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Study of functional materials by NMR dipolar echoes

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Influence of spin-echo signals $(2n+1) \cdot 90^{\circ}_{Y} - \tau - 90^{\circ}_{X} - Acq(t)$ has been studied in nuclear spin systems with dipolar interactions. In the case of rigid lattice ($M_2\tau_c^2>1$) and that of motionally narrowed NMR line ($M_2\tau_c^2<<1$), the maximum echo signals are shown to be observed at $t_e = 2\tau + t_2 - t_1/2$ where t_1 and t_2 are RF pulse durations. It has been shown also that in the slow motion region ($M_2\tau_c^2 \approx 1$) the dipolar echo signal amplitude decreases and the echo signal maximum shifts towards the end of second pulse. The theory developed agrees well with experimental data obtained for NH_4Cl polycrystal.

Исследуется влияние молекулярных движений на спин-эхо сигналы $(2n+1) \cdot 90^{\circ}_{Y} - \tau - 90^{\circ}_{X} - Acq(t)$ в ядерных спиновых системах с дипольными взаимодействиями. Показано, что в случае жесткой решетки ($M_2\tau_c^2>1$) и в случае суженной, в результате движений, линии ЯМР ($M_2\tau_c^2<<1$) максимум эхо сигналов наблюдается при $t_e = 2\tau + t_2 - t_1/2$, где t_1 и t_2 — длительности РЧ импульсов. Показано также, что в области медленных движений ($M_2\tau_c^2 \approx 1$) амплитуда дипольного эхо сигнала уменьшается, а максимум эхо сигнала сдвигается к концу к концу второго импульса. Развитая теория хорошо согласуется с эксперименатльными данными, полученными на поликристалле NH_4Cl.

In 1950, E. Hahn has demonstrated that a two-pulse sequence $90^{\circ} - \tau - 180^{\circ} - Acq(t)$ applied to an inhomogeneously broadened spin system (for example, nuclear spins in a liquid) gives rise to an echo signal at $t = 2\tau$ [1]. The amplitude of the Hahn echo does not depend on the time interval τ between RF pulses. For a homogeneously broadened spin system (for example, nuclear spins with dipole-dipole interaction between them), Powles, Mansfield and Strange proposed the "solid-echo" technique $90^{\circ}_{Y} - \tau - 90^{\circ}_{X} - Acq(t)$ [2, 3]. Today, this technique is a powerful NMR method for studying molecular structure of functional materials and dynamics in solid state. A general review on application of deuterium solid-echo technique has been published recently [4]. There are also numerous works on ^1H "solid-echo" technique and its application in studies of molecular dynamics in solids [5]. Assuming that the applied RF pulses are delta 90°_{XY} pulses (for the delta 90° pulse, it is assumed that $\omega_1 t_{1,2} = 90^{\circ}$ the pulse widths $t_{1,2} \to 0$ and the RF field amplitude $\omega_1 \to \infty$), it was shown that the solid-echo signal is also observed at $t = 2\tau$ [2, 3]. However, the solid-echo signal amplitude depends on τ and decays as τ^4, so the echo signal can be observed only for small τ values. Formation of this "solid-echo", in contrast to the Hahn one is not connected with sign invertion of dipole interaction Hamiltonian by RF pulses [6].

In this work, a general "solid-echo" technique $(2n+1) \cdot 90^{\circ}_{Y} - \tau - 90^{\circ}_{X} - Acq(t)$ is proposed. The two-pulse sequence is considered for the cases of rigid and mobile crystalline

lattice. It has been shown that the pulse sequence $(2n+1) \cdot 90_Y^\circ - \tau - 90_X^\circ - Acq(t)$ follows to obtain at $\tau \to 0$ the real dipolar echo signals. The amplitude of these echo signals does not depend on the RF pulse widths t_1 and t_2. The experimental results and discussions are presented.

At first, let a simple two- pulse model sequence $\alpha_Y^\circ - 90_X^\circ - Acq(t)$ be considered.The first RF pulse is a hard pulse α_Y°, for which rotational angle is $\alpha = (2n+1) \cdot (\pi/2)$ and $n = 1,3,5$. The RF field of this pulse lies along the $0Y$ axis in the rotating frame. After the first RF pulse, a density matrix has the form:

$$\rho(t_1) = \exp(-iHt_1) \cdot \rho(0) \cdot \exp(iHt_1), \quad (1)$$

where $\rho(0)$ is the density matrix at $t = 0$ and the interaction Hamiltonian H is [6, 7]:

$$H = -\omega_1 I_Y - \frac{1}{2} H_Y. \quad (2)$$

In Eq. (2), ω_1 is the RF pulse amplitude and

$$H_Y = \sum_{i,j} b_{ij}(2I_Y^i I_Y^j - I_X^i I_X^j - I_{Z_i} I_Z^j), \quad (3)$$

where b_{ij} is a dipolar coupling constant between i and j spins [8].

Assuming that $\rho(0) = I_Z$ and the RF pulse duration $t_1 = (2n+1) \cdot (\pi/2\omega_1)$ one obtains from Eq. (1):

$$\rho(t_1) = \quad (4)$$
$$= (-1)^n \exp\left(i\frac{1}{2}H_Y t_1\right) \cdot I_X \cdot \exp\left(-i\frac{1}{2}H_Y t_1\right).$$

If at the time t_1 the second delta 90_X° pulse is applied (it is assumed that $\omega_1 t_2 = 90^\circ$ and when $t_2 \to 0$, the RF field amplitude $\omega_1 \to \infty$), the density operator takes the form

$$\rho^+(t_1) = (-1)^n \exp\left(i\frac{1}{2}H_Z t_1\right) \cdot \exp\left(-i\frac{1}{2}H_Z t_1\right). \quad (5)$$

Here

$$H_Z = \sum_{i,j} b_{ij}(2I_Z^i I_Z^j - I_X^i I_X^j - I_{Y_i} I_Y^j). \quad (6)$$

After the second RF pulse, the Hamiltonian H_Z describes the free evolution of the density operator and at the time t (measured from the first pulse starting moment) the density operator has the form:

$$\rho(t_1, t) = (-1)^n \exp\left[-iH_Z\left(t - \frac{3}{2}t_1\right)\right] \cdot I_X \times$$
$$\times \exp\left[iH_Z\left(t - \frac{3}{2}t_1\right)\right]. \quad (7)$$

The observed transient response of the ensemble of spins is given by:

$$V(t_1, t) = (-1)^n \{Tr\left\{\exp\left[-iH_Z\left(t - \frac{3}{2}t_1\right] \cdot I_X \times\right.\right.$$
$$\left.\left. \times \exp\left[iH_Z\left(t - \frac{3}{2}t_1\right)\right] \cdot I_X\right\} \Big/ Tr(I_X^2). \quad (8)$$

It follows from (8) that at $t = 3t_1/2$, $V(t_1, t = 3t_1/2) = 1$, ,that is, an echo signal should be observed. The amplitude of this echo signal does not depend on t_1.

The considered model of the pulse sequence is difficult to verify experimentally. At first, the time between the end of the first RF pulse and the start of the second pulse, τ, is always finite. Besides, the second RF pulse having the finite width t_2, is not the delta pulse. All these factors cause attenuation and deformation of the echo signal.

Using the spin density matrix formalism and assuming that τ and t_2 are not equal to zero, we obtain the following expression for the dipolar echo signal observed after the two-pulse sequence $(2n+1) \cdot 90_Y^\circ - \tau - 90_X^\circ - Acq(t)$:

$$V(t, t_2, \tau, t_1) = (-1)^n \beta \cdot \left[1 - \frac{1}{4}\int_0^{t_1} dt'' \int_0^{t_1} h(t'', t')dt' - \right.$$
$$- \frac{1}{2}\int_{t_1}^{\tau} dt'' \int_0^{t_1} h(t'', t')dt' - \int_{t_1}^{\tau} dt'' \int_{t_1}^{t''} h(t'', t')dt' +$$
$$+ \frac{1}{2}\int_{\tau+t_2}^{t} dt'' \int_0^{t_1} h(t'', t')dt' + \int_{\tau+t_2}^{t} dt'' \int_{t_1}^{\tau} h(t'', t')dt' - \quad (9)$$
$$\left. - \int_{\tau+t_2}^{t} dt'' \int_{\tau+t_2}^{t''} h(t'', t')dt' + \ldots\right]$$

where

$$h(t'', t') = W \sum_{i,k} \overline{a_{ik}(t'')a_{ik}(t')}, \quad (10)$$

are the correlation functions of the dipolar local fields [8]. The overscribed bar denotes the average on the random motions of nuclei. In Eq. (10):

$$W = \frac{3}{4}\gamma^4\hbar^2 I(I+1)\frac{1}{N}; \qquad (11)$$

$$a_{ik}(t') = R_{ik}^{-3}(t')[1 - 3\cos^2\theta_{ik}(t')] \qquad (12)$$

To calculate the correlation function h (t'', t'), we consider the simple model for molecular motion of resonant nuclei between the equivalent potential wells determined in crystalline lattice by discrete lattice sites Ω_l ($l = 1,2...,n$). For this simple model, the correlation function $h(z)$ ($z = |tBB - tB| > 0$) is given by [5]:

$$h(z) = \overline{M_2} + \Delta M_2 \exp\left(-\frac{z}{\tau_c}\right), \qquad (13)$$

where

$$\Delta M_2 = M_2 - \overline{M_2} \qquad (14)$$

and τ_c is the correlation time characterising molecular motion. In Eq.(14), M_2 is the second moment of the NMR line of rigid crystalline lattice and $\overline{M_2}$ is the second moment of motionally narrowed NMR line [8]. Using the correlation function (13) and calculating the integrals in (9), we obtain:

$$V(t,t_2,\tau,t_1) = \qquad (15)$$
$$= (-1)^n\beta \cdot \{1 - \frac{1}{2}\overline{M_2}[t - (2\tau + t_2 - \frac{t_1}{2})]^2 -$$
$$- \Delta M_2\tau_c^2 \cdot R(t,t_2,\tau,t_1,\tau_c) + \ldots\},$$

where

$$R(t,t_2,\tau,t_1,\tau_c) =$$
$$= -\frac{7}{4} + \frac{t}{\tau_c} - 3\frac{t_1}{4\tau_c} - \frac{t_2}{\tau_c} - \frac{1}{4}\exp(-\frac{t_1}{\tau_c}) -$$
$$- \exp(-\frac{t_2}{\tau_c}) - \frac{1}{2}\exp(-\frac{t}{\tau_c}) + \frac{1}{2}\exp(-\frac{\tau - t_1}{\tau_c}) -$$
$$- \frac{1}{2}\exp(-\frac{t - t_1}{\tau_c}) + \frac{1}{2}\exp(-\frac{\tau + t_2}{\tau_c}) + \qquad (16)$$
$$+ \exp(-\frac{t - \tau}{\tau_c}) + \exp(-\frac{t - \tau - t_2}{\tau_c}) +$$
$$+ \frac{1}{2}\exp(-\frac{\tau}{\tau_c}) + \frac{1}{2}\exp(-\frac{\tau + t_2 - t_1}{\tau_c})$$

In the case of the polycrystalline sample, we must average (16) over all possible orientations of crystallites. If we denote the averaged values of $\overline{M_2}$ and ΔM_2 as $\langle\overline{M_2}\rangle$ and $\langle\Delta M_2\rangle$, then — for small τ and t — we can write:

$$V(t,t_2,\tau,t_1) = \qquad (17)$$
$$= (-1)^n\beta\left\{1 - \frac{1}{2}\langle\overline{M_2}\rangle\left[t - (2\tau + t_2 - \frac{t_2}{2})\right]^2 - \right.$$
$$\left. - \langle\Delta M_2\rangle\tau_c^2 R(t,t_2,\tau,t_1,\tau_c,) + \ldots\right\} \approx$$
$$\approx (-1)^n\frac{\hbar\omega_0}{kT}\exp\left\{-\frac{1}{2}\langle\overline{M_2}\rangle\left[t - (2\tau + t_2 - \frac{t_1}{2})\right]^2 - \right.$$
$$\left. - \langle\Delta M_2\rangle\tau_c^2 R(t,t_2,\tau,t_1,\tau_c,)\right\}$$

From Eq.(17), it follows that in the case of rigid crystalline lattice ($\langle M_2\rangle\tau_c^2 > 1$) and in the fast-motion region ($\langle M_2\rangle\tau_c^2 < 1$), the maximum of the dipolar echoes is observed at $t_e = 2\tau + t_2 - t_1/2$. In the slow-motion region ($\langle M_2\rangle\tau_c^2 \approx 1$), the amplitude of the solid echo signal is reduced and the maximum of the echo signal is shifted towards the second pulse end.

The theoretical results obtained have been applied to the analysis of temperature dependences of the solid echo signals observed in polycrystalline ammonium chloride (NH_4Cl). It is well established now that in NH_4Cl there are reorientations of the ammonium ions about threefold and twofold symmetry axes [9]. The ^1H NMR experiments were carried out using a pulse spectrometer operating at 60 MHz. in the temperature range of 133 to 273 K. The experimental dipolar echoes observed in NH_4Cl for the pulse sequences

$270_Y^\circ - \tau - 90_X^\circ - Acq(t)$,

$450_Y^\circ - \tau - 90_X^\circ - Acq(t)$,

$630_Y^\circ - \tau - 90_X^\circ - Acq(t)$

at the room temperature are shown in Fig. 1. It is seen that the maximum of the dipolar echoes is observed at $t_e = 2\tau + t_2 - t_1/2$.

The experimental temperature dependences of the maximum echo time position (t_e) for the pulse sequences

$270_Y^\circ - \tau - 90_X^\circ - Acq(t)$,

$450_Y^\circ - \tau - 90_X^\circ - Acq(t)$,

$630_Y^\circ - \tau - 90_X^\circ - Acq(t)$

obtained for polycrystalline NH_4Cl are shown in Fig. 2. The time positions of dipolar echo signals are seen to be independent of the temperature in the region $T > 160$ K. At $T > 160$ K, the time posi-

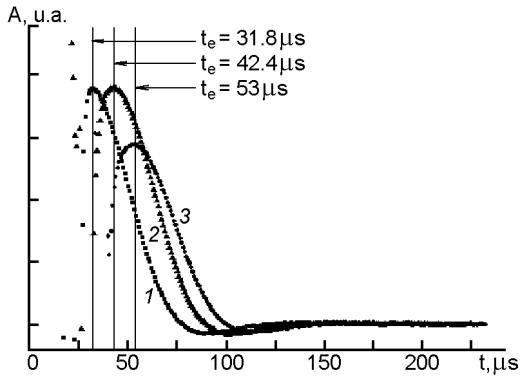

Fig. 1. Dipolar echoes in NH_4Cl at room temperature for the pulse sequences

$270_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$450_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$630_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$.

t_2 = 3.6 μs; $\tau - t_1$ = 5.8 μs.

tions of the echo signal maximum are shifted towards the end of the second pulse and echo signals disappear. The solid and broken lines in Fig. 2 are theoretical curves for the time positions of the echo maximum, as calculated from Eq. (17) using the results of the relaxation studies in this compound [9]. We have used the following parameters: $\tau_c = (2.16 \cdot 10^{-14}$ s)exp(19.85 kJ mol$^{-1}/RT$); $\overline{M_2} = 4.74 \cdot 10^{-8}$ T2; $\Delta M_2 = 46.15 \cdot 10^{-8}$ T2. The agreement between theory and experiment is quite reasonable, especially bearing in mind that parameters were not adjusted. The experimental temperature dependences of the maximum echo amplitudes for the pulse sequences

$270_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$450_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$630_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$

obtained for polycrystalline NH_4Cl are shown in Fig. 3. The solid and broken lines in Fig. 3 are theoretical curves obtained from Eq.(17) using the same parameters as for the theoretical curves in Fig. 2. From this Figure, it is seen that the developed theory describes rather well the observed temperature dependences of the dipolar echo amplitude.

In conclusion, it follows from our consideration that the time position and amplitude of the dipolar echo maximum depend on the correlation time τ_c of molecular mo-

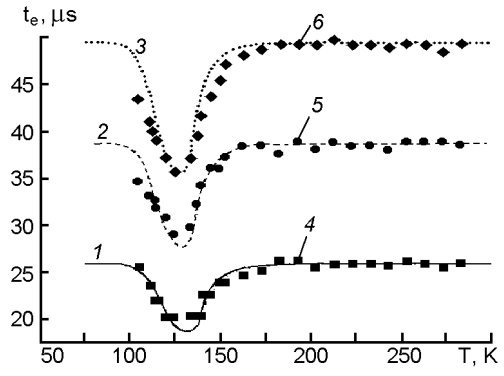

Fig. 2. Temperature dependences of the dipolar echoes maximum time positions in NH_4Cl for the pulse sequences

$270_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$450_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$630_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$.

t_2 = 3.6 μs; $\tau - t_1$ = 3.8 μs.

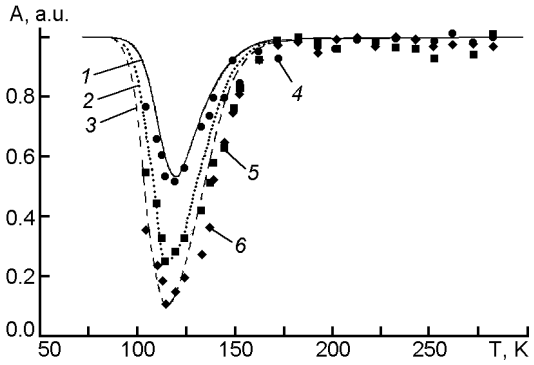

Fig. 3. Temperature dependences of the dipolar echo amplitude () in NH_4Cl for the pulse sequences:

$270_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$450_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$,

$630_{Y}^{\circ} - \tau - 90_{X}^{\circ} - Acq(t)$.

t_2 = 3.6 μs; $\tau - t_1$ = 2.8 μs.

tion as well as and on the RF pulse widths. Dramatic changes in the solid-echo behaviour are observed in the slow-motion region ($<M_{2II}>\tau_c^2 \approx 1$), where the amplitude of the dipolar echo signal is reduced and the maximum of the signal is shifted towards the end of the second pulse. It has been also shown that the study of the temperature dependence of the time position and amplitude of the dipolar echo maximum can yield valuable information about the dynamic process in solids.

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Дослідження функціональних матеріалів за допомогою ЯМР дипольних лун

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Досліджено вплив молекулярних рухів на спін-ехосигнали $(2n+1)\cdot 90^{\circ}_{Y} - \tau - 90^{\circ}_{X} - Acq(t)$ в ядерних спінових системах з дипольними взаємодіями. Показано, що у випадку жорсткої гратки ($M_2\tau_c^2<<1$) та у випадку звуженої внаслідок рухів лінії ЯМР ($M_2\tau_c^2<<1$) максимум ехосигналів спостерігається при $t_e = 2\tau + t_2 - t_1/2$, де t_1 і t_2 - тривалості РЧ імпульсів. Також показано, що в області повільних рухів ($M_2\tau_c^2 \approx 1$) амплітуда дипольної луни зменшується, а максимум ехосигнала зсувається в напрямі до кінця другого імпульсу. Розроблена теорія добре узгоджується з експериментальними даними, одержаними на полікристалі NH_4Cl.