Spin-Lattice Relaxation in the Rotating Frame : Weak-Collision Case

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A comprehensive theoretical expression for the spin-lattice relaxation time in the rotating frame $T_{1\rho}$ is derived for the case of weak collisions. Starting from the laboratory-frame dipolar Hamiltonian and retaining both secular and nonsecular terms, the doubly-rotating-frame Hamiltonian is determined and the relaxation expression derived, using standard density-matrix techniques. In limiting cases the derived expression reduces to established forms, including the normal expression for T_1. An experimental measurement of the angular dependence of $T_{1\rho}$ is described and the data for the sample of tetramethyl-ammonium iodide shown. The theoretical curve is in good agreement with the experimental data.

I. INTRODUCTION

NUCLEAR magnetic resonance has proved to be a very useful tool for the investigation of molecular and atomic motions. The motions are monitored by their effect on the nuclear resonance linewidth or the spin-spin relaxation time T_2 and the spin-lattice relaxation time T_1. The usual T_1 measurements at fields of the order of 10 kG are amenable to a weak-collision theory and are interpreted by means of the well-known relaxation treatment of Bloembergen, Purcell, and Pound.[1]

Low-field relaxation due to slow motion, i.e., $\tau_c > T_{2R.L.}$, where $T_{2R.L.}$ is the rigid lattice T_2 and τ_c is the motional correlation time, cannot be explained by means of the B.P.P. theory. This case has been treated in both the laboratory and the rotating frames in a recent series of papers by Slichter and Ailion,[2-4] employing a strong-collision approach. A weak-collision theory is still valid for low fields, in both the rotating and laboratory frames provided $\tau_c \ll T_{2R.L.}$.

In the rotating frame the effective field $\mathbf{H}_e$ is given by

$$\mathbf{H}_e = \omega_e/\gamma = [H_0 - (\omega/\gamma)]\hat{k} + H_1\hat{\imath}, \tag{1}$$

where $\hat{\imath}$ and $\hat{k}$ are unit vectors. $\mathbf{H}_e$ makes an angle θ with $\mathbf{H}_0$ where

$$\tan\theta = H_1/[H_0 - (\omega/\gamma)] = H_1/h_0. \tag{2}$$

The spin lattice relaxation time in the rotating frame[5] $T_{1\rho}$ is the characteristic decay time of the magnetization along H_e. Using the same nomenclature the transverse or spin-spin relaxation time in the rotating frame is designated $T_{2\rho}$.

A theoretical expression for $T_{1\rho}$ as a function of θ is derived for the weak-collision case. When θ becomes zero the expression agrees with the normal form for T_1. The angular dependence is compared with experimental data. The theoretical expression for $T_{1\rho}$ together with experimental T_1 and $T_{1\rho}(\theta = 90°)$ data at the same tem-

perature enables τ_c to be determined in appropriate cases.

II. THE HAMILTONIAN

The laboratory-frame Hamiltonian is given by

$$\hbar\mathcal{3C} = \hbar\mathcal{3C}_z + \hbar\mathcal{3C}_{rf} + \hbar\mathcal{3C}_d, \tag{3}$$

$$\hbar\mathcal{3C}_z = -\gamma\hbar H_0 \sum_p I_{pz}, \tag{4}$$

$$\hbar\mathcal{3C}_{rf} = -\gamma\hbar H_1 \sum_p e^{-iI_{z\omega t}} I_x e^{iI_{z\omega t}}. \tag{5}$$

Following the notation of Abragam[6] the random dipolar interaction is written

$$\hbar\mathcal{3C}_d(t) = \sum_{m=-2}^{+2} C^{(m)} F^{(m)} A^{(m)}. \tag{6}$$

The $A^{(m)}$ are spin operators, $F^{(m)}(t)$ time-dependent functions of the position coordinates, and the $C^{(m)}$ constants. They have the properties

$$A^{(m)} = A^{(-m)\dagger}, \quad F^{(m)} = F^{(-m)*}, \quad C^{(m)} = C^{(-m)}.$$

The dagger and asterisk denote the Hermitian conjugate and the complex conjugate, respectively.

$$A^{(0)} = I_{pz}I_{qz} - \tfrac{1}{4}(I_p^+I_q^- + I_p^-I_q^+),$$
$$A^{(1)} = I_{pz}I_q^+ + I_p^+I_{qz}, \tag{7}$$
$$A^{(2)} = I_p^+I_q^+,$$

where I^+ and I^- are the raising and lowering operators,

$$I^+ = I_x + iI_y, \quad I^- = I_x - iI_y;$$

$$C^{(0)} = \gamma^2\hbar, \quad C^{(1)} = -3\gamma^2\hbar/2, \quad C^{(2)} = -3\gamma^2\hbar/4. \tag{8}$$

$$F^{(0)} = (1 - 3\cos^2\beta_{pq})r_{pq}^{-3},$$
$$F^{(1)} = (\sin\beta_{pq}\cos\beta_{pq})e^{-i\phi_{pq}} r_{pq}^{-3}, \tag{9}$$
$$F^{(2)} = (\sin^2\beta_{pq})e^{-2i\phi_{pq}} r_{pq}^{-3}.$$

Calculation of the relaxation time in the rotating frame requires knowledge of the appropriate Hamiltonian. The laboratory-frame expression is transformed in three steps. The usual transformation procedure involving the unitary operator $e^{iI_{z\omega t}}$ gives the resonance rotating frame Hamiltonian. A new set of axes is chosen

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[1] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948), hereinafter referred to as B.P.P.
[2] D. Ailion and C. P. Slichter, Phys. Rev. Letters 12, 168 (1964).
[3] C. P. Slichter and D. Ailion, Phys. Rev. 135, A1099 (1964).
[4] D. C. Ailion and C. P. Slichter, Phys. Rev. 137, A235 (1965).
[5] A. G. Redfield, Phys. Rev. 98, 1787 (1955).

[6] A. Abragam, The Principles of Nuclear Magnetism (Clarendon Press, Oxford, England, 1961), p. 278 ff.

in the rotating frame with z' along H_e and x' in the H_0, H_1 plane. Finally a transformation into the frame rotating at velocity ω_e about H_e is accomplished using the operator $e^{iI_{z'}\omega_e t}$, i.e., into the doubly rotating frame.[7] Time-dependent terms are normally discarded from the rotating frame Hamiltonian, i.e., those arising from the nonsecular part of the laboratory frame expression. Since all relaxation mechanisms are to be taken into account it is imperative that the complete Hamiltonian be retained in this case. The final expression is:

$$
\begin{aligned}
\hbar\mathcal{K}_d' = \tfrac{1}{2}C^{(0)}F^{(0)}\Big[& (1-3\cos^2\theta)A^{(0)'} - \tfrac{3}{2}(\sin\theta\,\cos\theta)(A^{(1)'}e^{i\omega_e t}+A^{(-1)'}e^{-i\omega_e t}) \\
& -\tfrac{3}{4}(\sin^2\theta)(A^{(2)'}e^{i2\omega_e t}+A^{(-2)'}e^{-i2\omega_e t})\Big] + C^{(1)}F^{(1)}e^{i\omega_0 t}\big[(\sin 2\theta)A^{(0)'}+(\cos(\tfrac{3}{2}\theta)\,\cos(\tfrac{1}{2}\theta))A^{(1)'}e^{i\omega_e t} \\
& -(\sin(\tfrac{3}{2}\theta)\,\sin(\tfrac{1}{2}\theta))A^{(-1)'}e^{-i\omega_e t} - (\sin\theta\,\cos^2(\tfrac{1}{2}\theta))A^{(2)'}e^{i2\omega_e t}+(\sin\theta\,\sin^2(\tfrac{1}{2}\theta))A^{(-2)'}e^{-i2\omega_e t}\big] \\
& + C^{(-1)}F^{(-1)}e^{-i\omega_0 t}\big[(\sin 2\theta)A^{(0)'}-(\sin(\tfrac{3}{2}\theta)\,\sin(\tfrac{1}{2}\theta))A^{(1)'}e^{i\omega_e t}+(\cos(\tfrac{3}{2}\theta)\,\cos(\tfrac{1}{2}\theta))A^{(-1)'}e^{-i\omega_e t} \\
& +(\sin\theta\,\sin^2(\tfrac{1}{2}\theta))A^{(2)'}e^{i2\omega_e t}-(\sin\theta\,\cos^2(\tfrac{1}{2}\theta))A^{(-2)'}e^{-i2\omega_e t}\big] + C^{(2)}F^{(2)}e^{i2\omega_0 t} \\
& \times\big[(\sin^2\theta)A^{(0)'}+(\sin\theta\,\cos^2(\tfrac{1}{2}\theta))A^{(1)'}e^{i\omega_e t}-(\sin\theta\,\sin^2(\tfrac{1}{2}\theta))A^{(-1)'}e^{-i\omega_e t} \\
& +(\cos^4(\tfrac{1}{2}\theta))A^{(2)'}e^{i2\omega_e t}+(\sin^4(\tfrac{1}{2}\theta))A^{(-2)'}e^{-i2\omega_e t}\big] + C^{(-2)}F^{(-2)}e^{-i2\omega_0 t} \\
& \times\big[(\sin^2\theta)A^{(0)'}-(\sin\theta\,\sin^2(\tfrac{1}{2}\theta))A^{(1)'}e^{i\omega_e t}+(\sin\theta\,\cos^2(\tfrac{1}{2}\theta))A^{(-1)'}e^{-i\omega_e t} \\
& +(\sin^4(\tfrac{1}{2}\theta))A^{(2)'}e^{i2\omega_e t}+(\cos^4(\tfrac{1}{2}\theta))A^{(-2)'}e^{-i2\omega_e t}\big]. \quad (10)
\end{aligned}
$$

The $A^{(m)'}$ represent the spin operators defined with respect to the x', y', z' system of axes compared with the original x, y, z of the laboratory frame. The $F^{(m)}$ and $C^{(m)}$ components remain unchanged.

Inspection of the above expression shows the relevant frequencies for spin-lattice relaxation to be $\pm\omega_e$, $\pm 2\omega_e$, $\pm(\omega_0+\omega_e)$, $\pm(\omega_0-\omega_e)$, $\pm(\omega_0+2\omega_e)$, $\pm(\omega_0-2\omega_e)$, $\pm(2\omega_0+\omega_e)$, $\pm(2\omega_0-\omega_e)$, $\pm(2\omega_0+2\omega_e)$, and $\pm(2\omega_0-2\omega_e)$. The calculation of the relaxation time is carried out using the density-matrix master-equation procedure.

III. SPIN-LATTICE RELAXATION

Assuming an isotropic random motion of the spins, the correlation function $G^{(m)}(\tau)$ of $F^{(m)}(t)$ is defined[1]

$$\langle F^{(m)}(t)F^{(m)*}(t+\tau)\rangle_t = G^{(m)}(\tau).$$

$G(\tau)$ is assumed to be an even function of τ and independent of t, i.e., $G(\tau)$ is real. The spectral density $J^{(m)}(\tau)$ corresponding to $G^{(m)}(\tau)$ is real and even and given by

$$J^{(m)}(\omega) = \int_{-\infty}^{+\infty} G^{(m)}(\tau)e^{-i\omega\tau}d\tau.$$

Using the standard commutation relations between the components of angular momentum and the high-temperature approximation for the density matrix the doubly-rotating-frame Hamiltonian (10) yields for the two-spin case (rigorously for spin $\tfrac{1}{2}$)

$$
\begin{aligned}
\frac{1}{T_{1\rho}} = \tfrac{2}{3}I(I+1)\Big\{ & \tfrac{1}{4}(C^{(0)})^2\big[(9/4)(\sin^2\theta\,\cos^2\theta)J^{(0)}(\omega_e)+(9/4)(\sin^4\theta)J^{(0)}(2\omega_e)\big] \\
& + (C^{(1)})^2\big[(\cos^2(\tfrac{3}{2}\theta)\,\cos^2(\tfrac{1}{2}\theta))J^{(1)}(\omega_0+\omega_e)+(\sin^2(\tfrac{3}{2}\theta)\,\sin^2(\tfrac{1}{2}\theta))J^{(1)}(\omega_0-\omega_e)+4(\sin^2\theta\,\cos^4(\tfrac{1}{2}\theta))J^{(1)}(\omega_0+2\omega_e) \\
& + 4(\sin^2\theta\,\sin^4(\tfrac{1}{2}\theta))J^{(1)}(\omega_0-2\omega_e)\big] + (C^{(2)})^2\big[(\sin^2\theta\,\cos^4(\tfrac{1}{2}\theta))J^{(2)}(2\omega_0+\omega_e)+(\sin^2\theta\,\sin^4(\tfrac{1}{2}\theta))J^{(2)}(2\omega_0-\omega_e) \\
& + 4(\cos^8(\tfrac{1}{2}\theta))J^{(2)}(2\omega_0+2\omega_e)+4(\sin^8(\tfrac{1}{2}\theta))J^{(2)}(2\omega_0-2\omega_e)\big]\Big\}. \quad (11)
\end{aligned}
$$

This expression can be immediately generalized to the case when a large number of spins interact provided their motions are independent.

The correlation function $G^{(m)}(\tau)$ is normally assumed to be of the form

$$G^{(m)}(\tau) = \langle F^{(m)}(t)F^{(m)*}(t)\rangle_t e^{-|\tau|/\tau_c},$$

where τ_c is the correlation time. τ_c is further assumed to be the same for all the random functions where

$$J^{(m)}(\omega) = \langle F^{(m)}(t)F^{(m)*}(t)\rangle_t 2\tau_c(1+\omega^2\tau_c^2)^{-1},$$

and

$$J^{(0)}:J^{(1)}:J^{(2)} = |\langle F^{(0)}\rangle_t|^2 : |\langle F^{(1)}\rangle_t|^2 : |\langle F^{(2)}\rangle_t|^2 = 6:1:4.$$

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[7] A. Abragam, Ref. 6, p. 517 ff.

The expression (11) for $T_{1\rho}$ becomes

$$\frac{1}{T_{1\rho}} = K\left\{\frac{3}{2}\left[(\sin^2\theta\,\cos^2\theta)\frac{\tau_c}{1+\omega_e^2\tau_c^2}+(\sin^4\theta)\frac{\tau_c}{1+4\omega_e^2\tau_c^2}\right]\right.$$

$$+\left[(\cos^2(\tfrac{3}{2}\theta)\,\cos^2(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(\omega_0+\omega_e)^2\tau_c^2}+(\sin^2(\tfrac{3}{2}\theta)\,\sin^2(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(\omega_0-\omega_e)^2\tau_c^2}\right.$$

$$+(\sin^2\theta\,\cos^4(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(2\omega_0+\omega_e)^2\tau_c^2}+(\sin^2\theta\,\sin^4(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(2\omega_0-\omega_e)^2\tau_c^2}\Bigg]$$

$$+4\left[(\sin^2\theta\,\cos^4(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(\omega_0+2\omega_e)^2\tau_c^2}+(\sin^2\theta\,\sin^4(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(\omega_0-2\omega_e)^2\tau_c^2}\right.$$

$$+(\cos^8(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(2\omega_0+2\omega_e)^2\tau_c^2}+(\sin^8(\tfrac{1}{2}\theta))\frac{\tau_c}{1+(2\omega_0-2\omega_e)^2\tau_c^2}\Bigg]\Bigg\}. \quad (12)$$

This compares with the normal expression for T_1

$$\frac{1}{T_1}=K\left[\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right], \quad (13)$$

the K's being identical constants. Equation (12) becomes identical with Eq. (13) when θ becomes zero, i.e., ω_1 becomes zero or ω_e becomes infinite. For rapid motion, i.e., $\omega^2\tau_c^2\ll1$, both expressions reduce to $5K\tau_c$, $T_{1\rho}$ being independent of θ and equal to T_1.

Normally $T_{1\rho}$ is determined at exact resonance (i.e., $\theta=90°$) and with $\omega_1\ll\omega_0$. Under these conditions Eq. (12) becomes

$$\frac{1}{T_{1\rho}}=K\left[\frac{3}{2}\frac{\tau_c}{1+4\omega_e^2\tau_c^2}+\frac{5}{2}\frac{\tau_c}{1+\omega_0^2\tau_c^2}+\frac{\tau_c}{1+4\omega_0^2\tau_c^2}\right]. \quad (14)$$
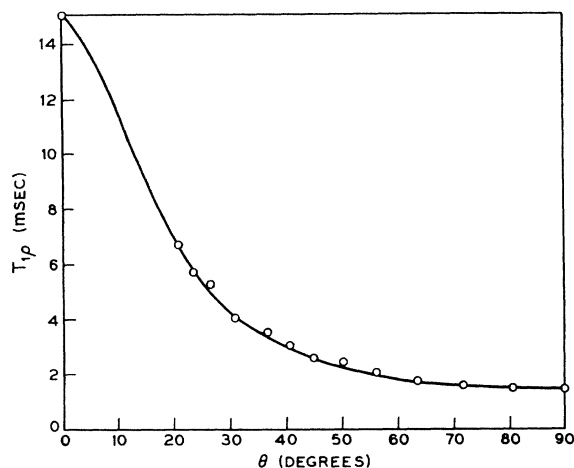

FIG. 1. $T_{1\rho}$ versus θ in tetramethylammonium iodide at 22°C. The circles denote the experimental data while the curve which is fitted at $\theta=0°$ γ 90° shows the predicted theoretical dependence. $H_1=3$ G and the rf frequency 30 MHz.

This is identical to an expression quoted by Look and Lowe.[8]

An experiment has been carried out to test the validity of the derived expression for the angular dependence of $T_{1\rho}$. Under the experimental conditions $\omega_e^2\tau_c^2\ll1$, $\omega_0^2\tau_c^2>1$, and $\omega_e\ll\omega_0$ the relevant expression from Eq. (12) becomes

$$\frac{1}{T_{1\rho}}=K\tau_c\left[\frac{3}{2}\sin^2\theta+\frac{1+\frac{3}{2}\sin^2\theta}{1+\omega_0^2\tau_c^2}+\frac{4-3\sin^2\theta}{1+4\omega_0^2\tau_c^2}\right]. \quad (15)$$

IV. EXPERIMENTAL

The apparatus used in this experiment is essentially the same as that previously described.[9] The rf field H_1 of 3 G was switched on with the main field-off resonance by h_0. The magnetization M_0 precesses about H_e, a component $M_0\cos\theta$ aligning itself along H_e in a time of approximately T_2. For large rf fields, i.e., $H_1\gg H_L$ (where H_L is the local nuclear dipolar field) the dipolar contribution to $T_{2\rho}$ is $\propto T_2|(1-3\cos^2\theta)^{-1}|$.[10] This reflects the behavior of the first term of the doubly-rotating-frame Hamiltonian [Eq. (10)], the secular component disappearing when $\theta=\cos^{-1}(1/\sqrt{3})$, the "magic angle." The longitudinal magnetization decays with the time constant $T_{1\rho}$, the progress of the decay being examined by means of the free induction signal following the termination of the rf pulse. In this experiment $T_{2\rho}\ll T_{1\rho}$ and did not complicate the interpretation.

All the experiments were carried out at room temperature (22°C). The material used was a solid (powder) sample of tetramethylammonium iodide obtained from K & K Laboratories, Plainview, New York. Proton re-

[8] D. C. Look and I. J. Lowe, Fourth Omnibus Conference on the Experimental Aspects of Nuclear Magnetic Resonance Spectroscopy, Mellon Institute, Pittsburgh, 1963 (unpublished).

[9] G. P. Jones, D. C. Douglass, and D. W. McCall, Rev. Sci. Instr. **36**, 1460 (1965).

[10] W. I. Goldburg and M. Lee, Phys. Rev. Letters **11**, 255 (1963).

laxation in the ammonium halides is thought to be due to reorientation of the ammonium ion[11,12] and in an analogous manner the relaxation in this case will be due to reorientation of the tetramethylammonium ion. Methyl group rotations will be very rapid at room temperature and their contribution to the relaxation time negligible. The ionic motion results in a sample T_2 of approximately 40 μsec at 22°C. $T_{1\rho}$ was determined for h_0's ranging from 0 to 8 G (from 90° to 20°) at an rf frequency of 30 MHz. T_1 was also determined at this frequency using the 180°–90° pulse sequence.

The $T_{1\rho}$ ($\theta = 90°$) minimum occurs at approximately $-30°C$ while the $T_1(30 \text{ MHz})$ minimum occurs above room temperature. The θ dependence of $T_{1\rho}$ at room temperature should therefore be given by Eq. (15). A plot of $T_{1\rho}$ versus θ is shown in Fig. 1. The experimental data are indicated by circles, the circle at $\theta = 0°$ being the T_1 point. Using the experimental data for $T_{1\rho}$ ($\theta = 90°$) and $T_1(30 \text{ MHz})$ and substituting in Eq. (15) gives a τ_c and K of 1.85×10^{-8} sec and 2.29×10^{10} sec^{-2},

respectively. The solid curve of Fig. 1 is the theoretical $T_{1\rho}$ determined from Eq. (15) using the above data for K and τ_c.

Under the experimental conditions, $\omega_0^2 \tau_c^2 = 12.1$ and therefore the second and third terms of Eq. (15) make only a second-order contribution to $T_{1\rho}$ for large θ's. As a result, the agreement of the experimental data and theoretical curve is mainly a test of the angular variation of that part of the Hamiltonian resulting from the secular terms in the laboratory frame. The relative importance of the terms can of course be varied by changing the temperature, i.e., varying τ_c.

The agreement between the theoretical curve and the experimental data is good being within the estimated experimental error of 6%. It can be concluded therefore that the weak-collision theory is valid in this case and the relaxation contributions at ω_e and $2\omega_e$ follow the expected dependency upon θ.

[11] A. H. Cooke and L. E. Drain, Proc. Phys. Soc. (London) A65, 894 (1952).
[12] H. S. Gutowsky, G. E. Pake, and R. Bersohn, J. Chem. Phys. 22, 643 (1954).

Photoelectric Effects in the Silver Halides*

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Measurements have been made of quantum yield for external photoemission from pure and doped silver halides and from samples with various surface preparations. Energy distribution curves for external photoelectrons were simultaneously determined. The quantum yield for external photoemission was found to rise smoothly from a threshold of about 6.2 eV to a yield of about 0.1 electrons per incident photon near 11-eV incident energy for pure AgCl. The bulk of external photoelectrons were found to emerge with a uniform distribution in energy between 0 and 2 eV for all incident energies (in contrast to alkali-halide results) with the exception of a small tail which moves in proportion to increasing incident energy. Only a slight indication of the onset of band-to-band scattering was found. Models to account for these results in terms of multiple electron-electron scattering, nonvertical transitions, and the contribution of the second valence band are discussed in light of the recent theoretical band scheme for the silver halides. Surface treatment and dopings of Cu$^+$ and Ni$^+$ (significant in terms of photographic and photoconductive effects) were found to have little effect on intrinsic photoelectric properties of AgCl.

I. INTRODUCTION

DESPITE the plethora of experimental observations on the optical and electrical properties of the silver halides,[1] surprisingly little about the details of

the energy bands has been inferred from first principles. Only in the last year has there been a band calculation available,[2] analogous to those for typical alkali halides or Si and Ge. Recent techniques have shown that con-

of Doctor of Philosophy at Cornell University, Ithaca, New York, 1964.
[1] See, e.g., F. C. Brown, J. Phys. Chem. 66, 2368 (1962) and cited references.
[2] R. S. Knox, F. Bassani, and W. B. Fowler, in *Photographic Sensitivity* (Maruzen and Company, Ltd., Tokyo, 1963), Vol. 3, p. 11; F. Bassani, R. S. Knox, and W. B. Fowler, Phys. Rev. 137, A1217 (1965).