SOLID ECHOES IN THE SLOW MOTION REGION

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Expressions describing the temperature dependence of the solid echo amplitude in the case of slow atomic and molecular motions for arbitrary ratios of the motion correlation times τ_c and intervals between the RF pulses τ have been obtained. Comparison with the experimental data measured in polycristalline cyclohexane in temperature ranges of slow reorientation and diffusion motions demonstrates a good agreement with the theoretical consideration made and shows new possibilities in measuring motion parameters using a simple solid echo experiment.

The study of slow atomic and molecular motions using the analysis of the NMR line shape $g(\omega)$ or free induction decay $G(t)$ is limited mainly by solids containing well isolated two- and three-spin groups (H_2O, D_2O, CH_2, CH_3, NH_3 etc.) [1]. This is due to the fact that the problem of the calculation of $g(\omega)$ or $G(t)$ allows in these cases an exact analytical solution. In the more general case a theoretical consideration of $g(\omega)$ and $G(t)$ is a complicated mathematical problem. Recently, for its solution Lowe et al. [2–4] have suggested to use a method similar to the moment method of Van Vleck [5]. The principle of the method consists in calculating the coefficients a_n in the time expansion of the function $G(t)$

$$G(t) = \sum_{n=0}^{\infty} (1/n!) a_n t^n \,. \tag{1}$$

In the case of a stochastic Markov process describing the thermal motion of the magnetic nuclei this expression can be written as [2–4,6]

$$G(t) = \left(1 - \frac{1}{2!} M_2 t^2 + \frac{1}{4!} M_4 t^4\right) + \left(\frac{1}{3!} \frac{\Delta M_2}{\tau_c} t^3 - \frac{1}{4!} \frac{\Delta M_2}{\tau_c^2} t^4 + \dots\right). \tag{2}$$

Here τ_c is the correlation time of the motion considered, M_2, M_4 are the second and fourth moments of the NMR line in the rigid lattice, $\Delta M_2 = M_2 - \bar{M}_2$, where $\bar{M}_2$ is the measured second moment of the motionally narrowed NMR line ($\tau_c^{-1} > M_2^{1/2}$). From (2) it follows that for the determination of the coefficients a_3 and a_4 which contain the information about the motion it is necessary to know the behaviour of $G(t)$ at $t \to 0$. However, the initial part of the FID cannot be measured usually because of the finite pulse length, the presence of a "dead" time of the receiver, etc.

Several methods were suggested for removing this "dead" time of the pulse experiment. The simplest method among them is the solid echo method in which a spin echo in solids is formed by the two-pulse sequence $90°-\tau-90°_{90°}$ [7,8]. It has been shown recently that for the Markov process the dependence of the solid echo amplitude at 2τ can be described as follows [9]

$$V(2\tau) - V_{rl}(2\tau) = 1 - \tfrac{2}{3}(\Delta M_2/\tau_c)\tau^3 + \tfrac{1}{2}(\Delta M_2/\tau_c^2)\tau^4 + \dots, \tag{3}$$

where $V_{rl}(2\tau)$ is the expression describing the decay of the solid echo amplitude in the rigid lattice [8]. The expressions (2) and (3) describe correctly the behaviour

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of the FID and solid echo amplitude for times $t < \tau_c$. In the present paper the calculation of the solid echo amplitude is performed for an arbitrary ratio t/τ_c. The same problem for the two-spin system was solved earlier [10–13].

It is known [1] that the function $G(t)$ can be expressed in the case of a dipole–dipole interaction spin system having space spin motion described by the stochastic Markov process as

$$G(t) = \exp\left(-\int_0^t (t-\tau)C(\tau)\,\mathrm{d}\tau\right), \tag{4}$$

where $C(\tau)$ is the autocorrelation function of the local dipole fields on the resonant nuclei. If $C(\tau)$ is chosen in the form [1]

$$C(\tau) = \bar{M}_2 + \Delta M_2 \exp(-\tau/\tau_c), \tag{5}$$

then we get from (4)

$$G(t) = \exp\{-\Delta M_2 \tau_c^2 [\exp(-t/\tau_c) - 1 + t/\tau_c] - \tfrac{1}{2}\bar{M}_2 t^2\}. \tag{6}$$

It follows from (6) that when $t/\tau_c < 1$,

$$G(t) = \left(1 - \frac{1}{2!}M_2 t^2 + \frac{1}{4!}(3M_2^2)t^4 + \ldots\right) + \left(\frac{1}{3!}\frac{\Delta M_2}{\tau_c}t^3 - \frac{1}{4!}\frac{\Delta M_2}{\tau_c^2}t^4 + \ldots\right), \tag{7}$$

which is in good agreement with (2) obtained using more strict initial conditions than (6). When $t/\tau_c \gg 1$ we have

$$G(t) = \exp(-\tfrac{1}{2}\bar{M}_2 t^2)\exp(-\Delta M_2 \tau_c t), \tag{8}$$

which corresponds to the motionally narrowed NMR line shape [1].

Using a method similar to the Abragam method presented above we have obtained for $V(2\tau)$ the following expression

$$V(2\tau) = \exp\left(-4\int_0^\tau (\tau - t')C(t')\,\mathrm{d}t' + \int_0^{2\tau} (2\tau - t')C(t')\,\mathrm{d}t'\right). \tag{9}$$

Then for the autocorrelation function of the form (we find from (9)

$$V(2\tau) = \exp\{-\Delta M_2 \tau_c^2 [1 + 2\tau/\tau_c - [2 - \exp(-\tau/\tau_c)]^2]\}. \tag{1}$$

In the slow motion region ($\tau/\tau_c < 1$) we have from (

$$V(2\tau) = 1 - \tfrac{2}{3}(\Delta M_2/\tau_c)\tau^3 + \tfrac{1}{2}(\Delta M_2/\tau_c^2)\tau^4 + \ldots, \tag{1}$$

which agrees well with the expression (3). For rapid motion ($\tau/\tau_c \gg 1$)

$$V(2\tau) \simeq \exp[-2\Delta M_2 \tau_c \tau]. \tag{1}$$

The calculated dependences of the solid echo amplitude on the ratio τ/τ_c are presented for some values of $\Delta M_2 \tau^2$ in fig. 1. It can be seen from it that the minimum of the temperature dependence of $V(2\tau)$ is always at $\tau/\tau_c = 1.8937$. Therefore the correlation time of the studied motion $\tau_c = 0.528\tau$ can be obtained with good accuracy from the temperature dependence of the solid echo amplitude. The minimum value of this dependence is determined by both the motion type and the parameter of the pulse sequence

$$V(2\tau) = \exp(-0.38\,\Delta M_2 \tau^2). \tag{1}$$

The measurements performed in polycristalline cyclohexane confirm well the obtained expressions. Fig. 2 shows a strong decrease of the solid echo amplitude in the slow motion regions of the reorientation of cyclohexane molecules about their threefold axes (at temperatures below the phase transition $T_c = 186$ K).

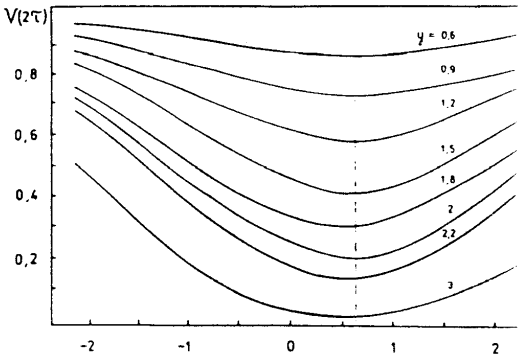

Fig. 1. The dependences of the solid echo amplitude $V(2\tau)$ on $\ln(\tau/\tau_c)$ for some values of $y = \Delta M_2 \tau^2$ calculated using eq. (10).

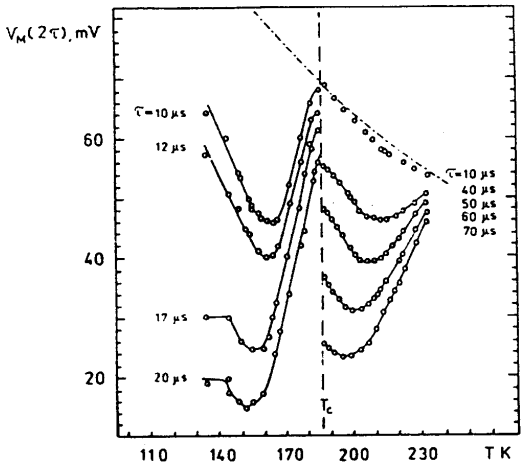

Fig. 2. The temperature dependences of the solid echo amplitudes in polycristalline cyclohexane for some values of the interval τ between RF pulses of the pulse sequence $90° - \tau - 90°_{90}°$. The length of the 90° pulses was 2.0 μs, the Larmor frequency was 30 MHz. The broken line shows the temperature dependence of the FID amplitude in polycristalline $Ca(OH)_2$ which is of rigid-lattice type in the whole measured temperature range.

diffusion (at $T > T_c$) [14–17]. The experimental values of the minimal $V(2\tau)$ for both studied motions agree well with the calculated ones. So, in the low temperature phase the $V(2\tau)$ values obtained using (13) and $\Delta M_2 = 19 \times 10^{-4}$ T [14,18] are equal to 0.58, 0.46, 0.21 and 0.12, for $\tau = 10$, 12, 17 and 20 μs, respectively. The corresponding experimental values are 0.58 ± 0.02, 0.50 ± 0.02, 0.29 ± 0.03 and 0.18 ± 0.03.

The correlation times of the cyclohexane molecule motions in two solid phases, obtained using the relation between τ and τ_c, $\tau/\tau_c = 1.8937$, at temperatures of the observed $V(2\tau)$ minima (164 ± 1, 162.5 ± 1, 157 ± 1, 154 ± 1 K and 195 ± 1, 200 ± 1, 206 ± 1, 211 ± 1 K) are described well by the Arrhenius expression $\tau_c = \tau_0 \exp(E_a/RT)$. The parameters of the cyclohexane diffusion motion in the plastic cubic phase at $T > 186$ K calculated in such a way $E_a = 9.5 \pm 0.2$ kcal/mole, $\tau_0 = (3.3 \times 2.0) \times 10^{15}$ s are in very good agreement with the known data of the previous studies of this phase made by the NMR pulse methods [15–17]. The parameters of the reorientation motion of the cyclohexane molecule around its threefold axis in the low-temperature monoclinic phase [14,18] are 5.4 ± 0.5 kcal/mole, $\tau_0 = (5.0 \pm 2.0) \times 10^{-13}$ s. It should be noted that it is the first time that the parameters of this reorientation motion are obtained. Previous attempts to measure the motion parameters in the low-temperature phase using the $T_{1\rho}$ and T_{2c} relaxation times were not succesfull due to the high local dipole field in this phase of cyclohexane which is comparable with the usually used RF field strengths of the spin-locking and MW-4 multipulse sequences [16,17].

Thus the obtained results demonstrate clearly that the study of the solid echoes in the slow motion region can give accurate information about the motions in solids within a wide range of dipole–dipole interactions.

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