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NUCLEAR SPIN RELAXATION IN PERIODICALLY PERTURBED SYSTEMS IV. THE RELAXATION IN THE PRESENCE OF DOUBLE ROTATION AND PULSE SEQUENCE*

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The effective relaxation times are calculated in the weak collision case for the system of identical nuclear spins perturbed by double rotation, periodic sequences of r.f. pulses and spin interactions.

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1. Introduction

The aim of this paper is to extend the calculation of the effective relaxation times $T_{1\mathrm{e}}$ and $T_{2\mathrm{e}}$ for a system of identical nuclear spins in the presence of the simultaneous perturbation by double rotation and periodic multi-pulse sequences.

In the previous papers [1–3] these two kinds of perturbations were considered separately. The influence of different pulse sequences on the effective spin–spin relaxation times was also presented in a series of papers [4–16].

2. General theory

Let us consider a system of identical nuclear spins $\boldsymbol{I}_i$ in a strong magnetic field $\boldsymbol{B}_0$ along z-axis, in the presence of double rotation around two axes z_1, z_2

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at the frequencies ω_1, ω_2 and polar angles $\Theta_1 = 54.7°$ and $\Theta_2 = 30.6°$, respectively [5–7], and periodic train of very short pulses

$$(\pi/2)_y - \left[\tau_0 - (\Theta'_1)_{\Phi'_1} - \tau_1 - (\Theta'_2)_{\Phi'_2} - \tau_2 - \ldots (\Theta'_N)_{\Phi'_N} - \tau_N\right]_n \tag{1}$$

at resonance frequency $\omega_0 = \gamma B_0$, where Θ'_n and Φ'_k are nutation and phase angles of the pulses with repetition period of the cycle $T_c = \sum_{k=0}^{N} \tau_k$ and cycle frequency $\omega_c = 2\pi/T_c$.

The relaxation time T_Q for the expectation value $\langle Q \rangle$ of an arbitrary spin operator Q in the weak collision case (WCC) can be calculated from the relation [1–3]

$$\frac{1}{T_Q} = \frac{\int_{-\infty}^{+\infty} \mathrm{Tr}\left\{[Q, \widetilde{\mathcal{H}}(t)][Q, \widetilde{\mathcal{H}}(t+\tau)]^\dagger\right\} \mathrm{d}\tau}{2\mathrm{Tr}(QQ^\dagger)}, \tag{2}$$

where $\widetilde{\mathcal{H}}(t)$ is a time dependent Hamiltonian in an interaction frame (interaction representation).

In the presence of dipole–dipole interactions of like spins 1/2 or axially symmetrical quadrupole interactions of spins $I = 1$, the Hamiltonian in the laboratory frame has the following form:

$$\mathcal{H}(t) = b \sum_{m=-2}^{+2} \mathcal{X}_m(t) \mathcal{T}^\dagger_{2m}(\boldsymbol{I}), \tag{3}$$

$$\mathcal{X}_m(t) = b\left[\mathcal{Y}_{2m}(\Theta(t)\Phi(t)) - \langle \mathcal{Y}_{2m}(\Theta(t)\Phi(t))\rangle\right], \tag{4}$$

where b is a coupling constant and $\mathcal{T}_{2m}(\boldsymbol{I})$ and $\mathcal{Y}_{2m}(\Theta, \Phi)$ are second rank spherical tensors and spherical functions, respectively.

All calculations have been done in the way described in the previous papers [1–3]. Using transformation properties for spherical tensors and spherical functions one gets the spin Hamiltonian in the interaction frame

$$\widetilde{\mathcal{H}}(t) = b \sum_{mm_1m_2m'=-2}^{+2} \mathcal{D}^*_{mm_1}(\Omega_1)\mathcal{D}^*_{m_1M_2}(\Omega_2)\mathcal{D}^*_{mm'}(\Omega'(t))X_{m_2}(t)\mathcal{T}^\dagger_{2m'}(\boldsymbol{I}), \tag{5}$$

where

$$\mathcal{D}_{mm'}(\Omega(t)) = \sum_{k=0}^{N-1} P_k(t)\mathcal{D}_{mm'}(\Omega'_k), \tag{6}$$

$$\mathcal{D}_{mm'}(\Omega) \equiv \mathcal{D}^{(2)}_{mm'}(\alpha, \beta, \gamma) = \exp(-\mathrm{i}m\alpha) d_{mm'}(\beta) \exp(-\mathrm{i}m\gamma), \tag{7}$$

$$P_k(t) = \sum_{n=-\infty}^{+\infty} c_{kn} \exp(+\mathrm{i}n\omega_c t), \tag{8}$$

$P_k(t)$ are periodic square pulses with the width τ_k. $\mathcal{D}_{mm'}(\Omega_k)$ and $d_{mm'}(\beta)$ are Wigner rotation matrices and Wigner functions, respectively,with $\Omega_k = (\alpha, \beta, \gamma) \equiv$

$(0, \Theta_k, \omega_k t)$ for $k = 1, 2$ and $\Omega'_k = (\Phi - \frac{\pi}{2}, \beta_k, \frac{\pi}{2} - \Phi)$ in the case of r.f. pulses with a fixed phase $\Phi_k = \Phi$.

Using Eqs. (1–7) and commutation relations for $Q = I_z$ and $I_x = \frac{1}{2}(I_+ + I_-)$ one gets the following general expressions for the effective relaxation times in the case of non-oriented (powder) samples:

$$\frac{1}{T_{1\mathrm{e}}} = \frac{\Delta M_2}{6} \sum_{mm_1m_2m'n} d^2_{mm'}(\Theta_1) d^2_{m_1m_2}(\Theta_2) \mid C^n_{mm'} \mid^2 (m')^2 \kappa_{m_2} \times \mathcal{J}_{m_2}(m_1\omega_1 + m_2\omega_2 - m\omega_0 - n\omega_\mathrm{c}), \tag{9}$$

$$\frac{1}{T_{2\mathrm{e}}} = \frac{\Delta M_2}{12} \sum_{mm_1m_2m'n} \left[\mid C^n_{mm'} \mid^2 \lambda_{m'} + C^n_{mm'} C^{n*}_{mm'+2} \lambda^+_{m'} + C^n_{mm'} C^n_{mm'-2} \lambda^-_{m'}\right] \times \mathcal{J}_{m_2}(m_1\omega_1 + m_2\omega_2 - m\omega_0 - n\omega_\mathrm{c}), \tag{10}$$

where

$$C^n_{mn'} = \sum_k c_{kn} \mathcal{D}_{mm'}(\Omega_k), \tag{11}$$

$$\lambda_m = 6 - m^2, \tag{12}$$

$$\lambda^\pm_m = \frac{1}{2}\sqrt{(1 \mp m)(2 \mp m)(3 \pm m)(4 \pm m)}, \tag{13}$$

$\mathcal{J}(\omega)$ is the reduced spectral density of the correlation function in the presence of molecular motion with correlation time τ_c:

$$\mathcal{J}_m(\omega) = \int_{-\infty}^{+\infty} \frac{\langle X_m(t) X_m(t+\tau)\rangle}{\langle \mid X_m \mid^2 \rangle} \mathrm{e}^{\mathrm{i}\omega\tau} \mathrm{d}\tau = \frac{2\tau_\mathrm{c}}{1 + \omega^2 \tau_\mathrm{c}^2} \tag{14}$$

and ΔM_2 is the change of the second moment of the resonance line in the case of motional narrowing.

In a special case of a train of identical, equidistant r.f. pulses along x-axis with $\Theta'_k = \Theta = 2\pi P/N, \Phi_k = 0$ and $\tau_k = 2\tau$ for $k = 1, \ldots, -N$ one gets

$$c_{kn} = \frac{1}{n\pi} \sin\frac{n\pi}{N} \mathrm{e}^{-\mathrm{i}2\pi kn/N}, \quad n \neq 0; \ c_{k0} = \frac{1}{N}, \tag{15}$$

$$\Omega_k = \left(\frac{\pi}{2}, +k\Theta, -\frac{\pi}{2}\right). \tag{16}$$

The numerical simulations of the effective relaxation time $T_{2\mathrm{e}}$ as a function of the correlation time τ_c at different values of cycle frequency ω_c, and rotation frequencies ω_1, ω_2 and $\Theta = \frac{\pi}{2}$ are presented in Figs. 1, 2 and 3 respectively, showing minima of $T_{2\mathrm{e}}$ at the region of $\omega_\mathrm{c}\tau_\mathrm{c}$ close to one.

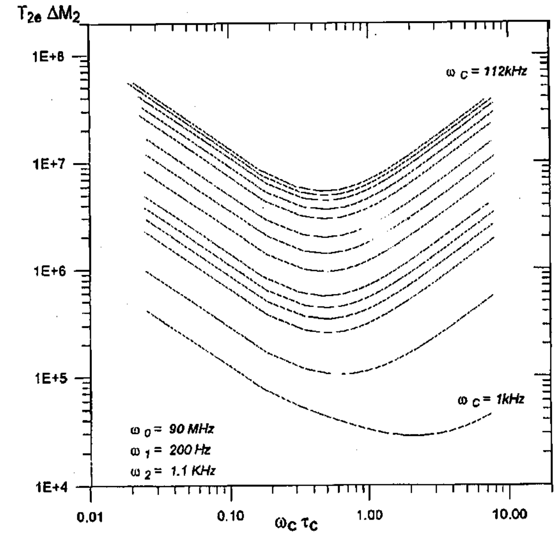

Fig. 1. T_{2e} as a function of the correlation time τ_c for ω_0 = 90 MHz, ω_1 = 200 Hz, ω_2 = 1.1 kHz and several values of ω_c (112 kHz, 102 kHz, 91 kHz, 75 kHz, 61 kHz, 41 kHz, 29 kHz, 19 kHz, 11 kHz, 9 kHz, 7.1 kHz, 5.3 kHz, 2.3 kHz, 1 kHz).

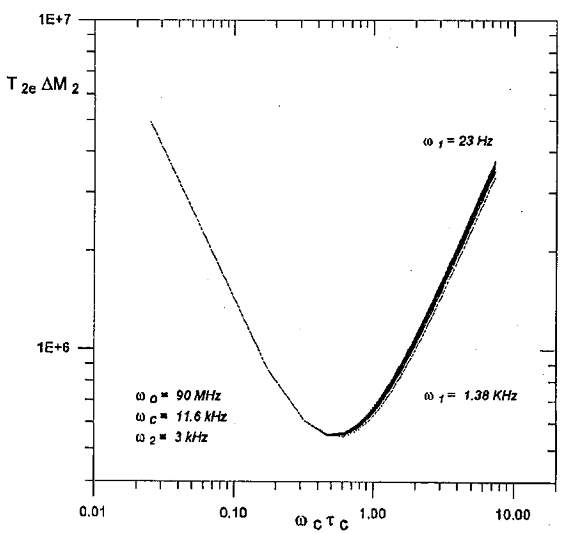

Fig. 2. T_{2e} as a function of the correlation time τ_c for ω_0 = 90 MHz, ω_c = 11.6 kHz, ω_2 = 3 kHz and several values of ω_1 (23 Hz, 57 Hz, 95 Hz, 193 Hz, 313 Hz, 503 Hz, 675 kHz, 893 kHz, 1 kHz, 1.38 kHz).

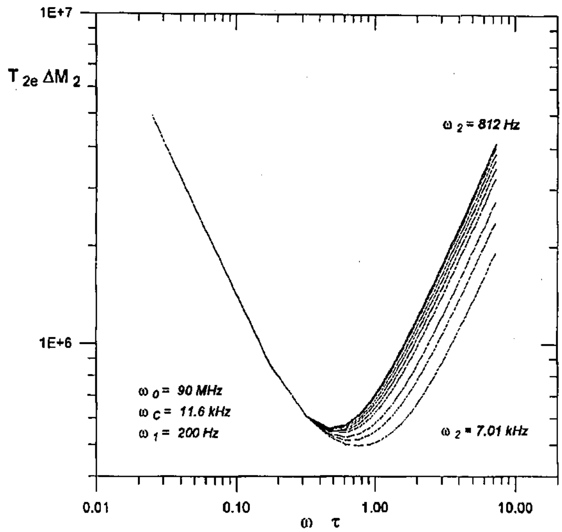

Fig. 3. T_{2e} as a function of the correlation time τ_c for ω_0 = 90Mhz, ω_c = 11.6 kHz, ω_1 = 200 Hz and several values of ω_2 (812 Hz, 1.1 kHz, 1.7 kHz, 2.5 kHz, 3.1 kHz, 3.7 kHz, 4.3 kHz, 5.4 kHz, 6.1 kHz, 7.01 kHz).

References

[1] J.S. Blicharski, A. Wolak, *Acta Phys. Pol. A* **79**, 591 (1991).

[2] J.S. Blicharski, A. Wolak, *Acta Phys. Pol. A* **82**, 511 (1992).

[3] J.S. Blicharski, G. Jasiński, *Acta Phys. Pol. A* **82**, 993 (1992).

[4] E.D. Ostroff, J.S. Waugh, *Phys. Rev. Lett.* **16**, 1097 (1966).

[5] P. Mansfield, D. Ware, *Phys. Lett.* **22**, 133 (1966).

[6] J.S. Waugh, C.H. Wang, *Phys Rev.* **162**, 209 (1967).

[7] P. Mansfield, D. Ware, *Phys. Rev.* **168**, 318 (1968).

[8] J.S. Waugh, L.M. Huber, U. Haeberlen, *Phys. Rev. Lett.* **20**, 180 (1968).

[9] U. Haeberlen, J.S. Waugh, *Phys. Rev.* **185**, 420 (1969).

[10] W. Grunde, H. Schmiedel, D. Freude, *Ann. Phys. (Leipzig)* **27**, 409 (1971).

[11] P. Mansfield, *Prog. Nucl. Magn. Reson. Spectrosc.* **8**, 43 (1971).

[12] A.N. Garroway, P. Mansfield, A.D. Stalker, *Phys. Rev. B* **11**, 121 (1975).

[13] R. Muller, R. Wilsh, *J. Mag. Resonance* **21**, 135 (1976).

[14] A. Jasiński, M. Stachurowa, *Acta Phys. Pol. A* **55**, 433 (1979).

[15] W.K. Rhim, P. Burum, A.D. Eleman, *J. Chem. Phys.* **68**, 692 (1978).

[16] A.J. Vega, R.W. Waughan, *J. Chem. Phys.* **68**, 1958 (1978).