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NUCLEAR MAGNETIC RELAXATION IN RAPIDLY ROTATED SOLIDS

By A. Jasiński

Institute of Nuclear Physics, Cracow*

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Rotating frame relaxation time for spinning sample $T_{1\varrho R}$ has been calculated in a weak collision case for the dipolar interaction and the chemical shift anisotropy interaction. It has been shown that in a special case of rapidly decreasing spectral density of the correlation function $T_{1\varrho R}$ measurements may be used to determine its shape in the frequency range from 0 to $2\omega_R$.

1. *Introduction*

One of the most important results of nuclear magnetic relaxation studies is a possibility of obtaining information about spectral density $J(\omega)$ of the correlation function $G(\tau)$ of molecular motion. Assuming that dipolar interaction is a dominant relaxation mechanism, the spectral density $J(\omega)$ of the correlation function at frequencies ω_0 and $2\omega_0$ (where ω_0 is the resonance frequency) may be obtained from Zeeman spin-lattice relaxation time T_1 [1]. Rotating frame nuclear magnetic relaxation time $T_{1\varrho}$ [2] gives information about $J(\omega)$ at the frequency ω_1 (where ω_1 is the amplitude of radiofrequency field (rf)), whereas $J(\omega)$ at the frequency ω_L (where ω_L measures the local field) may be obtained from the dipolar relaxation time T_{1D} [2]. For the rotating frame relaxation time $T_{1\varrho}$ to be meaningful the following condition must be satisfied $\omega_1 \geqslant \omega_L$. Therefore $J(\omega)$ in the frequency range from 0 to ω_L cannot be investigated using these techniques.

Nuclear magnetic resonance (NMR) experiments in rapidly spinning solids [3, 4] are now one of the well established techniques to study fine interactions in solids. Kessemeier and Norberg [5] considered spin-lattice relaxation in rapidly spinning solids due to paramagnetic impurities accompanied by spin diffusion, whereas Haeberlen and Waugh [6] considered relaxation due to thermally activated motion. They showed that macroscopic sample spinning has little effect on the spin-lattice relaxation.

In this paper the relaxation rate in the rotating frame, under the action of rf field for the spinning sample has been calculated for the dipolar interaction and the chemical shift anisotropy interaction. Preliminary results were published elsewhere [7]. The calculation

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* Address: Instytut Fizyki Jądrowej, Radzikowskiego 152, 31-342 Kraków, Poland.

has been performed in a weak collision case using a method similar to that one of Blicharski [8]. It has been shown that the rotating frame relaxation time $T_{1\varrho\mathrm{R}}$ for the spinning sample may give information about the spectral density $J(\omega)$ of the correlation function in the frequency range from 0 to $2\omega_\mathrm{R}$ (where ω_R is the sample spinning frequency), unavailable in standard relaxation experiments.

2. *Theory*

Consider a sample containing a system of nuclear spins I in a strong external magnetic field B_0, irradiated with a radiofrequency field (rf) of frequency ω and spun at a frequency ω_R around an axis inclined at an angle β_R with respect to B_0. Assume also that nuclear spins interact via the dipolar interaction and the chemical shift anisotropy interaction. The Hamiltonian $\hbar\mathcal{H}_\mathrm{L}$ in the laboratory frame "L" may be written as a sum of terms [1]

$$\hbar\mathcal{H}_\mathrm{L} = \hbar\mathcal{H}_\mathrm{L}^\mathrm{Z}+\hbar\mathcal{H}_\mathrm{L}^\mathrm{rf}+\hbar\mathcal{H}_\mathrm{L}^\mathrm{D}+\hbar\mathcal{H}_\mathrm{L}^\sigma, \tag{1}$$

where $\mathcal{H}_\mathrm{L}^\mathrm{Z}$, $\mathcal{H}_\mathrm{L}^\mathrm{rf}$, $\mathcal{H}_\mathrm{L}^\mathrm{D}$, $\mathcal{H}_\mathrm{L}^\sigma$ are Zeeman, rf-field, dipolar and chemical shift anisotropy terms, respectively.

The dipolar interaction term is written as a product of irreducible spherical tensors T_{2M}^D and tensor operators V_{2M}^D [9]

$$\mathcal{H}_\mathrm{L}^\mathrm{D} = \sum_{i>j}\sum_{M=-2}^{2}(-1)^M T_{2M}^\mathrm{D}(\vec{r}_{ij})V_{2-M}^\mathrm{D}(I_iI_j), \tag{2}$$

where

$$T_{2M}^\mathrm{D}(\vec{r}_{ij}) = -\sqrt{6}\,\frac{\hbar\gamma^2}{r_{ij}^3}\,\mathcal{D}_{M0}^{(2)*}(\Omega_{ij}), \tag{2a}$$

$$V_{2M}^\mathrm{D}(I_iI_j) = \sum_{M_1=-1}^{1}(1M1M-M_1|112M)I_i^{M_1}I_j^{M-M_1} \tag{2b}$$

and $\mathcal{D}_{M0}^{(2)}(\Omega)$ — Wigner rotation matrices, $(1M\,1M-M_1|112M)$ — Clebsch-Gordon coefficient, $\Omega_{ij} = (\alpha_{ij}, \beta_{ij}, 0)$ — Euler angles of $\vec{r}_{ij}$.

In a similar way the chemical shift anisotropy interaction term for symmetric chemical shift tensor is written as

$$\mathcal{H}_\mathrm{L}^\sigma = \sum_{k=1}^{N} T_{00}^\sigma(k)V_{00}^\sigma(I_k)+\sum_{k=1}^{N}\sum_{M=-2}^{2}(-1)^M T_{2M}^\sigma(k)V_{2-M}^\sigma(I_k), \tag{3}$$

where

$$T_{00}^\sigma(k) = \tfrac{1}{3}\,\mathrm{Tr}\,\{\gamma\sigma_{\alpha\beta}(k)\} = \gamma\sigma(k), \tag{3a}$$

$$T_{2\pm2}^\sigma(k) = \tfrac{1}{2}\,\gamma\{[\sigma_{xx}(k)-\sigma_{yy}(k)]\pm i2\sigma_{xy}(k)\}$$

$$T_{2\pm1}^\sigma(k) = \mp\gamma\{\sigma_{xz}(k)-i\sigma_{yz}(k)\}$$

$$T_{20}^\sigma(k) = \frac{\gamma}{\sqrt{6}}\{2\sigma_{zz}(k)-\sigma_{xx}(k)-\sigma_{yy}(k)\}, \tag{3b}$$

$$V_{00}^{\sigma}(I_k) = I_k^0 B^0, \tag{3c}$$

$$V_{2M}^{\sigma}(I_k) = \sum_{M_1/-1}^{1} (1M1M-M_1|112M) I_k^{M_1} B^{M-M_1} \tag{3d}$$

and $B^{\pm 1} = \mp \frac{1}{\sqrt{2}} (B_x \pm iB_y)$, $\sigma_{\alpha\beta}(k)$ — are elements of the chemical shift tensor for nuclei k. For homogeneous external magnetic field usually used in NMR experiment, $B_x = B_y = 0$, Eq. (3d) becomes

$$V_{2\pm 2}^{\sigma}(I_k) = 0, \quad V_{2\pm 1}^{\sigma}(I_k) = \frac{1}{\sqrt{2}} B^0 I_k^{\pm 1}, \quad V_{20}^{\sigma}(I_k) = \sqrt{\tfrac{2}{3}}\, B^0 I_k^0. \tag{3e}$$

The density matrix theory of relaxation is used to perform the calculation [1, 8]. The density matrix equation is transformed into the double rotating tilted frame DRFT, where Zeeman and rf field terms vanish. This transformation is equivalent to a rotation in the spin space by the Euler angles $\Omega_\varrho = (\alpha_\varrho, \beta_\varrho, \gamma_\varrho)$

$$\alpha_\varrho = \omega t, \quad \beta_\varrho = \operatorname{arctg} \frac{\omega_1}{\omega_0 - \omega}, \quad \gamma_\varrho = \omega_e t, \quad \omega_e = (\omega_1^2 + (\omega_0 - \omega)^2)^{1/2}, \tag{4}$$

where $\omega_1 = \gamma B_1$, B_1 is the amplitude of the rf field of frequency ω_1.

In order to describe the macroscopic sample spinning and the molecular motion, the spinning sample frame "R" and the molecular frame "M" are introduced. The orientation of "R" with respect to "L" and "M" with respect to "R" is described by the Euler angles $\Omega_R = (\omega_R t, \beta_R, 0)$ and $\Omega_M = (\alpha_M(t), \beta_M(t), \gamma_M(t))$ respectively. Ω_M is a random function of time describing the random motion of molecules. The space part of the Hamiltonian (1) is then transformed into the molecular frame "M" and the density matrix equation solved by successive approximation up to the second order. Calculating the expected value of $\langle I^0 \rangle$ the following equation is obtained [8]

$$\frac{d\langle I^0 \rangle}{dt} = -(\langle B(I^0) \rangle - \langle B(I^0) \rangle_0), \tag{5}$$

where

$$\langle B(I^0) \rangle = \tfrac{1}{2} \int_{-\infty}^{+\infty} d\tau \langle [\mathscr{H}_\varrho(t-\sigma), [\mathscr{H}_\varrho(t), I^0]] \rangle \tag{6}$$

and $\mathscr{H}_\varrho = \mathscr{H}_\varrho^{D} + \mathscr{H}_\varrho^{\sigma}$ is the interaction Hamiltonian in the DRTF frame for the spinning sample, $\langle\ \rangle_0$ is the average for the thermal equilibrium density matrix.

$$\mathscr{H}_\varrho^{D} = \sum_{i>j}^{N} \sum_{\substack{MM_1\\ M_2M_3}} (-1)^M \mathscr{D}_{MM_1}^{(2)*}(\Omega_R) \mathscr{D}_{M_1M_2}^{(2)*}(\Omega_M) T_{2M}^{D}(\vec{r}_{ij}^{\,M}) \mathscr{D}_{-MM_3}^{(2)*}(\Omega_\varrho) V_{2M_3}^{D}(I_i I_j), \tag{7}$$

where $\vec{r}_{ij}^{\,M}$ is expressed with respect to M. $\mathscr{H}_\varrho^{\sigma}$ has identical form to that one for $\mathscr{H}_\varrho^{D}$.

If $\langle B(I^0)\rangle$ is linear in $\langle I^0\rangle$ then the rotating frame relaxation time $T_{1\varrho\mathrm{R}}$ is given by

$$\frac{1}{T_{1\varrho\mathrm{R}}} = \frac{\langle B(I^0)\rangle}{\langle I^0\rangle}. \tag{8}$$

Assuming that the interference effects between the dipolar and the chemical shift anisotropy interaction are negligible [10] contributions to the relaxation rate from these interactions may be calculated separately

$$\frac{1}{T_{1\varrho\mathrm{R}}} = \left(\frac{1}{T_{1\varrho\mathrm{R}}}\right)^{\mathrm{D}} + \left(\frac{1}{T_{1\varrho\mathrm{R}}}\right)^{\sigma}. \tag{9}$$

a. Dipolar relaxation

After a rather tedious calculation, using (8), (7), (6) and (2), (2a), (2b), one can get the following expression for the dipolar interaction contribution to the relaxation rate in the rotating frame for the spinning sample

$$\left(\frac{1}{T_{1\varrho\mathrm{R}}}\right)^{\mathrm{D}} = \tfrac{1}{12} I(I+1) \sum_{i>j} \sum_{M/-2}^{2} \langle|\mathscr{D}^{(2)}_{M_1M_2}|^2\rangle_{\mathrm{av}} |T^{\mathrm{D}}_{2M}(\vec{r}^{\,\mathrm{M}}_{ij})|^2$$

$$\sum_{\substack{M_1M_2\\M_3}} d^{(2)^2}_{-MM_1}(\beta_\varrho) d^{(2)^2}_{MM_3}(\beta_\varrho) M_3^2 J(M\omega + M_1\omega_{\mathrm{R}} + M_3\omega_{\mathrm{e}}), \tag{10}$$

where: $\langle\ \rangle$ is the average over the motion, $J(\omega)$ — the spectral density of the correlation function

$$J(M\omega + M_1\omega_{\mathrm{R}} + M_3\omega_{\mathrm{e}}) = \int_{-\infty}^{+\infty} g(\tau) e^{-i(M\omega + M_1\omega_{\mathrm{R}} + M_3\omega_{\mathrm{e}})} d\tau \tag{11}$$

and $g(\tau)$ is the correlation function of the molecular motion. Let us assume that the correlation function is exponential with the correlation time τ_c.

Special cases may be obtained from Eq. (10). The Zeeman relaxation time T_1 is obtained, if

$$\beta_{\mathrm{R}} = 0, \quad \beta_\varrho = 0, \quad \omega_{\mathrm{R}} = 0, \quad \omega_{\mathrm{e}} = 0, \quad \omega = \omega_0. \tag{12}$$

Then from Eq. (10) one obtains the well known formula [1]

$$\left(\frac{1}{T_1}\right)^{\mathrm{D}} = \tfrac{1}{3} \Delta^2_{\mathrm{D}} (4J(2\omega_0) + J(\omega_0)), \tag{13}$$

where Δ^2_{D} is the second moment for the polycrystalline sample

$$\Delta^2_{\mathrm{D}} = \tfrac{1}{2} I(I+1) \sum_{i>j} \sum_{M_2} \langle|\mathscr{D}^{(2)}_{M_1M_2}|^2\rangle_{\mathrm{av}} |T^{\mathrm{D}}_{2M_2}(\vec{r}^{\,\mathrm{M}}_{ij})|^2. \tag{14}$$

The spin lattice relaxation time for the spinning sample $T_{1\mathrm{R}}$ is obtained from Eq. (10), if

$$\beta_{\mathrm{R}} \neq 0, \quad \beta_\varrho = 0, \quad \omega_{\mathrm{e}} = 0, \quad \omega = \omega_0, \tag{15}$$

than

$$\left(\frac{1}{T_{1\mathrm{R}}}\right)^{\mathrm{D}} = \tfrac{1}{6}\Delta_{\mathrm{D}}^{2}\sum_{MM_2} M^2 d^{(2)^2}_{-MM_1}(\beta_{\mathrm{R}})J(M\omega_0+M_1\omega_{\mathrm{R}}). \tag{16}$$

In an experiment the resonance frequency ω_0 is much larger than the spinning frequency ω_{R} so that for the spectral density of the correlation function one has

$$J(M\omega_0+M_1\omega_{\mathrm{R}}) \simeq J(M\omega_0) \tag{17}$$

and $(T_{1\mathrm{R}})^{\mathrm{D}} = (T_1)^{\mathrm{D}}$ in agreement with previous calculation of Haeberlen and Waugh [6].

Let us consider the relaxation in the rotating frame for the spinning sample in the special case when the molecular motion is slow and the correlation time τ_c long enough so that $\omega_0\tau_c \gg 1$. For $M \neq 0$ the spectral density of the correlation function is negligible. Exactly at resonance, spinning at the magic angle i.e.

$$\omega = \omega_0, \quad \beta_\varrho = \frac{\pi}{2}, \quad \beta_{\mathrm{R}} = \beta_{\mathrm{R}}^{\mathrm{M}} = 54°44', \tag{18}$$

one gets

$$\left(\frac{1}{T_{1\varrho\mathrm{R}}}\right)^{\mathrm{D}} = \frac{\Delta_{\mathrm{D}}^{2}}{12}\{J[2(\omega_{\mathrm{R}}+\omega_1)]+2J[\omega_{\mathrm{R}}+2\omega_1]+J[2(\omega_{\mathrm{R}}-\omega_1)+2J[\omega_{\mathrm{R}}-2\omega_1]\}. \tag{19}$$

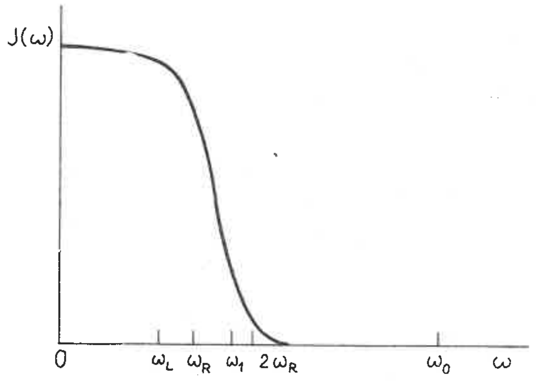

Fig. 1. The spectral density of the correlation function in the special case of slow molecular motion. ω_{L}, ω_1, ω_{R}, ω_0 are frequencies of the local field, the rf field, the sample spinning and the resonance frequency respectively

If the spectral density of the correlation function decreases rapidly as in shown in Fig. 1, so that

$$J[2(\omega_{\mathrm{R}}+\omega_1)],\ J[\omega_{\mathrm{R}}+2\omega_1] \ll J[2(\omega_{\mathrm{R}}-\omega_1)],\ J[\omega_{\mathrm{R}}-2\omega_1], \tag{20}$$

equation (19) becomes

$$\left(\frac{1}{T_{1\varrho\mathrm{R}}}\right)^{\mathrm{D}} = \frac{\Delta_{\mathrm{D}}^{2}}{12}\{J[2(\omega_{\mathrm{R}}-\omega_1)]+2J[\omega_{\mathrm{R}}-2\omega_1]\}. \tag{21}$$

In this special case one can obtain information about the spectral density of the correlation function $J(\omega)$ in the frequency range from 0 to $2\omega_R$. As is seen from Eq. (21) $J(\omega)$ can be measured directly in this range performing an experiment consisting of measuring $T_{1\varrho R}$ as a function of the spinning frequency ω_R and the rf field intensity ω_1.

This frequency range is not available to ordinary rotating frame relaxation time $T_{1\varrho}$ measurements on stationary sample, because it gives the spectral density of the correlation function at $2\omega_1$, and the field intensity cannot be made small enough otherwise $T_{1\varrho}$ looses its sense [2].

b. Chemical shift anisotropy relaxation

A contribution to the relaxation rate from the anisotropy of the chemical shift interaction $(1/T_{1\varrho R})^\sigma$ in the rotating frame for the spinning sample has been obtained after some algebra from Eqs. (3)—(3d), (6), and (8) is equal to

$$\left(\frac{1}{T_{1\varrho R}}\right)^\sigma = \frac{\omega_0^2\delta\sigma^2}{15}\sum_{M_1/-2}^{2}\sum_{MM_2/-1}^{1}(1M10|112M)^2 d^{(2)2}_{-MM_1}(\beta_R)$$

$$d^{(2)2}_{MM_2}(\beta_\varrho)M_2^2 J(M\omega+M_1\omega_R+M_2\omega_e), \tag{22}$$

where

$$\delta\sigma^2 = (\sigma_{zz}-\sigma_{xx})^2+(\sigma_{zz}-\sigma_{yy})(\sigma_{xx}-\sigma_{yy}). \tag{23}$$

From this general formula special cases can be obtained in a similar way as for the dipolar relaxation. The spin-lattice relaxation time $(T_1)^\sigma$ for stationary sample is obtained from formula (23) as a special case if conditions (12) are satisfied. The well known formula [1] is obtained

$$\left(\frac{1}{T_1}\right)^\sigma = \tfrac{1}{15}\,\omega_0^2\delta\sigma^2 J(\omega_0). \tag{24}$$

The spin-lattice relaxation time $(T_{1R})^\sigma$ for the spinning sample is obtained from formula (22) if conditions (15) are satisfied and is equal to

$$\left(\frac{1}{T_{1R}}\right)^\sigma = \frac{\omega_0^2\delta\sigma^2}{15}\sum_{M_1/-2}^{2}\sum_{M/-1}^{1}(1M10|112M)^2 d^{(2)2}_{-MM_1}(\beta_R)M^2 J(M\omega_0+M_1\omega_R). \tag{25}$$

Comparing formulas (24) and (25) it is easy to see that $(T_1)^\sigma = (T_{1R})^\sigma$ because of condition (17).

The rotating frame relaxation time $(T_{1\varrho})^\sigma$ calculated previously by Blicharski [11] is obtained from (22), if

$$\omega_R = 0, \quad \beta_R = 0, \quad \beta_\varrho = \frac{\pi}{2}, \quad \omega = \omega_0, \quad \omega_e = \omega_1, \tag{26}$$

and is equal to

$$\left(\frac{1}{T_{1\varrho}}\right)^{\sigma} = \tfrac{1}{90}\,\omega_0^2\delta\sigma^2\{3J(\omega_0)+4J(\omega_1)\}. \tag{27}$$

The rotating frame relaxation rate $(1/T_{1\varrho R})^{\sigma}$ for the spinning sample in the special case, when the molecular motion is slow and the correlation time τ_c is long enough so that $\omega_0\tau_c \gg 1$ is obtained from formula (22) if conditions (18) are satisfied. In a similar way as for the dipolar interaction one gets

$$\left(\frac{1}{T_{1\varrho R}}\right)^{\sigma} = \tfrac{1}{135}\,\omega_0^2\delta\sigma^2\{J[2\omega_R+\omega_1]+2J[\omega_R+\omega_1]+2J[\omega_R-\omega_1]+J[2\omega_R-\omega_1]\}. \tag{28}$$

For the rapidly decreasing spectral density of the correlation function satisfying conditions (20) Eq. (28) simplifies to

$$\left(\frac{1}{T_{1\varrho R}}\right)^{\sigma} = \tfrac{1}{135}\,\omega_0^2\delta\sigma^2\{J[2\omega_R-\omega_1]+2J[\omega_R-\omega_1]\}. \tag{29}$$

As is seen from this formula information about the spectral density of the correlation function in the frequency range from 0 to $2\omega_R$ can be obtained from measurements of $(T_{1\varrho R})^{\sigma}$. The same discussion as for the dipolar interaction applies here.

As has been shown here, measurements of the rotating frame relaxation time $T_{1\varrho R}$ for the spinning sample may open new possibilities in studying the spectral density of the correlation function in the very low frequency range, extending considerably the range of standard rotating frame relaxation experiments.

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