

SLOW MOLECULAR MOTIONS AND SOLID ECHO IN HYDRATE CRYSTALS

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The temperature dependences of the solid-echo amplitude have been measured in stilbite single crystal at temperatures of slow diffusion motions of water molecules. The obtained experimental data agree well with the derived theoretical expressions describing the two-pulse response of the isolated two-spin system performing jumps between two equilibrium positions.

It was shown recently [1-14] that the NMR spin-echo shape is very sensitive to the motion type of the molecular groups in solids. So in refs. [1-7,11] the influence of the isolated two-spin system motion on the shape and decay rate of the solid echo ($90^\circ-\tau-90^\circ_{90^\circ}-t$) was studied theoretically. It was found that certain correlations between the pulse interval τ , the motion correlation time τ_c and the geometric parameters of the two-spin system exist at which the molecular motions result in observable decreasing of the solid-echo amplitude. These theoretical results are of great interest from the point of view of practical applications, for example in studies of the internal thermal motions of water molecules in hydrate crystals. In the present letter the solid echo amplitudes are investigated in a stilbite single crystal ($\text{NaCa}_4[\text{Al}_{10}\text{Si}_{20}\text{O}_{72}] \cdot 28 \text{H}_2\text{O}$) in order to verify the theoretical results and to examine the possibility of the solid-echo method in measuring slow motions of water molecules.

In refs. [3,6] it was shown that the amplitude of the solid-echo in the case of an isolated two-spin system which performs jumps between two equilibrium positions in time moment after application of the two pulse sequences $90^\circ-\tau-90^\circ_{90^\circ}-t$ is described by the expressions

$$V(2\tau) = \frac{\exp(-t'/t_c)}{t_c^2 - 1} \left(t_c^2 - \cos \frac{t' \sqrt{t_c^2 - 1}}{t_c} + \sqrt{t_c^2 - 1} \sin \frac{t' \sqrt{t_c^2 - 1}}{t_c} \right), \quad t_c > 1, \quad (1a)$$

$$V(2\tau) = \exp(-t'/t_c) \left(1 + \frac{t'}{t_c} + \frac{t'^2}{2t_c^2} \right), \quad t_c = 1, \quad (1b)$$

$$V(2\tau) = \frac{\exp(-t'/t_c)}{t_c^2 - 1} \left(t_c^2 - \text{ch} \frac{t' \sqrt{1 - t_c^2}}{t_c} - \sqrt{1 - t_c^2} \text{sh} \frac{t' \sqrt{1 - t_c^2}}{t_c} \right), \quad t_c < 1, \quad (1c)$$

where

$$t_c = |a_1 - a_2| \tau_c, \quad t' = |a_1 - a_2| \tau,$$

$$a_i = 3\gamma^2 \hbar (1 - 3 \cos^2 \vartheta_i) / 4 R^3, \quad i = 1, 2.$$

\mathbf{R} is the internuclear vector, ϑ is the angle between \mathbf{R} and the external magnetic field \mathbf{B}_0 , and τ_c is the correlation time of the considered motion. The calculated dependence of $V^*(2\tau)$ values on $\ln t_c$ for different t' is shown in fig. 1. The molecular motions do not affect the solid-echo amplitude when the intervals between rf pulses are small ($\tau < |a_1 - a_2|^{-1}$). The solid-echo amplitude does not change also in the cases of the ultraslow ($\tau_c \gg |a_1 - a_2|^{-1}$) and very fast ($\tau_c \ll |a_1 - a_2|^{-1}$) motions. Therefore the measurement of the molecular motions of water molecules is possible only for certain intervals between the rf pulses of the applied pulse sequence ($\tau \approx |a_1 - a_2|^{-1}$) and for certain values of correlation times $\tau_c \approx |a_1 - a_2|^{-1}$. In this case as it follows from eqs. (1a)-(1c) the $V(2\tau)$ temperature dependence has a minimum at $\tau = \tau_c$. This minimum is observed for

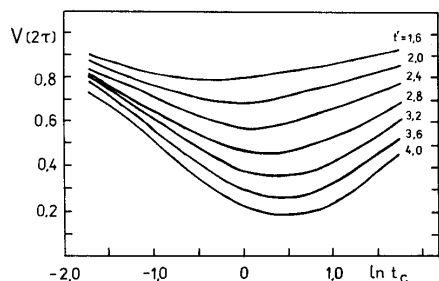


Fig. 1. The dependences of the solid echo amplitude $V(2\tau)$ on $\ln t_c$ for some values of $t' = |a_1 - a_2|\tau$ calculated using eqs. (1).

given τ only for definite correlation between τ and τ_c ($\tau/\tau_c = \alpha$). The results shown in fig. 1 were used when analysing the measured temperature dependences of the solid-echo in single crystal of stilbite $\text{NaCa}_4[\text{Al}_{10}\text{Si}_{26}\text{O}_{72}] \cdot 28 \text{H}_2\text{O}$ at $B_0 \parallel [100]$ (fig. 2). A natural crystal of stilbite (river Nidym, USSR) with dimensions $3 \times 6 \times 7$ mm was used in the experiments. The stilbite was chosen for proving the derived theoretical expressions (1) because of the simple mechanism of water diffusion in it. The stilbite, space group C 2/m, has 28 water molecules per unit cell. It was shown in ref. [15] by the wide-line ^1H NMR spectra analysis that the proton-proton (p-p) vectors of water molecules in the structure of stilbite shows a limited number of possible orientations. It was established in ref. [15] that twelve (p-p) vec-

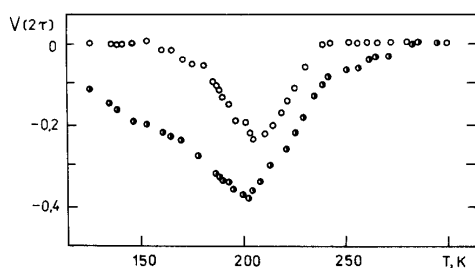


Fig. 2. The temperature dependences of the normalized solid-echo amplitudes in stilbite single crystal, $B_0 \parallel a$ for two values of the interval τ between rf pulses of the pulse sequence $90^\circ - \tau - 90^\circ_{90}$. The length of the 90° pulses was $2.0 \mu\text{s}$, the Larmor frequency was 30 MHz.

tors (3/7 of all vectors) are oriented along the $[001]$ direction, twelve vectors are parallel to the $[010]$ direction and small part of the p-p vectors (only four) is oriented at the angle of $\pm 55^\circ$ to the $[100]$ direction in the (001) plane which is very close to the so called "magic" angle $54^\circ 44'$. The slow diffusion of water molecules appears in the stilbite at temperatures above 170 K. In the stilbite structure the diffusion of water molecules goes in such way that the p-p vectors of diffusing water molecules occupy successively the orientations parallel either to $[001]$ or to $[010]$ directions. It means that the case of a two-spin system performing jumps between two positions exists really in stilbite from the NMR point of view. The value of $|a_1 - a_2|$ is equal to $1.5 \times 10^5 \text{ s}^{-1}$ at B_0 parallel to the $[100]$ direction in this crystal according to ref. [15].

The effect of diffusion of four other water molecules having different orientations of the p-p vectors is negligible due to low concentration and the specific orientation angle relatively to the $[100]$ direction.

The experimental dependences of $V(2\tau)$ were measured using a 30 MHz homemade pulse spectrometer. The obtained results (fig. 2) agree well with the theoretical predictions. The $V(2\tau)$ temperature dependences have distinct minima in the range of 205 K. At increasing τ the $V(2\tau)$ minimum value decreases and its temperature shifts to low temperatures, i.e. to longer τ_c values. The experimental values of the normalized minima at used values of interval between pulses $\tau = 10$ and $15 \mu\text{s}$ equal to 0.76 ± 0.01 , 0.63 ± 0.01 are in good agreement with calculated values correspondingly equal to 0.76 and 0.62. According to eqs. (1a)–(1c) and fig. 1 the values of α for $\tau = 10$ and $15 \mu\text{s}$ will be equal to 1.95 and 2.03. Using these values it is possible now to obtain in a simple way the correlation times of water molecule diffusion at temperatures of the $V(2\tau)$ minima $\tau_c = 0.51 \times 10^{-5} \text{ s}$ ($T = 205 \text{ K}$) and $0.74 \times 10^{-5} \text{ s}$ ($T = 202 \text{ K}$). The activation energy of this motion calculated using obtained values in assumption of the Arrhenius dependence of τ_c on temperature $\tau_c = \tau_0 \times \exp(E_{\text{act}}/RT)$ is equal to $32.65 \pm 2.5 \text{ kJ mol}^{-1}$ in good agreement with previous multipulse measurements in stilbite ($E_{\text{act}} = 31.0 \pm 1.3 \text{ kJ mol}^{-1}$) [16].

Thus, the obtained results show that the study of the temperature dependences of the solid-echo

amplitudes allow motion parameters to be measured in the case of the isolated two-spin systems, including water molecules in crystal hydrates.

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