

Nuclear Magnetic Relaxation in the Presence of Paramagnetic Ions. II*

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The influence of independent processes of relaxation of paramagnetic ions on nuclear magnetic relaxation in the presence of these ions is treated using the Kubo and Tomita method. The nuclei are assumed to relax as a result of their contact with the ions through isotropic spin-exchange coupling. The second-order terms in the perturbation expansion of the relaxation tensor yield contributions to the Bloch relaxation times of the nuclear spin system that agree with previous calculations by Solomon and Bloembergen. The fourth-order terms yield contributions to the nuclear relaxation times which are in agreement with the phenomenological relation suggested by Bloembergen and Morgan for this case, provided that the applied static field is not too strong and that the ionic motion can be described by a single Bloch relaxation time.

I. INTRODUCTION

DIPOLAR and spin-exchange interactions provide the basic mechanism for proton relaxation in aqueous solutions of paramagnetic ions; the detailed features of the relaxation may, however, be influenced by independent electronic relaxation. A phenomenological discussion of the influence of independent electronic relaxation on proton relaxation times has recently been given in the literature.^{1,2} An effective correlation time, obtained from the sum of the reciprocals of the correlation time of relative motion and ionic relaxation time, was inserted in the conventional expressions for the nuclear relaxation times. This assumption is supported by results obtained from quantum statistical methods in a previous study³ (referred to as I) where the dipolar contribution to the Bloch relaxation times T_1 and T_2 was treated using the Kubo and Tomita method.⁴ This paper is an extension of I to justify the phenomenological theory as applied by Bloembergen and Morgan to proton relaxation arising from proton electron spin exchange interaction.

This treatment is limited to isotropic spin exchange since it is not difficult to generalize the results to the more complicated anisotropic case using I.

The electronic relaxation is assumed to be a small correction to T_1 and T_2 so that perturbation theory provides an expansion in which the low-order terms are a good approximation to the whole series.

A brief outline of the present method and an explicit formulation of the problem, as well as a discussion of the choice of the Hamiltonian, are given in Sec. II. Expressions for T_1 and T_2 which include the contributions from independent electronic relaxation are obtained in Sec. III. A discussion of T_1 and T_2 for various limiting cases and a comparison with the phenomenological relations of Bloembergen and Morgan are given in Sec. IV.

II. FORMULATION OF THE PROBLEM

Consider a system of spins in the presence of a strong magnetic field H_z and an arbitrarily small disturbance given by

$$\begin{aligned} \mathbf{H}_1(t) &= \mathbf{H}_1 \quad (t \leq 0) \\ \mathbf{H}_1(t) &= 0 \quad (t \geq 0). \end{aligned} \quad (1)$$

The induced magnetic moment $\mathbf{M}^{\text{ind}}(t)$ will then be given by

$$\mathbf{M}^{\text{ind}}(t) = \phi(t) \mathbf{H}_1, \quad (2)$$

where $\phi(t)$ is called the relaxation tensor.

Assuming that the motion of the system can be described by single Bloch relaxation times,

$$\phi_{zz}(t) = \chi_0 e^{-t/T_1} \quad (3a)$$

and

$$\phi_{xx}(t) = \chi_0 e^{-t/T_2} \cos \omega t, \quad (3b)$$

where χ_0 is the static susceptibility, ω is the Larmor precessional frequency of the nuclear spins, and T_1 and T_2 are the longitudinal and transverse relaxation times, respectively.⁵ Expanding ϕ in a power series in t makes it possible to calculate the relaxation time. Contributions from $\phi_{zz}(t)$ and $\phi_{xx}(t)$ which lead to exponential damping and to exponential damping modulated by $\cos \omega t$ will be calculated for small values of (t/T_1) and (t/T_2) , respectively; the linear term in a time expansion is then a good approximation to the whole series.

It is convenient to start with the expansion of $\phi(t)$ in powers of the interaction Hamiltonian \mathcal{H}' between the individual spins obtained by Kubo and Tomita,

$$\phi_{\lambda\lambda}(t) = \sum_n \phi_{\lambda\lambda}^{(n)}(t), \quad (4)$$

where λ represents any one of the three Cartesian

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¹ N. Bloembergen and L. O. Morgan, J. Chem. Phys. **34**, 842 (1961).

² H. C. Torrey, D. O. Seever, and J. Korrington (to be published).

³ J. S. Dohnanyi, Phys. Rev. **125**, 1824 (1962).

⁴ R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

⁵ Actually, $M_x(t)$ will also include a term proportional to $M_y(0)e^{-t/T_2} \sin \omega t$ which we disregard since it does not lead to additional information on relaxation.

coordinates, and

$$\begin{aligned} \phi_{\lambda\lambda}^{(n)}(t) = & \beta(i\hbar)^{-n} \sum_{\alpha} \sum_{\beta} e^{i\omega_{\alpha}t} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{n-1}} dt_n \\ & \times \sum_{\gamma} \sum_{\delta} \cdots \sum_{\nu} \exp[i(\omega_{\gamma}t_1 + \omega_{\delta}t_2 + \cdots + \omega_{\nu}t_n)] \\ & \times \{ \langle [M_{\lambda}(\omega_{\alpha}); \mathcal{H}'^{\gamma}(t_1), \mathcal{H}'^{\delta}(t_2), \cdots, \mathcal{H}'^{\nu}(t_n) M_{\lambda}(\omega_{\beta})] \rangle \}; \end{aligned} \quad (5)$$

where the notation of I has been used. The properties of $\phi_{\lambda\lambda}^{(n)}(t)$ are discussed in references 3 and 4. The problem is to calculate the portions of $\phi_{xx}(t)$ linear in t and of $\phi_{zz}(t)$ linear in $t \cos \omega t$; the resulting expressions are then proportional to the reciprocals of T_1 and T_2 , respectively.

The Hamiltonian for the system of two different spins interacting with each other through spin exchange coupling may be written as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}', \quad (6)$$

where \mathcal{H}_0 is the total energy of the individual particles apart from their magnetic interactions but including their Zeeman energies and \mathcal{H}' is the sum of the proton-electron spin-exchange interaction and the magnetic interaction of the electrons with their environment.

The quantity \mathcal{H}' is given by

$$\mathcal{H}' = \mathcal{H}_{\text{ex}}' + \mathcal{H}_s', \quad (7)$$

where, denoting the j th nuclear and k th electronic spin operators by \mathbf{I}_j and \mathbf{S}_k , respectively, the spin-exchange coupling is given by

$$\mathcal{H}_{\text{ex}}' = \sum_{jk} A_{jk} \mathbf{I}_j \cdot \mathbf{S}_k, \quad (8)$$

and \mathcal{H}_s' is written as

$$\mathcal{H}_s' = \sum_k \mathbf{V}_k \cdot \mathbf{S}_k, \quad (9)$$

where \mathbf{V}_k is the effective magnetic local field operator for the electrons which may be caused by one or more of several factors, e.g., mutual dipole-dipole interaction between the paramagnetic ions, spin orbit coupling,^{3,6} etc. Using the interaction representation with I_z and S_z diagonal, the time dependence of \mathcal{H}' is given by

$$\mathcal{H}'(t) = \exp(i t \mathcal{H}_0 / \hbar) \mathcal{H}' \exp(-i t \mathcal{H}_0 / \hbar), \quad (10)$$

and hence

$$\mathcal{H}'(t) = \sum_{\gamma=-2}^{+2} \mathcal{H}'^{\gamma}(t) e^{i\omega_{\gamma}t} \quad (11)$$

where

$$\begin{aligned} \mathcal{H}'^{\pm 2}(t) &= \sum_k V_k^{\pm 1}(t) S_k^{\mp}, \\ \mathcal{H}'^{\pm 1}(t) &= \frac{1}{2} \sum_{jk} A_{jk}(t) I_j^{\pm} S_k^{\mp}, \\ \mathcal{H}'^0(t) &= \sum_{jk} [A_{jk}(t) I_{zj} S_{zk} + V_k^0(t) S_{zk}], \end{aligned} \quad (12)$$

and

$$\omega_{\pm 2} = \pm \Omega, \quad \omega_{\pm 1} = \pm (\Omega - \omega), \quad \omega_0 = 0. \quad (13)$$

In this expression ω and Ω are the Larmor precessional frequencies of the nuclei and electrons, respectively, in the static magnetic field H_z .

III. CALCULATION OF T_1 AND T_2

The Zeeman energy of the particles may be assumed to be sufficiently small⁴ compared with their total energy so that it can be disregarded in the expression for the density operator when computing averages over the spin variables. Then $\phi_{\lambda\lambda}^{(n)}(t)$ vanishes for odd n since the expectation value of any odd multiple of spin operators vanishes in this approximation.

The time dependence of the autocorrelation functions is taken to be

$$\langle A_{jk}(t) A_{jk}(0) \rangle = A^2 \exp(-|t|/\tau), \quad (14)$$

where τ is the correlation time for the proton-electron spin-exchange interaction. Also,

$$\langle V_k^{\delta}(t) V_k^{-\delta}(0) \rangle = \langle V_k^{\delta}(0) V_k^{-\delta}(0) \rangle \exp(-|t|/\sigma), \quad (15)$$

where σ is the correlation time for the electronic local field.

The results of I can be used to eliminate the amplitudes of the local field \mathbf{V}_k by the relations

$$\langle V_k^{\pm 1}(0) V_k^{\mp 1}(0) \rangle = \frac{1}{4} \hbar^2 (1 + \sigma^2 \Omega^2) (\sigma T_1^e)^{-1} \quad (16)$$

and

$$\langle V_k^0(0) V_k^0(0) \rangle = \hbar^2 [(\sigma T_2^e)^{-1} - (2\sigma T_1^e)^{-1}] \quad (17)$$

where T_1^e and T_2^e are the longitudinal and transverse electronic relaxation times subject to the condition $(T_1^e, T_2^e) \gg \sigma$.

Also, the relation

$$[A_{jk}(t), V_k^{\pm 1}(t)] \approx 0 \quad (18)$$

is assumed valid.

The relaxation times can now be calculated using Eqs. (3) and (5) together with (11) through (18). The zeroth order term gives the expression for the static susceptibility and does not include terms that describe a relaxation. The second-order terms agree with the expressions for the relaxation times obtained by Solomon and Bloembergen⁷ using a different method. The results are

$$(1/T_1)^{(2)} = c\tau(1 + \tau^2\Omega^2)^{-1} \quad (19)$$

and

$$(1/T_2)^{(2)} = \frac{1}{2} c\tau [1 + (1 + \tau^2\Omega^2)^{-1}], \quad (20)$$

where

$$c = \frac{2}{3} S(S+1)(n/N)\hbar^{-2}A^2, \quad (21)$$

and where n is the number of protons within the hydration sphere of the ion and N is the molar concentration of the protons. Equations (19) and (20) are subject to the condition $(T_1, T_2) \gg \tau$.

⁶ A. Abragam, Phys. Rev. **98**, 1729 (1955).

⁷ I. Solomon and N. Bloembergen, J. Chem. Phys. **25**, 261 (1956).

Calculation of $\phi_{\lambda\lambda}^{(n)}(t)$ to second order gives us no information about the influence of the ionic relaxation on T_1 and T_2 , because \mathcal{H}'_s commutes with the nuclear spin operators. In order to estimate this contribution, the portions of $\phi_{zz}^{(4)}(t)$ and $\phi_{xx}^{(4)}(t)$ which contain terms involving \mathcal{H}'_s are computed using Eqs. (3), (5), and (11) through (18), as well as the assumption $\tau^2\omega^2 \ll 1$. For $t \gg \tau$ and $\tau \gg \sigma$, the results are

$$(1/T_1)^{(4)} = -c\tau^2(1+\tau^2\Omega^2)^{-1}f(\Omega) \quad (22)$$

and

$$(1/T_2)^{(4)} = -\frac{1}{2}c\tau^2[(T_1^e)^{-1} + (1+\tau^2\Omega^2)^{-1}f(\Omega)], \quad (23)$$

where

$$f(\Omega) = \frac{(1-\tau^2\Omega^2)(1+\sigma^2\Omega^2)}{1+\tau^2\Omega^2} \times \left[\frac{1}{2T_1^e} + \frac{1}{(1+\sigma^2\Omega^2)^2} \left(\frac{1}{T_2^e} - \frac{1}{2T_1^e} \right) \right]. \quad (24)$$

The following formulas for the proton relaxation times with explicit correction factors for independent electron relaxation are obtained by combining Eqs. (19) through (24),

$$1/T_1 = (1/T_1)^{(2)} + (1/T_1)^{(4)} = c\tau(1+\tau^2\Omega^2)^{-1}[1-\tau f(\Omega)] \quad (25)$$

and

$$1/T_2 = (1/T_2)^{(2)} + (1/T_2)^{(4)} = \frac{1}{2}c\tau\{1-\tau/T_1^e + (1+\tau^2\Omega^2)^{-1}[1-\tau f(\Omega)]\}. \quad (26)$$

IV. DISCUSSION

It is evident from Eqs. (22) through (24) that the fourth-order corrections to T_1 and T_2 vanish as T_1^e and T_2^e become very large. Also, the fourth-order corrections become very large if $(T_1^e, T_2^e) \ll \tau$ and if, in addition, the field is weak, these corrections are negative. This indicates that the calculation is reliable only if $(T_1^e, T_2^e) > \tau$.

When the magnetic field H_z is weak, the conditions $\sigma^2\Omega^2 \ll 1$ and $\tau^2\Omega^2 \ll 1$ hold; the expressions (25) and (26) for the relaxation times then become

$$1/T_1 \approx c\tau(1-\tau/T_2^e) \quad (27)$$

and

$$1/T_2 \approx c\tau[1-\frac{1}{2}\tau(1/T_1^e + 1/T_2^e)]. \quad (28)$$

If the electronic relaxation times are equal,

$$T_1^e = T_2^e = T, \quad (29)$$

Equations (27) and (28) reduce to

$$1/T_1 \approx 1/T_2 \approx c\tau_e, \quad (30)$$

where

$$1/\tau_e = 1/\tau + 1/T. \quad (31)$$

Equation (30) has the same form as the second-order expressions (19) and (20) for the weak-field limit, provided that τ is replaced by τ_e , in agreement with the phenomenological theory of Bloembergen and Morgan.¹

Often experimental conditions are such that the applied field H_z is strong, i.e., $\tau^2\Omega^2 \gg 1$, but not so strong as to violate the condition $\tau^2\omega^2 \ll 1$. For this case, Eqs. (25) and (26) for the relaxation times become

$$\frac{1}{T_1} \approx \frac{c}{\tau\Omega^2} \left\{ 1 + \tau \left[\frac{1+\sigma^2\Omega^2}{2T_1^e} + \frac{1}{1+\sigma^2\Omega^2} \left(\frac{1}{T_2^e} - \frac{1}{2T_1^e} \right) \right] \right\} \quad (32)$$

and

$$\frac{1}{T_2} \approx c\tau \left\{ 1 - \frac{\tau}{T_1^e} + \frac{1}{\tau^2\Omega^2} \left[1 + \tau \left(\frac{1+\sigma^2\Omega^2}{2T_1^e} + \frac{1}{1+\sigma^2\Omega^2} \left(\frac{1}{T_2^e} - \frac{1}{2T_1^e} \right) \right) \right] \right\}. \quad (33)$$

Assuming further that $\sigma^2\Omega^2 \ll 1$, the relaxation times are then given by

$$1/T_1 \approx c(\tau\Omega^2)^{-1}(1+\tau/T_2^e)^{-1} \quad (34)$$

and

$$1/T_2 \approx c\tau[1-\tau/T_1^e + (\tau^2\Omega^2)^{-1}(1+\tau/T_2^e)^{-1}]. \quad (35)$$

If the ionic relaxation can be described by a single time constant $T = T_1^e = T_2^e$, then

$$1/T_1 \approx c(\tau_e\Omega^2)^{-1} \quad (36)$$

and

$$1/T_2 \approx c[\tau_e + (\tau_e\Omega^2)^{-1}], \quad (37)$$

with τ_e given by Eq. (31).

Thus, the suggestion of Bloembergen and Morgan is shown to be valid for weak and moderately strong fields, provided that $T_1^e = T_2^e$. The phenomenological theory appears, therefore, to have a wide range of applicability for typical experiments on liquids.

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