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SOLID-ECHO IN SOLIDS WITH FAST MOLECULAR MOTIONS. EFFECTS OF NONZERO PULSE WIDTH

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The effects of the widths of hard RF pulses (a width of RF pulses $t_i \neq 0$ and an amplitude of RF pulse $\omega_1 >> M_2^{1/2}$) on the solid echoes in solids with molecular motions have been discussed in [1]. It has been shown that in the slow-motion region ($M_2 \tau_c^2 \approx 1$) the amplitude of the echo signal is reduced and the maximum of the echo signal is shifted to the end of the second pulse. In the regions of the fast molecular motion ($\tau_c \to 0$) and the rigid lattice ($\tau_c \to \infty$) the maximum of the echo signal is observed at $t_e = 2\tau + t_2 - t_1/2$ [1, 2].

In this paper we consider the effects of the RF pulse widths on the solid echo signal assuming that there are the fast ($\omega_1 \tau_c << 1$) molecular motions in solids and the RF pulses are not so hard ($\omega_1 \geq M_2^{1/2}$). The difference between the present consideration and our early one [1] is the introduction of the nonsecular terms of the dipolar interaction Hamiltonian in the treatment of the dynamics of a spin system during the RF pulses.

The observed transient response of the ensemble of spins or the two-pulse signal, is given by [1-3]

$$V(t, t_2, \tau, t_1) = \frac{Tr\{\overline{\rho(t, t_2, \tau, t_1)} I_X\}}{Tr(I_X^2)} \tag{1}$$

where the upper bar denotes the average of the density operator on the random motions of nuclei; t_1 and t_2 are the widths of the first and the second RF pulses; τ is the time interval between the RF pulses; t is the time where the NMR signal is observed and this time is measured from the beginning of the first RF pulse.

Using the density matrix formalism [3] we obtain the following expression for the two-pulse signal ($90°_Y - \tau - 90°_X - t$)

$$\begin{aligned} V(t, t_2, \tau, t_1) &= \beta\{1 - F(t, t_2, \tau, t_1) - \Phi(t, t_2, \tau, t_1, \omega_1) - \Gamma(t, t_2, \tau, t_1, \omega_1) + \dots\} \\ &\approx \beta \exp[-F(t, t_2, \tau, t_1) - \Phi(t, t_2, \tau, t_1, \omega_1) - \Gamma(t, t_2, \tau, t_1, \omega_1)] \end{aligned} \tag{2}$$

Here $\beta = \hbar\omega_0/kT$, ω_0 is the nuclear Larmor frequency; T is the temperature of sample and

$$F(t,t_2,\tau,t_1) = \frac{1}{4}\int_0^{t_1} dt'' \int_0^{t''} h(t'',t')dt' + \frac{1}{2}\int_{t_1}^{\tau} dt'' \int_0^{t_1} h(t'',t')dt' +$$

$$+ \int_{t_1}^{\tau} dt'' \int_{t_1}^{t''} h(t'',t')dt' - \frac{1}{2}\int_{\tau+t_2}^{t} dt'' \int_0^{t_1} h(t'',t')dt' + \tag{3}$$

$$- \int_{\tau+t_2}^{t} dt'' \int_{t_1}^{\tau} h(t'',t')dt' + \int_{\tau+t_2}^{t} dt'' \int_{\tau+t_2}^{t''} h(t'',t')dt'$$

$$\Phi(t,t_2,\tau,t_1,\omega_1) = -\frac{1}{4}\int_0^{t_1} dt'' \int_0^{t''} h(t'',t')\cos(2\omega_1 t')dt' +$$

$$-\frac{1}{4}\int_0^{t_1} dt'' \int_0^{t''} h(t'',t')\cos(2\omega_1 t'')dt' - \frac{1}{2}\int_{t_1}^{\tau} dt'' \int_0^{t_1} h(t'',t')\cos(2\omega_1 t')dt' +$$

$$+ \frac{1}{2}\int_{\tau+t_2}^{t} dt'' \int_0^{t_1} h(t'',t')\cos(2\omega_1 t')dt' - \int_{\tau+t_2}^{t} dt'' \int_{\tau}^{\tau+t_2} h(t'',t')\cos[2\omega_1(t'-\tau)]dt' + \tag{4}$$

$$+ \int_{\tau}^{\tau+t_2} dt'' \int_{t_1}^{\tau} h(t'',t')\cos[2\omega_1(t''-\tau)]dt' + \frac{1}{2}\int_{\tau}^{\tau+t_2} dt'' \int_0^{t_1} h(t'',t')\cos[2\omega_1(t''-\tau)]dt'$$

$$\Gamma(t,t_2,\tau,t_1,\omega_1) = \frac{1}{4}\int_0^{t_1} dt'' \int_0^{t''} h(t'',t')\cos[2\omega_1(t''-t')]dt' +$$

$$-\frac{1}{2}\int_{\tau}^{\tau+t_2} dt'' \int_0^{t_1} h(t'',t')\cos[2\omega_1(t''-\tau)]\cos(2\omega_1 t')dt' +$$

$$-\frac{1}{2}\int_{\tau}^{\tau+t_2} dt'' \int_{\tau}^{t''} h(t'',t')\sin[2\omega_1(t''-\tau)]\sin[2\omega_1(t'-\tau)]dt' + \tag{5}$$

$$+ \int_{\tau}^{\tau+t_2} dt'' \int_{\tau}^{t''} h(t'',t')\cos[2\omega_1(t''-t')]dt'$$

In Eqs. (3)-(5)

$$h(t'',t') = W\sum_{i,j} \overline{a_{ij}(t'')a_{ij}(t')} \tag{6}$$

is the correlation function of the dipolar local fields [3].
In Eq. (6) [3]

$$W = \frac{3}{4}\gamma^4 \hbar^2 I(I+1)\frac{1}{N}, \tag{7}$$

$$a_{ij}(t') = R_{ij}^{-3}(t')[1 - 3\cos^2\theta_{ij}(t')]. \tag{8}$$

In order to calculate the integrals in Eqs. (3)-(5), we assume that the random process describing the molecular motions in solids is stationary Markov process and the correlation function $h(t'', t')$ has the form [1]

$$h(|t''-t'|) = \overline{M_2} + \Delta M_2 \exp\left(-\frac{|t''-t'|}{\tau_c}\right), \tag{9}$$

where τ_c is the correlation time for the random thermal motion of nuclei and

$$\overline{M_2} = W\sum_{i,j}\left\{\frac{1}{n}\sum_{k=1}^{n} a_{ij}(\Omega_k)\right\}^2 \equiv W\sum_{i,j}(\overline{a_{ij}})^2 \tag{10}$$

is the second moment of motionally narrowed NMR line [3];

$$\Delta M_2 = M_2 - \overline{M_2}. \tag{11}$$

In Eq. (11)

$$M_2 = W\sum_{i,j} a_{ij}^2 \tag{12}$$

is the second moment of NMR line for the rigid lattice [3].

Using the correlation function (9) and calculating the integrals in Eq. (3) we obtain the following expression for the function $F(t, t_2, \tau, t_1)$:

$$F(t,t_2,\tau,t_1) = \frac{1}{2}\overline{M_2}\left[t - \left(2\tau + t_2 - \frac{t_1}{2}\right)\right]^2 + \\ + \Delta M_2 \tau_c^2 R(t,t_2,\tau,t_1,\tau_c) + \dots , \tag{13}$$

where

$$R(t, t_2, \tau, t_1, \tau_c) = -\frac{7}{4} + \frac{t}{\tau_c} - \frac{3t_1}{4\tau_c} - \frac{t_2}{\tau_c} + $$
$$-\frac{1}{4}\exp\left(-\frac{t_1}{\tau_c}\right) - \exp\left(-\frac{t_2}{\tau_c}\right) - \frac{1}{2}\exp\left(-\frac{t}{\tau_c}\right) +$$
$$+\frac{1}{2}\exp\left(-\frac{\tau - t_1}{\tau_c}\right) - \frac{1}{2}\exp\left(-\frac{t - t_1}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau + t_2}{\tau_c}\right) + \quad (14)$$
$$+\exp\left(-\frac{t-\tau}{\tau_c}\right) + \exp\left(-\frac{t-\tau-t_2}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau + t_2 - t_1}{\tau_c}\right)$$

The expressions (13) and (14) were obtained earlier [1] describe the solid echo signal in the case of the hard RF pulses ($\omega_1 >> M_2^{1/2}$).

For the case of the fast molecular motions ($M_2^{1/2}\tau_c << 1$) from Eqs. (13), (14) we have

$$F(t, t_2, \tau, t_1) = \frac{1}{2}\overline{M_2}\left[t - \left(2\tau + t_2 - \frac{t_1}{2}\right)\right]^2 + \Delta M_2 \tau_c\left(t - \frac{3t_1}{4} - t_2\right). \quad (15)$$

So in the case of the hard RF pulses the solid echo signal is described by equation

$$V(t, t_2, \tau, t_1) \cong \beta\exp\left\{-\frac{1}{2}\overline{M_2}\left[t - \left(2\tau + t_2 - \frac{t_1}{2}\right)\right]^2 - \Delta M_2 \tau_c\left(t - \frac{3t_1}{4} - t_2\right)\right\}. \quad (16)$$

From Eq. (16) it follows that the maximum of the echo signal amplitude is observed at the time t_e:

$$t_e = 2\tau + t_2 - \frac{t_1}{2} - \frac{\Delta M_2}{\overline{M_2}}\tau_c . \quad (17)$$

Inserting Eq. (17) into Eq. (16) we obtain the following expression for the solid echo amplitude ($M_2^{1/2}\tau_c << 1$, $\omega_1 >> M_2^{1/2}$):

$$V(t_e, t_2, \tau, t_1) \cong \beta\exp\left[-\Delta M_2 \tau\tau_c\left(2 - \frac{5t_1}{4\tau}\right)\right]. \quad (18)$$

Let us consider the case of the RF pulses for which $\omega_1 \geq M_2^{1/2}$ and $\omega_1\tau_c << 1$. For this case we obtain from Eqs. (2)-(5)

$$V(t, t_2, \tau, t_1) \cong \beta \exp\left\{ -\frac{3}{8}\frac{\overline{M_2}}{\omega_1^2} - \frac{1}{2}\overline{M_2}\left[t - \left(2\tau + t_2 - \frac{t_1}{2} \right) \right]^2 - \Delta M_2 \tau_c \left(t - \frac{t_1}{2} - \frac{t_2}{4} \right) \right\} \quad (19)$$

From Eq. (19) it follows that the time position of the maximum of the echo signal amplitude is defined by Eq. (17). Inserting Eq. (17) into Eq. (19) we have

$$V(t_e, t_2, \tau, t_1) \cong \beta \exp\left[-\frac{1}{2}\frac{\overline{M_2}}{\omega_1^2} - \Delta M_2 \tau \tau_c \left(2 - \frac{4t_1 - 3t_2}{4\tau} \right) \right]. \quad (20)$$

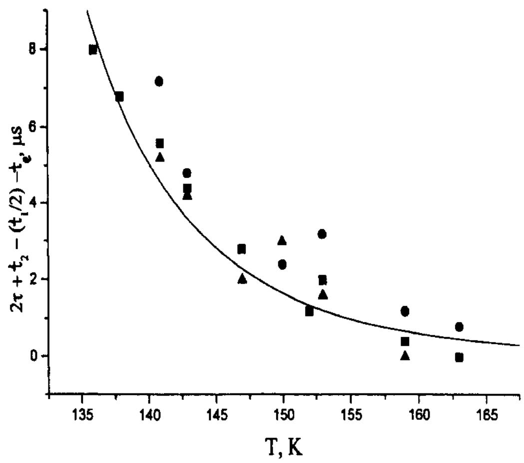

Fig. 1. The temperature dependence of ($2\tau + t_2 - t_1/2 - t_e$) for polycrystalline NH_4Cl at different pulse spacing ($t_1 = t_2 = 3.6$ μs). The solid line is the theoretical curve ($\Delta M_2 \tau_c/\overline{M_2}$). The values of τ were obtained from the high temperature values of the time position of the maximum solid echo amplitude using the equation: $t_e = 2\tau + t_2 - t_1/2$; ■ – τ = 22.3 μs; ● – τ = 29.7 μs; ▲ – τ = 38.1 μs.

From Eq. (17) we see that the time position of the maximum solid echo amplitude is simply connected with τ_c. Figure 1 shows the theoretical and experimental temperature dependences of $(2\tau + t_2 - t_1/2 - t_e) = \Delta M_2 \tau_c / \overline{M_2}$ obtained for polycrystalline NH_4Cl at different pulse spacings. The theoretical curve was obtained using the following parameters [1]: $\tau_c = (2.16 \times 10^{-14}$ s) exp (19.85 kJ· mol^{-1}/RT); $\overline{M_2} = 4.74 \times 10^{-8}$ T^2; $\Delta M_2 = 46.15 \times 10^{-8}$ T^2. The agreement between theory and experiment is reasonable though there are large errors at the t_e measurements.

References

[1] P. Bilski, N. A. Sergeev, J. Wąsicki, *Materiały XXXI Ogólnopolskiego Seminarium NMR* (Ed. J. Hennel) pp.139-142, Kraków, IFJ, 1999; Abstracts of RAMIS 99, Poznań-Kiekrz (1999) 56; Appl. Magn. Res. **18** (2000) (in press).

[2] N. A. Sergeev, Solid State NMR **10**, 45 (1997).

[3] C. P. Slichter, *Principles of Magnetic Resonance*, Springer, Berlin (1980).