# Spin echoes in solids with molecular motions

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A new approach to calculate the echo shape in solids with molecular motions is developed. It is shown that the study of the temperature dependence of the maximum solid echo amplitude in the region of rapid motions allows one to measure the activation energy of molecular motion with good accuracy.

Up to the present time, the evaluations of the two-pulse NMR echo shapes in solids with thermal motions of the magnetic nuclei are performed using the following approaches: (1) a power series expansion in times $\tau$ and $t$ ($\tau$ is the pulse separation time and $t$ is the time after the second pulse) [1]; (2) exact evaluations of the echo shape for simple two- and three-spin systems [2,3]; (3) the method of the stochastic local magnetic field [4]. The first approach permits one only to describe the short-time behaviour of the spin echo shape. The second approach is used mainly for solids containing the groups $H_2O$, $CH_2$, $CH_3$ etc. The last approach allows one to obtain the analytical expression for the echo shape for the stochastic Gauss–Markov process, describing the thermal motion of the magnetic nuclei. The following expression for the spin-echo amplitude was obtained [4],

$$V(2\tau)=\exp(-\mu_2\tau_c^2\{1+2\tau/\tau_c - [2-\exp(-\tau/\tau_c)]^2\}) . \quad (1)$$

Here $\tau_c$ is the correlation of the motion considered, $\mu_2$ is the second moment of the NMR line in the rigid lattice. Expression (1) was obtained for the case when the shape of the free induction decay (FID) had the Gauss form in the rigid lattice. However, the FID has no similar form in real solids.

Recently a new approach to calculate the echo shape in solids with a rigid lattice has been developed [5]. This approach allows one to obtain the general analytical expression for the shape of the two-pulse NMR echoes in solids. In this Letter we apply this approach to calculate the echo shape in solids with internal mobility of magnetic nuclei.

Using a method similar to that presented in refs. [5,6] we have obtained that the solid echo amplitude ($P_y(90°)$–$\tau$–$P_x(90°)$) in solids with molecular motions can be described as follows,

$$V(2\tau)=G_0^2(\tau)+\frac{1}{\mu_2}\left(\frac{dG_0}{d\tau}\right)^2+\dots , \quad (2)$$

where $G_0(\tau)$ is the shape of the FID.

If $G_0(\tau)$ is chosen in the Anderson form [7]

$$G_0(\tau)=\exp\{-\mu_2\tau_c^2[\exp(-\tau/\tau_c)-1+\tau/\tau_c]\}, \quad (3)$$

then from (2) we get

$$V(2\tau)=\{1+\mu_2\tau_c^2[1-\exp(-\tau/\tau_c)]^2\} \times\exp\{-2\mu_2\tau_c^2[\exp(-\tau/\tau_c)-1+\tau/\tau_c]\} . \quad (4)$$

It follows from (4) that if

$$\mu_2\tau_c^2[1-\exp(-\tau/\tau_c)]^2\ll 1$$

and

$$1+\mu_2\tau_c^2[1-\exp(-\tau/\tau_c)]^2 \approx\exp\{\mu_2\tau_c^2[1-\exp(-\tau/\tau_c)]^2\}$$

we get expression (1).

Thus we may conclude that expression (2) correctly describes the solid echo shape in solids with molecular motions.

The numerical evaluation of (4) shows that the minimum of $V(2\tau)$ with respect to the ratio $\tau/\tau_c$ is determined by the parameter $\mu_2\tau^2$.

Earlier we proposed to measure the minimum in the temperature dependence of $V(2\tau)$ and then determine $\tau_c$. However, as shown in our experiments, this method does not allow one to determine $\tau_c$ with good accuracy, so the minimum of $V(2\tau)$ is not well established. Therefore we propose to study the temperature dependence of the maximum solid echo amplitude in the region of rapid motions. Indeed, from (4) we obtain that if $\tau/\tau_c \gg 1$ (rapid motions) then

$$V(2\tau)=\exp(-2\mu_2\tau\tau_c)\,. \tag{5}$$

If we assume that $\tau_c$ is described by the Arrhenius expression

$$\tau_c=\tau_0\exp(U/RT)\,,$$

then we get from (5)

$$\ln[-\ln V(2\tau)]=\text{const}+U/RT\,. \tag{6}$$

Expression (6) was used in the analysis of temperature dependences of the solid echo in polycrystalline $CH_2Cl$–$CH_2Cl$. The experimental temperature dependences of $V(2\tau)$ at $\tau=30$ and 35 μs are shown in fig. 1. The experimental dependences of

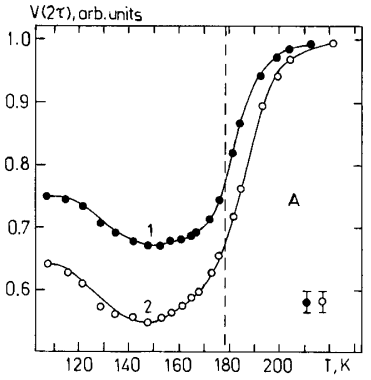


Fig. 1. Experimental temperature dependences of solid echo amplitude in polycrystalline $CH_2Cl$–$CH_2Cl$: (1) $\tau=30$ μs, (2) $\tau=35$ μs. (A) high temperature region.

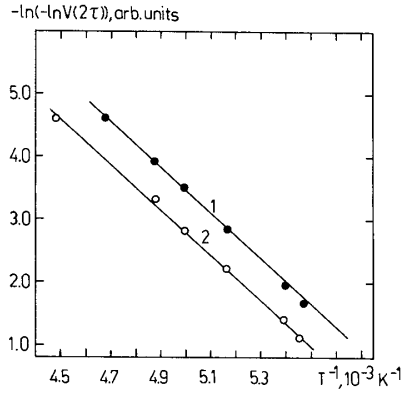


Fig. 2. Experimental temperature dependence of $-\ln[-\ln V(2\tau)]$ on $1/T$.

$V(2\tau)$ were approximated by expression (6) in the high temperature region (region A in fig. 1). The experimental temperature dependence of $-\ln[-\ln V(2\tau)]$ on $1/T$ is shown in fig. 2. From the results shown in fig. 2 we obtained that the activation energy of the molecular motion in $CH_2Cl$–$CH_2Cl$ is equal to

$$U=29.7\pm1.3\ \text{kJ mol}^{-1}\,,$$

and is in good agreement with the known data.

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