

Simple Two-pulse Time-reversal Sequence for Quadrupole-coupled Spin System

N. A. Sergeev and A. M. Panich^a

Institute of Physics, University of Szczecin, 70-451 Szczecin, Poland

^b Department of Physics, Ben-Gurion University of the Negev,

P. O. Box 653, Beer Sheva 84 105, Israel

Reprint requests to Prof. N. A. S.; E-mail: sergeev@wmf.univ.szczecin.pl

Z. Naturforsch. **58 a**, 33–35 (2003); received September 12, 2002

We demonstrate both theoretically and experimentally that the two-pulse sequence $(2n+1) \cdot 90_Y^\circ - 90_X^\circ - \text{Acq}(t)$ without delay between the pulses yields the reverse of the time evolution of spin systems with quadrupole interactions. This process results in refocusing of the spin magnetization into a magic echo at $t_e = t_1/2$ after the second pulse, where t_1 is the length of the first pulse.
33.25.+k; 76.20.+q; 76.60.-k; 76.60.Lz

Key words: Spin-echoes; 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 the evolution of the system from its state at a time $t > 0$ to its state at $t = 0$. The first time-reversal experiments on spin systems with dipolar interactions were proposed by Schneider and Schmiedel [1], Rhim *et al.* [2 - 4], and Takegoshi and McDowell [5]. They reported that it is possible to invert the sign of the dipolar Hamiltonian and obtain so-called “magic echoes”. Then Kimmich *et al.* [6] showed that the pulse sequences proposed in [2 - 5] are also suitable for the production of magic echoes in quadrupole-coupled systems with nuclear spin $I = 1$.

In the present paper we demonstrate that a simple two-pulse magic sequence $(2n+1) \cdot 90_Y^\circ - 90_X^\circ - \text{Acq}(t)$ [7], where n is an integer, yields the inversion of the sign of the quadrupole Hamiltonian and the reverse of the time evolutions of spin systems with quadrupole interactions.

Let us consider a transient response of the ensemble of quadrupolar nuclei to the two-pulse sequence $\alpha_Y^\circ - 90_X^\circ - \text{Acq}(t)$. Let the first rf pulse α_Y° rotates the nuclear magnetization by the angle $\alpha = (2n+1) \cdot (\pi/2)$, where $n = 1, 2, 3, \dots$. The rf field of this pulse lies along the

OY-axis in the rotating frame. After the first rf pulse, the density matrix of the spin system has the form

$$\rho(t_1) = \exp(-iH_1 t_1) \cdot \rho(t) \cdot \exp(iH_1 t_1). \quad (1)$$

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

$$H_1 = -\omega_1 I_Y + H_{qZ}, \quad (2)$$

where $I_Y = \sum I_{Yi}$, and

$$H_{qZ} = \sum_i \omega_{qi} \left[I_{Zi}^2 - \frac{1}{3} I(I+1) \right] \quad (3)$$

is the quadrupolar interaction Hamiltonian [8, 9]. In (2) ω_1 is the amplitude of the rf pulse. In (3) ω_{qi} is the quadrupolar coupling constant of the nucleus i [8, 9]. Writing the interaction Hamiltonian in the form (2) we neglect other interactions of quadrupolar nuclei (for example dipolar interactions). Writing the quadrupolar interaction Hamiltonian in the form (3) we assume that the approximation for a high magnetic field is fulfilled [8, 9].

If the first rf pulse is the “hard” pulse ($\omega_1 \gg \omega_{qi}$), the main contribution to the evolution of the spin system results from the terms of the quadrupolar Hamiltonian which commute with the Hamiltonian $(-\omega_1 I_Y)$

[10 - 12]. One can easily show [10 - 12] that these terms are $(-H_{qY}/2)$, where

$$H_{qY} = \sum_i \omega_{qi} \left[I_{Yi}^2 - \frac{1}{3} I(I+1) \right]. \quad (4)$$

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

$$\rho(t_1) = (-1)^n \exp\left(i\frac{1}{2}H_{qY}t_1\right) I_X \exp\left(-i\frac{1}{2}H_{qY}t_1\right). \quad (5)$$

At the time t_1 the second rf pulse (of the length 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

$$\rho^+(t_1+t_2) = \exp(-iH_2t_2) \cdot \rho(t_1) \cdot \exp(-iH_2t_2). \quad (6)$$

Here the interaction Hamiltonian H_2 has the form

$$H_2 = -\omega_1 I_X + H_{qZ}. \quad (7)$$

If the second rf pulse is also a “hard” pulse, only terms which commute with the Hamiltonian $(-\omega_1 I_X)$ appear in the interaction Hamiltonian H_{qZ} . Thus the Hamiltonian H_2 may be written as

$$H_2 = -\omega_1 I_X - \frac{1}{2} H_{qX}. \quad (8)$$

Here

$$H_{qX} = \sum_i \omega_{qi} \left[I_{Xi}^2 - \frac{1}{3} I(I+1) \right]. \quad (9)$$

If the second pulse is a 90° pulse ($t_2 = \pi/2\omega_1$), we obtain from (6)

$$\begin{aligned} \rho^+(t_1+t_2) = & (-1)^n \exp\left(i\frac{1}{2}H_{qX}t_2\right) \exp\left(i\frac{1}{2}H_{qZ}t_1\right) \\ & \cdot I_X \cdot \exp\left(-i\frac{1}{2}H_{qZ}t_1\right) \exp\left(-i\frac{1}{2}H_{qX}t_2\right). \end{aligned} \quad (10)$$

Usually $(\omega_{qi}/2\pi) \cdot t_2 = \omega_{qi}/(4\omega_1) \ll 1$, and if we assume that $t_2 \ll t_1$, (10) may be written as

$$\begin{aligned} \rho^+(t_1+t_2) \equiv \rho^+(t_1) \approx & (-1)^n \exp\left(i\frac{1}{2}H_{qZ}t_1\right) \\ & \cdot I_X \cdot \exp\left(-i\frac{1}{2}H_{qZ}t_1\right). \end{aligned} \quad (11)$$

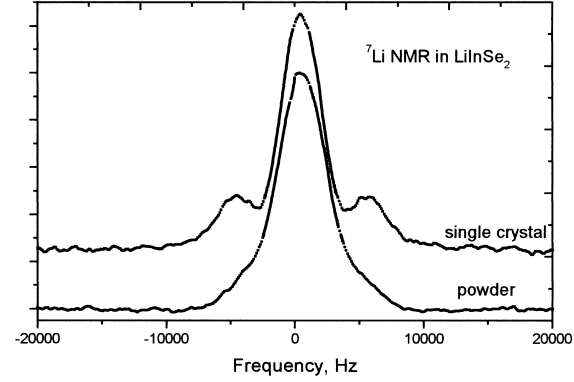


Fig. 1. Room temperature ^7Li NMR spectra of powder and single crystalline LiInSe_2 in an applied magnetic field of 8.0196 T. The orientation of the single crystal corresponds to the maximal splitting between satellites.

After the second rf pulse, the Hamiltonian H_{qZ} 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

$$\begin{aligned} \rho(t_1, t) = & \exp(-iH_{qZ}t) \cdot \rho^+(t_1) \cdot \exp(iH_{qZ}t) \\ = & (-1)^n \exp[-iH_{qZ}(t - \frac{1}{2}t_1)] \\ & \cdot I_X \cdot \exp[iH_{qZ}(t - \frac{1}{2}t_1)]. \end{aligned} \quad (12)$$

The observed transient response of the ensemble of spins is given by [8, 9]

$$V(t_1, t) = \frac{\text{Tr}[\rho(t_1, t) \cdot I_X]}{\text{Tr}(I_X^2)}. \quad (13)$$

Inserting (12) into (13) we obtain

$$\begin{aligned} V(t_1, t) = & (-1)^n \text{Tr}\{\exp[-iH_{qZ}(t - \frac{1}{2}t_1)] \cdot I_X \\ & \cdot \exp[iH_{qZ}(t - \frac{1}{2}t_1)] \cdot I_X\} \text{Tr}^{-1}(I_X^2). \end{aligned} \quad (14)$$

From (14), it follows that at $t = t_1/2$ we have $V(t_1 = t_1/2) = (-1)^n$ or, in the other words, we should observe the magic echo signal.

To confirm the results of the calculation, we have carried out ^3Li NMR echo measurements in powder of LiInSe_2 , applying the aforementioned pulse sequence. All measurements have been made in an applied magnetic field 8.0196 T (resonance frequency

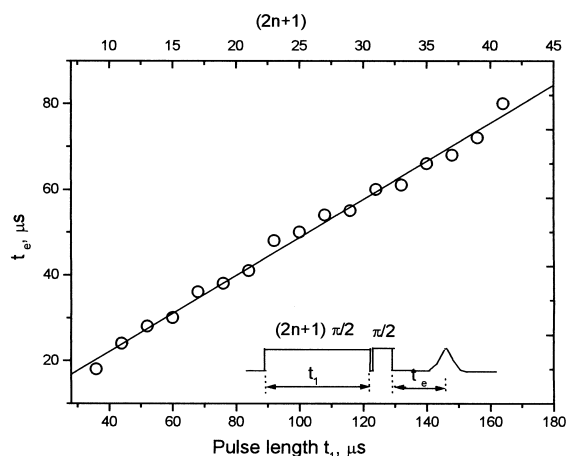


Fig. 2. Dependence of the echo position after the second pulse t_e versus the length of the first pulse $t_1 = (2n+1) \cdot \pi/2$ for the pulse sequence $(2n+1) \cdot 90_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$; ($\tau = 0.2 \mu\text{s}$). The pulse sequence is shown separately.

132.68 MHz) at ambient temperature. The echo signals were received using the $(2n+1) \cdot 90_Y^\circ - \tau - 90_X^\circ - \text{Acq}(t)$ pulse sequence. The length of the $\pi/2$ pulse was $4 \mu\text{s}$. The delay τ was chosen to be $0.2 \mu\text{s}$ (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 $\text{Pna}2_1$ [13]. The Li atoms are located at the centers of slightly distorted LiSe_4 tetrahedra. In such an environment, the quadrupole ^7Li nucleus ($I = 3/2$)

should exhibit three NMR lines. This is readily seen in Fig. 1 that shows ^7Li NMR spectra of powder and single crystalline LiInSe_2 [14]. Here the spectrum of the single crystal was measured at the orientation corresponding to the maximal splitting between the satellites. The powder spectrum, in which the central lines and the satellites are hardly resolved due to the overlap caused by the 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 $\omega_1 \gg \omega_{qi}$, which is necessary for the echo formation, is realized. Our measurements show that the aforementioned $(2n+1) \cdot 90_Y^\circ - 90_X^\circ - \text{Acq}(t)$ pulse sequence results in the spin echo that is seen after the second pulse. The echo position after the second pulse (t_e) versus the length of the first pulse, $t_1 = (2n+1) \cdot \pi/2$, is given in Figure 2. One can see that $t_e \approx t_1/2$. Linear fit of this dependence with the formula ($t_e = b \cdot t_1$) yields $b = 0.445$, that is close to the theoretical value of $1/2$. Thus one can see that the result of the calculation agrees well with the experimental data.

Acknowledgement

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

- [1] H. Schneider and H. Schmiedel, *Phys. Lett.* **30A**, 298 (1969).
- [2] W. K. Rhim, A. Pines, and J. S. Waugh, *Phys. Rev. Lett.* **25**, (1970) 218 (1970).
- [3] W. K. Rhim, A. Pines, and J. S. Waugh, *Phys. Rev.* **B3**, 684 (1971).
- [4] W. K. Rhim and H. Kessemeier, *Phys. Rev.* **B3**, 3655 (1971).
- [5] K. Takegoshi and D. A. McDowell, *Chem. Phys. Letters* **116**, 100 (1985).
- [6] R. Kimmich, J. Niess, and S. Hafner, *Chem. Phys. Lett.* **190**, 503 (1992).
- [7] This pulse sequence produces the magic echo in the dipolar coupled spin systems: P. Bilski, N. A. Sergeev, and J. Wąsicki, *Mol. Phys. Reports (Poland)* **34/2**, 75 (2001); *Functional Materials* **9**, (2002).
- [8] A. Abragam, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford 1961.
- [9] U. Haeberlen, *High Resolution NMR in Solids: Selective Averaging*, Academic Press, New York 1976.
- [10] D. Barnaal and I. J. Low, *Phys. Rev. Lett.* **11**, 258 (1963).
- [11] D. Barnaal, I. J. Low, *Phys. Rev.* **148**, 328 (1966).
- [12] N. A. Sergeev, *Solid State NMR* **10**, 45 (1997).
- [13] H. J. Beister, S. Ves, W. Hönl, and K. Syassen, *Phys. Rev. B*, **43**, 9635 (1991).
- [14] L. Isaenko, A. Yelisseyev, S. Lobanov, A. M. Panich, V. Vedenyapin, J. Smirnova, V. Petrov, J. J. Zondy, and G. Knippels, *Materials Research Society Symposium Proceedings* (2002), 692 (*Progress in Semiconductor Materials for Optoelectronic Applications*, 2001), p. 429-434.