

NUCLEAR SPIN RELAXATION IN PERIODICALLY PERTURBED SYSTEMS.

II. LIKE AND UNLIKE SPINS*

J.S. Blicharski and A. Wolak

Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland

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The effective relaxation time T_{2e} is calculated in the weak collision case for a system consisting of resonant nuclear spins I and nonresonant spins S , perturbed by periodic sequences of r.f. pulses and dipole-dipole interactions. PACS numbers: 76.60.-k

The aim of this paper is to calculate effective relaxation time T_{2e} for heteronuclear spin system in the presence of r.f. multipulse sequences of arbitrary phase and nutation angles. This theory may be applied for heterogeneous systems with slow molecular motion.

Dipolar interaction between resonant nuclear spins $I-I$ (like spins) as well as heteronuclear dipolar interactions $I-S$ between resonant and nonresonant spins (unlike spins) have been taken into account. A weak collision approximation has been applied. All calculations have been done in the way described in the previous paper (Part I of the series [7]) for homonuclear dipolar interactions. The results presented below are valid also in the case of the dipolar interactions $I-S$ between nuclear spins I and electron spins S (e.g. paramagnetic ions).

Let us consider generalized OWMW pulse sequence [1-7]

$$(\pi/2)_y - [-\tau - \beta_x - 2\tau - \beta_x - \dots - 2\tau - \beta_x - \tau]_n,$$

where $\beta_x = 2\pi P/N$ is the nutation angle of the very short (δ) r.f. pulse, $T_c = 2N\tau$ is the repetition period of the cycle, $\omega_c = 2\pi/T_c$ is the cycle frequency, P , N , n are natural numbers.

In the calculation we have taken into account secular and nonsecular terms of the dipolar interactions. Using the operator formalism presented in [7] and assuming $\omega_S \gg \omega_c$, $\omega_I \gg \omega_c$, one can calculate the effective relaxation time T_{2e} as a sum of relaxation contributions from homo- and heteronuclear dipolar interactions $I-I$ and $I-S$, respectively:

$$\frac{1}{T_{2e}} = \left(\frac{1}{T_{2e}} \right)_{II} + \left(\frac{1}{T_{2e}} \right)_{IS} \quad (1)$$

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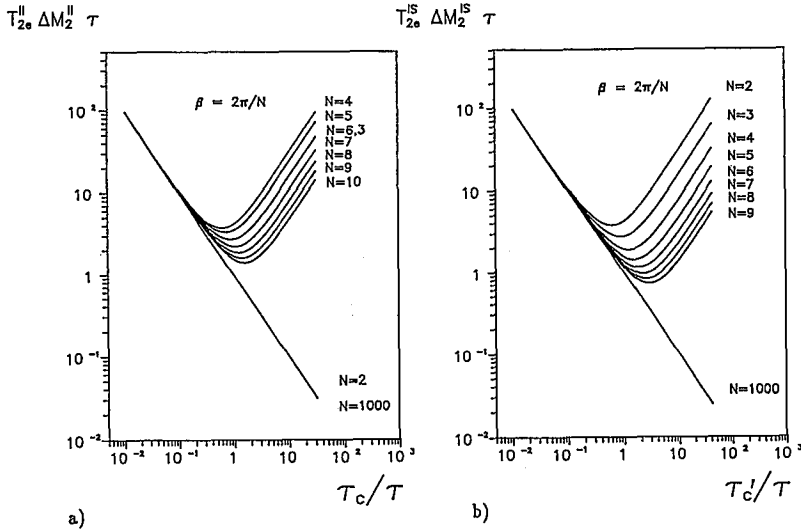


Fig. 1. Effective spin-spin relaxation time T_{2e} as a function of τ_c/τ (τ'_c/τ) for: (a) dipolar interactions between like spins ($I-I$), (b) dipolar interactions between unlike spins ($I-S$).

$$\left(\frac{1}{T_{2e}}\right)_{II} = \left(\frac{1}{T_2}\right)_{II} - \Delta M_2^{II} \tau \frac{\tanh u}{u^2} \frac{\sin^2 \beta}{1 - (\cos \beta / \cosh u)^2}, \quad (2)$$

$$\left(\frac{1}{T_{2e}}\right)_{IS} = \left(\frac{1}{T_2}\right)_{IS} - \Delta M_2^{IS} \tau \frac{\tanh(2w)}{2w^2} \frac{1 - \cos \beta}{1 - \cos \beta / \cosh 2w}, \quad (3)$$

$$\left(\frac{1}{T_2}\right)_{II} = \frac{\Delta M_2^{II}}{3} \left(3\tau_c + \frac{5\tau_c}{1 + \omega_I^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_I^2 \tau_c^2}\right), \quad (4)$$

$$\left(\frac{1}{T_2}\right)_{IS} = \frac{1}{4} \Delta M_2^{IS} \tau'_c \left(4 + \frac{3}{1 + \omega_I^2 \tau_c'^2} + \frac{1}{1 + (\omega_S - \omega_I)^2 \tau_c'^2} + \frac{6}{1 + \omega_S^2 \tau_c'^2} + \frac{6}{1 + (\omega_S + \omega_I)^2 \tau_c'^2}\right), \quad (5)$$

where

$$\Delta M_2^{II} = (M_2^{II})_{\text{RL}} - (M_2^{II}),$$

$$\Delta M_2^{IS} = (M_2^{IS})_{\text{RL}} - (M_2^{IS}),$$

$$\frac{1}{\tau'_c} = \frac{1}{\tau_c} + \frac{1}{\tau_s}, \quad w = \frac{\tau}{\tau'_c} = u + v, \quad u = \frac{\tau}{\tau_c}, \quad v = \frac{\tau}{\tau_s},$$

τ_c is the correlation time of molecular motions, τ_s is the relaxation time for spins S , τ'_c is effective correlation time, ΔM_2^{II} and ΔM_2^{IS} are changes of the second moment of the resonance line in the case of motional narrowing (compared with M_2 for a rigid lattice) for homo- and heteronuclear interactions, respectively.

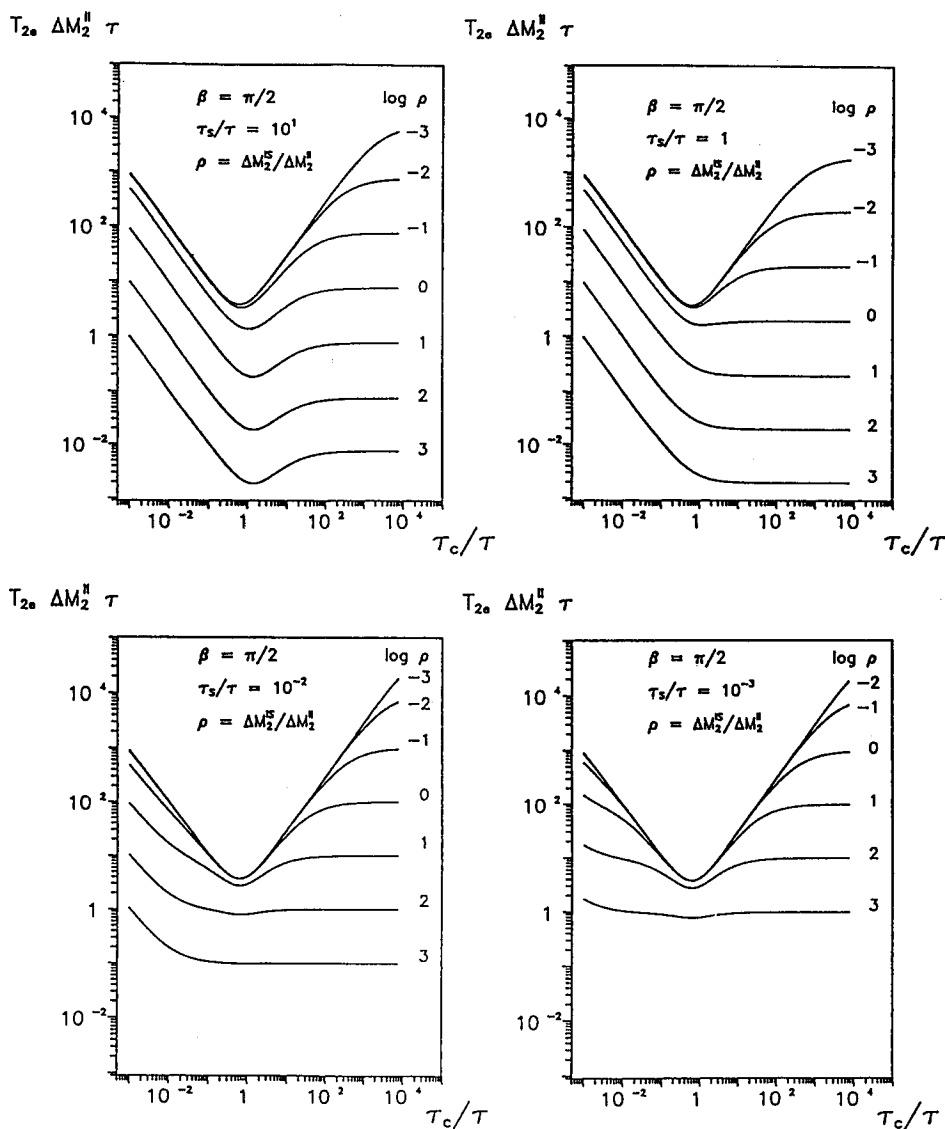


Fig. 2. Effective spin-spin relaxation time T_{2e} as a function of correlation time of molecular motions calculated for different values of the parameters τ_s/τ and $\rho = \Delta M_2^{IS}/\Delta M_2^{II}$. Calculations have been done for OWMW pulse sequence ($\beta = \pi/2$). Contributions from homo- and heteronuclear dipolar interactions have been taken into account.

Results of numerical calculations of the effective relaxation time T_{2e} as a function of correlation time τ_c are presented in Fig. 1 and Fig. 2. From Fig. 1a, one can see that for $\beta = \pi/2$ the relaxation time T_{2e}^{II} has a minimum for $\tau_c/\tau = 0.62$. If the

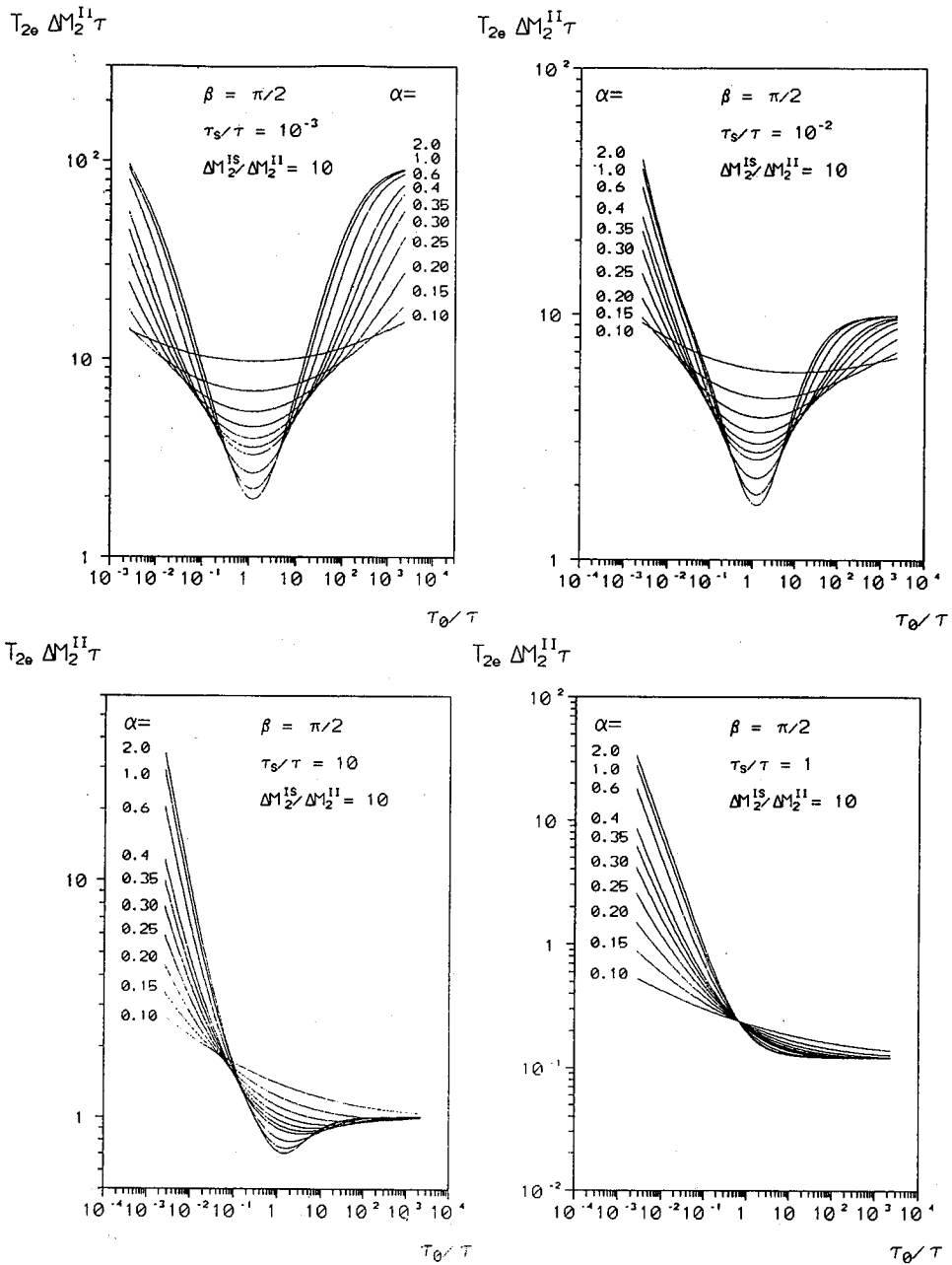


Fig. 3. Effective spin-spin relaxation time T_{2e} as a function of τ_0/τ in the presence of Log-Gauss distribution of correlation time τ_c of the molecular motion. Contributions from homo- and heteronuclear dipolar interactions have been taken into account. Calculations have been done for OWMW pulse sequence ($\beta = \pi/2$).

nutration angle β decreases, the value of $(T_{2e}^{II})_{\min}$ also decreases and the minimum of T_{2e}^{II} shifts in the direction of longer correlation times (lower temperatures). The relaxation time T_{2e}^{IS} exhibits a similar dependence on τ_c' as T_{2e}^{II} (Fig. 1b) but T_{2e}^{IS} has a minimum also for Carr-Purcell-Meiboom-Gill pulse sequence ($\beta = \pi$).

Results of calculation of the resultant relaxation time T_{2e} as a function of correlation time of molecular motions are presented in Fig. 2 for $\beta = \pi/2$ and for different values of the parameters τ_S/τ and $\rho = \Delta M_2^{IS}/\Delta M_2^{II}$. With increasing ρ , the contribution from the heteronuclear interaction increases. For large values of ρ and $\tau \ll \tau_S = \text{const.}$, the temperature dependence of T_{2e} is very weak. As ρ increases, the values of T_{2e} decreases. This effect is especially visible for $\tau_S \leq \tau$. For $\tau_S = \tau$ we observe shortening of T_{2e} as well as flattening of temperature dependence of T_{2e} in the region of low temperatures ($\tau_c < \tau$).

In the case of heterogeneous systems (e.g. biological systems) one can expect a presence of distribution of the correlation times τ_c for molecular motions. Assuming Log-Gauss distribution of the correlation times

$$f(s) = \frac{\alpha}{\sqrt{\pi}} \exp(-\alpha^2 s^2)$$

with $s = \ln \tau_c/\tau$ and fast exchange (or fast spin diffusion) one can calculate T_{2e} as a function of the average correlation time τ_0 in the logarithmic scale.

The results of numerical calculations are presented in Fig. 3 for $\rho = \Delta M_2^{IS}/\Delta M_2^{II} = 10$ at different values of τ_S/τ and parameters α .

The above presented theory will be applied for interpretation of the temperature dependence of T_{2e} for protons in the photosynthetic membranes.

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