MOLECULAR PHYSICS REPORTS **34/2** (2001) 75-78

DIPOLAR ECHOES IN SOLIDS AND MOLECULAR MOBILITY

P. BILSKI[1], N. A. SERGEEV[2], J. WĄSICKI[1]

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

Abstract: The general "solid-echo" technique $(2n+1)\cdot 90^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, which allows to inverting the dipolar Hamiltonian sign and to observe the echo signal, has been proposed.

In 1950 E. Hahn demonstrated that the two-pulse sequence $90^\circ - \tau - 180^\circ - Acq\ (t)$ applied to the inhomogeneously broadening spin system (for example the nuclear spins in liquid) leads to an appearance of the echo signal at $t = \tau$ [1]. The amplitude of the Hahn's echo does not depend on τ. When dephasing mechanisms do not operate. In the case of the homogeneously broadening spin system (for example the 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]. As it was shown [2, 3] in this case the echo signal is also observed at $t = \tau$. However the amplitude of solid-echo signal depends on τ as τ^4 and the echo signal may be observed only for small values of τ. The formation of solid-echo, contrary to the Hahn's echo is not connected with inverting of dipole interaction Hamiltonian sign by RF pulses [4]. In this report we consider the general "solid-echo" technique, which allows to inverting the dipolar Hamiltonian sign and to observe the echo signal.

Let us consider at a first the simple two- pulse model sequence: $\alpha^\circ_Y - 90^\circ_X - Acq\ (t)$. 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 OY-axis in the rotating frame. After the first RF pulse the density matrix has the form:

$$\rho(t_1) = \exp(-iHt_1)\cdot\rho(0)\cdot\exp(iHt_1)\,. \tag{1}$$

Here $\rho(0)$ is the density matrix at $t = 0$ and the interaction Hamiltonian H is [4-6]:

$$H = -\omega_1 I_Y - \frac{1}{2}H_Y\,. \tag{2}$$

In Eq. (2) ω_1 is the frequency of RF pulse and

$$H_Y = \sum_{i,j} b_{ij}\left(2I_Y^i I_Y^j - I_X^i I_X^j - I_Z^i I_Z^j\right). \tag{3}$$

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

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

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

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

where

$$H_Z = \sum_{i,j} b_{ij}\left(2I_Z^i I_Z^j - I_X^i I_X^j - I_Y^i I_Y^j\right). \tag{6}$$

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

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

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

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

From Eq. (8), it follows that at $t = 3t_1/2$ we have $V(t_1, t = 3t_1/2) = 1$ or we should observe the echo signal. The amplitude of this echo signal does not depend on t_1.

The considered model of pulse sequence cannot be applied in real experiments. At first there is always a finite time between the end of the first RF pulse and the beginning of the second pulse. Also the second RF pulse has the finite width and one is not the delta pulse. All these factors induce an attenuation and deformation of the echo signal. It is easily shown that for real two-pulse sequence $(2n + 1) \cdot 90^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$ the maximum of echo signal is observed at [4]:

$$t_e = 2\tau + t_2 - \frac{t_1}{2}, \tag{9}$$

where τ is the time distance between the beginning of the first RF pulse and the beginning of the second RF pulse.

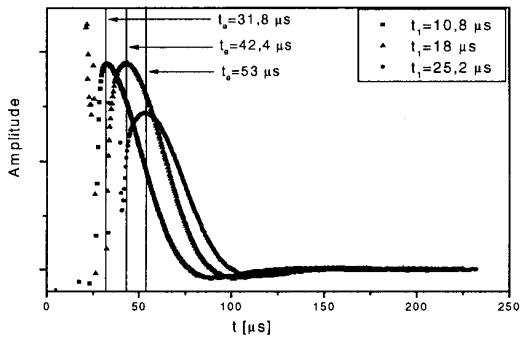

Fig. 1. The dipolar echoes in NH_4Cl at the room temperature for the pulse sequences: $270^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, $450^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$. $t_2 = 3.6$ µs; $\tau - t_1 = 5.8$ µs

Experimental measurements of the echo signals for the pulse sequences $270^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, $450^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$ for polycrystalline NH_4Cl are shown in Fig. 1. Experimental values of time positions of the echo signals are in good agreement with Eq. (9).

We considered also the influence of molecular mobility on the echo signal observed after the two-pulse sequence $(2n+1)\cdot 90^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, and obtained [7, 8]

$$V(t, t_2, \tau, t_1,) = \beta \cdot \exp\left\{-\frac{1}{2}\bar{M}_2\left[t - \left(2\tau + t_2 - \frac{t_1}{2}\right)\right]^2 - \Delta M_2\, \tau_c^2 \cdot R(t, t_2, \tau, t_1, \tau_c)\right\}, \tag{10}$$

where $\beta = \hbar\omega_0/kT$ and

$$\begin{aligned} R(t, t_2, \tau, t_1, \tau_c) = &-\frac{7}{4} + \frac{t}{\tau_c} - \frac{3t_1}{4\tau_c} - \frac{1}{4}\exp\left(-\frac{t_1}{\tau_c}\right) - \exp\left(-\frac{t_2}{\tau_c}\right) - \frac{1}{2}\exp\left(-\frac{t}{\tau_c}\right) \\ &+ \frac{1}{2}\exp\left(-\frac{\tau - t_1}{\tau_c}\right) - \frac{1}{2}\exp\left(-\frac{t - t_1}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau + t_2}{\tau_c}\right) \\ &+ \exp\left(-\frac{t - \tau}{\tau_c}\right) + \exp\left(-\frac{t - \tau - t_2}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau}{\tau_c}\right) + \frac{1}{2}\exp\left(-\frac{\tau + t_2 - t_1}{\tau_c}\right) \end{aligned} \tag{11}$$

In Eq. (10) $\Delta M_2 = M_2 - \bar{M}_2$, where M_2 is the second moment of NMR line for a rigid lattice; $\bar{M}_2$ is the second moment of motional narrowed NMR line. In Eq. (11) τ_c is the correlation time which describes the molecular mobility in solid.

From Eqs. (10) and (11) it follows that in the case of rigid lattice ($M_2\tau_c^2 \gg 1$) and motionaly narrowed NMR line ($M_2\tau_c^2 \ll 1$) the time position of the echo signal is determined by Eq. (9). The dramatically changes in echo signal behavior are observed in the slow-motion region ($M_2\tau_c^2 \approx 1$). In this region the amplitude of dipolar echo signal is reduced and the time position of the echo signal maximum is shifted to the end of the second pulse. The obtained Eqs. (10) and (11) have been applied to the analysis of the temperature dependencies of dipolar echo signals in ammonium chloride NH_4Cl. The experimental and theoretical data are shown in Fig. 2 and Fig. 3.

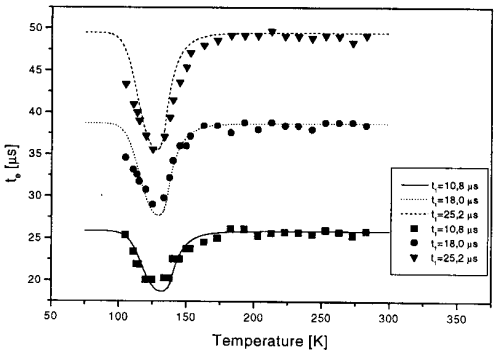

Fig. 2. The temperature dependencies of the time positions of the dipolar echoes maximum in NH_4Cl for the pulse sequences:
$270^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$,
$450^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$,
$630^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$.
$t_2 = 3.6$ μs; $\tau - t_1 = 3.6$ μs

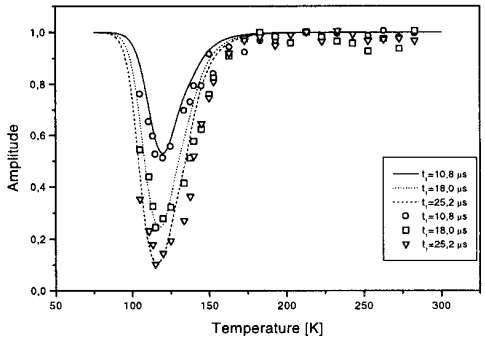

Fig. 3. The temperature dependencies of the dipolar echoes amplitude in NH_4Cl for the pulse sequences: $270^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, $450^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq\ (t)$. $t_2 = 3.6$ µs; $\tau - t_1 = 3.6$ µs

A comparison of the developed theory with experimental results demonstrates a good agreement between them.

References

[1] Hahn E. L., Phys. Rev. **80,** 580 (1950).
[2] Powles J. G. and Masfield P., Phys. Rev. Lett. **2**, 58 (1962).
[3] Powles J. G. and Strange J. H., Proc. Phys. Soc. **82**, 7 (1963).
[4] Sergeev N. A., Solid State NMR **10**, 45 (1997).
[5] Barnaal D. and Low I. J., Phys. Rev. Lett. **11**, 258 (1963).
[6] Barnaal D. and Low I. J., Phys. Rev. **148**, 328 (1966).
[7] Bilski P., Sergeev N. A. and Wąsicki J., Appl. Magn. Reson. **18**, 115 (2000).
[8] Bilski P., Sergeev N. A. and Wąsicki J., Molec. Phys. Rep. **29**, 55 (2000).