their effect upon the ground state. The criterion for selecting the extended basis states was to include those vectors with significant ^6G composition (greater than 4%), since the major interactions between ground and excited states involves excited-state ^6G components only. Examination of the composition of the ground-state vector and all higher-lying multiplets indicates that the J-mixing contribution to the ground splitting from any other multiplets should be negligible.

No attempt was made to fit the data with this extended basis, since the matrices are so large. We merely assumed the previously calculated values of B_0^4 and B_0^6 and computed the crystal-field matrices with the extended basis and diagonalized them. This, of course, causes the quality of the previous fit to deteriorate somewhat; however, it was too slight to justify attempting a new fit with such large matrices, especially since we were seeking an effect in the ground state. The effect, unfortunately, did not appear. The over-all splitting of the ground state was only increased from 0.072 to 0.074 cm^{-1}. Thus, we were able to account for about half of the ground-state splitting with a calculation which is good to all orders within the basis used. It is felt then that further investigation of the ground-state free-ion state vector is merited.

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Spin-Lattice Relaxation in Periodically Perturbed Systems*

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Spin-lattice relaxation theory is examined, in the perturbation-theory regime, for nuclear spin systems which experience time-dependent forces not only from fluctuating spin-lattice interactions but also from externally produced periodic disturbances. These include strong steady rf fields (spin-locking and the Lee-Goldburg experiments), amplitude and phase-modulated rf fields (pulsed narrowing experiments), and modulation of the secular dipolar fields through rotation of the sample. It is shown for relatively slow molecular motions ($T_2 > \tau \gg \omega_0^{-1}$, where T_2 is the relaxation time, τ the correlation time, and ω_0 the rf frequency) that uncoupled Bloch equations can be obtained for suitably defined components of the magnetization. The spin-lattice relaxation times, which limit the degree of narrowing that can be obtained, depend in every case on Fourier components of the thermal motion in the neighborhood of the frequency of the periodic disturbance, and are of the same order of magnitude for all the experiments. Various narrowing experiments on substances having molecular motion are discussed.

I. INTRODUCTION

In recent years, a number of magnetic resonance experiments have been developed in which the behavior of the spins is influenced in an important way by a strong perturbation which is periodic in time. We have in mind the resonant spin locking[1,2] and Lee-Goldburg (LG) experiments,[3] in which the perturbation is a rf magnetic field applied on or off resonance; various multiple-pulse experiments,[4–8] in which a similar field is amplitude and/or phase modulated by a pulse train; and the sample-spinning experiments,[9–11] where a field inhomogeneity or an internal local field is modulated by rotating the sample with respect to the Zeeman field.

All these experiments have in common that, in a suitable frame of reference, some or all of the secular terms of the internal Hamiltonian become time-dependent and very often much less effective for spin-spin relaxation. It can be shown[8] that the secular decay of magnetization becomes describable by a weaker effective time-independent Hamiltonian. Therefore, speaking in terms of the Fourier transform of the decay, we may say that the periodic disturbance provides a means of line narrowing. Perhaps with the exception of the first one, all of the above-mentioned experiments have been motivated by this very fact and, correspondingly, have been treated theoretically and exploited

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experimentally most extensively for the rigid-lattice case, though molecular motions have also been considered by a number of authors.[8,12]

The ultimate limit of line narrowing achievable with these methods will be set by spin-lattice relaxation processes for which some kind of lattice motion is a prerequisite. This fact must be considered carefully in connection with any attempts to apply the narrowing experiments to samples which already display some degree of motional narrowing through thermal lattice motion. It seems that in a number of experiments where nonrigid samples have been used, spin-lattice relaxation is the cause of failure to achieve line narrowing[13] whereas in other instances, still with nonrigid samples, some line narrowing has been obtained with these methods.[13–16] It is the purpose of this paper to provide a consistent treatment of spin-lattice relaxation processes for these kinds of NMR experiments. We include some well-known cases in order to exhibit existing analogies and to facilitate comparisons. To end up with simple explicit results, we will ultimately specialize in each case to simple molecular motions characterized by a single correlation time τ_c, ignoring any correlations of the dipolar interactions of different pairs of nuclei.

A word about terminology may be in order: One is accustomed to use the terms "longitudinal," "spin lattice," and "T_1" more or less interchangeably. The same goes for "transverse," "spin spin," and "T_2". In the experiments discussed here, this is distinctly impossible. We choose to speak of spin-lattice relaxation whenever the lattice is involved in the relaxation process as an emitter or absorber of energy, and of spin-spin relaxation when the process can occur in an isolated spin system.

II. HAMILTONIAN AND FRAME OF REFERENCE

The Hamiltonian of the systems we shall consider consists in general, of three terms, which represent, respectively, the Zeeman, the rf, and the dipolar Hamiltonians:

$$\mathcal{H}=\mathcal{H}_Z+\mathcal{H}_{rf}+\mathcal{H}_d. \tag{1}$$

Nothing needs to be said about $\mathcal{H}_Z$. $\mathcal{H}_{rf}$ varies greatly from experiment to experiment. It is expressed most conveniently and also most directly not in the laboratory, but in the rotating spin frame. We shall do so in our examples. $\mathcal{H}_d$, the dipolar Hamiltonian (of a pair of identical spins i and k) in units of $\hbar$ and in its irreducible tensor notation assumes the form

$$\mathcal{H}_d=-\sqrt{(6\pi/5)}\gamma^2\hbar r_{ik}^{-3}(-1)^m Y_{2,-m}T_{2m}$$
$$=-\text{const}\times(-1)^m Y_{2,-m}T_{2m}. \tag{2}$$

The Einstein summation convention is used. The T_{2m}'s are second-rank tensor operators, formed with the components of the spin operators $\mathbf{I}^i$ and $\mathbf{I}^k$ (see Ref. 17). The remaining symbols have their usual meaning.

$\mathcal{H}_d$ is time-dependent explicitly through the dependence on time of the arguments of the Y_{2m}'s. The origin of this time dependence may be twofold: (i) molecular motion, (ii) physical motion of the bulk sample, as in the spinning-sample experiment. We indicate such and only such a physical motion of the bulk sample by writing $Y_{2m}(t)$ and $\mathcal{H}_d(t)$.

In Sec. III, we shall approach relaxation processes by perturbation theory. In order to do it successfully, it is necessary to choose an interaction representation which "removes" the Zeeman and the rf parts from the total Hamiltonian. In other words, it is necessary to go into a frame of reference in which no external fields show up explicitly. These frames of reference, and the form the total Hamiltonian assumes in them, are quite different in each case we shall investigate, and we shall rather carefully state them now.

A. Relaxation in the Zeeman Field

$\mathcal{H}_{rf}$ is zero, and $\mathcal{H}_Z$ is removed from $\mathcal{H}$ in the usual way by going into the rotating spin frame, laboratory space frame, in which

$$\mathcal{H}=-\text{const}\times(-1)^m Y_{2,-m}T_{2m}e^{im\omega_0 t}, \tag{3}$$

where $\omega_0=|\gamma|H$ and H is the strength of the static Zeeman field.

We note in passing that $\mathcal{H}$ as given by (3) does *not* transform as a scalar. Consequently, the density matrix ρ in the rotating frame is not a scalar either. This circumstance, rather surprising at first sight, arises from the fact that spin and space variables are measured with respect to different frames of reference which are accelerated with respect to one another.

B. Spin-Locking, LG, and Spinning-Sample Experiments

These experiments, seemingly so different, are in fact closely related and, in order to display the analogy, we shall treat them in parallel. Since they are fairly well known with respect to the matter we treat in this section, we do so briefly:

In the spin-locking and LG experiments, one writes the Hamiltonian in a frame which rotates in spin space but is stationary with respect to lattice variables, so as to make the rf field $2H_1\cos\omega t$ stationary:

$$\mathcal{H}=\Delta\omega I_z+\omega_x I_x-\text{const}\times(-1)^m Y_{2,-m}T_{2m}e^{im\omega_0 t}. \tag{4a}$$

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For the spinning-sample experiment, one begins in the same way, but recognizes that the lattice variables are time-dependent:

$$\mathcal{H}=-\text{const}\times(-1)^m Y_{2,-m}(t)T_{2m}e^{im\omega_0 t}. \quad (4b)$$

The time dependence of the Y_{2m}'s due to the spinning of the sample offsets in some sense the lack in Eq. (4b) of the first two terms in (4a), which originate from $\mathcal{H}_{rf}$ and a resonance offset characteristic of the LG experiment. In (4a), a tilting of the *spin* frame about the y axis through $\theta=\tan^{-1}(\omega_x/\Delta\omega)$ brings the (new) z axis along the effective field H_{eff} with $|\gamma|H_{\text{eff}}=\omega_e=(\omega_x^2+\Delta\omega^2)^{1/2}$. In (4b), a tilting of the *space* frame about the y axis through θ_r brings the (new) z axis along the rotation axis. Thus we have in the rotating, tilted spin, laboratory space frame for the spin-locking and LG experiments

$$\mathcal{H}=\omega_e I_z-\text{const}\times\mathfrak{D}_{mm'}{}^2 Y_{2,-m}T_{2m'}e^{im\omega_0 t}(-1)^m, \quad (5a)$$

and in the rotating spin, tilted space frame for the spinning-sample experiment

$$\mathcal{H}=-\text{const}\times(-1)^m\mathfrak{D}_{-m,-m'}{}^2 Y_{2,-m'}(t)T_{2m}e^{im\omega_0 t}. \quad (5b)$$

The Wigner rotation matrices[18] $\mathfrak{D}(\alpha,\beta,\gamma)$ are understood to have arguments $(0,\theta,0)$ in (5a) and $(0,\theta_r,0)$ in (5b), since these sets of Eulerian angles correspond to the indicated tiltings.

A rotation of the spin frame about the new z axis with angular velocity ω_e "removes" the term $\omega_e I_z$ from Eq. (5a). A similar rotation with angular velocity ω_r about the space-frame z axis "removes" the explicit time dependence from the Y_{2m}'s in Eq. (5b). Thus, we have in the rotating, tilted, rotating spin, laboratory space frame

$$\mathcal{H}=-\text{const}\times\mathfrak{D}_{mm'}{}^2 Y_{2,-m}T_{2m'}(-1)^m e^{im\omega_0 t}e^{im'\omega_e t}, \quad (6a)$$

and in the rotating spin, tilted, rotating space frame

$$\mathcal{H}=-\text{const}\times\mathfrak{D}_{-m,-m'}{}^2 Y_{2,-m'}T_{2m}(-1)^m \times e^{im\omega_0 t}e^{-im'\omega_r t}. \quad (6b)$$

The last space frame of reference in the spinning-sample experiment [Eq. (6b)] is a sample-fixed frame. In this frame, the space variables depend upon time only through molecular motion, and, consequently, we have dropped the argument (t) from the Y_{2m}'s in Eq. (6b).

Note that every factor in (6a) has its exact counterpart in Eq. (6b). Note also, to which indices the "slow" (ω_e,ω_r) and the "fast" (ω_0) oscillatory terms are related. In this respect, Eqs. (6a) and (6b) are different, and the difference is quite significant, since from now on spin and space variables are treated differently in the usual way.

By choosing $\theta=\frac{1}{2}\pi$ and dropping $m\neq 0$ terms, (6a) goes over into Redfield's dipolar Hamiltonian [Ref. 1, Eq. (21)]. By choosing $\theta=\cos^{-1}(3^{-1/2})$ and dropping $m\neq 0$ terms, (6a) goes over into the Hamiltonian pertaining to the LG experiment. Similarly, Eq. (6b) assumes the form usually used in the spinning-sample experiments, if we drop $m\neq 0$ terms.

[18] A. R. Edmonds, *Angular Momentum in Quantum Mechanics* (Princeton University Press, Princeton, N. J., 1957).

C. Combined Sample-Spinning and LG Experiment

One might be tempted to try to improve resolution in high-resolution NMR in solids (including high-molecular-weight solutions and highly viscous liquids) by performing at the same time two of the line-narrowing experiments. To see if something can be gained by such a procedure, we examine the simplest—at least conceptually, if not practically—of these experiments, which is the combined sample-spinning and LG experiment. A brief, more intuitive account has been given previously (8). The Hamiltonian pertinent to this case is obtained by combining Eqs. (6a) and (6b) with the result

$$\mathcal{H}=-\text{const}\times\mathfrak{D}_{-m,-m''}{}^2\mathfrak{D}_{mm'}{}^2(-1)^m Y_{2,-m''}T_{2m'}e^{im\omega_0 t} \times e^{im'\omega_e t}e^{-im''\omega_r t}. \quad (7)$$

The spin coordinates are measured [as in (6a)] in the rotating, tilted, rotating frame, the space coordinates [as in (6b)], in the tilted, rotating frame—the body-fixed frame. The arguments of the Wigner rotation matrices are the same as given in the text following Eqs. (5a) and (5b).

D. WHH Four-Pulse Experiment

In the rotating spin, laboratory space frame,

$$\mathcal{H}=\mathcal{H}_v(t)-\text{const}\times(-1)^m Y_{2,-m}T_{2m}e^{im\omega_0 t}. \quad (8)$$

$\mathcal{H}_v(t)$ is shown in Fig. 1(a). The index v suggests video and has been chosen for the characteristic time dependence of this Hamiltonian.

In a frame, moving as indicated in Fig. 1(b)—we call it the rotating, toggling spin frame of reference—$\mathcal{H}_v(t)$ drops out, and in this frame

$$\mathcal{H}=-\text{const}\times(-1)^m Y_{2,-m}\{\mathfrak{D}_{mm'}{}^2(0,0,0)P_z(t) +\mathfrak{D}_{mm'}{}^2(\tfrac{1}{2}\pi,-\tfrac{1}{2}\pi,-\tfrac{1}{2}\pi)P_x(t) +\mathfrak{D}_{mm'}{}^2(0,\tfrac{1}{2}\pi,0)P_y(t)\}T_{2m'}e^{im\omega_0 t}. \quad (9)$$

The space coordinates are still measured in the laboratory frame of reference. $P_x(t)$, $P_y(t)$, $P_z(t)\equiv P_r(t)$ are shown in Figs. 1(c)–1(e). Equation (9) results from Eq. (8) by expressing the T_{2m}'s of Eq. (8) in terms of the spin coordinates of the toggling frame by use of the Wigner rotation matrices. Equation (9) is a generalization of the $\bar{\mathcal{H}}(t)$ we used in Ref. 8, inasmuch as it encompasses the total dipolar Hamiltonian, not only its secular terms.

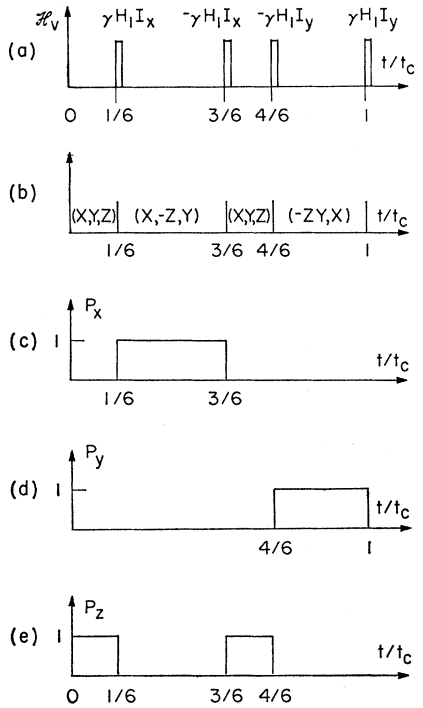

FIG. 1. (a) $\mathcal{H}_v(t)$. The widths t_p of the pulses are thought of as being infinitely short, but such that $\gamma H_1 t_p = \frac{1}{2}\pi$. Between the pulses $\mathcal{H}_v(t) = 0$. The sequence of pulses, shown above, is repeated at a rate $\omega_c/2\pi = 1/t_c$. (b) Rotating toggling spin frame of reference. The row vectors give the direction of the x, y, and z axes of the toggling frame in terms of the axes of the rotating frame. They are valid in the indicated intervals. (c), (d), and (e); $P_x(t)$, $P_y(t)$, and $P_z(t)$.

We expand $P_x(t)$ in Fourier series:

$$P_x(t) = \sum_{n=-\infty}^{+\infty} \mathbf{r}_n e^{in\omega_c t}, \quad \omega_c = 2\pi/t_c. \tag{10}$$

For the coefficients $\mathbf{r}_n$, we find $x_0 = y_0 = z_0 = \frac{1}{3}$ and, for $n \neq 0$,

$$y_n = (1/n\pi) e^{in\pi/3} \sin(n\pi/3), \tag{11a}$$

$$x_n = (-1)^n y_n, \tag{11b}$$

$$z_n = -(x_n + y_n). \tag{11c}$$

Note that $\mathbf{r}_{-n} = \mathbf{r}_n^*$. Inserting (10) into (9) gives

$$\mathcal{H} = -\text{const} \times (-1)^m Y_{2,-m} T_{2,m'} \times \sum_{n=-\infty}^{+\infty} \mathcal{C}_{mm'}{}^n e^{in\omega_c t} e^{im\omega_0 t}, \tag{12}$$

where

$$\mathcal{C}_{mm'}{}^n = \{\mathfrak{D}_{mm'}{}^2(0,0,0) z_n + \mathfrak{D}_{mm'}{}^2(\tfrac{1}{2}\pi, -\tfrac{1}{2}\pi, -\tfrac{1}{2}\pi) x_n + \mathfrak{D}_{mm'}{}^2(0, \tfrac{1}{2}\pi, 0) y_n\}.$$

The coefficients $\mathcal{C}_{mm'}{}^n$ are completely determined by the Wigner rotation matrices and Eqs. (11a)–(11c). Since we will not need all of them, we will postpone their further evaluation.

III. RELAXATION THEORY

We choose as our starting point the following equation of motion of the reduced-spin density matrix ρ [19]:

$$\frac{d\rho}{dt} = -\int_0^\infty d\tau \langle [\mathfrak{IC}(t), [\mathfrak{IC}(t-\tau), \rho]] \rangle_{\text{av}}. \tag{13}$$

The approximations inherent in Eq. (13) are thoroughly discussed by Abragam and will not be repeated here. $\mathfrak{IC}$ is the relaxation-causing Hamiltonian and is given, for our cases, by Eqs. (3), (6a), (6b), (7), and (12). We recall that these Hamiltonians are expressed in totally different frames of reference, and the same will be true for ρ. Contrary to our convention in Sec. II, here (t) includes all time dependences of $\mathfrak{IC}$ or Y_{2m} arising from thermal lattice motion or elsewhere.

A. Relaxation in the Zeeman Field

We include this case primarily to show how our approach applies to a well-known case. Also we believe that the exploitation of the properties of tensor operators renders the reasoning more direct than in the standard approach,[19] especially with regard to the step from the equation of motion of the density matrix to Bloch equations.

Insertion of (3) into (13) gives

$$\frac{d\rho}{dt} = -\frac{6\pi}{5}\frac{\gamma^4\hbar^2}{r^6}(-1)^{m+m'} e^{i(m+m')\omega_0 t} [T_{2,m}, [T_{2,m'}, \rho]] \times \int_0^\infty \langle Y_{2,-m}(t) Y_{2,-m'}(t-\tau) \rangle_{\text{av}} e^{-im'\omega_0\tau} d\tau. \tag{14}$$

Using the definition

$$\mathfrak{F}^m(\omega) = \int_0^\infty \langle Y_{2,-m}(t) Y_{2,m}(t-\tau) \rangle_{\text{av}} e^{i\omega\tau} d\tau = (-1)^m \int_0^\infty \langle Y_{2,m}{}^*(t) Y_{2,m}(t-\tau)_{\text{av}} \rangle e^{i\omega\tau} d\tau, \tag{15}$$

and restriction to secular terms in (14) leaves

$$\frac{d\rho}{dt} = -\frac{6\pi}{5}\frac{\gamma^4\hbar^2}{r^6} [T_{2,m}, [T_{2,-m}, \rho]] \mathfrak{F}^m(m\omega_0). \tag{16}$$

We multiply both sides of (16) by I_μ ($\mu = 1, 0, -1$) and take the trace, thus getting equations of motion for the expectation values of $I_1 = -(1/\sqrt{2}) I_+$, $I_0 = I_z$, $I_{-1} = (1/\sqrt{2}) I_-$.

The traces over the double commutators

$$\text{tr}\{[T_{2m}, [T_{2,-m}, \rho]] I_\mu\} = \text{tr}\{[T_{2,-m}, [T_{2,m}, I_\mu]] \rho\} \equiv \langle [T_{2,-m}, [T_{2,m}, I_\mu]] \rangle \tag{17}$$

are reduced to traces over single commutators by use

[19] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961), Chap. VIII, Eq. 33.

of the following commutation relations, valid for tensor operators[20]:

$$[I_{\pm1},T_{l,m}]=\mp[\tfrac{1}{2}(l\mp m)(l\pm m+1)]^{1/2}T_{l,m\pm1},\qquad [I_0,T_{l,m}]=mT_{l,m}. \tag{18}$$

Thus, we get

$$\left\langle\frac{dI_0}{dt}\right\rangle=-\frac{6\pi}{5}\frac{\gamma^4\hbar^2}{r^6}\langle[T_{2,m},T_{2,-m}]\rangle m\mathfrak{F}^m(m\omega_0), \tag{19}$$

$$\left\langle\frac{dI_{\pm1}}{dt}\right\rangle=-\frac{6\pi}{5}\frac{\gamma^4\hbar^2}{r^6}\langle[T_{2,m\pm1},T_{2,-m}]\rangle(\mp1)\times[\tfrac{1}{2}(2\mp m)(3\pm m)]^{1/2}\mathfrak{F}^m(m\omega_0). \tag{20}$$

From

$$T_{l_1m_1}T_{l_2m_2}=\sum_{l,m}T_{l,m}(l_1l_2lm\,|\,l_1m_1l_2m_2), \tag{21}$$

where $(\cdots|\cdots)$ are Clebsch-Gordan coefficients (in the notation of Edmonds), we get

$$[T_{2,m_1},T_{2,m_2}]=\sum_{l,m}T_{l,m}\{(22lm\,|\,2m_12m_2)-(22lm\,|\,2m_22m_1)\}, \tag{22}$$

and, because of the following symmetry relation [Ref. 18, Eq. (3.5.14)]

$$(l_1l_2lm\,|\,l_1m_1l_2m_2)=(-1)^{l_1+l_2-l}(l_2l_1lm\,|\,l_2m_2l_1m_1), \tag{23}$$

the only terms that survive in (22) are those with l odd, that is, $l=1,3$.

The $l=3$ terms cause trouble, for they lead to an equation of motion for $\langle I_\mu\rangle$ not consistent with the Bloch equations. Fortunately for $I=\frac{1}{2}$, $\langle T_{3m}\rangle=\mathrm{tr}\{T_{3m}\rho\}$ vanishes because in the matrix elements $(j_1m_1|T_{3m}|j_2m_2)$ the "triangle condition" $3+j_2\geqslant j_1\geqslant 3-j_2$ can never be met with j_1, $j_2=0$ or 1, which are the only values j_1 and j_2 can assume in a spin-$\frac{1}{2}$ system.

For the $l=1$ terms, we have by virtue of the Wigner-Eckart theorem[17]

$$\langle T_{1m}\rangle=c\langle I_m\rangle, \tag{24}$$

where c is a constant (with respect to m) and for which we get by direct evaluation of $\langle T_{10}\rangle$,

$$c=(\tfrac{1}{3}\sqrt{10})I(I+1). \tag{25}$$

Combining Eq. (25) with Eq. (22) and inserting the Clebsch-Gordan coefficients, we get (completely for $I=\frac{1}{2}$ and the $l=1$ contributions for $I\geqslant1$)

$$\langle[T_{22},T_{2,-2}]\rangle=\tfrac{4}{3}I(I+1)\langle I_0\rangle, \tag{26a}$$

$$\langle[T_{21},T_{2,-1}]\rangle=-\tfrac{2}{3}I(I+1)\langle I_0\rangle, \tag{26b}$$

$$\langle[T_{22},T_{2,-1}]\rangle=\tfrac{2}{3}\sqrt{2}I(I+1)\langle I_1\rangle, \tag{26c}$$

$$\langle[T_{21},T_{20}]\rangle=-(2/\sqrt{3})I(I+1)\langle I_1\rangle, \tag{26d}$$

$$\langle[T_{21},T_{2,-2}]\rangle=\tfrac{2}{3}\sqrt{2}I(I+1)\langle I_{-1}\rangle, \tag{26e}$$

$$\langle[T_{20},T_{2,-1}]\rangle=-(2/\sqrt{3})I(I+1)\langle I_{-1}\rangle. \tag{26f}$$

[20] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 84.

Inserting (26a) and (26b) in (19), we see immediately that we get a Bloch equation with

$$\frac{1}{T_0}=+\frac{4\pi}{5}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\{-\mathfrak{F}^1(\omega_0)-\mathfrak{F}^{-1}(-\omega_0)+4\mathfrak{F}^2(2\omega_0)+4\mathfrak{F}^{-2}(-2\omega_0)\}. \tag{27}$$

Inserting (26c)-(26f) into (20) we again get Bloch equations with

$$\frac{1}{T_{\pm1}}=\frac{4\pi}{5}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\{3\mathfrak{F}^0(0)+2\mathfrak{F}^{\mp2}(\mp2\omega_0)-2\mathfrak{F}^{\pm1}(\pm\omega_0)-3\mathfrak{F}^{\mp1}(\mp\omega_0)\}. \tag{28}$$

For random stationary motions, $\mathfrak{F}^{-m}(-\omega)=\mathfrak{F}^{m*}(\omega)$, the star indicating conjugate complex, so Eq. (27) gives a real quantity identical to $1/T_1$, whereas Eq. (28) give complex quantities, the real parts of which are equal and may be identified with $1/T_2$. The imaginary parts correspond to shifts. For a Gaussian-Markoff process with correlation time τ

$$\mathrm{Re}[\mathfrak{F}^m(\omega)]=(-1)^m(1/4\pi)[\tau/(1+\omega^2\tau^2)], \tag{29}$$

and with this we recover from (27) and (28) the familiar expressions[15] for T_1 and T_2:

$$\frac{1}{T_1}=\frac{2}{5}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\left(\frac{\tau}{1+\omega_0^2\tau^2}+\frac{4\tau}{1+4\omega_0^2\tau^2}\right), \tag{30}$$

$$\frac{1}{T_2}=\frac{1}{5}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\left(3\tau+\frac{5\tau}{1+\omega_0^2\tau^2}+\frac{2\tau}{1+4\omega_0^2\tau^2}\right). \tag{31}$$

B. Spin-Lattice Relaxation in the Spinning-Sample Experiment

By comparing the Hamiltonians of (3) and (6b), we see immediately that we can take over all our formulas from case A, provided we replace

$$Y_{2,-m}(t)\quad\text{by}\quad\mathfrak{D}_{-m,-m'}{}^2Y_{2,-m'}(t)e^{-im'\omega_rt},$$

which gives, consequently,

$$\mathfrak{F}_m(m\omega_0)=\mathfrak{D}_{-m,-m'}{}^2\mathfrak{D}_{m,m''}{}^2e^{-i(m'-m'')\omega_rt}\times\int_0^\infty\langle Y_{2,-m'}(t)Y_{2,m''}(t-\tau)\rangle_{\mathrm{av}}e^{i(m\omega_0-m''\omega_r)\tau}d\tau. \tag{32}$$

Now

$$\mathfrak{D}_{-m,-m'}{}^2=(-1)^{m-m'}\mathfrak{D}_{mm'}{}^{2*}$$

and

$$Y_{2,-m'}(t)=(-1)^{m'}Y_{2,m'}{}^*(t),$$

and, for *random* molecular motion,

$$\langle Y_{2m'}{}^*(t)Y_{2m''}(t-\tau)\rangle_{\mathrm{av}}=\delta_{m'm''}\langle Y_{2m'}{}^*(t)Y_{2m'}(t-\tau)\rangle_{\mathrm{av}},$$

which reduces (32) to

$$\mathfrak{F}^m(m\omega_0)=(-1)^m\sum_{m'}|\mathfrak{D}_{mm'}{}^2|^2 \times\int_0^\infty\langle Y_{2m'}{}^*(t)Y_{2m'}(t-\tau)\rangle_{\rm av}e^{i(m\omega_0-m'\omega_r)\tau}d\tau. \quad (33)$$

For a Gaussian-Markoff process, Eq. (33) gives

$$\mathfrak{F}^m(m\omega_0)=(-1)^m\frac{1}{4\pi}\sum_{m'}|\mathfrak{D}_{mm'}{}^2|^2\frac{\tau}{1+(m\omega_0-m'\omega_r)^2\tau^2}. \quad (34)$$

For $\omega_0\gg\omega_r$ and $m\neq0$, and thus for T_1, there is no dramatic change as compared to ordinary spin-lattice relaxation, treated in case A. However, in $1/T_{\pm1}$ or $1/T_2$, there is the term $m=0$, $\mathrm{Re}\mathfrak{F}^0(0)$ which dominates the others greatly for $\omega_0\tau\gg1$. This term changes by spinning the sample from $\tau/4\pi$ to

$$\frac{\tau}{4\pi}\sum_{m'}|\mathfrak{D}_{0m'}{}^2(0,\theta_r,0)|^2\frac{1}{1+(m'\omega_r\tau)^2} =\frac{\tau}{4\pi}\left(\frac{3\cos^2\theta_r-1}{2}+3\sin^2\theta_r\cos^2\theta_r\frac{1}{1+\omega_r{}^2\tau^2} +\tfrac{3}{4}\sin^4\theta_r\frac{1}{1+4\omega_r{}^2\tau^2}\right), \quad (35a)$$

which, for the magic angle $\theta_r=\tan^{-1}\sqrt{2}$, is

$$\frac{\tau}{4\pi}\frac{1}{3}\left(\frac{2}{1+\omega_r{}^2\tau^2}+\frac{1}{1+4\omega_r{}^2\tau^2}\right). \quad (35b)$$

This makes $1/T_2$ essentially become

$$\frac{1}{T_2}\approx\frac{1}{5}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\left(\frac{2\tau}{1+\omega_r{}^2\tau^2}+\frac{\tau}{1+4\omega_r{}^2\tau^2}\right). \quad (36)$$

We note that the condition for T_2 in the spinning-sample experiment to be considerably longer than the ordinary T_2 is not only $\omega_0\tau\gg1$, but also $\omega_r\tau\gg1$. It is very likely that failure to meet this last condition is the cause of the failure of some recent experiments,[13] in which it had been attempted to narrow broad lines of high-molecular-weight solutions by spinning the sample at the magic angle.

C. Relaxation in Tilted-Rotating Frame (Spin-Locking and LG Experiments)

Things get more complicated here. Elimination of the high-frequency terms in the equation of motion of the density matrix, that is, those terms which contain factors $e^{in\omega_0t}$, $n=m+m''\neq0$, does not select the proper T_{2m}'s in the sense that the rate of change of the $\langle I_\mu\rangle$, $\mu=1, 0, -1$, should be proportional to $\langle I_\mu\rangle$. The resulting "Bloch equations" are no longer decoupled. By inspecting the limiting case $\omega_e\to0$, θ finite, we see that this must be so indeed: In this limiting case, physically we come back to our case A. However, we are now in a different frame of spin coordinates. Rather than elaborate the general case, we shall restrict ourselves to $m=0$ in Eq. (6a). This amounts to discarding all high-frequency terms from the Hamiltonian itself, which then reads

$$\mathfrak{H}=-\mathrm{const}\times\mathfrak{D}_{0m}{}^2(0,\theta,0)Y_{20}(t)T_{2m}e^{im\omega_et}. \quad (37)$$

After putting $m=0$ in Eq. (6a), we have changed m' to m. By comparing (37) with (3) and recalling the results from Sec. III A, we find (i) $\langle I_1\rangle$, $\langle I_0\rangle$, $\langle I_{-1}\rangle$ in the rotating, tilted, rotating frame relax independently and exponentially with time constants T_0, T_{+1}, T_{-1}, and (ii) we get these time constants by replacing everywhere $(-1)^mY_{2m}(t)$ by $\mathfrak{D}_{0m}{}^2Y_{20}(t)$, and ω_0 by ω_e, which consequently gives

$$\mathfrak{F}^m(m\omega_e)=(-1)^m|\mathfrak{D}_{0m}{}^2|^2 \times\int_0^\infty\langle Y_{20}(t)Y_{20}(t-\tau)\rangle_{\rm av}e^{im\omega_e\tau}d\tau, \quad (38)$$

and, for a Markoff process,

$$\mathrm{Re}\mathfrak{F}^m(m\omega_e)=(-1)^m|\mathfrak{D}_{0m}{}^2|^2\frac{1}{4\pi}\frac{\tau}{1+(m\omega_e\tau)^2}. \quad (39)$$

We get T_0, $T_{\pm1}$ by inserting (38) or (39) into (27) and (28).

We proceed to discuss two important special cases.

1. $\theta=\frac{1}{2}\pi$: *Resonant-Spin Locking*

$$|\mathfrak{D}_{0,\pm2}{}^2|^2=\tfrac{3}{8},\ |\mathfrak{D}_{0,\pm1}{}^2|^2=0,\ |\mathfrak{D}_{00}{}^2|^2=\tfrac{1}{4} \quad \text{for } (\alpha,\beta,\gamma)=\left(0,\frac{\pi}{2},0\right),$$

which gives

$$\frac{1}{T_0}=\frac{3}{5}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\frac{\tau}{1+4\omega_e{}^2\tau^2}. \quad (40)$$

T_0 is identical with what is generally called $T_{1\rho}$ in the literature. We get also an expression for what might be called $T_{2\rho}$:

$$\mathrm{Re}\frac{1}{T_{\pm1}}=\frac{1}{T_{2\rho}}=\frac{3}{20}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\left(\tau+\frac{\tau}{1+4\omega_e{}^2\tau^2}\right). \quad (41)$$

In the "extreme narrowing" case $\omega_e\tau\ll1$ (but still $\omega_0\tau\gg1$), we get $T_{2\rho}=2T_{1\rho}$; for $\omega_e\tau\gg1$, $T_{1\rho}$ becomes larger than $T_{2\rho}$. Note that $T_{2\rho}$ is always longer than T_2, itself.

2. $\theta=\tan^{-1}\sqrt{2}$: Lee-Goldburg Experiment

$$|\mathfrak{D}_{0,\pm 2}{}^2|^2=\tfrac{1}{6},\quad |\mathfrak{D}_{0\pm 1}{}^2|^2=\tfrac{1}{3},\quad |\mathfrak{D}_{00}{}^2|^2=0,$$

$$\frac{1}{T_0}=\frac{2}{15}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\left(\frac{\tau}{1+\omega_e{}^2\tau^2}+\frac{2\tau}{1+4\omega_e{}^2\tau^2}\right), \quad (42)$$

$$\mathrm{Re}\frac{1}{T_{\pm 1}}=\frac{1}{15}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\left(\frac{5\tau}{1+\omega_e{}^2\tau^2}+\frac{\tau}{1+4\omega_e{}^2\tau^2}\right). \quad (43)$$

We postpone a discussion and a comparison of these times until we have completed cases D and E.

D. Combined LG and Sample-Spinning Experiment

We will treat this case only far enough to recognize the essential point, which is the following. The term in Eq. (31) that causes T_2 to become very short, when the correlation time τ becomes very long, is the term 3τ in the large parentheses, which has no large denominator. The outstanding feature of the magic angle experiments is the lack of such a term in the expressions for the relaxation times, see (36), (42), and (43). Now, in a combined LG and sample-spinning experiment such terms with no large denominators are reintroduced when $\omega_e=\omega_r$, but essentially also, when $\omega_e\approx\omega_r$. In the following, we confine ourselves to demonstrating this point.

From the Hamiltonian, as given by (7), we keep, of course, again only the terms with $m=0$.

By comparing the resulting Hamiltonian with (3), we see that we get the desired relaxation times by making the replacement in (3):

$$Y_{2,-m}(t)\rightarrow(-1)^m\mathfrak{D}_{0,-m'}{}^2(0,\theta_r,0)\times\mathfrak{D}_{0,m}{}^2(0,\theta,0)Y_{2,-m'}(t)e^{-im'\omega_r t},$$

which subsequently gives, after some manipulations including change of indices and for a Gaussian-Markoff process

$$\mathrm{Re}\mathfrak{F}^m(m\omega_e)=(-1)^m|\mathfrak{D}_{0m}{}^2(0,\theta,0)|^2\times\sum_{m'}|\mathfrak{D}_{0m'}{}^2(0,\theta_r,0)|^2\frac{1}{4\pi}\frac{\tau}{1+(m\omega_e-m'\omega_r)^2\tau^2}. \quad (44)$$

These expressions, for $m=-2\cdots+2$, have to be plugged into (27) and (28).

For the magic angle conditions $\theta=\theta_r=\tan^{-1}\sqrt{2}$,

$$|\mathfrak{D}_{00}{}^2(0,\theta,0)|^2=|\mathfrak{D}_{00}{}^2(0,\theta_r,0)|^2=0,$$

so in the equation for $1/T_{\pm 1}$, (28), the term $\mathfrak{F}^0(0)$ drops out. The other ones, $m=\pm 1,\pm 2$, however, for $\omega_e=\omega_r$ will all contain terms, where $m'\omega_r$ cancels $m\omega_e$ with the effect that for $\tau\rightarrow\infty$, T_2 does not become long as predicted by (36) and (43), but short as predicted by (31).

There may still be situations, where a combined LG–spinning-sample experiment might be useful: i.e., when anisotropic chemical-shift broadenings, which are unaffected by an LG type of experiment (or any of the multipulse experiments) prove to be troublesome. They may be removed by spinning the sample. The preceding considerations show that one should avoid choosing $\omega_e=\omega_r$, a better choice usually being $\omega_e\gg\omega_r$.

E. WHH Four-Pulse Experiment

The reader will accept it as only fair if again we restrict ourselves to the terms $m=0$. The Hamiltonian we have to deal with then reads

$$\mathcal{H}=-\text{const}\times Y_{20}T_{2m'}\sum_{n=-\infty}^{+\infty}\mathcal{C}_{0m'}{}^n e^{in\omega_c t}. \quad (45)$$

It is troublesome that the frequencies $n\omega_c$ are not related to the index m' of $T_{2m'}$. In our previous examples, frequencies had always been related to the components of the spherical tensors, and this had quite important consequences: Restriction to secular terms in the equation of motion of the density matrix left only such commutators $[T_{2m_1},T_{2m_2}]$ as to give decoupled Bloch equations.

However, as we shall show presently, the symmetry relations among the Wigner rotation matrices and the relations among the x_n, y_n, and z_n as given by (11a), (11b), (11c) result in

$$\mathcal{C}_{0\pm 1}{}^n\equiv 0,\quad \mathcal{C}_{00}{}^n=0 \text{ for } n \text{ odd, and } \mathcal{C}_{0\pm 2}{}^n=0 \text{ for } n \text{ even.}$$

So, essentially, we recover a relationship between the index m' of $T_{2m'}$ and the associated frequencies.

Table I gives the Wigner rotation matrices $\mathfrak{D}_{0m'}{}^2(\alpha,\beta,\gamma)$ for our three sets of (α,β,γ). We deduce immediately that $\mathcal{C}_{0\pm 1}{}^n\equiv 0$. This results from our applying only $\frac{1}{2}\pi$ pulses. With $x_0=y_0=z_0=\frac{1}{3}$ we also find $\mathcal{C}_{0m'}{}^0=0$.

By plugging x_n, y_n, and z_n as given by (11a), (11b), and (11c) and the numbers from Table I into the defining equation for $\mathcal{C}_{mm'}{}^n$, we get

$$\mathcal{C}_{00}{}^n=-\tfrac{3}{2}[1+(-1)^n]y_n=-\tfrac{3}{2}[1+(-1)^n]\frac{1}{n\pi}e^{in\pi/3}\sin(n\pi/3), \quad (46a)$$

$$\mathcal{C}_{0\pm 2}{}^n=\tfrac{1}{2}(\sqrt{\tfrac{3}{2}})[1-(-1)^n]y_n=\tfrac{1}{2}(\sqrt{\tfrac{3}{2}})[1-(-1)^n]\frac{1}{n\pi}e^{in\pi/3}\sin(n\pi/3). \quad (46b)$$

TABLE I. Numerical values for the Wigner rotation matrices.

m'	+2	+1	0	−1	−2
$\mathfrak{D}_{0m'}{}^2(0,0,0)$	0	0	1	0	0
$\mathfrak{D}_{0m'}{}^2(\frac{1}{2}\pi,-\frac{1}{2}\pi,-\frac{1}{2}\pi)$	$-\frac{1}{2}\sqrt{\frac{3}{2}}$	0	$-\frac{1}{2}$	0	$-\frac{1}{2}\sqrt{\frac{3}{2}}$
$\mathfrak{D}_{0m'}{}^2(0,\frac{1}{2}\pi,0)$	$\frac{1}{2}\sqrt{\frac{3}{2}}$	0	$-\frac{1}{2}$	0	$\frac{1}{2}\sqrt{\frac{3}{2}}$

Next, we insert the Hamiltonian (45) into the equation of motion of the density matrix ρ (Eq. 13), and get

$$\frac{d\rho}{dt}=-\text{const}^2\times\sum_{n'n''}e^{i(n'+n'')\omega_c t}\mathcal{C}_{0m'}{}^{n'}\mathcal{C}_{0m''}{}^{n''}\times[T_{2m'},[T_{2m''},\rho]]\int_0^\infty d\tau\times\langle Y_{20}(t)Y_{20}(t-\tau)\rangle_{\text{av}}e^{-in''\omega_c\tau}. \quad (47)$$

Restriction to secular terms ($n=n'=-n''$) leaves

$$\frac{d\rho}{dt}=-\text{const}^2\times\sum_n\mathcal{C}_{0m'}{}^n\mathcal{C}_{0m''}{}^{-n}[T_{2m'},[T_{2m''},\rho]]\times\int_0^\infty d\tau\langle Y_{20}(t)Y_{20}(t-\tau)\rangle_{\text{av}}e^{in\omega_c\tau}. \quad (48)$$

Multiplication of (48) by $I_0(=I_z)$, taking the trace, and using

$$\text{tr}\{[T_{2m'},[T_{2m''},\rho]I_0\}=\text{tr}\{[T_{2m''},[T_{2m'},I_0]]\rho\}=m'\langle[T_{2m'},T_{2m''}]\rangle \quad (49)$$

gives

$$\left\langle\frac{dI_0}{dt}\right\rangle=-\text{const}^2\times\sum_n\mathcal{C}_{0m'}{}^n\mathcal{C}_{0m''}{}^{-n}m'\times\langle[T_{2m'},T_{2m''}]\rangle\mathfrak{F}^0(n\omega_c). \quad (50)$$

We proceed to examine the double sum over m' and m'': Because $\mathcal{C}_{0\pm1}{}^n=0$, all terms with $m',m''=\pm1$ vanish. For n even, the only coefficients that do not vanish are the $\mathcal{C}_{00}{}^n$'s. But then the commutator vanishes, because $m'=m''=0$. We are thus left with n odd, and $m',m''=2,-2$ and $-2,2$. Using $\mathcal{C}_{0,2}{}^n\mathcal{C}_{0,-2}{}^{-n}=\mathcal{C}_{0,-2}{}^n\mathcal{C}_{0,2}{}^{-n}=|\mathcal{C}_{02}{}^n|^2$, which follows from (46b), and $\langle[T_{22},T_{2,-2}]\rangle=\frac{4}{3}I(I+1)\langle I_0\rangle$ [Eq. (26a)], we get

$$\left\langle\frac{dI_0}{dt}\right\rangle=-\text{const}^2\times\sum_{n\text{ odd}}|\mathcal{C}_{02}{}^n|^2\times(16/3)I(I+1)\langle I_0\rangle\mathfrak{F}^0(n\omega_c). \quad (51)$$

By inserting

$$\text{const}^2=(6\pi/5)(\gamma^4\hbar^2/r^6),$$

$$|\mathcal{C}_{02}{}^n|^2=(9/8\pi^2)(1/n^2)\quad\text{for } n \text{ odd, but not a multiple of 3,}$$

$$=0\quad\text{otherwise [see (46b)],}$$

and

$$\text{Re}\mathfrak{F}^0(n\omega_c)=\frac{1}{4\pi}\frac{\tau}{1+(n\omega_c\tau)^2}$$

into Eq. (51), and summing only over positive n, which brings in another factor 2, we finally get

$$\frac{1}{T_1}=\frac{2}{5}\frac{9}{\pi^2}I(I+1)\frac{\gamma^4\hbar^2}{r^6}\sum_n{}'\frac{1}{n^2}\frac{\tau}{1+(n\omega_c\tau)^2}. \quad (52)$$

The summation is over n positive, odd and not a multiple of 3. The term $n=1$ dominates all other ones. The weight of the next one, $n=5$ is already down by a factor of 25.

Turning now to $I_1=-(1/\sqrt{2})I_+$, the equation of motion, analogous to (50), becomes

$$\langle dI_1/dt\rangle=-\text{const}^2\times\sum_n\mathcal{C}_{0m'}{}^n\mathcal{C}_{0m''}{}^{-n}[\tfrac{1}{2}(2-m')(3+m')]^{1/2}\times\langle[T_{2m''},T_{2,m'+1}]\rangle\mathfrak{F}^0(n\omega_c). \quad (53)$$

From the double sum over m' and m'', only three terms survive, due to the properties of the $\mathcal{C}_{0m}{}^n$:

$m'=-2, m''=-2$: The T_{lm}'s contained in $[T_{2,-2}, T_{2,-1}]$ have $m=-3$, and so we can have only $l=4$ or 3. However, T_{lm}'s with l even are not contained in the commutator, and so we are left with $l=3$. We have shown, in Sec. III A, that for $I=\frac{1}{2}$, $\langle T_{3m}\rangle=0$ and, to be consistent, we drop these terms for any I.

$m'=-2, m''=2$: These terms vanish for n even but do survive for n odd.

$$\mathcal{C}_{0,-2}{}^n\mathcal{C}_{0,+2}{}^{-n}[\tfrac{1}{2}(4)(1)]^{1/2}\times\langle[T_{2,+2},T_{2,-1}]\rangle=(3/2\pi^2)(1/n^2)I(I+1)\langle I_1\rangle \quad (54)$$

for n odd, but not a multiple of 3.

$m'=0, m''=0$: These terms vanish for n odd, but do survive for n even $\neq0$.

$$\mathcal{C}_{00}{}^n\mathcal{C}_{00}{}^{-n}[\tfrac{1}{2}(2)(3)]^{1/2}\langle[T_{20},T_{21}]\rangle=(27/2\pi^2)(1/n^2)I(I+1)\langle I_1\rangle \quad (55)$$

for n even, but not a multiple of 3.

Inserting (54), (55), and the expressions for const and $\mathfrak{F}^0(n\omega_c)$ into (53), we get a Bloch equation decoupled from the equations of motion for $\langle I_{-1}\rangle$ and $\langle I_0\rangle$ with a time constant:

$$\text{Re}\frac{1}{T_{+1}}=\frac{1}{T_2}=\frac{3}{10}\frac{9}{\pi^2}\frac{\gamma^4\hbar^2}{r^6}I(I+1)\times\left\{3\sum_n\frac{1}{n^2}\frac{\tau}{1+(n\omega_c\tau)^2}+\frac{1}{3}\sum_m\frac{1}{m^2}\frac{\tau}{1+(m\omega_c\tau)^2}\right\}. \quad (56)$$

The sum over n runs over $n>0$, even and not a multiple of 3, the sum over m runs over $m>0$, odd and not a multiple of 3.

IV. SUMMARY AND DISCUSSION

We have shown that in a wide variety of NMR experiments Eq. (13),

$$\frac{d\rho}{dt}=-\int_0^\infty d\tau\langle[\mathfrak{IC}(t),[\mathfrak{IC}(t-\tau),\rho]]\rangle_{\text{av}},$$

with $\mathcal{H}$ being the dipolar Hamiltonian coupling two identical spins, under certain conditions leads to decoupled Bloch equations for the components of $\langle \mathbf{I} \rangle$. The required conditions are (i) we choose an appropriate frame of reference, which is the one in which no external fields, static or oscillatory, appear explicitly. (ii) We restrict ourselves to the famous secular terms of the dipolar Hamiltonian whenever—in the laboratory frame—rf fields are present during the relaxation process. (iii) We are dealing with spins with $I=\frac{1}{2}$ or we discard, for $I \geqslant 1$ terms, $\langle T_{3m} \rangle$ from the equations of motion of the components of $\langle \mathbf{I} \rangle$.

As we have noted earlier, the characteristic feature of the line-narrowing experiments is the removal of terms without "soaring" denominators from the expressions for the relaxation times. The remaining terms are very similar in all of these experiments. The decisive parameter is always some frequency Ω which is provided by the experimenter himself,

$\Omega=\omega_e$ in the spin-locking and LG experiments
$=\omega_r$ in the spinning-sample experiment
$=\omega_c$ in the WHH four-pulse experiment (and also in the other versions of the multipulse experiments).

The magnitude of Ω in practical experiments of all these types tends to be roughly the same (say, 10^4–10^5 sec^{-1}), and so the corresponding spin-lattice relaxation times T^+ and the limit they set to the narrowing are also similar. It is important to realize that this T^+ is *not* the ordinary spin-lattice relaxation time T_1 which limits the resolution of conventional NMR experiments, but is invariably shorter, and often, for relatively slow lattice motions, very much shorter. Of the various relaxation times in question, perhaps the most familiar is $T_{1\rho}$, the "rotating frame" spin-lattice relaxation time in a spin-locked system at resonance. Accordingly, one may use $T_{1\rho}^{-1}$ as a reasonable guide to the limiting resolution of any of the narrowing experiments.

T^+, like T_1, depends strongly on the rapidity of molecular motion. It is helpful to discuss various experimental situations in terms of the familiar schematic plot of Fig. 2: Consider first the situation labeled A, appropriate to a nearly rigid lattice. A narrowing experiment will apparently be highly successful, since $T^+ \gg T_2$. However, if really high resolution of, say, 1 Hz is desired, one must have $T^+ \approx 1$ sec. But if this is true, T_1, being several orders of magnitude longer, may be so long as to make the experiment unfeasible. (One must wait several T_1's for the spins to polarize before the experiment is performed or to recover to equilibrium after applications of a strong rf field.)

Now suppose the correlation time is shortened (perhaps by raising the temperature) until T_1 decreases to the convenient value of a few sec (case B). Since T^+ is still smaller than T_1 by several orders of magnitude, the degree of line narrowing which can be obtained is sharply curtailed. This situation is appropriate to many substances, including polymers near room temperature, which show some degree of motional narrowing. In several fluorocarbon polymers (including Teflon), we have observed limiting linewidths of 1–2 kHz near room temperature.[14]

The situation labeled C is even worse. It applies, for example, to viscous-liquid solutions of many high-molecular-weight substances, where a residue of dipolar broadening persists because of the relatively long rotational correlation time of the molecule. In such a case, it may well be that $T^+=T_2$, i.e., *no* further narrowing is obtainable. We believe this is the explanation for several reported failures[13] of the sample-spinning technique to narrow the NMR spectra of protein solutions.

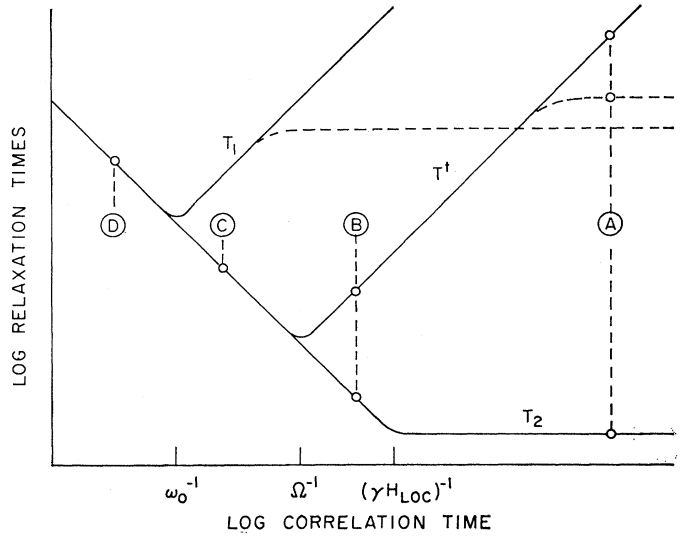

FIG. 2. Schematic dependence of relaxation times on correlation time for a simple lattice motion. The labels A–D refer to situations discussed in the text. The dashed curves emanating from the lines labeled T_1 and T^+ indicate the behavior of systems in which spin-lattice relaxation through the molecular motion is short circuited by spin-diffusion-controlled relaxation through paramagnetic centers.

Case D of Fig. 2 corresponds to extreme narrowing in a mobile liquid, where the narrowing experiments again fail ($T^+=T_2$), but are in any case academic ($T_1=T_2$).

Evidently, partial narrowing of a resonance through thermal motions is not a blessing, but a curse to the seeker after narrow resonances. Is there a way to defeat nature in this quest? The answer is in a sense affirmative, but requires, paradoxically, that the motion and the partial narrowing it provides be first eliminated. Imagine that the sample is cooled to a low temperature or otherwise immobilized, restoring case A. To avoid the problem of unbearably long T_1 we supply a suitable concentration of paramagnetic centers, either chemically or, perhaps, by suitable irradiation. The dominant spin-lattice process now becomes dependent on nuclear-electronic spin flips involving the nuclei near the paramagnetic centers, and equilibration of the nuclear system through spin diffusion. When, as often occurs, the bottleneck is the spin-diffusion process, T_1 becomes independent of temperature. The same is true of T^+, which may be longer or shorter than T_1. Under the conditions of effective narrowing experiments, it is in fact typically longer (and the relaxation is nonexponential).[12,21] These were the conditions of our successful experiments in paramagnetically doped CaF_2 [7,8] and $CaSO_4 \cdot 2H_2O$, in which there is not much effective molecular motion even at room temperature. We believe that similar results could be obtained rather generally in more mobile molecular solids by suitable doping and freezing. One should keep in mind that relaxation centers introduced by irradiation at a low temperature are likely to disappear unless the sample is kept cold until the NMR spectrum is obtained. Low temperatures —even that of liquid helium—are, of course, advantageous for obtaining intense magnetic resonance signals.

Before concluding, we hasten to emphasize that few substances have molecular motions as simple as Fig. 2 implies. More complex motions may well be involved in the few cases of motionally narrowed substances in which narrowing experiments have had a degree of success.[13–16] Consider the case of silicone rubber, whose ordinary NMR spectrum is much narrower than the rigid-lattice width at room temperature, yet in which both magic angle rotations[13] and the WHH experiment[16] are successful. One can imagine that the motional narrowing is due to rotation of the $-CH_3$ side chains at a rate so high as to have no appreciable spectral density near Ω, and that the residual width exists because the over-all motion of the chain is so slow that the spectral density of the inter $-CH_3$ interactions lies almost entirely at frequencies smaller than Ω. Under these circumstances any of the narrowing experiments will succeed in removing the inter $-CH_3$ dipolar coupling. One would also predict that $T_{1\rho}$, measured in an rf field of a few gauss, would be "anomalously" long. The case of aqueous solutions of poly-γ-benzyl glutamate in the helical configuration, reported by Cohn[13] to give narrowing of the aromatic proton resonances only in a spinning experiment, is more puzzling: Still, this is certainly another case of two or more different molecular motions on rather different time scales.

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[21] S. Clough and K. W. Gray, Proc. Phys. Soc. (London) **79**, 457 (1962).