mathcal{H}_{dd} is the dipole-dipole interaction, summed over all spin pairs; and $\mathcal{H}_1 = \sum_j h_{1j}$ is the spin-lattice relaxation perturbation Hamiltonian. The z axis is defined as the direction of maximum electric field gradient, eq is the field gradient in that direction, and Q is the nuclear quadrupole moment (in cm^2). It is specifically assumed in Eq. (2b) that the electric field gradient is axially symmetric. Henceforth the units of γ , the gyromagnetic ratio, and K the quadrupole coupling constant, are defined so that $\hbar = 1$, and energy is expressed by ω in radians/sec.

The dynamics of the spin system and its relaxation will be handled by the density matrix method,^{10,11} which deals with a solution of the fundamental equation

$$i \frac{d}{dt} \rho(t) = [\mathcal{H}, \rho(t)]. \quad (4)$$

The density matrix $\rho(t)$ lends itself conveniently to a transformation into the interaction representation, which effectively eliminates the main constant interaction term \mathcal{H}_0 from \mathcal{H} , Eq. (1). Therefore $\rho(t)$ transforms to $\rho^*(t)$ according to

$$\rho^*(t) = T \rho(t) T^{-1} = e^{i\mathcal{H}_0 t} \rho(t) e^{-i\mathcal{H}_0 t}. \quad (5)$$

Now $\rho^*(t)$ obeys the equation

$$i \frac{d\rho^*(t)}{dt} = [\mathcal{H}^*, \rho^*(t)], \quad (6)$$

and

$$\mathcal{H}^* = e^{i\mathcal{H}_0 t} \mathcal{H} e^{-i\mathcal{H}_0 t} - \mathcal{H}_0. \quad (7)$$

Equation (6) restricts itself to the influence of lattice and rf field perturbations, but contains terms with a coherent time dependence $e^{i\omega_0 t}$ and $e^{2i\omega_0 t}$, where ω_0 is the transition frequency between eigenlevels of \mathcal{H}_0 . These terms are dropped as nonsecular high-frequency oscillations whose average effect upon $\rho^*(t)$ is negligibly small, since we are interested in relatively slow changes in $\rho^*(t)$. This truncation procedure will be signified by the use of $\mathcal{H}^{*'}$ in place of \mathcal{H}^* . The random time dependence of lattice variables contained in \mathcal{H}_1^* is still included in $\mathcal{H}^{*'}$, however, because terms in \mathcal{H}_1^* contribute to the relaxation in second order.

Particular attention must be given to the transformations indicated by Eqs. (5) and (7) when dealing with pure nuclear quadrupole coupling as the dominant interaction Hamiltonian. If the dominant Hamiltonian is instead given by the familiar Zeeman term

$$\mathcal{H}_0 = -\gamma H_0 \sum_j I_{zj},$$

⁹ T. P. Das and E. L. Hahn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Suppl. I.

¹⁰ Charles P. Slichter, *Principles of Magnetic Resonance* (Harper & Row, Publishers, Inc., New York, 1963), Chap. 5.

¹¹ Reference 1, Chap. VIII.

where H_0 is the applied dc magnetic field, the transformations (5) and (7) are linear in the spin operators, and they therefore represent simple rotations. However, if \mathcal{H}_0 is given by the form of Eq. (2a), which is quadratic in spin operator I_z^2 , the transformations (5) and (7) are no longer simple rotations. Before such transformations can be applied, a scheme must be devised in which the usual rules for unitary transformations can still be used. This method is outlined in a separate section to follow, which is then applied to relaxation calculations in different interaction representations applicable to our experiments.

II. TRANSFORMATION TO THE QUADRUPOLE INTERACTION REPRESENTATION; CASE OF $I = \frac{3}{2}$

Consider any four-by-four matrix, and let it be divided up into quadrants, each of which is a two-by-two matrix:

$$\left(\begin{array}{c|c} a & u \\ \hline l & b \end{array} \right). \quad (8)$$

Each quadrant labeled a , u , l , and b will be chosen so that it can be represented by any of the three Pauli spin matrices σ_x , σ_y , σ_z or the identity matrix ϵ , given as follows:

$$\begin{aligned} \sigma_x &= \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, & \sigma_z &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \\ \sigma_y &= \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, & \epsilon &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \end{aligned} \quad (9)$$

By adding the appropriate subscripts a , u , l , or b to the matrices in (9), and combining them with the necessary coefficients, the matrix given by (8) can be used to represent required expressions. For example, σ_{ax} is the four-by-four matrix with zeros in all quadrants, except the upper left one in (8), namely:

$$\sigma_{ax} \equiv \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}.$$

For $I = \frac{3}{2}$, the matrix representation of the operator I_z is

$$\begin{pmatrix} \frac{3}{2} & 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & 0 \\ 0 & 0 & 0 & -\frac{3}{2} \end{pmatrix} \equiv \frac{1}{2}(\sigma_{az} + 2\epsilon_a + \sigma_{bz} - 2\epsilon_b). \quad (10)$$

The quadrupole interaction, Eq. (2b), can be written as

$$h_Q = 3K(\sigma_{ax} - \sigma_{bx}). \quad (11)$$

It will be useful for later calculations to obtain the transformed density matrix and Hamiltonian, given by (5) and (7), respectively, in terms of the Pauli matrix

notation outlined above. If the relaxation term \mathcal{H}_1 and the dipolar term \mathcal{H}_{dd} in \mathcal{H} , Eq. (1), are omitted for the time being, we write

$$\begin{aligned} \mathcal{H} &= 3K \sum_j (\sigma_{az}^j - \sigma_{bz}^j) \\ &\quad - 2\gamma H_1 \sum_j [(\sqrt{3}/2)(\sigma_{ax}^j + \sigma_{bx}^j) \\ &\quad\quad + \frac{1}{2}(\sigma_{uy}^j + \sigma_{ly}^j)] \cos \omega t, \end{aligned} \quad (12)$$

where the superscripts are particle indices and

$$\sigma_{\pm} = \sigma_x \pm i\sigma_y.$$

The term $-2\gamma H_1 \cos \omega t$ represents a linearly polarized rf Hamiltonian \mathcal{H}_{rf} . According to Eqs. (3), (5), and (11),

$$\begin{aligned} T &= \exp\{\frac{1}{2}i\omega t \sum_j (\sigma_{az}^j - \sigma_{bz}^j)\} \\ &= \prod_j T_j, \end{aligned} \quad (13)$$

where $T_j = \exp\{\frac{1}{2}i\omega t (\sigma_{az}^j - \sigma_{bz}^j)\}$. If O^j is an operator which acts only on the j th spin, then $TO^jT^{-1} = T_j O^j T_j^{-1}$. Furthermore, if O^j has only a and b quadrants [see (8)], with zeros in the u and l quadrants, then using T of Eq. (13),

$$\begin{aligned} TO^jT^{-1} &= e^{i\omega t \sigma_{az}^j/2} O_a^j e^{-i\omega t \sigma_{az}^j/2} \\ &\quad + e^{-i\omega t \sigma_{az}^j/2} O_b^j e^{i\omega t \sigma_{az}^j/2}. \end{aligned} \quad (14)$$

Note particularly that (14) comes about because of the general property that any a operator acting on any b operator gives zero, and vice versa. The first term in (14) is a rotation of O_a^j in a given direction about the z axis, and the second term is a rotation of O_b^j in the opposite direction about the z axis. Therefore, the concept of two rotating frames precessing in opposite directions can be retained: One direction involves the $m_I = \frac{3}{2} \leftrightarrow \frac{1}{2}$ transition and the other direction involves the $m_I = -\frac{3}{2} \leftrightarrow -\frac{1}{2}$ transition. The linearly polarized rf field given in Eq. (12) is a sum of two circularly polarized fields, each of which precess opposite to one another, and couple only to those spins having the corresponding sense of precession.

If some terms in the Hamiltonian to be transformed are of the type O_u or O_l , it proves to be easier to operate, as in (14), by an explicit expansion of $e\{i\omega t \sigma_{az}/2\}$. These expansions are

$$e^{(i\omega t/2)\sigma_{az}} = \frac{1}{2}(\epsilon_a + \sigma_{az})e^{i\omega t/2} + \frac{1}{2}(\epsilon_a - \sigma_{az})e^{-i\omega t/2} + \epsilon_b,$$

and

$$e^{(i\omega t/2)\sigma_{bz}} = \frac{1}{2}(\epsilon_b + \sigma_{bz})e^{i\omega t/2} + \frac{1}{2}(\epsilon_b - \sigma_{bz})e^{-i\omega t/2} + \epsilon_a. \quad (15)$$

These expressions apply as well for x and y substituted for z , but do not apply if the σ operator in the exponential is σ_u or σ_l .

With the transformation (13) now applied to the entire Hamiltonian, Eq. (1), therefore Eq. (7) becomes

$$\begin{aligned} \mathcal{H}^* &= (3K - \frac{1}{2}\omega) \sum_j (\sigma_{az}^j - \sigma_{bz}^j) - \frac{1}{2}3\gamma H_1 \sum_j (\sigma_{ax}^j + \sigma_{bx}^j) \\ &\quad + \mathcal{H}_{dd}^* + \text{terms in } e^{i\omega t} \text{ and } e^{2i\omega t}. \end{aligned} \quad (16)$$

The truncated dipole-dipole Hamiltonian in this repre-

sensation is expressed as

$$\mathfrak{H}_{dd}^{*'} = \sum_{j>k} h_{jk}^{*'}, \quad (17)$$

where $h_{jk}^{*'}$ is the spin-pair interaction. Exact rf resonance, $3K - \frac{1}{2}\omega = 0$, will be assumed. Again the non-secular high-frequency terms in $e^{i\omega t}$ and $e^{2i\omega t}$ are dropped. When a short intense rf pulse is applied, it is assumed that H_1 greatly exceeds the dipolar field, and the term (17) appearing in (16) is neglected during the pulse. At time $t=0$, the initial equilibrium density matrix is

$$\rho(0) = e^{-\beta_L \mathfrak{H}_Q} / \text{Tr} \rho = (-3\beta_L(0)K / \text{Tr} 1) \times \sum_j (\sigma_{az}^j - \sigma_{bz}^j), \quad (18)$$

where $\beta_L(0) = (1/kT_L)$, and T_L is the lattice temperature. The high-temperature approximation is made, and the identity operator is dropped because operators whose expectation values will be of interest are traceless. With $\rho(0) = \rho^*(0)$ and the spin temperature fixed at its initial value, it follows from Eqs. (5) and (14) that

$$\rho^*(t) = (-3\beta_L(0)K / \text{Tr} 1) \sum_j (e^{(i\omega_1 t/2)\sigma_{ax}^j} \times \sigma_{az}^j e^{(-i\omega_1 t/2)\sigma_{ax}^j} - e^{(i\omega_1 t/2)\sigma_{bx}^j} \sigma_{bz}^j e^{(-i\omega_1 t/2)\sigma_{bx}^j}), \quad (19)$$

where $\omega_1 = \sqrt{3}\gamma H_1$. Although the ensemble consists of a pair of two-level systems, each behaving as though the spin $I = \frac{1}{2}$, the operator connecting the levels introduces a factor $\sqrt{3}$ because of the degenerate levels associated with the actual spin $I = \frac{3}{2}$. Each term in (19) represents a rotation of magnetization about H_1 along the x axis in the rotating frame, associated with a given sense of rf field precession. At the rf pulse-width time $t = t_w = (\pi/2\omega_1)$, a 90° pulse transformation follows from Eq. (19), giving

$$\rho^*(t_w) = (-3\beta_L(0)K / \text{Tr} 1) \sum_j (\sigma_{ay}^j - \sigma_{by}^j). \quad (20)$$

The spin temperature becomes a function of t for $t > t_w$. Each rotating frame now has a magnetization along its respective y axis. Spin locking is subsequently achieved if the phase of the applied rf is shifted by $\pi/2$ at t_w in a time $\Delta t \ll t_w$. Therefore, the rf Hamiltonian (16) becomes

$$\mathfrak{H}_{rf}^{*'} = \sum_j h_{rfj}^{*'} = \frac{1}{2}\omega_1 \sum_j (\sigma_{ay}^j - \sigma_{by}^j). \quad (21)$$

For $\gamma H_1 \gg |\mathfrak{H}_{dd}^{*'}|$, one need retain only those parts of $\mathfrak{H}_{dd}^{*'}$ which are secular with respect to $\mathfrak{H}_{rf}^{*'}$, which can be denoted $\mathfrak{H}_{dd}^{*''}$. In this event, however, because of its form, $\rho^*(t_w)$ will commute with $\mathfrak{H}_{rf}^{*'}$ + $\mathfrak{H}_{dd}^{*''}$, with the consequence that for $t > t_w$, the order represented by the two magnetizations will persist in time, except that it is slowly diminished by spin-lattice relaxation effects not yet included.

The assumption of a spin-locked rotating-frame spin temperature T_S leads to the use of the density matrix

$$\rho^*(t) = (-\beta_S(t) / \text{Tr} 1) \mathfrak{H}_{rf}^{*'}, \quad (22)$$

where $\mathfrak{H}_{rf}^{*'}$ compares to \mathfrak{H}_Q of Eq. (18), and $\beta_S(t)$

$= [kT_S(t)]^{-1}$. At $t = t_w \approx 0$, the lattice (L) and spin (S) temperatures are related by

$$\beta_S = \beta_L(\omega_0/\omega_1), \quad (23)$$

and T_S corresponds to a lower spin temperature. The spin-locked state sets the stage from which order in the rotating magnetization can be transferred to the dipole-dipole interaction reservoir. This is carried out, as previously described, by turning off H_1 slowly. The initial spin temperature in this state (ADRF) is again a low one, expressed as

$$\beta_S(\text{ADRF}) = \beta_L \left[\frac{\text{Tr}\{\mathfrak{H}_Q^2\}}{\text{Tr}\{\mathfrak{H}_{dd}^{*'}\}^2} \right]^{1/2}, \quad (24)$$

where $\mathfrak{H}_{dd}^{*'}$ is given by Eq. (17).

Spin-Lattice Relaxation Times

A generalized procedure has been established¹¹ for the evaluation of relaxation times from a master equation for the density matrix. A second-order perturbation evaluation of the relaxation rate is carried out when the irreversible relaxation process is determined by stationary random functions of lattice and spin variables. The quadrupole relaxation term of the total Hamiltonian [Eq. (1)] is written as

$$\mathfrak{H}_1(t) = \sum_j h_{1j}(t) = \sum_q F^{(q)}(t) A^{(q)}, \quad (25)$$

where $h_{1j}(t) = F_j^{(q)}(t) A_j^{(q)}$. Any contribution to pure magnetic relaxation involving fluctuations in lattice coordinates of \mathfrak{H}_{dd} is assumed negligible, and magnetic relaxation is therefore excluded. The $F^{(q)}(t)$ terms represent stationary random functions of lattice vibrations which impose fluctuating electric field gradients arising from sources such as ionic vibrations, torsional vibrations of molecular groups, fluctuations in covalency, or hindered rotations. The superscript (q) designates a given change in spin quantum number Δm at which a given component of lattice vibration is effective. The $A^{(q)}$ terms represent the quadrupole spin operators which allow these relaxation transitions. When $A^{(q)}$ is associated with the appropriate spectrum of lattice frequencies which are at the allowed quadrupole transition frequencies, the relaxation transitions are most probable. In order that $\mathfrak{H}_1(t)$ be Hermitian, the restrictions $F^{(q)} = F^{(-q)*}$ and $A^{(q)} = A^{(-q)\dagger}$ are made. The master equation for the density matrix in operator form is

$$\frac{d}{dt} \sigma^*(t) = -\frac{1}{2} \sum_{q,p} J_q(\omega_p^{(q)}) [B_p^{(-q)}, [B_p^{(q)}, \sigma^*(t)]], \quad (26)$$

where

$$\sigma^*(t) = \rho^*(t) - \rho^*(\infty), \quad (27)$$

and $\rho^*(t)$ is given by (22). Note that for the Pauli matrix notation of Sec. II the use of σ is distinguished from its symbol as a density matrix by the use of sub-

scripts. At thermal equilibrium, $\beta_S = \beta_L$ and the density matrix is defined by $\rho(\infty)$. Any deviation of the density matrix $\rho(t)$ from thermal equilibrium at time t is defined by $\sigma(t)$, while $\rho^*(t)$ and $\sigma^*(t)$ are the corresponding quantities in the interaction representation. The terms $B_p^{(a)}$ are related to $A^{(a)}$ by

$$A^{(a)}(t) = e^{i\mathcal{H}_0 t} A^{(a)} e^{-i\mathcal{H}_0 t} = \sum_p B_p^{(a)} e^{i\omega_p^{(a)} t}, \quad (28)$$

where $B_p^{(a)} = \sum_j B_p^{(a)}(t)$. Subscript p sums over the eigenfrequencies of the spin system, and $\omega_p^{(a)}$ signifies frequencies in the lattice spectrum for which the $A^{(a)}$ operators can connect eigenlevels of \mathcal{H}_0 as secular terms. High-frequency nonsecular terms are dropped in Eq. (26). The spectral density function is given by

$$J_q(\omega_p^{(a)}) = \int_{-\infty}^{\infty} d\tau g_q(\tau) e^{i\omega_p^{(a)} \tau}, \quad (29)$$

and $g_q(\tau)$ is the autocorrelation function of $F^{(a)}(t)$:

$$g_q(\tau) = \langle F^{(a)}(t) F^{(a)}(t-\tau) \rangle_{av}. \quad (30)$$

This represents an ensemble average over many spins, and it is independent of the time t when a slowly changing spin temperature is defined. An arbitrarily chosen even function of τ is prescribed for $g_q(\tau)$, so that it follows from Eq. (29) that $J_q(\omega_p^{(a)}) = J_q(-\omega_p^{(a)})$.

III. LABORATORY-FRAME SPIN-LATTICE RELAXATION

In the laboratory frame the spin-lattice relaxation process involves the axially symmetric quadrupole-interaction Hamiltonian

$$\mathcal{H}_0 = 3K \sum_j (\sigma_{az}^j - \sigma_{bz}^j), \quad (31)$$

as obtained from Eqs. (2) and (11). The matrix notation introduced in Sec. II is applied to the determination of T_{1L} . By usual perturbation methods the result for T_{1L} has already been obtained.¹² However, a re-determination of T_{1L} here is instructive because it will be carried out in the new interaction representation, and will aid the reader in obtaining clearer understanding of the new calculations of T_{1SL} and T_{1AD} to follow. For any time t the spin temperature has a slow time dependence, so that the density matrix is now

$$\rho(t) = (-3K\beta_S(t)/\text{Tr}1) \sum_j (\sigma_{az}^j - \sigma_{bz}^j), \quad (32)$$

which is identical to the form of Eq. (18). Because \mathcal{H}_0 and $\rho(t)$ above commute with one another, Eqs. (5) and (27) imply that $\rho^*(t) = \rho(t)$ and that

$$\sigma^*(t) = \sigma(t) = (-3K/\text{Tr}1) [\beta_S(t) - \beta_L] \times \sum_j (\sigma_{az}^j - \sigma_{bz}^j). \quad (33)$$

Upon substituting the sums of single spin operators into the master equation (26), the commutators will be nonzero only when all operators pertain to the same spin. Therefore, for simplicity in notation, the summation index j over the spins may be dropped. If the double commutator $[B_p^{(-a)}, [B_p^{(a)}, (\sigma_{az} - \sigma_{bz})]]$ of Eq. (26) reduces to some factor multiplied by the operator $(\sigma_{az} - \sigma_{bz})$, which commutes with (32), then the perturbing lattice does not cause the spin system to depart from a state of internal equilibrium. Instead the relaxation development in time of the spin system reflects a smooth change in the spin temperature T_S , and a unique relaxation time is specified from the equation

$$\frac{d}{dt} \beta_S(t) = -\frac{1}{T_{1L}} [\beta_S(t) - \beta_L].$$

However, if the commutator does not commute with the main interaction Hamiltonian, and a common spin temperature can still be defined, then the internal dipole-dipole interaction among the spins must provide the mechanism¹³ by which a spin temperature is maintained. In such a case the rate equation of the total spin energy must be solved, which involves the derivative of the expectation value of the energy. In the determination of the three relaxation times T_{1L} , T_{1SL} , and T_{1AD} , of concern in the pure quadrupole relaxation of Cl^{35} , the total spin energy need be considered only in the determination of T_{1AD} . The unique times T_{1L} and T_{1SL} are measured when the $\pm m$ degenerate levels of the quadrupole system are equally excited, and when the sum of the population differences associated with both the $+m$ and $-m$ levels is measured.¹² An apparent spin temperature in NQR can then be defined for the case of $I = \frac{3}{2}$ (without requiring the mechanism of dipole-dipole coupling) with respect to a main independent interaction energy reservoir which is (a) quadrupolar in the laboratory frame, or (b) is Zeeman, with respect to the rf field H_1 in the rotating frame of the quadrupole system.

The single spin-relaxation Hamiltonian [Eq. (25)] for equivalent spin sites is

$$h_1(t) = \sum_{q=-2}^{+2} F^{(-q)}(t) A^{(q)} \quad (34)$$

and

$$\begin{aligned} A^{(0)} &= 3I_z^2 - I(I+1), \\ A^{(\pm 1)} &= \frac{1}{2}\sqrt{6}(I_z I_{\pm} + I_{\pm} I_z), \\ A^{(\pm 2)} &= \frac{1}{2}\sqrt{6}I_{\pm}^2, \\ F^{(0)}(t) &= \frac{1}{2}V_{zz}, \\ F^{(\pm 1)}(t) &= (1/\sqrt{6})(V_{xz} \pm iV_{yz}), \\ F^{(\pm 2)}(t) &= (1/2\sqrt{6})(V_{xx} - V_{yy} \pm 2iV_{xy}). \end{aligned} \quad (35)$$

¹² M. J. Weber and E. L. Hahn, Phys. Rev. **120**, 365 (1960); M. J. Weber, J. Phys. Chem. Solids **17**, 267 (1961).

¹³ A. Abragam and W. G. Proctor, Phys. Rev. **106**, 160 (1957); R. L. Mieher, Phys. Rev. Letters **4**, 57 (1960); Phys. Rev. **125**, 1537 (1962).

Here the electrostatic potential V is a random function of the time. Its subscripts indicate derivatives with respect to the given coordinates. The constant axial component V_{zz} is included in h_Q , Eq. (2b).

Now the transformation of (26) to the interaction representation is obtained, using T of Eq. (13):

$$\begin{aligned} h_1^*(t) &= T h_1(t) T^{-1} \\ &= F^{(0)}(t) 3(\sigma_{az} - \sigma_{bz}) + F^{(-1)}(t) (3/\sqrt{2})(\sigma_{a+} e^{i\omega_0 t} - \sigma_{b+} e^{-i\omega_0 t}) + F^{(+1)}(t) (3/\sqrt{2})(\sigma_{a-} e^{-i\omega_0 t} - \sigma_{b-} e^{i\omega_0 t}) \\ &\quad + F^{(-2)}(t) (3/\sqrt{2})[(\epsilon_u + \sigma_{uz}) e^{i\omega_0 t} + (\epsilon_u - \sigma_{uz}) e^{-i\omega_0 t}] + F^{(+2)}(t) (3/\sqrt{2})[(\epsilon_l - \sigma_{lz}) e^{i\omega_0 t} + (\epsilon_l + \sigma_{lz}) e^{-i\omega_0 t}]. \end{aligned} \quad (36)$$

By using Eq. (28), the operators $B_p^{(a)}$ may be identified from an inspection of Eq. (36). Eqs. (33) and (36) are used to evaluate the commutators of Eq. (26), which yield zero or $(\sigma_{az} - \sigma_{bz})$ times a number. These numbers, when summed, produce $3K/T_{1L}$. Note that since $A^{(0)}$ commutes with $\sigma^*(t)$, the lattice vibrations represented by $F^{(0)}$ can not contribute to the relaxation. The relaxation rate is finally obtained as

$$T_{1L}^{-1} = 2(W_1 + W_2). \quad (37)$$

The $\Delta m = \pm 1$ ($m = \pm \frac{1}{2} \leftrightarrow m = \pm \frac{3}{2}$) transition rate is $W_1 = 18J_1(\omega_0)$, the $\Delta m = \pm 2$ ($m = \mp \frac{1}{2} \leftrightarrow m = \pm \frac{3}{2}$) transition rate is $W_2 = 18J_2(\omega_0)$, and J is defined from Eq. (29).

action after the transformation, a second transformation is made into another representation in order to eliminate h_{rfj}^* . Again, using expressions for single-particle interactions, $h_1^*(t)$ is transformed to

$$\begin{aligned} h_1^{**}(t) &= T_{rf} h_1^*(t) T_{rf}^{-1} \\ &= F^{(0)}(t) \frac{3}{2} [(\sigma_{az} + i\sigma_{ax} - \sigma_{bz} + i\sigma_{bx}) e^{i\omega_1 t} + (\sigma_{az} - i\sigma_{ax} - \sigma_{bz} - i\sigma_{bx}) e^{-i\omega_1 t}] \\ &\quad + F^{(-1)}(t) (3/\sqrt{2}) \left\{ \frac{1}{2} [(\sigma_{ax} - i\sigma_{az}) e^{i\omega_0 t} - (\sigma_{bx} + i\sigma_{bz}) e^{-i\omega_0 t}] e^{-i\omega_1 t} + \frac{1}{2} [(\sigma_{ax} + i\sigma_{az}) e^{i\omega_0 t} - (\sigma_{bx} - i\sigma_{bz}) e^{-i\omega_0 t}] e^{-i\omega_1 t} \right. \\ &\quad \left. + i\sigma_{ay} e^{i\omega_0 t} - i\sigma_{by} e^{-i\omega_0 t} \right\} + \text{Hermitian conjugate} + F^{(-2)}(t) (3/\sqrt{2}) \left[\frac{1}{2} (\epsilon_u + \sigma_{uy}) (e^{i\omega_0 t} + e^{-i\omega_0 t}) e^{i\omega_1 t} \right. \\ &\quad \left. + \frac{1}{2} (\epsilon_u - \sigma_{uy}) (e^{i\omega_0 t} + e^{-i\omega_0 t}) e^{-i\omega_1 t} + \sigma_{uz} e^{i\omega_0 t} - \sigma_{uz} e^{-i\omega_0 t} \right] + \text{Hermitian conjugate}, \end{aligned} \quad (38)$$

where

$$T_{rf} = e^{(i\omega_1 t/2)(\sigma_{ay} - \sigma_{by})}. \quad (39)$$

The rf interaction is assumed to be very large compared to the dipolar interaction, and therefore \mathcal{H}_{dd} of Eq. (1) plays no role in the calculation of T_{1SL} .

Using Eqs. (20), (21), and (27), the density matrix during spin locking becomes

$$\begin{aligned} \sigma^{**}(t) &= e^{i\mathcal{H}_{rf}^*/t} \sigma^*(t) e^{-i\mathcal{H}_{rf}^*/t} \\ &= -3K(\beta_S - \beta_L)(\sigma_{ay} - \sigma_{by}). \end{aligned} \quad (40)$$

The same procedure for evaluation of the relaxation rate coefficient in Eq. (26) is carried out as before in the determination of $1/T_{1L}$. It should be noted that the $q=0$ term of $h_1^*(t)$, Eq. (36), now does not commute with the new density matrix given by (40), and, as a consequence, there will be a contribution to the relaxation from the $q=0$ component of vibration. The $q=\pm 1$ term is now the double commutator of an I_+ operator with an I_y operator, whereas for the $1/T_{1L}$ calculation, I_+ was associated with I_z . The present commutator is smaller by a factor of 2. For the $q=\pm 2$ terms, half of them are dropped as a nonsecular because of exponential

IV. SPIN-LATTICE RELAXATION IN THE ROTATING rf FRAME

Calculation of the spin-locked relaxation rate $1/T_{1SL}$ proceeds along the lines used to obtain the rate $1/T_{1L}$. The total Hamiltonian, Eq. (1), is now used, and the \mathcal{H}_{rf} term is retained and transformed according to Eq. (21). The applied rf frequency ω is assumed to be at exact quadrupole resonance. First, the main interaction term \mathcal{H}_0 is transformed away, which converts the perturbation term $h_1(t)$ into the first interaction representation term $h_1^*(t)$, given by Eq. (36). With the retention of the rf term, Eq. (21), which appears as a constant inter-

time-dependent terms which are functions of $\omega_1 t$. With one exception all double commutators reproduce the operator $\sigma_{ay} - \sigma_{by}$, but even this exception (from $q=\pm 2$ terms) is cancelled when the property $J_q(\omega) = J_q(-\omega)$ is used. The spin-locked relaxation rate becomes

$$\begin{aligned} T_{1SL}^{-1} &= 18J_0(\omega_1) + 9[J_1(\omega_0 + \omega_1) + J_2(\omega_0 + \omega_1) \\ &\quad + J_1(\omega_0 - \omega_1) + J_2(\omega_0 - \omega_1)]. \end{aligned} \quad (41)$$

If $\omega_1 \ll \omega_0$ is assumed, then

$$T_{1SL}^{-1} \approx 18[J_0(\omega_1) + J_1(\omega_0) + J_2(\omega_0)]. \quad (42)$$

When this result is compared with Eq. (37), it is seen that it is possible for T_{1SL} to be as much as twice as large as T_{1L} .

V. SPIN-LATTICE RELAXATION AFTER ADIABATIC DEMAGNETIZATION IN THE ROTATING FRAME (ADRF)

The third relaxation time T_{1AD} is the most difficult to analyze because the interaction representation Hamiltonian—after transforming out the quadrupole term [Eq. (2)]—is now the truncated secular dipole-

dipole Hamiltonian $\mathcal{H}_{dd}^{*'}$, which is a sum of two spin operators. Only one spin species is assumed to be present. If a second species (denoted by B spins to distinguish from the primary species, the A spins) were included, the complexity of the calculation would be greatly and unrewardingly increased. However, the presence of B spins is more often the real case in experiments, and can, as we shall see, have a profound effect upon the apparent relaxation of the A spins.

The spin pair dipole-dipole interaction is

$$h_{jk} = \gamma^2 r_{jk}^{-3} [A_{jk} I_{zj} I_{zk} + B_{jk} (I_{+j} I_{-k} + I_{-j} I_{+k}) + C_{jk} (I_{zj} I_{+k} + I_{+j} I_{zk}) + D_{jk} (I_{zj} I_{-k} + I_{-j} I_{zk}) + E_{jk} (I_{+j} I_{+k} + F_{jk} I_{-j} I_{-k})]; \quad (43)$$

and

$$\begin{aligned} A_{jk} &= 1 - 3 \cos^2 \theta, \\ B_{jk} &= -\frac{1}{4} (1 - 3 \cos^2 \theta), \\ C_{jk} &= D_{jk}^* = -\frac{3}{2} \sin \theta \cos \theta e^{-i\varphi}, \\ E_{jk} &= F_{jk}^* = -\frac{3}{4} \sin^2 \theta e^{-2i\varphi}. \end{aligned}$$

θ and φ are spherical coordinates of the \mathbf{r}_{jk} distance connecting j and k spins. Transformation of h_{jk} to the interaction representation is indicated by Eqs. (16) and (17), giving

$$\begin{aligned} h_{jk}^{*'} &= \gamma^2 r_{jk}^{-3} \{ A_{jk} I_{zj} I_{zk} + B_{jk} [\frac{3}{4} (\sigma_{a+}^j \sigma_{a-}^k + \sigma_{a-}^j \sigma_{a+}^k + \sigma_{b+}^j \sigma_{b-}^k + \sigma_{b-}^j \sigma_{b+}^k) + \sigma_{u-}^j \sigma_{l+}^k + \sigma_{l+}^j \sigma_{u-}^k] \\ &+ C_{jk} (I_{zj} \sigma_{u-}^k + \sigma_{u-}^j I_{zk}) + C_{jk}^* (I_{zj} \sigma_{l+}^k + \sigma_{l+}^j I_{zk}) \\ &+ E_{jk} [\frac{3}{4} (\sigma_{a+}^j \sigma_{b+}^k + \sigma_{b+}^j \sigma_{a+}^k) + \sigma_{u-}^j \sigma_{u-}^k] \\ &+ E_{jk}^* [\frac{3}{4} (\sigma_{a-}^j \sigma_{b-}^k + \sigma_{b-}^j \sigma_{a-}^k) + \sigma_{l+}^j \sigma_{l+}^k] \}. \quad (44) \end{aligned}$$

The once-transformed Hamiltonian is

$$\mathcal{H}^{*'} = \sum_{j>k} h_{jk}^{*'} + \sum_j h_{1j}^{*'}(t),$$

where $h_{1j}^{*'}(t)$ is the transformed lattice perturbation given by Eq. (36). The master equation, Eq. (26), is now presented with the summation over k spins:

$$\begin{aligned} \frac{d\sigma^{**}}{dt} &= - \sum_{k,q} \int_0^\infty d\tau \langle F_k^{(q)}(t) F_k^{(-q)}(t-\tau) \rangle_{av} [\exp(i \sum_l h_{lk}^{*'} t) A_k^{(q)}(t) \exp(-i \sum_m h_{mk}^{*'} t), \\ &[\exp[i \sum_n h_{nk}^{*'}(t-\tau)] A_k^{(-q)}(t-\tau) \exp[-i \sum_j h_{jk}^{*'}(t-\tau)], \sigma^{**}(t)]]]. \quad (45) \end{aligned}$$

The lattice vibrations affecting spins at site k determine the autocorrelation function of F_k , and are assumed to be randomly independent of similar vibrations at other equivalent sites. The expressions in F and A , given by Eqs. (29), (30), and (28), respectively, implicitly carry the summation index over p . In analogy to Eqs. (33) or (40),

$$\sigma^{**}(t) = \sigma^*(t) = -[\beta_S(t) - \beta(\infty)] \sum_{j>k} h_{jk}^{*'}, \quad (46)$$

where the simple operator $\sigma_{az} - \sigma_{bz}$ or $\sigma_{ay} - \sigma_{by}$ is replaced by $\mathcal{H}_{dd}^{*'} = \sum_{j>k} h_{jk}^{*'}$. The second transformed density matrix in the ADRF representation of $\mathcal{H}_{dd}^{*'}$ is given by $\sigma^{**}(t)$. Now we must take note of the fact that a transformation of $A_k^{(q)}$ of the type given by Eq. (28), when $\mathcal{H}_{dd}^{*'}$ replaces \mathcal{H}_0 , is not possible in Eq. (45). $A_k^{(q)}(t)$ itself is expandable in a series of terms signified by the sum over p , where the ω_p transition frequencies are between discrete levels established by the large quadrupole interactions \mathcal{H}_0 . When $\mathcal{H}_{dd}^{*'}$ replaces \mathcal{H}_0 , the ω_p would correspond to one frequency out of a continuum of dipolar frequencies in the spectrum of the

dipolar linewidth. These frequencies are negligibly small compared to accompanying quadrupole resonance frequencies, and we shall drop them for the same reason that ω_1 is dropped relative to ω_0 in Eq. (41), which yields Eq. (42). Therefore, in Eq. (45) we let $\exp[\pm i h_{qk}^{*' t}] = 1$, where q is any of the indices summed over.

The double commutator in Eq. (45) does not reproduce $h_{jk}^{*'}$, and therefore with Eq. (46) the master equation does not reduce to a simple rate equation in the density matrix. Instead, the density matrix

$$\rho^*(t) = -\beta_S \sum_{j>k} h_{jk}^{*'} \quad (47)$$

is assumed, and we consider the time rate of change of the dipolar energy:

$$\frac{d}{dt} \text{Tr} \{ \rho^* \mathcal{H}_{dd}^{*' } \} = - \frac{d\beta_S}{dt} \sum_{j>k} \text{Tr} \{ h_{jk}^{*'2} \}. \quad (48)$$

Now with the properties that $d\rho^*(t)/dt = d\sigma^*(t)/dt = d\sigma^{**}(t)/dt$, and the summation rule $\sum_{j>k} = \frac{1}{2} \sum_{j \neq k}$, Eq. (45) is now written as

$$\frac{d\sigma^{**}(t)}{dt} = - \sum_{k,q} \int_0^\infty d\tau \langle F_k^{(q)}(t) F_k^{(-q)}(t-\tau) \rangle_{av} [A_k^{(q)}(t), [A_k^{(-q)}(t-\tau), \sigma^{**}(t)]]].$$

Therefore, Eq. (48) yields

$$-d\beta_S(t)/dt = T_{1AD}^{-1} [\beta_S(t) - \beta_L],$$

where

$$\frac{1}{T_{1AD}} = \frac{2}{\sum_{j>k} \text{Tr}\{h_{jk}^{*'/2}\}} \sum_{j>k} \int_0^\infty d\tau \langle F^{(q)}(t) F^{(-q)}(t-\tau) \rangle_{\text{av}} \text{Tr}\{[A_{j^{(q)}}(t), [A_{j^{(-q)}}(t-\tau), h_{jk}^{*'}]] h_{jk}^{*'}\}. \quad (49)$$

The $A^{(q)}(t)$ terms are obtained from Eq. (36) and $h_{jk}^{*'}$ is obtained from Eq. (44). Equation (49) is evaluated and the result is

$$T_{1AD}^{-1} = [\sum_k r_{jk}^{-6} (25A_{jk}^2 + 68B_{jk}^2 + 80|C_{jk}^2| + 68|E_{jk}^2|)]^{-1} \sum_k r_{jk}^{-6} [36J_0(0)(36B_{jk}^2 + 36|E_{jk}^2|) + 36J_1(\omega_0)(10A_{jk}^2 + 68B_{jk}^2 + 56|C_{jk}^2| + 68|E_{jk}^2|) + 36J_2(\omega_0)(40A_{jk}^2 + 68B_{jk}^2 + 114|C_{jk}^2| + 68|E_{jk}^2|)]. \quad (50)$$

Upon substituting the definitions of A_{jk} , B_{jk} , etc. from Eq. (43) into (50), $1/T_{1AD}$ finally becomes

$$T_{1AD}^{-1} = [\sum_k r_{jk}^{-6} (67.5 - 72Z_{jk}^2 + 121.5Z_{jk}^4)]^{-1} \sum_k r_{jk}^{-6} [36J_0(0)(22.5 - 54Z_{jk}^2 + 40.5Z_{jk}^4) + 36J_1(\omega_0)(52.5 - 36Z_{jk}^2 + 40.5Z_{jk}^4) + 36J_2(\omega_0)(82.5 - 18Z_{jk}^2 + 112.5Z_{jk}^4)], \quad (51)$$

and Z_{jk} is the direction cosine between the z axis and \mathbf{r}_{jk} .

An exact numerical lattice sum required by Eq. (51) for a specific case is not applicable to our measurements, where more than one spin species is present, nor would the effort be justifiable. The similarity of the terms in both the numerator and denominator of Eq. (51) suggests possibly that the value of $1/T_{1AD}$ may not be very sensitive to the specific form of the lattice. It suffices to present an approximate crude expression for $1/T_{1AD}$ by assuming that the distribution of spin sites around a given spin is spherically symmetric. The angular functions Z of θ may be averaged over a sphere giving

$$Z_{\text{av}}^2 = \langle \cos^2\theta \rangle_{\text{av}} = \frac{1}{3},$$

and

$$Z_{\text{av}}^4 = \langle \cos^4\theta \rangle_{\text{av}} = \frac{1}{5}.$$

Therefore, with this approximation,

$$T_{1AD}^{-1} \approx 6.7J_0(0) + 25.8J_1(\omega_0) + 52.6J_2(\omega_0). \quad (52)$$

VI. DISCUSSION OF RESULTS AND CONCLUSIONS

The particular mechanisms which cause quadrupolar relaxation are of no concern to the present analysis, but they do account for the relative magnitudes of the spectral density functions J_0 , J_1 and J_2 which appear in the derived relaxation rates. To a large extent all the lattice excitation frequencies are represented by a smooth spectrum, and the spectral density function $J_q(\omega)$ should be essentially constant over the range of NQR frequencies present. In Eq. (41) we assume $J_0(\omega_1) = J_0(0)$, which implies a constant spectral density at the low-frequency end of the spectrum. This applies as well to Eq. (50) where the $J_0(0)$ term corresponds physically to the spectral density function over local dipolar frequencies near zero. The three relaxation rates from Eqs. (37), (41) and (52), now collected together, are, respectively,

$$\begin{aligned} T_{1L}^{-1} &= 36[J_1(\omega_0) + J_2(\omega_0)], \\ T_{1SL}^{-1} &= 18[J_0(0) + J_1(\omega_0) + J_2(\omega_0)], \end{aligned} \quad (53)$$

and

$$T_{1AD}^{-1} \approx 6.7J_0(0) + 25.8J_1(\omega_0) + 52.6J_2(\omega_0).$$

From measurements of T_{1L} and T_{1SL} , the spectral density function $J_0(\omega_1) \approx J_0(0)$ may be obtained directly as

$$J_0(0) = \frac{1}{36} \left(\frac{2}{T_{1SL}} - \frac{1}{T_{1L}} \right), \quad (54)$$

where $T_{1S} \leq 2T_{1L}$, since $J \geq 0$ for any J . The low-frequency spectral distribution function $J_0(\omega_1) \approx J_0(0)$ is a new parameter which can be determined; it never plays a role in affecting usual laboratory-frame T_{1L} measurements. Where low-frequency perturbations are particularly important, the shape of $J_0(\omega_1)$ could be measured as a function of ω_1 if $J_0(\omega_1)$ is not necessarily flat near zero frequency.

It is worthwhile to compare the experimental results of Table I with the predictions of Eqs. (53) in spite of the rather inexact expression for $1/T_{1AD}$. Eqs. (53), together with the data for KClO_3 at 77°K, yield the following spectral intensity function values:

$$\begin{aligned} J_0(0) &= (1.93 \pm 0.41) \times 10^{-2} \text{ sec}^{-1}, \\ J_1(\omega_0) &= (4.78 \pm 0.68) \times 10^{-2} \text{ sec}^{-1}, \\ J_2(\omega_0) &= (1.83 \pm 0.47) \times 10^{-2} \text{ sec}^{-1}, \\ J_1/J_2 &= 2.61 \pm 0.76; \end{aligned}$$

and at 20°K, the values are

$$\begin{aligned} J_0(0) &= (2.89 \pm 0.13) \times 10^{-4} \text{ sec}^{-1}, \\ J_1(\omega_0) &= (5.31 \pm 0.19) \times 10^{-4} \text{ sec}^{-1}, \\ J_2(\omega_0) &= (1.72 \pm 0.13) \times 10^{-4} \text{ sec}^{-1}, \\ J_1/J_2 &= 3.08 \pm 0.26, \end{aligned}$$

where J_1/J_2 is roughly independent of the temperature. By an independent method,¹² the ratio $J_1/J_2 = 3.4 \pm 1.3$ for Cl^{35} nuclei in KClO_3 was determined at 77 and 298°K, apparently independent of the temperature. This rough agreement with the present estimate of J_1/J_2 , although possibly accidental, justifies some confidence in the use

of the spin-lattice relaxation rates given by Eqs. (53), particularly because the inexact expression for $1/T_{1AD}$ is not involved. There is an additional consistency which is found when the relaxation data for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$ are used to obtain J_0 , J_1 , and J_2 from Eqs. (53). Although a small negative value of $J_1(\omega_0)$ is found, which is forbidden, and not surprising because of our crude estimate of $1/T_{1AD}$, we set $J_1(\omega_0) \approx 0$ as a justifiable physical possibility. As seen from Eqs. (29), (30), and the definition of $F^{(\pm 1)}$ in Eqs. (35), this implies that lattice vibrations of field gradient components V_{zz} and V_{yz} contribute very little to the relaxation rate. We have not justified this property from a detailed study of the actual field gradient characteristics in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$. If use is made of the measured $1/T_{1SL}$ to solve for $J_2(\omega_0)$, and if the measured $1/T_{1L}$ is used to solve for $J_0(0)$, a predicted value of T_{1AD} can be found from the $1/T_{1AD}$ equation. The results for $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$ are

$$\begin{aligned} J_1(\omega_0) &\approx 0, \\ J_2(\omega_0) &= (1.68 \pm 0.02) \times 10^{-2} \text{ sec}^{-1}, \\ J_0(0) &= (1.14 \pm 0.09) \times 10^{-2} \text{ sec}^{-1}, \\ T_{1AD}(\text{predicted}) &= 1.04 \pm 0.04 \text{ sec}, \\ T_{1AD}(\text{measured}) &= 1.00 \pm 0.08 \text{ sec}. \end{aligned}$$

No independent measurements of J_1/J_2 are available in this case, but the consistency between $T_{1AD}(\text{predicted})$ and $T_{1AD}(\text{measured})$ is evident on the basis that $J_1(\omega_0) \approx 0$.

The above apparent rough consistencies of relaxation rate theory with experiment are not to be taken too seriously. At best the important conclusion to be drawn is that there is no general relationship between relaxation rates in the laboratory and transformed representations which is independent of the particular quadrupole system studied, because of the roles played by the spectral density functions. Note in particular that T_{1SL} and T_{1AD} are longer than expected from simple arguments. Moreover, the reader is reminded that Eqs. (53) are derived on the basis that a single species of spins is relaxing, whereas actually several isotopes are present in the chlorates which were measured. For H_1 large compared to the dipolar field, the presence of such foreign "B spins" would not be expected to distort the measured values of T_{1SL} , because the B spins couple and relax independently to the lattice. However, for the determination of T_{1AD} , all spin species form a common coupled reservoir during the ADRF state, and the apparent spin-lattice relaxation, reflected in the recovered Cl^{35} signal, is determined by the B spins as well and by their separate dipolar heat capacities. The data in Table I for NaClO_3 indicate this effect, which is more marked in this respect than that for KClO_3 and $\text{Ba}(\text{ClO}_3)_2 \cdot \text{D}_2\text{O}$. In NaClO_3 particularly, the gyromagnetic ratio γ for Na^{23} is $\frac{5}{2}$ that of Cl^{35} , whereas in the latter two compounds, the γ of all foreign neighbors of significant isotopic abundance is smaller than the γ

of Cl^{35} . Consequently, the Na-Na dipolar interaction has a much larger heat capacity than that of the Cl-Cl interaction, and will contain a larger part of the spin ordering during the ADRF state. The Na nuclear quadrupole interaction in NaClO_3 corresponds to a frequency in the range of 400 to 500 kc/sec about 75 times smaller than that for Cl^{35} , so that Na would have a relatively long spin-lattice relaxation time compared to Cl^{35} . Consequently, upon remagnetization of the Cl^{35} nuclei, the apparent T_{1AD} of Cl^{35} is longer than expected because the ADRF ordered state relaxes mostly according to the lower relaxation rate of the Na nuclei. This effect occurs even for T_{1SL} measurements because of the difficulty of obtaining sufficiently large rf fields H_1 to decouple Cl^{35} completely from the dipolar reservoir of the Na nuclei. In addition, the effect manifests itself by the fact that the measured decay functions are not truly exponential.

The measured relaxation time of Cl^{35} in $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ illustrates a case where the disappearance of Cl^{35} signal is not due to coupling with the lattice, but rather with the proton dipolar reservoir with its dominant heat capacity. The proton spin-lattice relaxation time is extremely long, and has no effect on the measurements. In Table I, the value of T_{1L} in the hydrate is the same as in the deuterate, but the values of $T_{1SL} = 0.3$ sec and $T_{1AD} = 0.1$ sec in the hydrate are shorter than the corresponding values for the deuterate. The measured decay curves were far from exponential in character. In the measurement of T_{1SL} , even a 10 G rotating rf field H_1 was insufficient to decouple the Cl^{35} spin reservoir from the proton dipolar reservoir, with its associated larger dipolar field and heat capacity. After the Cl^{35} order transfers predominantly into the proton system, little of this order could be restored to the Cl^{35} reservoir, following adiabatic remagnetization, because the rf intensities H_1 available in the experiment were insufficient to make this possible, i.e., by imparting a sufficient rotating-frame Zeeman heat capacity to the Cl^{35} nuclei.

The calculations of relaxation rates have been carried out in the special case of exact quadrupole resonance. If this condition is removed, and the off-resonance parameter were to be considered in our analysis, the relaxation rates will change in such a manner as to approach the normal relaxation rate $1/T_{1L}$, as one gets farther off resonance. Such a behavior is qualitatively observed in our experiments, but no attempt is made here to investigate this effect. With this additional information, combined with the on-resonance relaxation behavior, it appears that the spectral density functions J_1 , J_2 , and J_3 could be more accurately determined. It is shown, with the evaluation of different relaxation rates in different frames of reference, that one can measure in principle the separate magnitudes of these density functions or their ratios.

The lengthened spin-lattice relaxation times dis-

cussed in this paper were in fact first observed in the course of making nuclear double resonance measurements. The fact that the lifetimes of ordered states are in general lengthened favors the enhancement of the sensitivity of double resonance experiments.⁷

The calculations in this investigation present a change from the qualitative, phenomenological approach which argues that nuclear quadrupole systems can be described by analogy with ordinary pure magnetic resonance phenomena. The unitary transformation one uses to transform the total Hamiltonian to the interaction representation is a simple rotation about the axis of the applied magnetic field, when handling pure magnetic resonance problems. Calculations for quadrupole systems can now be extended to the interaction representation where the corresponding transformation for pure quadrupole resonance is not a simple rotation, but can be decomposed into a subset of unitary transformations by a superposition of Pauli matrices which represent the higher order quadrupole operators. The ex-

ample handled in this paper is explicitly for spin $I = \frac{3}{2}$ in an axially symmetric, electric field gradient in zero magnetic field. The new representation can be developed to handle the problem of an asymmetric electric field gradient combined with an applied magnetic field, and it is applicable to some problems which involve spins other than $I = \frac{3}{2}$. Other problems, not necessarily involving spin-lattice relaxation, which deal with the dynamic behavior of nuclear-quadrupole-coupled spin ensembles, such as in nuclear double resonance experiments,⁷ should now be amenable to a more rigorous treatment.

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Theory of Exchange-Narrowed Magnetic-Resonance Linewidth at Finite Temperature

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General formulas are derived for the width of an exchange-narrowed magnetic-resonance absorption line at a finite temperature where the Zeeman and/or exchange energies can be comparable to the thermal energy kT . The perturbation which gives rise to line broadening also is allowed to be comparable to kT in our treatment, and this marks a departure from previous theories of exchange narrowing. The relaxation-function approach of Kubo and Tomita is used, and it is assumed, as in the infinite-temperature limit, that the appropriate correlation times are sufficiently short. We show that the correlation function $\langle M_x(t)M_x(0) \rangle$ of the x component of the magnetization has an apparent relaxation rate which is given by an obvious extension of the Van Vleck moments formula to finite temperature. This relation holds for an arbitrary ratio of perturbation energy to kT . However, it appears that only if the perturbation energy is much less than kT can this relaxation function be simply related to $\bar{M}_x(t)$, which describes relaxation of the macroscopic magnetization. If this is the case, then an unambiguous result for the linewidth is obtained which is clearly related to Van Vleck's infinite-temperature theory.

I. INTRODUCTION

It is well known¹⁻³ that paramagnetic resonance lines are considerably narrowed under the influence of a large isotropic exchange interaction between identical spins. This effect is semiquantitatively described by the formula

$$\gamma\Delta H \approx \langle \Delta\omega^2 \rangle / \omega_e, \quad (1)$$

where $\gamma\Delta H$ is the linewidth expressed in frequency units, $\langle \Delta\omega^2 \rangle^{1/2}$ is the frequency width in the absence of an exchange interaction, and ω_e , the "exchange fre-

quency," is proportional to the exchange coupling expressed in frequency units. The physical interpretation¹ of (1) is that the perturbation which gives rise to $\langle \Delta\omega^2 \rangle$ is randomly modulated by spin flips occurring at a characteristic rate $\omega_e \gg \langle \Delta\omega^2 \rangle^{1/2}$.

The quantities $\langle \Delta\omega^2 \rangle$ and ω_e are given in Refs. 1-3 for the infinite-temperature limit, in which case

$$\langle \Delta\omega^2 \rangle = M_2 \quad (2)$$

and

$$\omega_e = (M_4/M_2)^{1/2}, \quad (3)$$

where M_2 and M_4 are the Van Vleck second and fourth moments, respectively. In this paper we investigate the temperature dependence of ΔH , which involves a treatment for arbitrary values of $\hbar\omega_e/kT$ and $\hbar\omega_0/kT$, where

¹ P. W. Anderson and P. R. Weiss, *Rev. Mod. Phys.* **25**, 269 (1953).

² J. H. Van Vleck *Phys. Rev.* **74**, 1168 (1948).

³ R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).