

## MOLECULAR MOTIONS AND ECHO IN SOLIDS

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**Abstract:** The effect of the non-secular terms of the dipolar interaction Hamiltonian on the echo signal for the case of the fast molecular motions in solids is considered.

It is now well established that solid-echo signal can be significantly distorted in the so-called slow-motion region and the nature of this distortion may be used to obtain information about the motional mechanism and the motional parameters in solids. At the recent time, there have been published a great number of papers describing analysis and application of “solid-echo” technique to molecular dynamic investigations in solids (see Refs in [1-2]). In all the papers the secular part of the dipolar interaction Hamiltonian has been only considered. This approximation is not good enough for the case of the fast molecular motion when the correlation frequency of the molecular motion  $\omega_c = 2\pi/\tau_c$  is comparable with the resonant NMR frequency of nucleus  $\omega_0 = \gamma B_0$  [3].

In this paper we consider the effects of the non-secular terms of the dipolar interaction Hamiltonian on the solid echo signal for the case, when there are fast ( $\omega_c \approx \omega_0$ ) molecular motions in solids.

Using the density matrix formalism and assuming that the RF pulses are the delta-functions [4], we obtain the following expression for the two-pulse signal ( $90^\circ_Y - \tau - 90^\circ_X - Acq(t)$ ):

$$V(t, \tau) = \beta \{1 - F(t, \tau) - \Gamma(t, \tau, \omega_0)\} + \dots \approx \beta \exp[-F(t, \tau) - \Gamma(t, \tau, \omega_0)]. \quad (1)$$

Here the function

$$F(t, \tau) = \int_0^\tau dt'' \int_0^{t''} h(t'', t') dt' - \int_0^t dt'' \int_0^\tau h(t'', t') dt' + \int_0^t dt'' \int_0^{t''} h(t'', t') dt' \quad (2)$$

describes the secular dipolar interaction contribution to the echo signal decay [1, 2]. The non-secular dipolar contribution to the echo signal decay is described by the function

$$\begin{aligned}
\Gamma(t, \tau, \omega_0) = & \frac{5}{3} \int_0^\tau dt'' \int_0^{t''} h(t'', t') \cos \omega_0(t'' - t') dt' + \\
& - \frac{4}{3} \int_\tau^t dt'' \int_0^\tau h(t'', t') \cos \omega_0(t'' - t') dt' + \frac{5}{3} \int_\tau^t dt'' \int_0^{t''} h(t'', t') \cos \omega_0(t'' - t') dt' + \\
& + \frac{2}{3} \int_0^\tau dt'' \int_0^{t''} h(t'', t') \cos 2\omega_0(t'' - t') dt' - \frac{1}{3} \int_\tau^t dt'' \int_0^\tau h(t'', t') \cos 2\omega_0(t'' - t') dt' + \\
& + \frac{2}{3} \int_\tau^t dt'' \int_0^{t''} h(t'', t') \cos 2\omega_0(t'' - t') dt' .
\end{aligned} \tag{3}$$

In Eqs. (2) and (3)

$$h(t'', t) = W \left\langle \sum_{i,k} \overline{b_{ik}(t'') b_{ik}(t')} \right\rangle \tag{4}$$

and

$$W = \frac{3}{4} \gamma^4 \hbar^2 I(I+1) \frac{1}{N}, \tag{5}$$

$$b_{ik}(t) = r_{ik}^{-3}(t) [1 - 3 \cos^2 \vartheta_{ik}(t)]. \tag{6}$$

In order to calculate the correlation function  $h(t'', t')$  we consider a simple model of the molecular motion in solids between discrete lattice sites  $\Omega_m$  ( $m = 1, 2, \dots, n$ ) [1, 2]. For this model the correlation function  $h(t'', t')$  has the form [1, 2]:

$$h(|t'' - t'|) = \langle \bar{M}_2 \rangle + \langle \Delta M_2 \rangle \exp\left(-\frac{|t'' - t'|}{\tau_c}\right). \tag{7}$$

Here  $\langle \bar{M}_2 \rangle$  is the second moment of motionally narrowed *NMR* line in polycrystalline sample and  $\langle \Delta M_2 \rangle = \langle M_2 \rangle - \langle \bar{M}_2 \rangle$ ;  $\langle M_2 \rangle$  is the second moment of *NMR* spectrum in polycrystalline rigid lattice. In Eq. (7)  $\tau_c^{-1}$  is the rate constant which describes the probability that the random variable  $\Omega(t)$  changes from  $\Omega_l$  to  $\Omega_m$  ( $l \neq m$ ) by one jump [1, 2].

Using the correlation function (7) and assuming that the molecular motions in solid are fast ( $M_2^{1/2} \tau_c \ll 1$ ,  $\tau_c \ll \tau$ ), we obtain from Eq. (2) and Eq. (3):

$$F(t, \tau) = \frac{1}{2} \langle \bar{M}_2 \rangle (t - 2\tau)^2 + \langle \Delta M_2 \rangle \tau_c t \tag{8}$$

and

$$\Gamma(t, \omega_0) = \frac{1}{3} [5J(\omega_0) + 2J(2\omega_0)] t. \quad (9)$$

In Eq. (9)

$$J(m\omega_0) = \langle \Delta M_2 \rangle \int_0^{\infty} e^{-\frac{t}{\tau_c}} \cos m\omega_0 t \, dt = \langle \Delta M_2 \rangle \frac{\tau_c}{1 + (m\omega_0 \tau_c)^2}. \quad (10)$$

Inserting Eqs. (8)-(10) into Eq. (1) we have

$$V(t, \tau, \omega_0) \approx \beta \exp \left[ -\frac{1}{2} \langle \bar{M}_2 \rangle (t - 2\tau)^2 - \frac{1}{3} \langle \Delta M_2 \rangle t \left( 3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right) \right]. \quad (11)$$

From Eq. (11) it follows that the maximum of solid echo signal is observed at the time  $t_e$ :

$$t_e = 2\tau - \frac{\langle \Delta M_2 \rangle}{3 \langle \bar{M}_2 \rangle} \left( 3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right). \quad (12)$$

The shift of the echo signal due to non-secular terms of dipolar interaction is determined by the term

$$\left( \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right)$$

in Eq. (12). This term has maximum value at  $\tau_c \approx \omega_0^{-1}$  and for NMR spectrometers is  $< 0.1 \mu\text{s}$ . So, the shift of the echo signal due to non-secular terms of dipolar interaction is very small and may be ignored in consideration. Thus omitting the non-secular contribution to Eq. (12), we have

$$t_e \approx 2\tau - \frac{\langle \Delta M_2 \rangle}{\langle \bar{M}_2 \rangle} \tau_c. \quad (13)$$

Inserting Eq. (13) into Eq. (11) we obtain the following expression for the solid echo amplitude:

$$V(t_e, \tau, \omega_0) \approx \beta \exp(-\langle \Delta M_2 \rangle t_e \tau_c). \quad (14)$$

From Eq. (14) it follows the simple formula for the activation energy  $E_a$  of a molecular motion:

$$\ln \{-\ln [T V(t_e)]\} = \text{const} + \frac{E_a}{RT}. \quad (15)$$

We have applied the Eq. (15) for the analysis of temperature dependencies of the solid echo signals in polycrystalline benzene ( $\text{C}_6\text{H}_6$ ) and polycrystalline ammonium chloride ( $\text{NH}_4\text{Cl}$ ). These

compounds were chosen because they have been extensively studied by different experimental *NMR* techniques (see Refs in [1, 2]). It is now well established that in  $\text{NH}_4\text{Cl}$  there are the reorientations of the ammonium ions about threefold and twofold symmetry axes and in solid benzene there are the reorientations of  $\text{C}_6\text{H}_6$  molecules about its sixfold symmetry axis. The experimental temperature dependencies of  $-\ln[-\ln(TV)(t_e)]$  on  $1/T$  in polycrystalline benzene ( $\text{C}_6\text{H}_6$ ) and polycrystalline ammonium chloride ( $\text{NH}_4\text{Cl}$ ) are shown in Fig. 1 and Fig. 2. From the results shown in Fig. 1 we obtained the activation energy of the molecular motion in polycrystalline benzene ( $\text{C}_6\text{H}_6$ )

$$E_a = (18.3 \pm 1) \text{ kJ} \cdot \text{mol}^{-1}.$$

This value is in reasonable agreement with the known data  $E_a = 17.5 \text{ kJ mol}^{-1}$ [1].

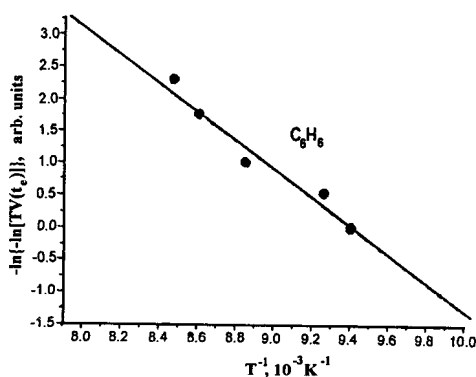


Fig. 1. Experimental temperature dependence of  $-\ln[-\ln TV(t_e)]$  on  $1/T$  in polycrystalline  $\text{C}_6\text{H}_6$ .  $\tau = 29.4 \mu\text{s}$

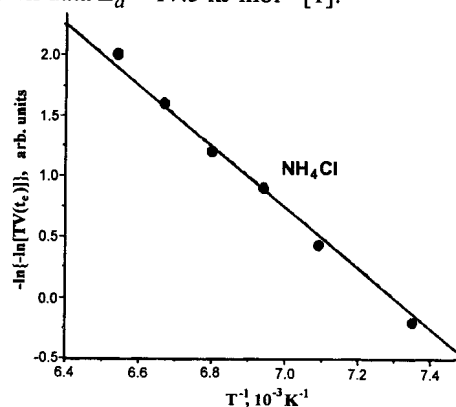


Fig. 2. Experimental temperature dependence of  $-\ln[-\ln TV(t_e)]$  on  $1/T$  in polycrystalline  $\text{NH}_4\text{Cl}$ .  $\tau = 20.4 \mu\text{s}$

From the results shown in Fig. 2 we obtained the activation energy of the molecular motion in ammonium chloride ( $\text{NH}_4\text{Cl}$ ) equal to

$$E_a = (20.8 \pm 1) \text{ kJ} \cdot \text{mol}^{-1}.$$

This value is in agreement also with the known data  $E_a = 19.85 \text{ kJ} \cdot \text{mol}^{-1}$ [1].

## References

- [1] P. Bilski, N. A. Sergeev, J. Waśicki, *Appl. Magn. Res.* **18**, 115 (2000).
- [2] P. Bilski, N. A. Sergeev, J. Waśicki, *Mol. Phys. Rep.* **29**, 55 (2000).
- [3] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford (1961).
- [4] In the delta-function approximation of the *RF* pulse it is assumed that for the amplitude and the width of the *RF* pulse  $\omega_1 t_i = \text{const}$  at  $t_i \rightarrow 0$  and  $\omega_1 \rightarrow \infty$ .