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THEORY OF NUCLEAR RESONANCE IN PARAMAGNETIC MEDIA. II. SPIN-LATTICE RELAXATION

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The longitudinal relaxation rate of nuclear magnetization in paramagnetic media is calculated in the two limiting cases of fast and slow thermal motion in the medium. It is assumed that the interaction between the nuclear and the electron spins in the system is due to dipole-dipole and contact forces. Precession, relaxation, and exchange motions in the electron spin system are taken into account.

1. In an earlier article [1] a calculation was given of the shape, width and shift of nuclear magnetic resonance lines in paramagnetic media. In this article we shall give within the framework of the same theory a calculation of the nuclear spin-lattice (longitudinal) relaxation time $T_{\|}$. We shall utilize the method of calculation and the notation adopted in [1].

As Kubo and Tomita [2] have shown, the relaxation time $T_{\|}$ can be calculated in the linear approximation by means of the formula

$$T_{\|}^{-1} = \frac{1}{2} \sum_{\gamma \neq 0} \sigma_{\gamma}^{(z)2} \int_{-\infty}^{\infty} f_{\gamma}(\tau) \exp(i\gamma\omega_I \tau)\, d\tau; \tag{1}$$

$$\sigma_{\gamma}^{(z)2} = \hbar^{-2} \langle | [\hat{M}_z, \hat{\mathscr{H}}'_{\gamma}(0)] |^2 \rangle / \langle \hat{M}_z^2 \rangle, \tag{2}$$

$$f_{\gamma}(\tau) = \langle [\hat{M}_z, \hat{\mathscr{H}}'_{\gamma}(\tau)]\, [\hat{\mathscr{H}}'_{-\gamma}(0), \hat{M}_z] \rangle / \langle | [\hat{M}_z, \hat{\mathscr{H}}'_{\gamma}(0)] |^2 \rangle. \tag{3}$$

The quantity $\sigma_{\gamma}^{(z)2}$ can be interpreted as the rms z component of the internal field (in frequency units) produced at the nuclear site by the nonsecular part of the perturbation $\hat{\mathcal{H}}'_{\gamma}$, $\gamma \neq 0$. This perturbation varies with time as a result of precession, relaxation and exchange motions in the electron spin system and of thermal motion of the particles of the medium; as a result of the variable perturbation a transfer of energy occurs from the nuclear spins to the other degrees of freedom of the system; the rate of this process is characterized by the parameter $T_{\|}$ calculated here.

The correlation function $f_{\gamma}(\tau)$ of the form (3) describes the rate of variation of the internal fields; in the case under consideration we have in accordance with [1]

$$\sigma_{\gamma}^{(z)2} f_{\gamma}(\tau) = \sum_{\beta,\alpha} \sigma_{\gamma\beta,\alpha}^{(z)2} f_{\gamma\beta,\alpha}(\tau), \tag{4}$$

$$f_{\gamma\beta,\alpha}(\tau) = \exp(i\beta\omega_S\tau - |\tau| T_{\beta}^{-1} - F(\tau)\,\omega_e^2 - |\tau|\,\tau_{\alpha}^{-1}). \tag{5}$$

$\gamma\beta$	$\sigma_{\gamma\beta}^{(z)2}$	
	$\sigma_{\gamma\beta,1}^{(z)2} = \sigma_{-\gamma,-\beta,2}^{(z)2}$	$\sigma_{\gamma\beta,2}^{(z)2} = \sigma_{-\gamma,-\beta,2}^{(z)2}$
10	$^1/_4\, S(S+1)\, \sigma_{IS}^2$	0
11	$^1/_2\, S(S+1)\, \sigma_{IS}^2$	0
1, −1	$^1/_{12} S(S+1) \sigma_{IS}^2$	$^1/_3 S(S+1) \langle A^2 \rangle$

The values of the quantity $\sigma_{\gamma\beta,\alpha}^{(z)2}$ are given in the table. The individual terms in the exponent in (5) describe the effect on the internal field of the precession ($i\beta\omega_S\tau$), the relaxation ($-|\tau| T_{\beta}^{-1}$), the exchange ($-F(\tau)\,\omega_e^2$) and the thermal ($-|\tau|\,\tau_{\alpha}^{-1}$) motions in the system.

On taking (4) and (5) into account formula (1) can be rewritten in the form

$$T_{\|}^{-1} = \frac{1}{2} \sum_{\gamma=\pm 1} \sum_{\beta=0,\pm 1} \sum_{\alpha=1,2} \sigma_{\gamma\beta,\alpha}^{(z)2} \int_{-\infty}^{+\infty} \exp(i\gamma\omega_I\tau)\, f_{\gamma\beta,\alpha}(\tau)\, d\tau \tag{6}$$

On comparing (6) with formula (22) in [1] we can verify that

$$T_{\|}^{-1} = 2\,(\Delta\omega_{1/2})_{nS}, \tag{7}$$

where $(\Delta\omega_{1/2})_{nS}$ is the contribution to the width of the resonance line due to the (nonsecular) part of the perturbation $\mathcal{H}'_{\gamma}$, $\gamma \neq 0$ which is nondiagonal with respect to the nuclear spin. As a result of (7) we can immediately obtain the expression for $T_{\|}^{-1}$ by taking appropriate terms from the formulas for the total half width $\Delta\omega_{1/2}$ from [1]. The formal identifying characteristic of the terms required by us is the presence in them of the frequencies $\pm\omega_I$ of nuclear relaxation transitions.

2. In the case of fast thermal motion in the system ($T_{\perp}^{0} \gg \tau_e$) we obtain, in accordance with (7), from formula (23) of [1]

$$T_{\parallel}^{-1}=2\left[S(S+1)\sigma_{IS}^{2}\left(\frac{1}{4}\frac{K_{01}^{-1}}{K_{01}^{-2}+\omega_I^2}+\frac{1}{2}\frac{K_{11}^{-1}}{K_{11}^{-2}+(\omega_S+\omega_I)^2}+\frac{1}{12}\frac{K_{11}^{-1}}{K_{11}^{-2}+(\omega_I-\omega_S)^2}\right)+\frac{1}{3}S(S+1)\langle A^2\rangle\frac{K_{12}^{-1}}{K_{12}^{-2}+(\omega_I-\omega_S)^2}\right];$$

$$K_{0\alpha}^{-1}=\tau_\alpha^{-1}+T_1^{-1}+\tau_e\omega_e^2,\qquad K_{1\alpha}^{-1}=\tau_\alpha^{-1}+T_2^{-1}+\tau_e\omega_e^2;\qquad \alpha=1,2. \tag{8}$$

Here τ_1, τ_2 are the characteristic times of the correlation functions of the dipole ($\alpha = 1$) and the contact ($\alpha = 2$) interactions of the nuclear and the electron spins perturbed by the thermal motion; T_1 and T_2 are the relaxation times for the longitudinal and the transverse electron magnetization, τ_e is the characteristic time for the variation of the exchange energy under the influence of the thermal motion of the system. In the case of solvated ions σ_{IS}^2 and $\langle A^2\rangle$ in (8) (and also in the formulas of [1]) coincide with the standard expressions $(4/5)\gamma_I^2\gamma_S^2\hbar^{-2}(mN_S/N_I)b^{-6}$ and $A^2(mN_S/N_I)$, where m is the number of nuclei in the first sphere surrounding the ion at a distance b from its center.

3. In the case of slow thermal motion in the system ($T_\perp^0 \ll \tau_e$) we have from formulas (28), (30)—(32) in [1]

$$T_{\parallel}^{-1}=2\sqrt{\frac{\pi}{2}}\frac{1}{\omega_e}\sum_{\gamma=\pm1}\sum_{\beta=0,\pm1}\sigma_{\gamma\beta}^{(z)2}\operatorname{Re}L(z_{\gamma\beta});$$

$$L(z)=e^{-z^2}\left(1-2i\pi^{-1/2}\int_0^z e^{x^2}dx\right),$$

$$z_{\gamma\beta}=\omega_e^{-1}(\gamma\omega_I+\beta\omega_S-iT_\beta^{-1})/\sqrt{2},\qquad \sigma_{\gamma\beta}^{(z)2}=\sigma_{\gamma\beta,1}^{(z)2}+\sigma_{\gamma\beta,2}^{(z)2} \tag{9}$$

From (9) we obtain in the case of strong exchange and for $T_\beta^{-1} \ll \omega_S$

$$T_{\parallel}^{-1}=2\sqrt{\frac{\pi}{2}}\frac{1}{\omega_e}\left[\sigma_{10}^2+\sigma_{11}^2\exp\left\{-\frac{(\omega_I+\omega_S)^2}{2\omega_e^2}\right\}+\sigma_{1,-1}^2\exp\left\{-\frac{(\omega_I-\omega_S)^2}{2\omega_e^2}\right\}\right] \tag{10}$$

[cf. also formula (33) in [1]].

In the case of weak fields (or of very short T_1, T_2) we can for strong exchange set $z_{\gamma\beta} = -iT_\beta^{-1}/\sqrt{2}\,\omega_e$, and then

$$T_{\parallel}^{-1}=2\sqrt{\pi/2}\,\omega_e^{-1}[\sigma_{10}^2L(-iT_1^{-1}/\sqrt{2}\omega_e)+(\sigma_{11}^2+\sigma_{1,-1}^2)L(-iT_2^{-1}/\sqrt{2}\omega_e)] \tag{11}$$

[cf. formula (35) in [1]].

In the case of very strong exchange $\omega_e \gg \omega_S$, ω_I, T_1^{-1}, T_2^{-1} formulas (10) and (11) reduce in accordance with the table to

$$T_{\parallel}^{-1}=2\sqrt{\pi/2}\,\omega_e^{-1}\left[\frac{5}{6}S(S+1)\sigma_{IS}^2+\frac{1}{3}S(S+1)\langle A^2\rangle\right]. \tag{12}$$

As can be seen from formulas (8)—(12), the rate $T_\parallel^{-1}$ of the longitudinal relaxation of nuclear spins is determined by the same factors as the rate $T_\perp^{-1}$ of the transverse relaxation, and will exhibit similar dependence on the concentration of the paramagnetic substance, on the external field, on the temperature, and on the other parameters of the medium. A detailed discussion of such dependences is given in [1]. At the same time $T_\parallel$ and $T_\perp$ will not, in general, coincide numerically. The differences are due not only to the difference in the dependence on the Larmor frequencies ω_S and ω_I, but also to the presence of a contact interaction between the nuclear and the electron spins. Therefore, an analysis of the ratio $T_\parallel/T_\perp$ enables us, in particular, to evaluate the magnitude of the contact interaction between paramagnetic particles and nuclear spins.[3]

The parameter $T_\parallel$, as well as $T_\perp$, can be experimentally determined with great accuracy by the spin echo method (the notation T_1, T_2 is utilized in the corresponding literature in place of $T_\parallel$, $T_\perp$).

[1] R. Kh. Timerov and K. A. Valiev, JETP **41**, 1566 (1961), Soviet Phys. JETP **14**, 1116 (1962).

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

[3] N. Bloembergen, J. Chem. Phys. **27**, 572 (1957).

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