# Echoes in spin systems with dipolar interactions

P. BILSKI[1], N. A. SERGEEV [2]* and J. WASICKI[1]

[1] Faculty of Physics, Adam Mickiewicz University, 61-614 Poznan, Poland
[2] Institute of Physics, University of Szczecin, 70-451 Szczecin, Poland

The effects of molecular motions on spin–echo signals $(2n + 1)90_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ in nuclear spin systems with dipolar interactions have been investigated. It was found that in the case of a rigid lattice $(M_2\tau_c^2 \gg 1)$ and a motionally narrowed NMR line $(M_2\tau_c^2 \ll 1)$ a maximum of echo signals is observed at $t_e = 2\tau + t_2 - t_1/2$, where $t_1$ and $t_2$ are the widths of the RF pulses. It also was found that in the slow motion region $(M_2\tau_c^2 \approx 1)$ an amplitude of the dipolar echo signal is reduced and the maximum of the echo signal is shifted to the end of the second pulse. The theory developed is confirmed by the experimental results obtained for $C_6H_6$.

## 1. Introduction

In 1950 E. Hahn demonstrated that a two-pulse sequence $90^\circ - \tau - 180^\circ - \text{Acq}(t)$ applied to an inhomogeneously broadened spin system (for example nuclear spins in a liquid) leads to the appearance of an echo signal at $t = 2\tau$ [1]. For the homogeneously broadened spin system (for example the nuclear spins with dipole–dipole interaction between them), Powles, Mansfield and Strange [2, 3] proposed the 'solid-echo' technique $90_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$, which is a powerful NMR method for studying molecular structure and dynamics in solid state. General reviews of applications of the deuterium solid-echo technique may be found in [4, 5]. Also there are many papers on the $^1$H solid-echo technique and its application to the study of molecular dynamics in solids [6–20]. Assuming that the applied RF pulses are delta $90_{X,Y}^\circ$ pulses (for the delta $90^\circ$ pulse it is assumed that $\omega_1 t_{1,2} = 90^\circ$ with the widths of pulses $t_{1,2} \to 0$ and the amplitude of the RF field $\omega_1 \to \infty$), it was shown that the solid-echo signal is observed also at $t = 2\tau$ [2, 3]. However, the amplitude of the solid-echo signal depends on $\tau$ and it decays as $\tau^4$, so the echo signal may be observed only for small values of $\tau$.

In this paper, a general solid-echo technique $(2n + 1)90_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ is proposed. It has been shown that the pulse sequence $(2n + 1)90_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ makes it possible to obtain at $\tau \to 0$ the real dipolar echo signals.

## 2. Theory

Let us consider an ensemble of nuclear spins in a high static magnetic field $\mathbf{B}_0(\mathbf{B}\|OZ)$. We should assume that there is molecular reorientation in the solid, the rate of which is smaller than the Larmor frequency $\omega_0 = \gamma B_0$ ($\gamma$ is the magnetogyric ratio of the nuclei). In this adiabatic approximation we may restrict our consideration to the secular part of the dipolar interaction Hamiltonian [23]

$$H_Z(t) = \sum_{i,j} b_{ij}(t)(2I_Z^i I_Z^j - I_X^i I_X^j - I_Y^i I_Y^j), \quad (1)$$

where $b_{ij}$ is a dipolar coupling constant between $i$ and $j$ spins [23].

We consider the transient response of the ensemble of nuclear spins after a simple two-pulse sequence: $\alpha_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$. The first RF pulse is the hard pulse $\alpha_Y^\circ$, for which the rotational angle is $\alpha = (2n + 1)(\pi/2)$ and $n = 1, 3, 5 \ldots$. The RF field of this pulse lies along the $OY$ axis in the rotating frame. The second RF pulse is the hard pulse $90_X^\circ$, and the RF field of this pulse lies along the $OX$ axis in the rotating frame.

Using the general formalism, described in [16], the following expression is found for the transient response of the ensemble of spins on the two-pulse sequence $\alpha_Y^\circ - \tau - 90_Y^\circ - \text{Acq}(t)$:

*Author for correspondence. e-mail: sergeev@uoo.univ. szczecin.pl

$$V(t,t_2,\tau,t_1) = (-1)^n\beta\left[1 - \frac{1}{4}\int_0^{t_1}\mathrm{d}t''\int_0^{t''}h(t'',t')\mathrm{d}t\right.$$

$$-\frac{1}{2}\int_{t_1}^{\tau}\mathrm{d}t''\int_0^{t_1}h(t'',t')\mathrm{d}t$$

$$-\int_{t_1}^{\tau}\mathrm{d}t''\int_{t_1}^{t''}h(t'',t')\mathrm{d}t'$$

$$+\frac{1}{2}\int_{\tau+t_2}^{t}\mathrm{d}t''\int_0^{t_1}h(t'',t')\mathrm{d}t'$$

$$+\int_{\tau+t_2}^{t}\mathrm{d}t''\int_{t-1}^{\tau}h(t'',t')\mathrm{d}t'$$

$$\left.-\int_{\tau+t_2}^{t}\mathrm{d}t''\int_{\tau+t_2}^{t''}h(t'',t')\mathrm{d}t' + \cdots\right]. \tag{2}$$

Here $\beta = (\hbar\omega_0/kT)[Tr(E)]^{-1}$ with $E$ the unit operator, $T$ is the temperature of a lattice, and

$$h(t'',t') = W\sum_{i,k}\overline{a_{ik}(t'')a_{ik}(t')} \tag{3}$$

is the correlation function of the dipolar local fields [23]. The upper bar denotes the average of $a_{ik}(t'')a_{ik}(t')$ on the random motions of nuclei.

In equation (3),

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

$$a_{ik}(t') = R_{ik}^{-3}(t')[1 - 3\cos^2\theta_{ik}(t')]. \tag{5}$$

Let us first consider the case of a 'rigid' lattice with no molecular motions in the crystal. Then one obtains, from equation (3),

$$h(0,0) = W\sum_{i,k}a_{ik}^2 = M_2, \tag{6}$$

where $M_2$ is the second moment of the NMR line. Inserting equation (6) into (3) and calculating integrals we obtain the well known result [16]

$$V(t,t_2,\tau,t_1) = \beta\left[1 - \frac{1}{2}M_2\left(t - 2\tau - t_2 + \frac{1}{2}t_1\right)^2 + \cdots\right]. \tag{7}$$

In the case of the fast motion region ($M^{1/2} \ll \tau_c^{-1} \ll \omega_0/2\pi$), when the correlation function $h(t'',t')$ does not depend on time [23], one obtains

$$h(0,0) = W\sum_{i,k}\bar{a}_{ik}^2 = \bar{M}_2. \tag{8}$$

In equation (8) $\bar{M}_2$ is the second moment of the motionally narrowed NMR line [23, 24].

Inserting equation (8) into (3) and calculating integrals we obtain [16]

$$V(t,t_2,\tau,t_1) = (-1)^n\beta\left[1 - \frac{1}{2}\bar{M}_2\left(t - 2\tau - t_2 + \frac{1}{2}t_1\right)^2 + \cdots\right] \tag{9}$$

Note that if $\bar{M}_2 = 0$ and we have liquid-like mobility, from equation (9) we have $V(t,t_2,\tau,t_1) = (-1)^n\beta$. This trivial result indicates that the echo signal is not observed in the fast motion region ($M_2^{1/2} \ll \tau_c^{-1} \ll \omega_0/2\pi$) in this case.

From equations (7) and (9) it follows that in the case of rigid lattice ($M_2\tau_c^2 \gg 1$) and for the case of a motionally narrowed NMR line ($M_2\tau_c^2 \ll 1$) the maximum of the echo signals is observed at $t_e = 2\tau + t_2 - t_1/2$.

In order to calculate the correlation function $h(t'',t')$ we assume that the random molecular motions in solids are described by a stationary Markovian process. For this process the correlation function $h(t'',t')$ depends only on $z = |t'' - t'| > 0$. In this case we can write equation (2) as

$$V(t,t_2,\tau,t_1) = (-1)^n\beta\left[1 - \frac{1}{4}\int_0^{t-1}(t_1 - z)h(z)\mathrm{d}z\right.$$

$$-\frac{1}{2}\int_0^{t_1}zh(z)\mathrm{d}z - \frac{t_1}{2}\int_{t_1}^{\tau-t_1}h(z)\mathrm{d}z$$

$$-\frac{1}{2}\int_{\tau-t_1}^{\tau}(\tau - z)h(z)\mathrm{d}z$$

$$-\int_0^{\tau-t_1}[(\tau - t_1) - z]h(z)\mathrm{d}z$$

$$-\frac{1}{2}\int_{\tau+t_2-t_1}^{\tau+t_2}[(\tau + t_2 - t_1) - z]h(z)\mathrm{d}z$$

$$+\frac{t_1}{2}\int_{\tau+t_2}^{t-t_1}h(z)\mathrm{d}z + \frac{1}{2}\int_{t-t_1}^{t}(t - z)h(z)\mathrm{d}z$$

$$-\int_{t_2}^{\tau+t_2-t_1}(t_2 - z)h(z)\mathrm{d}z$$

$$+(\tau - t_1)\int_{\tau+t_2-t_1}^{t-\tau}h(z)\mathrm{d}z$$

$$+\int_{t-\tau}^{t-t_1}[(t - t_1) - z]h(z)\mathrm{d}z$$

$$\left.-\int_0^{t-\tau-t_2}[(t - \tau - t_2) - z]h(z)\mathrm{d}z + \cdots\right]. \tag{10}$$

In order to calculate the correlation function $h(z)$ we consider a simple model of the molecular motion of resonant nuclei between the equivalent potential wells determined in crystal lattice by discrete lattice sites $\Omega_l$ ($l = 1, 2, \ldots, n$). For this simple model the correlation function $h(z)$ is given by [16, 24]

$$h(z) = \bar{M}_2 + \Delta M_2\exp\left(-\frac{z}{\tau_c}\right), \tag{11}$$

where

$$\Delta M_2 = M_2 - \bar{M}_2 \qquad (12)$$

and $\tau_c$ is the correlation time characterizing molecular motion.

Using the correlation function (11) and calculating the integrals in equation (10) we obtain

$$V(t, t_2, \tau, t_1) = (-1)^n \beta \left\{ 1 - \frac{1}{2}\bar{M}_2 \left[ t - \left( 2\tau + t_2 - \frac{t_1}{2} \right) \right]^2 \right.$$

$$\left. - \Delta M_2 \tau_c^2 R(t, t_2, \tau, t_1, \tau_c) + \cdots \right\}, \qquad (13)$$

where

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

$$- \exp\left(\frac{t_2}{\tau_c}\right) - \frac{1}{2}\exp\left(-\frac{t}{\tau_c}\right)$$

$$+ \frac{1}{2}\exp\left(-\frac{\tau - t_1}{\tau_c}\right) - \frac{1}{2}\exp\left(-\frac{t - t_1}{\tau_c}\right)$$

$$+ \frac{1}{2}\exp\left(-\frac{\tau + t_2}{\tau_c}\right) + \exp\left(-\frac{t - \tau}{\tau_c}\right)$$

$$+ \exp\left(-\frac{t - \tau - t_2}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau}{\tau_c}\right)$$

$$+ \frac{1}{2}\exp\left(-\frac{\tau + t_2 - t_1}{\tau_c}\right) \qquad (14)$$

In the case of the polycrystalline sample we must average equation (13) over all possible orientations of the crystallites. If we denote the averaged values of $\bar{M}_2$ and $\Delta M_2$ as $\langle \bar{M}_2 \rangle$ and $\langle \Delta M_2 \rangle$, then for small $\tau$ and $t$ we may write

$$V(t, t_2, \tau, t_1) = (-1)^n \beta \left\{ 1 - \frac{1}{2}\langle \bar{M}_2 \rangle \left[ t - \left( 2\tau + t_2 - \frac{t_1}{2} \right) \right]^2 \right.$$

$$\left. - \langle \Delta M_2 \rangle \tau_c^2 R(t, t_2, \tau, t_1, \tau_c) + \cdots \right\}$$

$$\approx (-1)^n \frac{\hbar \omega_0}{kT}\exp\left\{ -\frac{1}{2}\langle \bar{M}_2 \rangle \left[ t - \left( 2\tau + t_2 - \frac{t_1}{2} \right) \right]^2 \right.$$

$$\left. - \langle \Delta M_2 \rangle \tau_c^2 R(t, t_2, \tau, t_1, \tau_c) \right\}. \qquad (15)$$

It should be noted that for $n = 0$ equation (15) coincides with the equation obtained in [16].

From equation (15) it follows that in the slow motion region $(\langle M_2 \rangle \tau_c^2 \approx 1)$ the amplitude of the sold-echo signal is reduced and the maximum of the echo signal is shifted to the end of the second pulse.

## 3. Experimental results and discussion

The theoretical results obtained were applied to an analysis of the temperature dependence of the solid-echo signals observed in benzene ($C_6H_6$). It is now well established that in $C_6H_6$ there is a reorientation of the benzene ring around its sixfold symmetry axis [11]. $^1H$ NMR experiments were performed using a pulse spectrometer operating at $60\,MHz$ in the temperature range 95–180 K. The experimental dipolar echoes observed in $C_6H_6$ for the pulse sequences $450_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$, $630_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ and $810_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ at the $T = 180\,K$ are shown in figure 1. One can see that the maximum of the dipolar echoes is observed at $t_e = 2\tau + t_2 - t_1/2$.

The experimental temperature dependence of the maximum echo time position $t_e$ for the pulse sequences $450_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$, $630_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ and $810_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ obtained for $C_6H_6$ are shown in figure 2. The time positions of dipolar echo signals do not depend on the temperature in the region $T > 130\,K$. At $T < 130\,K$ the time positions of the maximum of the echo signals are shifted to the end of the second pulse and echo signals disappear. The solid and broken lines in figure 2 are the theoretical curves for the time positions of the echo maximum, as calculated from equation (15) using the results of the relaxation studies of this compound [25]. We have used the following parameters: $\tau_c = (3.14 \times 10^{-15}\,\text{s})\exp(19.01\,\text{kJ}\,\text{mol}^{-1}/RT)$; $\bar{M}_2 = 1.58 \times 10^{-8}T^2$; $\Delta M_2 = 8.32 \times 10^{-8}T^2$. The agreement between theory and experiment is reasonable, especially since no parameters have been adjusted.

The experimental temperature dependence of the maximum echo amplitudes for the pulse sequence
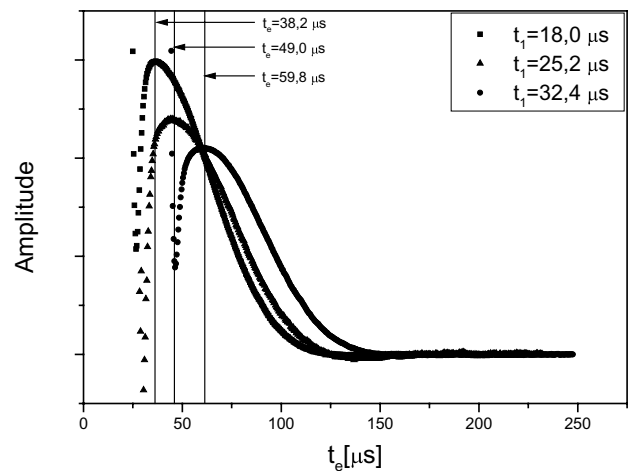


Figure 1. Dipolar echoes in $C_6H_6$ at room temperature for the pulse sequences $450_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$, $630_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ and $810_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$: $t_2 = 3.6\,\mu s$ $\tau - t_1 = 2.8\,\mu s$.
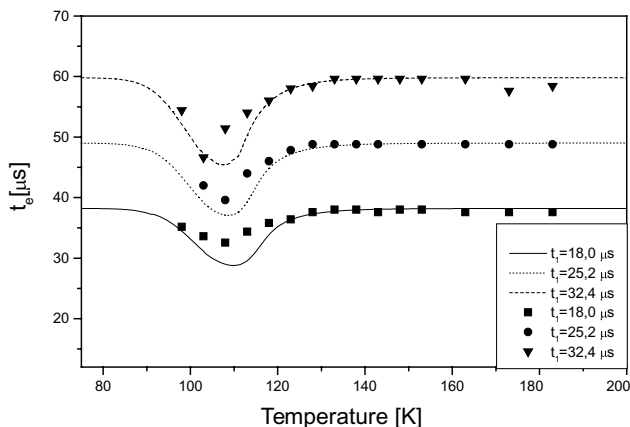
Figure 2. Temperature dependence of the time positions of the dipolar echoes maximum in $C_6H_6$ for the pulse sequences $450_Y^\circ - \tau - 90_X^\circ - Acq(t)$, $630_Y^\circ - \tau - 90_X^\circ - Acq(t)$ and $810_Y^\circ - \tau - 90_X^\circ - Acq(t)$: $t_2 = 3.6\,\mu s$; $\tau - t_1 = 2.8\,\mu s$.
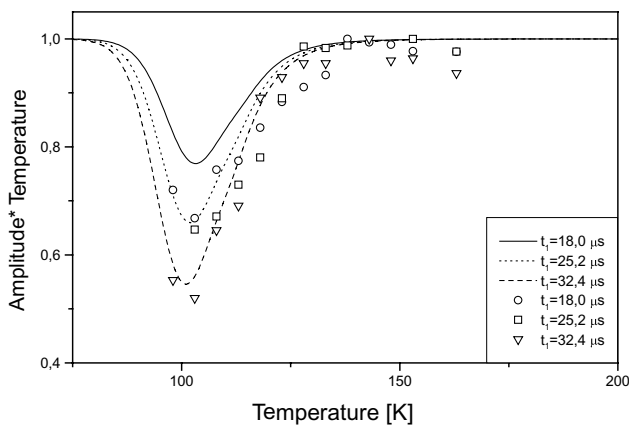


Figure 3. Temperature dependence of the dipolar echoes amplitude $(V(t_e) \times T)$ in $C_6H_6$ for the pulse sequences $450_Y^\circ - \tau - 90_X^\circ - Acq(t)$, $630_Y^\circ - \tau - 90_X^\circ - Acq(t)$ and $810_Y^\circ - \tau - 90_X^\circ - Acq(t)$: $t_2 = 3.6\,\mu s$; $\tau - t_1 = 2.8\,\mu s$.

$450_Y^\circ - \tau - 90_X^\circ - Acq(t)$, $630_Y^\circ - \tau - 90_X^\circ - Acq(t)$ and $810_Y^\circ - \tau - 90_X^\circ - Acq(t)$ obtained for benzene are shown in figure 3. The solid and broken lines in figure 3 are the theoretical curves obtained from equation (15) using the same parameters as for the theoretical curves in figure 2. From this figure one can see that the theory developed describes rather well the observed temperature dependence of the dipolar echo amplitude.

## 4. Conclusion

From our study it follows that the time position and amplitude of the dipolar echo maximum depend on the correlation time $\tau_c$ of molecular motion and on the RF pulse widths. Dramatic changes in the solid-echo

behaviour are observed in the slow motion region $(\langle M_{2H} \rangle \tau_c^2 \approx 1)$, where the amplitude of the dipolar echo signal is reduced and the maximum of the echo signal is shifted to the end of the second pulse. It has been shown also that a study of the temperature dependence of the time position and amplitude of the dipolar echo maximum can yield valuable information about dynamic processes in solids.

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