Available online at www.sciencedirect.com
SCIENCE DIRECT®
Solid State Nuclear Magnetic Resonance 25 (2004) 76–79
Solid State Nuclear Magnetic Resonance
http://www.elsevier.com/locate/ssnmr

Simple two-pulse time-reversal sequence for dipolar and quadrupolar-coupled spin systems

P. Bilski,[a] A.M. Panich,[b] N.A. Sergeev,[c,*] and J. Wąsicki[a]

[a] *Faculty of Physics, Adam Mickiewicz University, 61-614 Poznań, Poland*
[b] *Department of Physics, Ben-Gurion University of the Negev, P.O.Box 653, Beer Sheva 84105, Israel*
[c] *Institute of Physics, University of Szczecin, 70-451 Szczecin, Poland*

Received November 7, 2002; revised February 5, 2003

Abstract

We demonstrate, both theoretically and experimentally, that two-pulse sequence $(2n+1)\cdot 90^\circ_Y - 90^\circ_X - Acq(t)$ without delay between pulses, yields the reverse of time evolution of spin system with dipolar and quadrupole interactions. This process results in refocusing of the spin magnetization into magic echo at $t_e = t_1/2$ after the second pulse, where t_1 is the length of the first pulse.

PACS: 33.25.+k; 76.20.+q; 76.60.−k; 76.60.Lz

Keywords: Spin-echoes; Dipolar and quadrupolar interactions; Finite width RF pulses

1. Introduction

One of the interesting and practically important features of pulse NMR spectroscopy is the possibility to reverse the time evolution of a spin system, resulting in evolution of the system from its state at $t>0$ to its state at time $t=0$. The first and simplest time-reversal experiment in NMR was the Hahn echo experiment, in which the two-pulse sequence $90^\circ - \tau - 180^\circ - Acq(t)$, applied to a spin system in an inhomogeneous external magnetic field, leads to the occurrence of the echo signal at $t=2\tau$ [1]. In the case of a homogeneous broadening of the resonance line (e.g., if one considers nuclear spins with dipole–dipole coupling), the first attempts to change the sign of the interaction Hamiltonian were carried out by Powles, Mansfield and Strange [2,3]. Assuming that the applied RF pulses are delta $90^\circ_{X,Y}$ pulses (that supposes that $\omega_1 t_{1,2} = 90^\circ$ at the pulse length $t_{1,2}\to 0$ and the amplitude of the RF field $\omega_1 \to \infty$), it was shown that the two-pulse sequence $90^\circ_Y - \tau - 90^\circ_X - Acq(t)$ yields the echo signal observed at $t=2\tau$ [2,3]. The amplitude of the solid echo depends on τ [2,3]: the echo decays as τ^4 and thus may be observed only for small values of τ ($\tau < T_2 \equiv 2\pi/\sqrt{M_2}$, where M_2 is the second moment of the NMR line in $(\mathrm{rad/s})^2$). The time-reversal experiments on spin systems with dipolar interactions were proposed also by Schneider and Schmiedel [4] and Rhim et al. [5–8]. They reported that it is possible to invert the sign of the dipolar Hamiltonian and obtain the "magic" echo signal, which can be observed at $t > T_2 \equiv 2\pi/\sqrt{M_2}$. Then Kimmich et al. [9] showed that pulse sequences proposed in [5–8] are also suitable for the production of magic echoes in quadrupole-coupled system with nuclear spin $I=1$.

In this paper we propose a simple two-pulse magic sequence $(2n+1)\cdot 90^\circ_Y - 90^\circ_X - Acq(t)$, where n is an integer, which yields the inversion of the signs of dipolar and quadrupole Hamiltonians and the reverse of the time evolutions of spin systems with dipolar and quadrupole interactions. Some preliminary results were reported in [10–12]. We note that in spite of some similarity between our pulse sequence, $(2n+1)\cdot 90^\circ_Y - 90^\circ_X - Acq(t)$, and that proposed by Rhim et al. $90^\circ_Y - \alpha^\circ_X - Acq(t)$, (Fig. 1b in Ref. [6]), these sequences do not coincide.

*Corresponding author.
E-mail address: sergeev@wmf.univ.szczecin.pl (N.A. Sergeev).

0926-2040/$ - see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/j.ssnmr.2003.03.020

2. Theory

Let us consider a simple two-pulse sequence $\alpha^\circ_Y - 90^\circ_X - Acq(t)$. The first RF pulse α°_Y rotates the nuclear magnetization with the angle $\alpha = (2n+1)\cdot(\pi/2)$, where $n = 1, 2, 3, \ldots$ 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

$$\rho(t_1) = \exp(-iH_1 t_1)\rho(0)\exp(iH_1 t_1). \tag{1}$$

Here $\rho(0)$ is the density matrix at $t = 0$ and $H_1(\hbar = 1)$ is the interaction Hamiltonian of nuclear spins in the rotating frame:

$$H_1 = -\omega_1 I_Y + H_Z, \tag{2}$$

where ω_1 is the amplitude of RF pulse. Let the interaction Hamiltonian H_Z contain the secular parts of dipolar and quadrupolar Hamiltonians [13]

$$H_Z = \sum_i \omega_{qi}\left[I_Z^2 - \frac{1}{3}I(I+1)\right] + \sum_{i,j} b_{ij}(2I_Z^i I_Z^j - I_X^i I_X^j - I_Y^i I_Y^j). \tag{3}$$

Here b_{ij} is dipolar coupling constant between the spins i and j and ω_{qi} is the quadrupolar coupling constant of the nucleus i [13]. Writing the interaction Hamiltonian in the form (3) we assume that the approximation of high magnetic field is fulfilled [13].

If the first RF pulse is a "hard" pulse ($\omega_1 \gg ||H_Z||$), the main contribution to the evolution of spin system results from the terms of the interaction Hamiltonian H_Z which commute with the Hamiltonian $(-\omega_1 I_Y)$ [13]. One can easily show [14–16] that these terms are

$$\tilde{H}_Z = -\frac{1}{2}H_Y, \tag{4}$$

where

$$H_Y = \sum_i \omega_{qi}\left[I_Y^2 - \frac{1}{3}I(I+1)\right] + \sum_{i,j} b_{ij}(2I_Y^i I_Y^j - I_X^i I_X^j - I_Z^i I_Z^j). \tag{5}$$

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

$$\rho(t_1) = (-1)^n \exp\left(i\frac{1}{2}H_Y t_1\right) I_X \exp\left(-i\frac{1}{2}H_Y t_1\right). \tag{6}$$

At the time t_1 the second RF pulse (of the length of t_2) is applied to the spin system. The RF field of this pulse lies along the OX-axis in the rotating frame. After the second RF pulse the spin density operator becomes:

$$\rho^+(t_1+t_2) = \exp(-iH_2 t_2)\rho(t_1)\exp(iH_2 t_2). \tag{7}$$

Here the interaction Hamiltonian H_2 has the form

$$H_2 = -\omega_1 I_X + H_Z. \tag{8}$$

If the second RF pulse is also a "hard" pulse, only terms which commute with the Hamiltonian $(-\omega_1 I_X)$ retain in the interaction Hamiltonian H_Z. Thus the Hamiltonian H_2 may be written as

$$H_2 = -\omega_1 I_X - \frac{1}{2}H_X. \tag{9}$$

Here

$$H_X = \sum_i \omega_{qi}\left[I_X^2 - \frac{1}{3}I(I+1)\right] + \sum_{i,j} b_{ij}(2I_X^i I_X^j - I_Z^i I_Z^j - I_Y^i I_Y^j). \tag{10}$$

If the second pulse is a 90° pulse ($t_2 = \pi/2\omega_1$), we obtain from Eq. (7)

$$\rho^+(t_1+t_2) = (-1)^n \exp\left(i\frac{1}{2}H_X t_2\right)\exp\left(i\frac{1}{2}H_Z t_1\right) \times I_X \exp\left(-i\frac{1}{2}H_Z t_1\right)\exp\left(-i\frac{1}{2}H_X t_2\right). \tag{11}$$

Usually $||H_{Z,X}||\cdot t_2 = ||H_{Z,X}||\cdot\pi/(2\omega_1) \ll 1$, and if we assume that $t_2 \ll t_1$, Eq. (11) may be written as

$$\rho^+(t_1+t_2) \equiv \rho^+(t_1) \approx (-1)^n \exp\left(i\frac{1}{2}H_Z t_1\right) \times I_X \exp\left(-i\frac{1}{2}H_Z t_1\right). \tag{12}$$

After the second RF pulse, the Hamiltonian H_Z describes the free evolution of the spin density operator. At the time t measured from the end of the second RF pulse, the density operator has the form:

$$\rho(t_1, t) = \exp(-iH_Z t)\rho^+(t_1)\exp(iH_Z t) = (-1)^n \exp\left[-iH_Z\left(t - \frac{1}{2}t_1\right)\right] \times I_X \exp\left[iH_Z\left(t - \frac{1}{2}t_1\right)\right]. \tag{13}$$

The observed transient response of the ensemble of spins is determined by the equation [13]

$$V(t_1, t) = (-1)^n \frac{Tr[\rho(t_1, t)I_X]}{Tr(I_X^2)}. \tag{14}$$

Inserting Eq. (13) into Eq. (14) we obtain

$$V(t_1, t) = (-1)^n \times \frac{Tr\left\{\exp\left[-iH_Z\left(t - \frac{1}{2}t_1\right)\right] I_X \exp\left[iH_Z\left(t - \frac{1}{2}t_1\right)\right] I_X\right\}}{Tr(I_X^2)}. \tag{15}$$

From Eq. (15), it follows that at $t = t_1/2$ we have $V(t_1, t = t_1/2) = (-1)^n$ or, in other words, we should observe the magic echo signal.

Concerning the experimental verification of our calculation, we note that in experiment (i) there is a

finite time τ between the end of the first RF pulse and the beginning of the second pulse and (ii) the second RF pulse has a finite width t_2 and thus is not a delta pulse. These factors yield some attenuation and deformation of the echo signal. In analogy to [17], it is easy to show that for the proposed pulse sequence, $(2n+1)\cdot 90^\circ_Y - \tau - 90^\circ_X - Acq(t)$, the maximum of the echo signal should be observed at the time $t_e = \tau + t_1/2$.

3. Experimental results

3.1. Quadrupolar-coupled spin system

To confirm the results of the calculation, we have carried out ^{7}Li NMR echo measurements in powder $LiInSe_2$, applying the aforementioned pulse sequence. All measurements were done, performed in the applied magnetic field 8.0196 T (resonance frequency 132.68 MHz) at ambient temperature. The echo signals were received using $(2n+1)90^\circ_Y - \tau - 90^\circ_X - Acq(t)$ pulse sequence. The length of $\pi/2$ pulse was 4 μs. Delay τ was chosen to be 0.2 μs (which is twice as much the minimal time interval available in our spectrometer); one can see that τ is negligibly small in comparison to the pulse length.

We note that the crystal structure of $LiInSe_2$ belongs to the orthorhombic symmetry, the space group is $Pna2_1$ [18]. The Li atoms are located at the centre of slightly distorted $LiSe_4$ tetrahedra. In such an environment, quadrupole ^{7}Li nucleus ($I = 3/2$) should exhibit three NMR lines. This is readily seen in Fig. 1 that shows ^{7}Li NMR spectra of powder and single crystalline $LiInSe_2$ [19]. Here the spectrum of the single crystal was measured at the orientation corresponding to the maximal splitting between satellites. The powder spectrum, in which the central line and the satellites are hardly resolved due to the overlap caused by angular dependence of the resonance frequency, shows a line width of 4.6 kHz. Thus one can realize that the pulses used in our experiment excite the whole spectrum of the powder sample, which was utilized for the echo measurements. The value of the RF field ω_1 was calculated to be 63 kHz (in the frequency units), that significantly exceeds the line width. Thus the above condition $\omega_1 \gg ||H_Z||$, which is necessary for the echo formation, is realized. Our measurements show that the aforementioned $(2n+1)\cdot 90^\circ_Y - 90^\circ_X - Acq(t)$ pulse sequence results in spin echo that is seen after the second pulse. Dependence of the echo position after the second pulse (t_e) on the length of the first pulse, $t_1 = (2n+1)\pi/2$, is given in Fig. 2. One can see that $t_e \approx t_1/2$. A linear fit of this dependence with formula ($t_e = bt_1$) yields $b = 0.445$ that is close to the theoretical value of 1/2. Thus one can see that the result of the calculation is in good agreement with the experimental data.

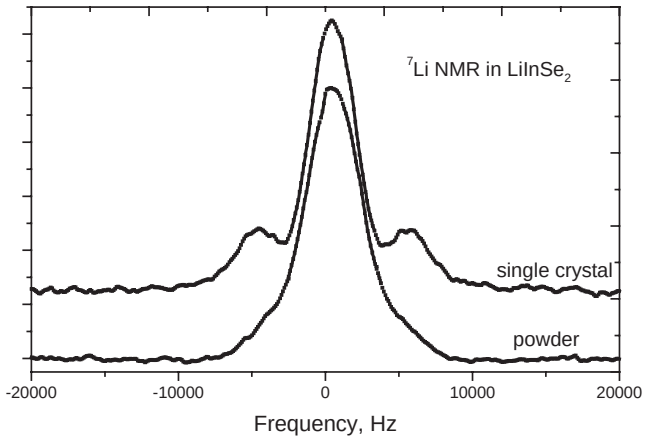

Fig. 1. Room temperature ^{7}Li NMR spectra of powder and single crystalline $LiInSe_2$ in the applied magnetic field of 8.0196 T. The orientation of the single crystal corresponds to the maximal splitting between satellites.

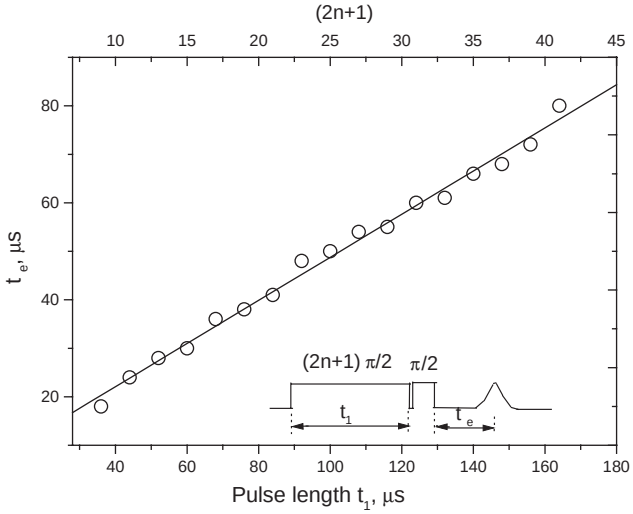

Fig. 2. Dependence of the echo position after the second pulse t_e versus the length of the first pulse $t_1 = (2n+1)\cdot\pi/2$ for the pulse sequence $(2n+1)\cdot 90^\circ_Y - \tau - 90^\circ_X - Acq(t)$ ($\tau = 0.2$ μs). The pulse sequence is shown separately.

3.2. Dipolar-coupled spin systems

To confirm the results of the calculation, we have also carried out ^{1}H NMR echo measurements in powder benzene (C_6H_6) and ammonium chloride (NH_4Cl). ^{1}H NMR experiments were performed at $T = 200$ K using a pulse spectrometer operating at 60 MHz. The experimental echoes observed in C_6H_6 for the pulse sequences: $450^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $810^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $990^\circ_Y - \tau - 90^\circ_X - Acq(t)$ are

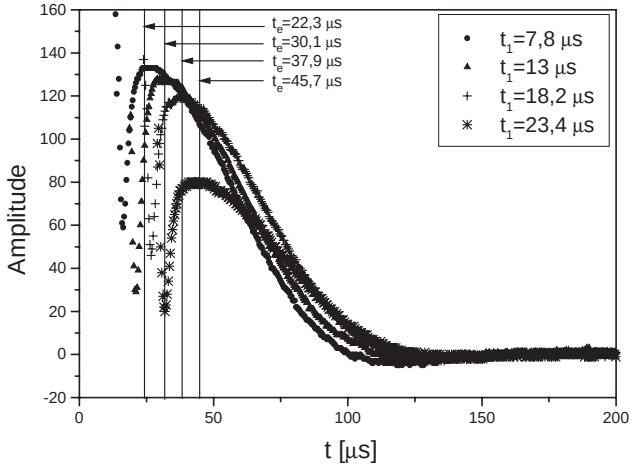

Fig. 3. The dipolar echoes in C_6H_6 at $T = 200\,\mathrm{K}$ for the pulse sequences: $450^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $810^\circ_Y - \tau - 90^\circ_X - Acq(t)$, and $990^\circ_Y - \tau - 90^\circ_X - Acq(t)$. $t_2 = 2.6\,\mu\mathrm{s}$; $\tau = 2.8\,\mu\mathrm{s}$.

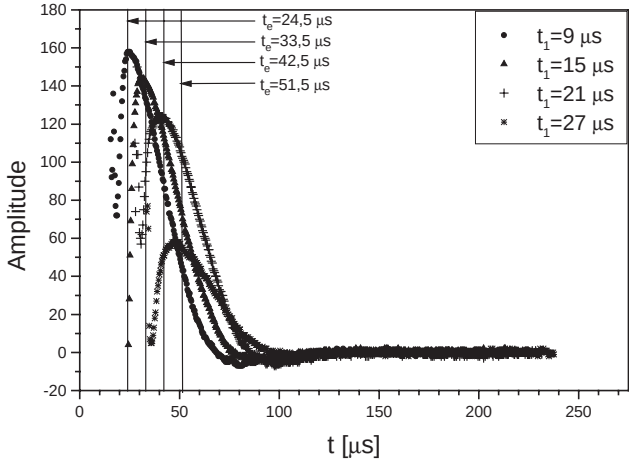

Fig. 4. The dipolar echoes in NH_4Cl at $T = 200\,\mathrm{K}$ for the pulse sequences: $90^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $270^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $450^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq(t)$, and $990^\circ_Y - \tau - 90^\circ_X - Acq(t)$. $t_2 = 3.0\,\mu\mathrm{s}$; $\tau = 5.8\,\mu\mathrm{s}$.

shown in Fig. 3. One can see that the maximum of the dipolar echoes is observed at $t_e = \tau + t_1/2$. The dipolar echoes observed in NH_4Cl for the pulse sequences: $450^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $630^\circ_Y - \tau - 90^\circ_X - Acq(t)$, $810^\circ_Y - \tau - 90^\circ_X - Acq(t)$, and $990^\circ_Y - \tau - 90^\circ_X - Acq(t)$ at $T = 200\,\mathrm{K}$ are shown in Fig. 4. One can see that the maximum of the dipolar echoes is observed at $t_e = \tau + t_1/2$.

Acknowledgments

We thank A. Yelisseyev (Design and Technical Institute of Monocrystals, Novosibirsk) for supplying us with $LiInSe_2$ samples.

References

[1] E.L. Hahn, Phys. Rev. 80 (1950) 580.
[2] J.G. Powles, P. Mansfield, Phys. Rev. Lett. 2 (1962) 58.
[3] J.G. Powles, J.H. Strange, Proc. Phys. Soc. 82 (1963) 7.
[4] H. Schneider, H. Schmiedel, Phys. Lett. 30A (1969) 298.
[5] W.K. Rhim, A. Pines, J.S. Waugh, Phys. Rev. Lett. 25 (1970) 218.
[6] W.K. Rhim, A. Pines, J.S. Waugh, Phys. Rev. B3 (1971) 684.
[7] W.K. Rhim, H. Kessemeier, Phys. Rev. B3 (1971) 3655.
[8] K. Takegoshi, D.A. McDowell, Chem. Phys. Lett. 116 (1985) 100.
[9] R. Kimmich, J. Niess, S. Hafner, Chem. Phys. Lett. 190 (1992) 503.
[10] P. Bilski, N.A. Sergeev, J. Wąsicki, Mol. Phys. Reports (Poland) 34/2 (2001) 75.
[11] P. Bilski, N.A. Sergeev, J. Wąsicki, Funct. Mater. 9 (2002) 130.
[12] P. Bilski, A.M. Panich, N.A. Sergeev, J. Wąsicki, Book of Abstracts of 31th Congress AMPERE on Magnetic Resonance and Related Phenomena, Poznan, Poland, July 2002, p. 87.
[13] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford, 1961.
[14] D. Barnaal, I.J. Low, Phys. Rev. Lett. 11 (1963) 258.
[15] D. Barnaal, I.J. Low, Phys. Rev. 148 (1966) 328.
[16] N.A. Sergeev, Solid State NMR 10 (1997) 45.
[17] P. Bilski, N.A. Sergeev, J. Wąsicki, Appl. Magn. Res. 18 (2000) 115.
[18] H.J. Beister, S. Ves, W. Hönle, K. Syassen, Phys. Rev. B 43 (1991) 9635.
[19] L. Isaenko, A. Yelisseyev, S. Lobanov, A.M. Panich, V. Vedenyapin, J. Smirnova, V. Petrov, J.J. Zondy, G. Knippels, Materials Research Society Symposium Proceedings, 2002, 692 (Progress in Semiconductor Materials for Optoelectronic Applications, 2001), p. 429–434.