NUCLEAR SPIN RELAXATION IN PERIODICALLY PERTURBED SYSTEMS. III. THE RELAXATION IN THE PRESENCE OF DOUBLE ROTATION*

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The effective spin relaxation times are calculated in the presence of double rotation in the weak collision case.

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1. Introduction

The commonly applied high resolution NMR methods in solids (magic angle spinning (MAS) [1, 2] and pulse method proposed by Waugh, Huber, Haeberlen [3, 4]) do not give a possibility of elimination of second order anisotropy effects of dipole–dipole or quadrupole interactions. These effects cause broadening of resonance lines. One can eliminate them by sample rotation about more than one axis. During the last few years new methods were developed, which eliminate the effects of second order anisotropy: namely double rotation (DOR) [5–7] and dynamic angle spinning (DAS) [8–11].

Spin relaxation processes in the presence of above-mentioned methods have not been studied yet. It is known that the spectral resolution is restricted by the rates of these processes. It is possible to describe these processes by spin–lattice and spin–spin effective relaxation times. The aim of this paper is to calculate "effective" spin relaxation times in the presence of double rotation.

In the double rotation method a sample rotates simultaneously about two axes z_1, z_2 at frequencies ω_1, ω_2 and polar angles θ_1, θ_2, respectively, which fulfil a condition $P_L(\cos\theta_1)P_L(\cos\theta_2) = 0$ for $L = 2, 4$, where $P_L(\cos\theta)$ are Legendre polynomials. These conditions have been satisfied by construction of a double rotor BETA (Berkeley-Tallin) [5, 7], which consists of the outer rotor and the inner rotor with a sample. The outer rotor rotates about a stable axis z_1, which forms the magic angle $\theta_1 = 54.7°$ with the direction of the magnetic field $\boldsymbol{B}_0$. The

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magic angle satisfies the condition $P_2(\cos\theta_1) = 0$. The inner rotor rotates about the axis z_2, which is inclined by $\theta_2 = 30.6^0$ with respect to the axis z_1. The angle θ_2 fulfils the condition $P_4(\cos\theta_2) = 0$. Other possible values of the angles are not used because of lower filling factors [7].

2. Theory of effective spin relaxation in the presence of double rotation

The relaxation time T_Q for the expectation value $< Q >$ of an arbitrary spin operator Q in the weak collision approximation (WCC) can be calculated from the relation [12]:

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

where $\tilde{\mathcal{H}}(t)$ is a spin Hamiltonian in an interaction frame (interaction representation).

In the presence of dipole–dipole interaction of two identical spins 1/2 or in the presence of axially symmetrical quadrupole interaction of spins $I = 1$, the spin Hamiltonian in the laboratory frame can be written as follows:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}(t), \tag{2}$$

$$\mathcal{H}_0 = -\omega_0 I_z + b\sum_m < Y_{2m}(\Theta,\Phi) > T^+_{2m}(\mathcal{I}), \tag{3}$$

$$\mathcal{H}(t) = \sum_m T_{2m}(\mathcal{I})X^*_m(t) = \sum_m X_m(t)T^+_{2m}(\mathcal{I}), \tag{4}$$

$$X_m(t) = b\left[Y_{2m}(\Theta(t),\Phi(t)) - < Y_{2m}(\Theta(t),\Phi(t)) >\right], \tag{5}$$

where $T^+_{2m} = (-1)^m T_{2-m}$ and $Y_{2m}(\Theta,\Phi)$ are respectively second rank spherical tensors and spherical functions, $\omega_0 = \gamma B_0$ is the Larmor frequency, and b is a coupling constant.

In the strong field approximation, when $\omega_0 \gg b$, $\mathcal{H}_0 \approx -\omega_0 I_z$ and in the presence of double rotation one gets

$$\tilde{\mathcal{H}}(t) = \sum_{mm_1m_2}\mathcal{D}^*_{mm_1}(\Omega_1)\mathcal{D}^*_{m_1m_2}(\Omega_2)X_{m_2}(t)T^+_{2m}\exp(-\mathrm{i}m\omega_0 t), \tag{6}$$

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

where $\mathcal{D}_{mm'}(\Omega_k)$ are the Wigner functions [13] expressed by the Euler angles $(\alpha,\beta,\gamma) = (0,\theta_k,\omega_k t)$ for $k = 1, 2$. Using Eqs. (1–7), commutation relations for spherical tensors, orthogonality and normalization of tensors in spherical functions one can get expressions for effective spin–lattice and spin–spin times $T_{1\mathrm{R}}$ and $T_{2\mathrm{R}}$ for $Q = I_z$ and I_x, respectively, in the presence of double rotation:

$$\frac{1}{T_{1\mathrm{R}}} = \frac{\Delta M_2}{6}\sum_{mm_1m_2} d^2_{mm_1}(\theta_1)d^2_{m_1m_2}(\theta_2)m^2\mathcal{J}(m_1\omega_1 + m_2\omega_2 - m\omega_0), \tag{8}$$

$$\frac{1}{T_{2\mathrm{R}}} = \frac{\Delta M_2}{12}\sum_{mm_1m_2} d^2_{mm_1}(\theta_1)d^2_{m_1m_2}(\theta_2)(6-m^2)\mathcal{J}(m_1\omega_1 + m_2\omega_2 - m\omega_0), \tag{9}$$

where $d_{mm'}(\theta_k) = \mathcal{D}^{(2)}_{mm'}(0, \theta_k, 0)$ are reduced Wigner functions. In the presence of isotropic molecular reorientations described by a correlation time τ_c, the reduced spectral density of the correlation function $\mathcal{J}(\omega)$ may be expressed in the form:

$$\mathcal{J}(\omega) = \frac{2\tau_c}{1 + \omega^2\tau_c^2}. \tag{10}$$

It follows from Eqs. (8–10) that relaxation times T_{1R} and T_{2R} show their minima for correlation times about $1/\omega_0$ and $1/\omega_1$, respectively. In the case of slow molecular motions in solids, the secular part $(m_1 = m_2 = m = 0)$ gives the main contribution to the spin–spin relaxation rate. However in the double rotation method this part vanishes because of the condition $d_{00}(\theta_1) = P_2(\cos\theta_1) = 0$. Moreover in the DOR method the condition $\omega 2/\omega 1 \neq n$, $1/n$ for $n = 1, 4/3, 3/2, 2, 3, 4$ (in practice $\omega_2/\omega_1 > 5$) [5] is satisfied, which gives $m_1\omega_1 + m_2\omega_2 \neq 0$ for $m_1, m_2 \neq 0$. It means that in strong fields ($\omega_0 \gg \omega_1, \omega_2$) and slow molecular motions the widths of NMR lines $\Delta\omega = 1/T_{2R}$ in the DOR method will be very small in comparison with $1/T_2$. In the absence of rotation, when $\omega_1 = \omega_2 = 0$, from Eqs. (8–9) one gets the well-known equations for the relaxation times T_1 i T_2 in the laboratory frame [14]. If $\omega_2 = 0$, one can get T_{1R} and T_{2R} in the presence of magic angle spinning (MAS) [15].

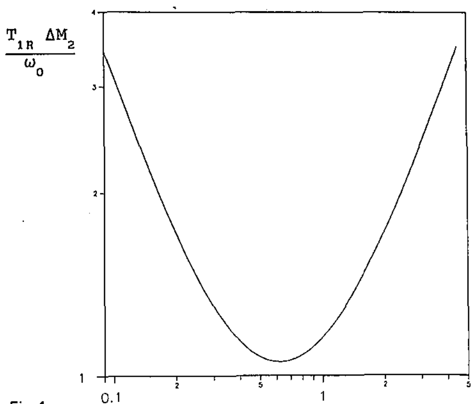

Fig. 1

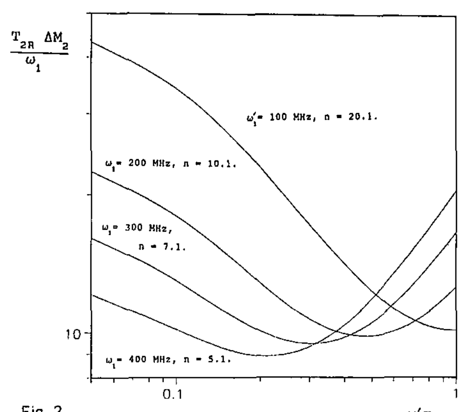

Fig. 2

Fig. 1. Effective spin–lattice relaxation time T_{1R} as a function of correlation time, in the presence of double rotation DOR ($\omega_0 = 90$ MHz, $\omega_1 = 200$ Hz, $n = \omega_2/\omega_1 = 5.1$).
Fig. 2. Effective spin–spin relaxation time T_{2R} as a function of correlation time in the presence of double rotation DOR for several values of ω_1 and n ($\omega_0 = 90$ MHz).

We made numerical simulations of Eqs. (1) and (2) for resonance frequency $\omega_0 = 90$ MHz in the wide range of $n = \omega_2/\omega_1$ for T_{2R}. Figure 1 shows the $\omega_0\tau_c$ dependence of T_{1R}. Figures 2, 3 and 4 show T_{2R} dependence on $\omega_1\tau_c$ in logarithmic-logarithmic plot, as well in fixed as in variable values of ω_1 and n.

As it was predicted above, relaxation times T_{1R} and T_{2R} show minimum values for correlation times about $1/\omega_0$ and $1/\omega_1$, respectively. Moreover, one can see that T_{2R} minimum is slightly shifted according to changes of ω_1 and n. Assuming

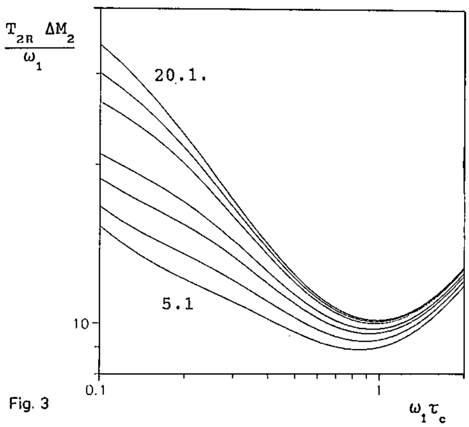

Fig. 3

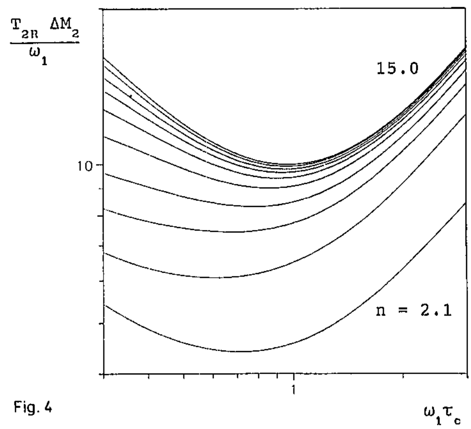

Fig. 4

Fig. 3. Effective spin–spin relaxation time T_{2R} as a function of correlation time in the presence of double rotation DOR for several values of n ($\omega_0 = 90$ MHz, $\omega_1 = 200$ Hz, $n = 5.1, 6.1, 7.6, 9.1, 13.1, 16.1, 20.1$).

Fig. 4. Effective spin–spin relaxation time T_{2R} as a function of correlation time in the presence of double rotation DOR for several values of n ($\omega_0 = 90$ MHz, $\omega_1 = 300$ Hz, $n = 2.1, 3.1, 4.1, 5.1, 6.5, 8.0, 9.5, 11.0, 13.0, 15.0$).

exponential dependence of correlation time τ_c on $1/T$ (Arrhenius equation) [14] by simple translation and changing of X axis scale, one can get activation dependence of T_{1R} and T_{2R} on 1000/T.

In the next paper we shall present spin relaxation theory in the presence of dynamic angle spinning (DAS).

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