

NUCLEAR MAGNETIC RELAXATION IN ROTATING FRAME

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The relaxation times $T_{1\theta}$ and $T_{2\theta}$ in the rotating frame are calculated in a weak-collision case. The dipolar, quadrupolar, spin-rotational, and scalar interactions are taken into account.

1. Introduction

The problem of nuclear magnetic relaxation in a rotating frame has been considered in several papers (Redfield 1955, Provotorov 1961, Ailion and Slichter 1964, 1965, Jones 1966, Look and Lowe 1966, Strange and Morgan 1970, Mansfield 1971). Redfield showed that when a spin system is subjected to an intense radiofrequency magnetic field H_1 the steady-state nuclear magnetization will be parallel to the effective field H_e in the rotating frame. This effect is called rotary saturation. The approach of longitudinal magnetization (along H_e) in the rotating frame to the steady-state value is characterized by the spin-lattice relaxation time in the rotating frame $T_{1\theta}$. Using the same nomenclature, the transverse or spin-spin relaxation time in the rotating frame is designated $T_{2\theta}$.

In the previous papers the problem of spin-lattice relaxation in the rotating frame was treated employing a strong-collision approach (Ailion and Slichter 1964, 1965) and a weak-collision approach (Jones 1966). The last approach is valid if the motional correlation time τ_c is much smaller than the spin-spin relaxation time in a rigid lattice.

The purpose of this paper is to calculate $T_{1\theta}$ and $T_{2\theta}$ in the weak-collision case in the presence of different types of random interactions.

2. Theory

Consider a system of identical nuclear spins I_i in the presence of an external magnetic field H_0 along z axis and radio-frequency field $2H_1 \cos \omega t$ along x axis of the laboratory frame. The oscillating field can be decomposed to two components rotating in the opposite

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senses in the xy plane. Only one of two rotating components is effective in inducing transitions between Zeeman levels of nuclear spins. The other component, which rotates in reverse sense to the precession of nuclear spins in the magnetic field H_0 , can be neglected unless H_1 is comparable to H_0 (Abragam 1961). The total spin Hamiltonian in the laboratory frame may be written in the form:

$$\mathcal{H} = \hbar(G_0 + G_1 + G(t)) \quad (1)$$

$$G_0 = -\gamma_I H_0 I_z \quad (2)$$

$$G_1 = -\gamma_I H_1 e^{-i\omega t I_z} I_x e^{i\omega t I_z} \quad (3)$$

$$G(t) = \sum_{m=-l}^l (-1)^m A_{lm} F_{l-m}(t) \quad (4)$$

$$I_z = \sum_i I_{zi} \quad (5)$$

where γ_I is the gyromagnetic ratio, G_0 and G_1 are Zeeman interactions of nuclear spins with the static field H_0 and radiofrequency field H_1 respectively, and $G(t)$ is a random interaction. This last can be presented as a scalar product of irreducible spherical tensors A_{lm} and F_{lm} , dependent on spin coordinates and random (*e.g.* spatial) coordinates respectively. The spin dependent tensors A_{lm} , called tensor operators, are considered in the Appendix. The time dependent tensors $F_{lm}(t)$ are treated as orthogonal and stationary random functions.

Generally, instead of a single random interaction one should take into account the sum of all possible random interactions. However, one can consider each of them separately provided that the time correlations between different random interactions are negligible. In this case the total relaxation rate (inverse of relaxation time) will be the sum of the rates following from the respective random interactions.

To calculate the relaxation times in the rotating frame one has to know the appropriate spin Hamiltonian. For this purpose it is necessary to transform the spin Hamiltonian (1) expressed in the laboratory frame, into a double rotating tilted frame (DRTF), in which the Zeeman terms G_0 and G_1 disappear and random interaction gives the only non-vanishing term $G_e(t)$ of the spin Hamiltonian.

According to the transformation properties of the tensor operators under rotation (Eq. (A.7)), the spin Hamiltonian $G_e(t)$ in DRTF may be presented in the form:

$$G_e(t) = O_R^{-1} G(t) O_R = \sum_{mm'} (-1)^m D_{mm'}^{(l)}(\alpha, \beta, \gamma) A_{lm} F_{l-m}(t). \quad (6)$$

The Euler angles α, β, γ for this transformation may be written in the form:

$$\begin{aligned} \alpha &= \omega t \simeq \omega_0 t \\ \beta &= \arctg \left(\frac{\omega_1}{\omega_0 - \omega} \right) \\ \gamma &= \omega_e t \end{aligned} \quad (7)$$

with

$$\begin{aligned}\omega_0 &= \gamma_I H_0 \\ \omega_1 &= \gamma_I H_1 \\ \omega_e &= \gamma_I H_e = \sqrt{(\omega_0 - \omega)^2 + \omega_1^2}\end{aligned}\quad (8)$$

where ω_0 and ω_e are Larmor precession angular frequencies of nuclear spins in the laboratory and rotating frame respectively, and β is the angle between direction of the field H_0 and H_e .

The time dependence of the expectation value $\langle Q \rangle(t)$ of an operator $Q = (I_z, I_{\pm})$ can be calculated on the basis of the theory of density operator σ , which gives

$$\langle Q \rangle(t) = \langle Q \sigma(t) \rangle. \quad (9)$$

Starting from the quantum mechanical equation of motion of density operator in DRTF

$$\frac{d\sigma}{dt} = -i[G_e(t), \sigma] \quad (10)$$

and using the method of successive approximations up to the second order (Abragam 1961), one can get

$$\frac{d\langle Q \rangle}{dt} = -(\langle B(Q) \rangle - \langle B(Q) \rangle_0) \quad (11)$$

$$\langle B(Q) \rangle = \frac{1}{2} \int_{-\infty}^{+\infty} \langle [G_e(t), [G_e(t-\tau), Q]] \rangle d\tau \quad (12)$$

where $\langle B(Q) \rangle_0$ is the statistical average of $B(Q)$ at the thermal equilibrium.

If $\langle B(Q) \rangle$ is the linear function of $\langle Q \rangle$ then one can calculate the relaxation times T_{1e} and T_{2e} in the rotating frame from the following equations:

$$\frac{1}{T_{1e}} = \frac{\langle B(I_z) \rangle}{\langle I_z \rangle} \quad (13)$$

$$\frac{1}{T_{2e}} = \frac{\langle B(I_+) \rangle}{\langle I_+ \rangle}. \quad (14)$$

The explicit form of $\langle B(Q) \rangle$ may be obtained by applying Eqs (6)–(7), (12), and (A8)–(A10). Taking into account only the secular part of $\langle B(Q) \rangle$, one gets

$$\begin{aligned}\langle B(Q) \rangle &= \frac{1}{2} \sum_{mm'} \langle |F_{lm}|^2 \rangle (d_{mm'}^{(l)}(\beta))^2 \times \\ &\times \langle [A_{lm'}, [A_{lm'}^*, Q]] \rangle j(m\omega_0 + m'\omega_e)\end{aligned}\quad (15)$$

where $j(\omega)$ is the reduced spectral density

$$j(\omega) = \int_{-\infty}^{+\infty} \frac{\langle F_{lm}(0)F_{lm}^*(\tau) \rangle}{\langle |F_{lm}|^2 \rangle} e^{i\omega\tau} d\tau. \quad (16)$$

Under the assumption that the correlation function $\langle F_{lm}(0)F_{lm}^*(\tau) \rangle$ obeys the relation

$$\langle F_{lm}(0)F_{lm}^*(\tau) \rangle = \langle |F_{lm}|^2 \rangle e^{-\frac{|\tau|}{\tau_c}} \quad (17)$$

one can get

$$j(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2} \quad (18)$$

where

$$\pi^{-1} \int_0^{\infty} j(\omega) d\omega = 1. \quad (19)$$

In the detailed calculation of the relaxation rate in the rotating frame presented below we consider separately the relaxation contributions produced by different interactions. In the first approximation we neglect the interference of different types of interactions (Blicharski 1969). The interference effect in nuclear magnetic relaxation in the rotating frame will be considered elsewhere.

3. Dipolar relaxation

We consider a system of two identical and equivalent nuclei of spin I . The Hamiltonian of dipolar interaction between these nuclei can be written in the form

$$G_d(t) = \sum_{m=-2}^{+2} (-1)^m A_{2m}(I_1, I_2) F_{2-m}(t) \quad (20)$$

with

$$F_{2m}(t) = -2\hbar\gamma_1^2 r^{-3} C_{2m}(\theta(t), \varphi(t)) \quad (21)$$

where $\theta(t)$ and $\varphi(t)$ are the time dependent angles defining the orientation of internuclear vector $\mathbf{r} = \mathbf{r}_{12}$ joining the two nuclei, with respect to the laboratory frame.

To calculate the dipolar contributions to the relaxation rate in the rotating frame from the Eqs (13)–(15) and Eqs (20)–(21) we have to find the average values $\langle |C_{lm}|^2 \rangle$ and $\langle [A_{lm}, [A_{lm}^*, Q]] \rangle$. In the calculation we assume isotropic molecular reorientations. Under the last assumption one finds

$$\langle |C_{lm}|^2 \rangle = \frac{1}{2I+1}. \quad (22)$$

From the commutation relations for the tensor operators $A_{lm}(I_1 I_2)$ it follows that

$$\langle [A_{2m}, [A_{2m}^*, I_z]] \rangle = \frac{1}{4} m^2 I(I+1) \langle I_z \rangle \quad (23)$$

$$\langle [A_{2m}, [A_{2m}, I_+]] \rangle = \frac{1}{8} (m+2)(3-m)I(I+1) \langle I_+ \rangle. \quad (24)$$

Finally from Eqs. (13)–(15) and (21)–(24) one finds the general expression for T_{1e} and T_{2e} :

$$\frac{1}{T_{1e}} = \frac{I(I+1)\hbar^2\gamma^4 r^{-6}}{10} \sum_{mm'} (d_{mm'}^{(2)}(\beta))^2 \times \\ \times m'^2 j(m\omega_0 + m'\omega_e) \quad (25)$$

$$\frac{1}{T_{2e}} = \frac{I(I+1)\hbar^2\gamma^4 r^{-6}}{20} \sum_{mm'} (d_{mm'}^{(2)}(\beta))^2 \times \\ \times (m'+2)(3-m')j(m\omega_0 + m'\omega_e). \quad (26)$$

Introducing Eqs (18), (A.10), and Table II into Eq. (25) one gets a formula for T_{1e} identical with that presented by Jones (1966), whereas Eq. (26) leads to the following expressions for T_{2e}

$$\frac{1}{T_{1e}} = \frac{I(I+1)\hbar^2\gamma^4 r^{-6}}{5} \left[\frac{3}{4} (3 \cos^2 \beta - 1)^2 \tau_c + \frac{15}{8} \sin^2 2\beta \frac{\tau_c}{1 + \omega_e^2 \tau_c^2} + \right. \\ \left. + \frac{3}{4} \sin^4 \beta \frac{\tau_c}{1 + 4\omega_e^2 \tau_c^2} + \frac{9}{4} \sin^2 2\beta \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \right. \\ \left. + 5 \left(\cos \frac{3\beta}{2} \cos \frac{\beta}{2} \right)^2 \frac{\tau_c}{1 + (\omega_0 + \omega_e)^2 \tau_c^2} + 5 \left(\sin \frac{3\beta}{2} \sin \frac{\beta}{2} \right)^2 \frac{\tau_c}{1 + (\omega_0 - \omega_e)^2 \tau_c^2} + \right. \\ \left. + 2 \sin^2 \beta \cos^4 \frac{\beta}{2} \frac{\tau_c}{1 + (\omega_0 + 2\omega_e)^2 \tau_c^2} + 2 \sin^2 \beta \sin^4 \frac{\beta}{2} \frac{\tau_c}{1 + (\omega_0 - 2\omega_e)^2 \tau_c^2} + \right. \\ \left. + \frac{9}{4} \sin^4 \beta \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} + 5 \sin^2 \beta \cos^4 \frac{\beta}{2} \frac{\tau_c}{1 + (2\omega_0 + \omega_e)^2 \tau_c^2} + \right. \\ \left. + 5 \sin^2 \beta \sin^4 \frac{\beta}{2} \frac{\tau_c}{1 + (2\omega_0 - \omega_e)^2 \tau_c^2} + 2 \cos^8 \frac{\beta}{2} \frac{\tau_c}{1 + (2\omega_0 + 2\omega_e)^2 \tau_c^2} + \right. \\ \left. + 2 \sin^8 \frac{\beta}{2} \frac{\tau_c}{1 + (2\omega_0 - 2\omega_e)^2 \tau_c^2} \right]. \quad (27)$$

As a special case we can get from Eqs (25)–(26) and (18) the well-known expressions for relaxation times T_1 and T_2 in the laboratory frame (Abragam 1961). Namely, for $\omega_e = 0$, $\beta = 0$, and $d_{mm'}^{(l)}(0) = \delta_{mm'}$ ($\delta_{mm'}$ — Kronecker's delta) it follows that:

$$\frac{1}{T_1} = \left(\frac{1}{T_{1e}} \right)_{\omega_e = \beta = 0} = \frac{1}{5T_D} \sum_{m=1}^2 \frac{m^2}{1+m^2\tau_c^2} \quad (28)$$

$$\begin{aligned} \frac{1}{T_2} &= \left(\frac{1}{T_2} \right)_{\omega_e = \beta = 0} = \frac{1}{20T_D} \sum_{m=-2}^{+2} \frac{(m+2)(3-m)}{1+m^2\omega_0^2\tau_c^2} = \\ &= \frac{1}{10T_D} \left[3 + \frac{5}{1+\omega_0^2\tau_c^2} + \frac{2}{1+4\omega_0^2\tau_c^2} \right] \end{aligned} \quad (29)$$

where T_D is the asymptotic value of T_1 and T_2 in the extreme narrowing case $\omega_0\tau_c \ll 1$ (rapid motion)

$$\frac{1}{T_D} = 2I(I+1)\hbar^2\gamma^4r^{-6}\tau_c. \quad (30)$$

In the case $\omega_0 \gg \omega_e$, which usually take place under experimental conditions, one can get

$$\begin{aligned} \frac{1}{T_{1e}} &= \frac{1}{10T_D} \left[\frac{3 \sin^2 \beta \cos^2 \beta}{1+\omega_e^2\tau_c^2} + \frac{3 \sin^4 \beta}{1+4\omega_e^2\tau_c^2} + \right. \\ &\quad \left. + \frac{2+3 \sin^2 \beta}{1+\omega_0^2\tau_c^2} + \frac{8-6 \sin^2 \beta}{1+4\omega_0^2\tau_c^2} \right] \end{aligned} \quad (31)$$

$$\begin{aligned} \frac{1}{T_{2e}} &= \frac{1}{40T_D} \left[3(3 \cos^2 \beta - 1)^2 + \frac{30 \sin^2 \beta \cos^2 \beta}{1+\omega_e^2\tau_c^2} + \right. \\ &\quad \left. + \frac{3 \sin^4 \beta}{1+4\omega_e^2\tau_c^2} + \frac{20-6 \sin^2 \beta}{1+\omega_0^2\tau_c^2} + \frac{8+12 \sin^2 \beta}{1+4\omega_0^2\tau_c^2} \right]. \end{aligned} \quad (32)$$

Using Eqs (31)–(32) one can easily find that in the case $\omega_0 \gg |\omega - \omega_0| \gg \omega_1$ the values T_{1e} and T_{2e} are equal to T_1 and T_2 respectively, whereas for $\omega_0\tau_c \ll 1$ all four considered relaxation times are equal to T_D . The last situation can be present in liquids of low viscosity.

Normally T_{1e} is determined at exact resonance, for $\omega = \omega_0$, $\beta = \pi/2$ and $\omega_1 \ll \omega_0$. The same definition can be applied for T_{2e} . After substitution of $\beta = \pi/2$ and $\omega_e = \omega_1$ into Eqs (21) and (32) it follows that

$$\frac{1}{T_{1e}} = \frac{1}{10T_D} \left[\frac{3}{1+\omega_1^2\tau_c^2} + \frac{5}{1+\omega_0^2\tau_c^2} + \frac{2}{1+4\omega_0^2\tau_c^2} \right] \quad (33)$$

$$\frac{1}{T_{2e}} = \frac{1}{40T_D} \left[3 + \frac{3}{1+4\omega_1^2\tau_c^2} + \frac{14}{1+\omega_0^2\tau_c^2} + \frac{20}{1+4\omega_0^2\tau_c^2} \right] \quad (34)$$

where the expression (33) is identical to that quoted by Look and Lowe (1966). One can easily observe that in the case $\omega_1\tau_c \ll 1$ it follows that $T_{1e} = T_2$, whereas for $\omega_0\tau_c \ll 1$ each of the relaxation times is equal to T_D .

4. Quadrupole relaxation

As an example we consider a nucleus of spin $I = 1$. This nucleus, possessing the quadrupole moment eQ , can interact with the gradient of electric field eq produced by molecular surroundings. If we assume the axial symmetry of the electric field tensor then the Hamiltonian of the quadrupole interaction may be written in the form

$$G_Q(t) = \sum_{m=-2}^{+2} (-1)^m A_{2m}(I) F_{2-m}(t) \quad (35)$$

$$F_{2m}(t) = \frac{e^2 Q q}{2I(2I-1)\hbar} C_{2m}(\theta(t), \varphi(t)) \quad (36)$$

where $\theta(t)$ and $\varphi(t)$ are the time dependent angles defining the orientation of the symmetry axis.

To calculate the quadrupole contribution to the relaxation rate we observe that in the case $I = 1$ the tensor operators $A_{2m}(I)$ obey commutation relations similar to those for the tensors $A_{2m}(I_1, I_2)$, namely:

$$\langle [A_{2m}(I), [A_{2m}^*(I), I_z]] \rangle = \frac{3}{4} m^2 \langle I_z \rangle \quad (37)$$

$$\langle [A_{2m}(I), [A_{2m}^*(I), I_+]] \rangle = \frac{3}{8} (m+2)(3-m) \langle I_+ \rangle. \quad (38)$$

As a final result one gets the quadrupole contributions $1/T_{1e}$ and $1/T_{2e}$ which are similar to the dipolar ones.

$$\frac{1}{T_{1e}} = \frac{3}{40} \left(\frac{e^2 q Q}{\hbar} \right)^2 \sum_{mm'} (d_{mm'}^{(2)}(\beta))^2 m'^2 j(m\omega_0 + m'\omega_e) \quad (39)$$

$$\frac{1}{T_{2e}} = \frac{3}{80} \left(\frac{e^2 q Q}{\hbar} \right)^2 \sum_{mm'} (d_{mm'}^{(2)}(\beta))^2 (m'+2)(3-m') j(m\omega_0 + m'\omega_e). \quad (40)$$

In the extreme narrowing case ($\omega_0\tau_c \ll 1$) and for $\beta = 0$ and $\beta = \pi/2$ the asymptotic value of the considered times are equal to T_Q , where

$$\frac{1}{T_Q} = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar} \right)^2 \tau_c. \quad (41)$$

One can easily see that Eqs (27)–(29) and (31)–(34) are valid also for quadrupole relaxation contributions for nuclear spin $I = 1$ provided that one replaces T_D by T_Q . Moreover, if there is not axial symmetry of the electric field tensor then T_Q may be expressed in the form (Abragam 1961)

$$\frac{1}{T_Q} = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar} \right)^2 \left(1 + \frac{\eta^2}{3} \right) \tau_c \quad (42)$$

where η is the asymmetry parameter.

5. Spin-rotational relaxation

As a simple example we consider a nucleus of spin I in a linear molecule with molecular angular momentum J . The interaction between the magnetic moment of the nucleus and the magnetic field $H_J = H'J$ produced by molecular rotation, called spin-rotation interaction, may be written in the form (Ramsey 1956, Abragam 1961)

$$G_r(t) = -\gamma_I \mathbf{I} \cdot \mathbf{H}_J(t) = -c_I \mathbf{I} \cdot \mathbf{J}(t) \quad (43)$$

where $c_I = \gamma_I H'$ is the spin-rotation constant and the components of $\mathbf{J}(t)$ are random functions of time. The above expression may be written as a special case of Eqs (4), namely

$$G_r(t) = \sum_{m=-1}^{+1} (-1)^m A_{1m}(\mathbf{I}) F_{1-m}(t) \quad (44)$$

$$F_{1m}(t) = -c_I A_{1m}(\mathbf{J}(t)) \quad (45)$$

To calculate the spin-rotational contributions to the relaxation times T_{1e} and T_{2e} it is necessary to evaluate the double commutators and spectral density of the correlation functions in Eqs (15)–(16). From the commutation relations (A5)–(A6) and Bloch equations for the vector \mathbf{J} in the field H_0 it follows that

$$\langle [A_{1m}(\mathbf{I}), [A_{1m}^*(\mathbf{I}), I_z]] \rangle = m^2 \langle I_z \rangle \quad (46)$$

$$\langle [A_{1m}(\mathbf{I}), [A_{1m}^*(\mathbf{I}), I_+]] \rangle = \frac{1}{2}(1+m)(2-m) \langle I_+ \rangle \quad (47)$$

$$\langle F_{1m}(0) F_{1m}^*(\tau) \rangle = \frac{1}{3} c_I^2 \langle J(J+1) \rangle e^{-m\omega_J \tau} e^{-\frac{|\tau|}{\tau_c}} \quad (48)$$

$$j(\omega) = \frac{2\tau_c}{1 + (\omega - m\omega_J)^2 \tau_J^2} \quad (49)$$

where ω_J is Larmor precession angular frequency for the vector \mathbf{J} and τ_J is the correlation time for the spin-rotational interaction.

Using the above-presented expressions and Eqs (13)–(15) one can find that

$$\begin{aligned} \frac{1}{T_{1e}} &= \frac{1}{6} c_I^2 \langle J(J+1) \rangle \sum_{mm'} (d_{mm'}^{(1)}(\beta))^2 m'^2 j(m\omega_0 + m'\omega_e) = \\ &= \frac{1}{2T_R} \left[\frac{\sin^2 \beta}{1 + \omega_e^2 \tau_J^2} + \frac{2 \sin^4 \frac{\beta}{2}}{1 + (\omega_0 - \omega_J - \omega_e)^2 \tau_J^2} + \frac{2 \cos^4 \frac{\beta}{2}}{1 + (\omega_0 - \omega_J + \omega_e)^2 \tau_J^2} \right] \end{aligned} \quad (50)$$

$$\begin{aligned} \frac{1}{T_{2e}} &= \frac{1}{12} c_I^2 \langle J(J+1) \rangle \sum_{mm'} (d_{mm'}^{(1)}(\beta))^2 (1+m')(2-m') j(m\omega_0 + m'\omega_e) = \\ &= \frac{1}{4T_R} \left[2 \cos^2 \beta + \frac{\sin^2 \beta}{1 + \omega_e^2 \tau_J^2} + \frac{2 \sin^2 \beta}{1 + (\omega_0 - \omega_J)^2 \tau_J^2} + \right. \\ &\quad \left. + \frac{2 \sin^4 \frac{\beta}{2}}{1 + (\omega_0 - \omega_J - \omega_e)^2 \tau_J^2} + \frac{2 \cos^4 \frac{\beta}{2}}{1 + (\omega_0 - \omega_J + \omega_e)^2 \tau_J^2} \right] \end{aligned} \quad (51)$$

$$\frac{1}{T_R} = \frac{2}{3} c_I^2 \langle J(J+1) \rangle \tau_J. \quad (52)$$

Under the resonance conditions ($\beta = \pi/2$) and for $\omega_1 \ll |\omega_0 - \omega_J|$ one finds

$$\frac{1}{T_{1e}} = \frac{1}{2T_R} \left(\frac{1}{1 + \omega_1^2 \tau_J^2} + \frac{1}{1 + (\omega_0 - \omega_J)^2 \tau_J^2} \right) \quad (53)$$

$$\frac{1}{T_{2e}} = \frac{1}{4T_R} \left(\frac{1}{1 + \omega_1^2 \tau_J^2} + \frac{1}{1 + (\omega_0 - \omega_J)^2 \tau_J^2} \right). \quad (54)$$

6. Scalar relaxation

Consider a system of two non-identical nuclei of spins I and S , where I is the resonant spin and S is the non-resonant one. These two nuclear spins may be coupled *via* electron spins. This coupling, called indirect spin-spin interaction or scalar interaction, may be expressed by the following Hamiltonian (Gutowsky and McCall 1951)

$$G_{Sc} = -J_{IS} \mathbf{I} \cdot \mathbf{S} \quad (55)$$

where J_{IS} is the scalar coupling constant.

In the case of a sufficiently fast spin exchange characterized by the exchange time constant τ_e (where $\tau_e \ll J_{IS}^{-1} \ll T_1$), the above Hamiltonian may be treated as time dependent perturbation where $J_{IS} = J_{IS}(t)$ is a random function obeying the following relation

(Solomon and Bloembergen 1956)

$$\langle J_{IS}(0)J_{IS}(\tau) \rangle = J_{IS}^2 e^{-\frac{|\tau|}{\tau_e}} \quad (56)$$

There is also a second mechanism which gives a fast modulation of the scalar interaction. Namely, in the case of spins $I = 1/2$ and $S \geq 1$ the quadrupole interaction leads to very short relaxation times τ_1 and τ_2 for spin S ($\tau_1 \ll J_{IS}^{-1}$), whereas relaxation times T_1 and T_2 for spin I are much longer than those for spin S . Under these circumstances, the spins S may be considered as a part of the lattice and the components of the vector \mathbf{S} in the Hamiltonian (55) may be treated as random functions (Abragam 1961), where

$$\langle S_z(0)S_z(\tau) \rangle = \frac{1}{3}S(S+1)e^{-\frac{|\tau|}{\tau_1}} \quad (57)$$

$$\langle S_{\pm}(0)S_{\pm}^*(\tau) \rangle = \frac{2}{3}S(S+1)e^{\mp i\omega_S \tau} e^{-\frac{|\tau|}{\tau_2}} \quad (58)$$

Taking into account both mechanisms of the scalar relaxation and Eqs (A11)–(A12), one can present the Hamiltonian (55) in the general form

$$G_{Sc}(t) = \sum_{m=-1}^{+1} (-1)^m A_{1m}(I) F_{1-m}(t) \quad (59)$$

$$F_{1m}(t) = -J_{IS}(t)A_{1m}(S(t)). \quad (60)$$

Moreover, according to Eqs (56)–(58) and (60), the correlation function may be written as follows

$$\langle F_{1m}(0)F_{1m}^*(\tau) \rangle = \frac{1}{3}J_{IS}^2 S(S+1)e^{-im\omega_S \tau} e^{-\frac{|\tau|}{\tau_m}} \quad (61)$$

where τ_m is the effective correlation time for scalar interaction

$$\frac{1}{\tau_m} = \begin{cases} \frac{1}{\tau_{c1}} = \frac{1}{\tau_e} + \frac{1}{\tau_1}, & (m = 0) \\ \frac{1}{\tau_{c2}} = \frac{1}{\tau_e} + \frac{1}{\tau_2}, & (m = \pm 1). \end{cases} \quad (62)$$

The scalar contributions to the relaxation rate of spin I in the rotating frame may be calculated from Eqs (13)–(16), (46)–(47), and (61)–(62). As a result of the calculation one gets

$$\frac{1}{T_{1e}} = \frac{1}{3} J_{IS}^2 S(S+1) \sum_{mm'} (d_{mm'}^{(1)}(\beta))^2 \frac{m'^2 \tau_m}{1 + (m\omega_0 - m\omega_S + m'\omega_e)^2 \tau_m^2} \quad (63)$$

$$\frac{1}{T_{2e}} = \frac{1}{6} J_{IS}^2 S(S+1) \sum_{mm'} (d_{mm'}^{(1)}(\beta))^2 \frac{(1+m')(2-m')\tau_m}{1 + (m\omega_0 - m\omega_S + m'\omega_e)^2 \tau_m^2}. \quad (64)$$

After substitution of $d_{mm'}^{(1)}(\beta)$ from Table II into Eq. (62) one can obtain an expression for T_{1e} identical to that quoted by Strange and Morgan (1970), provided that $1/\tau_e = 0$, whereas T_{2e} may be written in the form

$$\frac{1}{T_{2e}} = \frac{1}{6} J_{IS}^2 S(S+1) \left[2\tau_{c1} \cos^2 \beta + \frac{\tau_{c1} \sin^2 \beta}{1 + \omega_e^2 \tau_{c1}^2} + \frac{2\tau_{c2} \sin^2 \beta}{1 + (\omega_0 - \omega_S)^2 \tau_{c2}^2} + \frac{2\tau_{c2} \sin^4 \frac{\beta}{2}}{1 + (\omega_0 - \omega_S - \omega_e)^2 \tau_{c2}^2} + \frac{2\tau_{c2} \cos^4 \frac{\beta}{2}}{1 + (\omega_0 - \omega_S + \omega_e)^2 \tau_{c2}^2} \right]. \quad (65)$$

In the case of $\omega_1 \ll |\omega_0 - \omega_S|$ and under the resonance condition ($\beta = \pi/2$) one gets

$$\frac{1}{T_{1e}} = \frac{1}{3} J_{IS}^2 S(S+1) \left(\frac{\tau_{c1}}{1 + \omega_e^2 \tau_{c1}^2} + \frac{\tau_{c2}}{1 + (\omega_0 - \omega_S)^2 \tau_{c2}^2} \right) \quad (66)$$

$$\frac{1}{T_{2e}} = \frac{1}{6} J_{IS}^2 S(S+1) \left(\frac{\tau_{c1}}{1 + \omega_e^2 \tau_{c1}^2} + \frac{3\tau_{c2}}{1 + (\omega_0 - \omega_S)^2 \tau_{c2}^2} \right). \quad (67)$$

7. Discussion and remarks

It was found that in the presence of dipolar and quadrupole interaction the relaxation time T_{1e} under the resonance conditions is equal to T_2 , provided that $\omega_e \tau_e \ll 1$. The same equality $T_{1e} = T_2$ is usually fulfilled in the presence of other considered interaction. Thus, if the molecular motion is not slow ($\omega_e \tau_e \ll 1$) one can measure T_{1e} instead of T_2 .

In the case of very slow molecular motion and in the presence of a sufficiently high radiofrequency field ($\omega_e^2 \tau_e^2 \gg 1$) it follows that $T_{1e} \gg T_{2e}$ and

$$\frac{1}{T_{2e}} = \frac{1}{T_2} (d_{00}^{(0)}(\beta))^2. \quad (68)$$

One has to note that a transversal component of the precessing nuclear magnetization in the rotating frame may be damped even in the case of a perfectly rigid lattice. The damping may be produced by the dipolar interactions, which cause the nuclei to get increasingly out of phase as time progresses (Goldburg and Lee 1963). In the above case one finds

$$\left(\frac{I}{T_{2e}} \right)_{RL} = \left(\frac{1}{T_2} \right)_{RL} \frac{|3 \cos^2 \beta - 1|}{2} \quad (69)$$

where the relaxation times $(T_2)_{RL}$ and $(T_{2e})_{RL}$ for a rigid lattice are proportional to the inverse of the resonance linewidth in the laboratory and rotating frame respectively.

The spin-spin relaxation time T_{2e} in the rotating frame could be measured using an additional receiving coil aligned along the direction of the field H_0 . The received signal in this case should be proportional to the transversal magnetization M_{\perp} in the rotating

frame. Under the resonance conditions and for $M_{\perp}(0) = M_0$ one can get

$$M_{\perp}(t) = M_0 e^{-\frac{t}{T_{2e}}} \cos \omega_1 t. \quad (70)$$

The above equation may be a basis for the measurements both of the relaxation time T_{2e} and the amplitude of the radiofrequency field H_1 .

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APPENDIX

In the calculations it is convenient to use the tensor operators A_{lm} built on the basis of spherical harmonics $r^l Y_{lm}$ multiplied by the factor $(4\pi/2l+1)^{\frac{1}{2}}$. These tensor operators can be constructed by polarization of the spherical harmonics, *i. e.* by introducing the spin components I_x, I_y, I_z , in the place of the position variables x, y, z , respectively (Edmonds 1957).

Including the multiplication factor one gets:

$$A_{lm} = \begin{cases} A_{lm}(I_1 \dots I_l) = \prod_{k=1}^l (I_k \cdot \nabla) r^l C_{lm} & (A1) \\ A_{lm}(I) = (I \cdot \nabla)^l r^l C_{lm} & (A2) \end{cases}$$

where

$$C_{lm} \equiv C_{lm}(\theta, \varphi) = \left(\frac{4\pi}{2l+1} \right)^{\frac{1}{2}} Y_{lm}(\theta, \varphi) = \frac{(-1)^{l+m}}{2^l l!} \left[\frac{(l-m)!}{(l+m)!} \right]^{\frac{1}{2}} \sin^m \theta \frac{d^{l+m} \sin^{2l} \theta e^{im\varphi}}{(d \cos \theta)^{l+m}}, \quad (m \geq 0) \quad (A3)$$

$$C_{l-m} = (-1)^m C_{lm}^* \quad (A4)$$

According to the definition of the tensor operators given by Racah (1942), the following commutation relations are fulfilled

$$[I_z, A_{lm}] = m A_{lm} \quad (A5)$$

$$[I_{\pm}, A_{lm}] = [(l \mp m)(l \pm m + 1)]^{\frac{1}{2}} A_{lm \pm 1} \quad (A6)$$

where

$$I_{\pm} = I_x \pm iI_y.$$

The other definition, which is equivalent to Eq. (A5)–(A6), can be given by the condition that $2l+1$ components of the tensor operator A_{lm} transform under rotation of the reference frame as follows (Edmonds 1957, Wigner 1959)

$$O_R^{-1} A_{lm} O_R = \sum_{mm'} D_{mm'}^{(l)}(\alpha, \beta, \gamma) A_{lm}, \quad (A7)$$

where

$$D_{m'm}^{(l)}(\alpha, \beta, \gamma) = e^{im'\alpha} d_{m'm}^{(l)}(\beta) e^{im\gamma} \quad (\text{A8})$$

$$d_{m'm}^{(l)}(\beta) = \left[\frac{(l+m')!(l-m)!}{(l+m)!(l-m)!} \right]^{\frac{1}{2}} \sum_{\sigma} (-1)^{l-m'-\sigma} \binom{l+m}{l-m'-\sigma} \binom{l-m}{\sigma} \times \\ \times \left(\cos \frac{\beta}{2} \right)^{2\sigma+m'+m} \left(\sin \frac{\beta}{2} \right)^{2l-2\sigma-m'-m} \quad (\text{A9})$$

$$d_{mm}^{(l)}(\beta) = d_{m'm}^{(l)}(-\beta) = (-1)^{m'-m} d_{-m'-m}^{(l)}(-\beta) = (-1)^{l-m} d_{m'-m}^{(l)}(\pi-\beta) \quad (\text{A10})$$

O_R is the unitary operator of rotation through the Euler angles γ , β and α around the fixed axes z , y and z respectively. The same operation of the rotation O_R can be carried out by three successive Euler rotations α , β and γ around the rotated axes z , y' and z'' respectively (Rose 1957).

The tensor operators are applicable and very useful in quantum-mechanical calculations. Taking into account the applications in this paper, we consider the tensor operators A_{lm} of the first and second rank ($l = 1$ and 2). From the Eqs (A1)–(A4) it follows that

$$A_{10}(\mathbf{I}) = I_z \quad (\text{A11})$$

$$A_{1\pm 1}(\mathbf{I}) = \mp \frac{I_{\pm}}{\sqrt{2}} \quad (\text{A12})$$

$$A_{20}(\mathbf{I}) = I_z^2 - \frac{1}{4} I_+ I_- - \frac{1}{4} I_- I_+ = \frac{3I_z^2 - I(I+1)}{2} \quad (\text{A13})$$

$$A_{2\pm 1}(\mathbf{I}) = \mp \sqrt{\frac{3}{8}} (I_z I_{\pm} + I_{\pm} I_z) \quad (\text{A14})$$

$$A_{2\pm 2}(\mathbf{I}) = \sqrt{\frac{3}{8}} I_{\pm}^2 \quad (\text{A15})$$

$$A_{20}(\mathbf{I}_j, \mathbf{I}_k) = I_{zj} I_{zk} - \frac{1}{4} I_{+j} I_{-k} - \frac{1}{4} I_{-j} I_{+k} = \frac{3I_{zj} I_{zk} - I_j I_k}{2} \quad (\text{A16})$$

$$A_{2\pm 1}(\mathbf{I}_j, \mathbf{I}_k) = \mp \sqrt{\frac{3}{8}} (I_{zj} I_{\pm k} + I_{\pm j} I_{zk}) \quad (\text{A17})$$

$$A_{2\pm 2}(\mathbf{I}_j, \mathbf{I}_k) = \sqrt{\frac{3}{8}} I_{\pm j} I_{\pm k} \quad (\text{A18})$$

Generally the spherical tensors A_{lm} of any rank can be constructed from the tensors of lower rank by a relation analogous to that for C_{lm} functions, namely:

$$A_{lm} = \sum_{m_1 m_2} A_{l_1 m_1} A_{l_2 m_2} \frac{(l_1 m_1 l_2 m_2 | lm)}{(l_1 0 l_2 0 | lm)} \quad (\text{A19})$$

where $(l_1 m_1 l_2 m_2 | lm)$ are Clebsch-Gordan coefficients. Using Eqs (A11)–(A12) and (A19) one can obtain the tensors A_{2m} given by Eqs (A13)–(A18).

The transformation matrices $d_{m'm}^{(l)}(\beta)$ for the considered tensor operators of the first and second rank are given in Tables I and II respectively, for positive numbers of m' and m . The missing elements of $d_{m'm}^{(l)}(\beta)$ can be easily obtained using the properties of the symmetry given by Eq. (A10).

TABLE I

$d_{m'm}^{(1)}(\beta)$		
$m' \backslash m$	1	0
1	$\cos^2 \frac{\beta}{2}$	$\frac{\sin \beta}{\sqrt{2}}$
0	$-\frac{\sin \beta}{\sqrt{2}}$	$\cos \beta$

TABLE II

$d_{m'm}^{(2)}(\beta)$			
$m' \backslash m$	2	1	0
2	$\cos^4 \frac{\beta}{2}$	$\sin \beta \cos^2 \frac{\beta}{2}$	$\sqrt{\frac{3}{8}} \sin^2 \beta$
1	$-\sin \beta \cos^2 \frac{\beta}{2}$	$\cos \frac{3\beta}{2} \cos \frac{\beta}{2}$	$\sqrt{\frac{3}{8}} \sin 2\beta$
0	$\sqrt{\frac{3}{8}} \sin^2 \beta$	$-\sqrt{\frac{3}{8}} \sin 2\beta$	$\frac{3 \cos^2 \beta - 1}{2}$

REFERENCES

- Abragam, A., *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford 1961.
 Ailion, D. C., Slichter, C. P., *Phys. Rev.*, **137**, A235 (1965).
 Blicharski, J. S., *Acta Phys. Polon.*, **36**, 211 (1969).
 Edmonds, A. R., *Angular Momentum in Quantum Mechanics*, Princeton University Press, 1957.
 Goldburg, W. I., Lee, M., *Phys. Rev. Letters*, **11**, 255 (1963).
 Gutowsky, H. S., McCall, D. W., *Phys. Rev.*, **82**, 748 (1951).
 Jones, G. P., *Phys. Rev.*, **148**, 332 (1966).
 Look, D. C., Lowe, I. J., *J. Chem. Phys.*, **14**, 2995 (1966).
 Mansfield, P., *Progress in NMR Spectroscopy*, **8**, 43, (1971).
 Provotorov, B. N., *Zh. Eksper. Teor. Fiz.*, **41**, 1582 (1961).
 Ramsey, N. F., *Molecular Beams*, Clarendon Press, Oxford 1956.
 Redfield, A. G., *Phys. Rev.*, **98**, 1787 (1955).
 Rose, M. E., *Elementary Theory of Angular Momentum*, Wiley, New York 1957.
 Solomon, I., Bloembergen, N., *J. Chem. Phys.*, **25**, 261 (1956).
 Strange, J. H., Morgan, R. E., *J. Phys. C. Solid State Phys.*, **3**, 1999 (1970).
 Wigner, E. P. *Group Theory*, Academic Press, New York 1959.