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Journal of Magnetic Resonance 177 (2005) 173–183
JMR Journal of Magnetic Resonance
www.elsevier.com/locate/jmr

A study of the spin–echo spin-locking effect in multi-pulse sequences in ^{14}N nuclear quadrupole resonance

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Received 18 November 2004; revised 10 March 2005
Available online 24 May 2005

Abstract

Experimental evidence of observing a rather unusual spin-locking spin echo (SLSE) effect in the fields of two multi-pulse sequences $(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n$ and $(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_n$ in ^{14}N nuclear quadrupole resonance is presented. It was demonstrated that the SLSE effect is observed only in the even pulse intervals of both sequences. All experiments were carried out at room temperature on a powder sample of $NaNO_2$. A theoretical description of the effect is given.

Keywords: Nuclear quadrupole resonance; Multi-pulse sequence; Spin-locking; Spin–echo; Solid echo

1. Introduction

The discovery of the multi-pulse spin-locking spin–echo (SLSE) effect in the nuclear quadrupole resonance (NQR) spectroscopy [1] greatly stimulated the development of this area of spectroscopy. The possibility presented by the SLSE effect to accumulate multiple signals radically increased the range of compounds that could be studied as it permitted to detect directly even the weak signals in nitrogen-containing substances. The practical significance of this was recently confirmed by a whole new range of NQR applications [2–6].

Therefore, the great interest of researchers in the SLSE effect reflected in numerous publications of both experimental and theoretical nature [1,7–18], is justified.

Until now the SLSE effect in NQR has been observed experimentally in the fields of only three multi-pulse sequences:

MW-4 [1]

$$(\varphi_0)_y - (\tau - \varphi_x - \tau)_n, \quad (1)$$

MW-2 [7]

$$(\varphi_0)_x - (\tau - \varphi_x - 2\tau - \varphi_{-x} - \tau)_n \quad (2)$$

and [18]

$$(\varphi_0)_{\pi/4} - (\tau - \varphi_x - 2\tau - \varphi_y - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-y} - \tau)_n. \quad (3)$$

(φ_0 and φ are the flip angles of the preparatory pulse and the other pulses of the sequence, respectively).

In the case of the quadrature detection the signals observed after all the three sequences do not display any significant differences. This becomes obvious if we consider the equations for the spin system magnetisation obtained for each of the three sequences [14,18] which vary only by the value of the resonance offset of the effective field of the sequence.

This communication presents data on a rather unusual SLSE effect that is generated by sequences of the following type:

$$(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_x - 2\tau - \varphi_{-x} - 2\tau - \varphi_{-x} - \tau)_n \quad (4)$$

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1090-7807/$ - see front matter
doi:10.1016/j.jmr.2005.03.011

and

$$(\varphi_0)_\phi - (\tau - \varphi_x - 2\tau - \varphi_y - \tau)_n, \qquad (5)$$

where ϕ is the preparatory pulse phase.

The peculiarity of the effect consists in its being observed only in the even pulse intervals of each of the sequences and whatever the phase of the preparatory pulse ϕ is set, it is never observed in the odd intervals.

A theoretical analysis given in the paper confirms that the focusing properties of the spin-system with homonuclear dipole interactions can only be observed in the even pulse intervals of sequences (4) and (5). The analysis was carried out on the basis of a two-particle model.

All experimental data presented in this communication was obtained for powder $NaNO_2$ at room temperature.

2. Theory

2.1. Preliminaries

To display the principal peculiarities of the formation of the echo signal to sequences (4) and (5) we will use a two-particle model and a detailed formalism of two-particle operators (TO) [19]. The relations between TO and ordinary one-particle operators of a fictitious spin-1/2 are presented in Tables 1–3.

Table 1
Definitions of two-particle operators

$$K_1^p = I_{p,e}I_{p,1} + I_{p,1}I_{p,e},\ K_2^p = I_{p,2}I_{p,3} + I_{p,3}I_{p,2}$$
$$K_3^p = I_{p,3}I_{p,3} - I_{p,2}I_{p,2},\ K_1^q = I_{p,e}I_{p,2} + I_{p,2}I_{p,e},$$
$$K_2^q = I_{p,3}I_{p,1} + I_{p,1}I_{p,3},\ K_3^q = I_{p,1}I_{p,1} - I_{p,3}I_{p,3},$$
$$K_1^r = I_{p,e}I_{p,3} + I_{p,3}I_{p,e},\ K_2^r = I_{p,1}I_{p,2} + I_{p,2}I_{p,1},$$
$$K_3^r = I_{p,2}I_{p,2} - I_{p,1}I_{p,1},\ K_e^p = I_{p,1}I_{p,1} + I_{p,e}I_{p,e},$$
$$K_e^q = I_{p,2}I_{p,2} + I_{p,e}I_{p,e},\ K_e^r = I_{p,3}I_{p,3} + I_{p,e}I_{p,e},$$
$$K_E = I_{p,1}I_{p,1} + I_{p,2}I_{p,2} + I_{p,3}I_3 + 3I_{p,e}I_{p,e},$$
$$L_1 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,1} + I_{p,1}(I_E - 2I_{p,e}) + I_{q,1}I_{r,2} + I_{r,1}I_{q,2} + I_{q,2}I_{r,1} + I_{r,2}I_{q,1}],$$
$$L_2 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,2} + I_{p,2}(I_E - 2I_{p,e}) + I_{q,1}I_{r,1} + I_{r,1}I_{q,1} - I_{q,2}I_{r,2} - I_{r,2}I_{q,2}],$$
$$L_3 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,3} + I_{p,3}(I_E - 2I_{p,e}) - I_{q,1}I_{q,1} - I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2}],$$
$$L_e = \tfrac{1}{2}(I_{q,1}I_{q,1} + I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2}) - 2I_{p,2}I_{p,1} + \tfrac{1}{2}(I_EI_{p,e} + I_{p,e}I_E),$$
$$M_1 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,1} + I_{p,1}(I_E - 2I_{p,e}) - I_{q,1}I_{r,2} - I_{r,1}I_{q,2} - I_{q,2}I_{r,1} - I_{r,2}I_{q,1}],$$
$$M_2 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,2} + I_{p,2}(I_E - 2I_{p,e}) - I_{q,1}I_{r,1} - I_{r,1}I_{q,1} + I_{q,2}I_{r,2} + I_{r,2}I_{q,2}],$$
$$M_3 = \tfrac{1}{2}[(I_E - 2I_{p,e})I_{p,3} + I_{p,3}(I_E - 2I_{p,e}) + I_{q,1}I_{q,1} + I_{q,2}I_{q,2} - I_{r,1}I_{r,1} - I_{r,2}I_{r,2}],$$
$$M_e = -\tfrac{1}{2}(I_{q,1}I_{q,1} + I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2}) - 2I_{p,2}I_{p,e} + \tfrac{1}{2}(I_EI_{p,e} + I_{p,e}I_E),$$
$$N_1 = I_{p,e}I_{p,e},\ N_2 = I_{q,1}I_{q,1} + I_{q,2}I_{q,2} + I_{r,1}I_{r,1} + I_{r,2}I_{r,2} = L_e - M_e,$$
$$N_3 = \tfrac{1}{2}[(I_{q,3} - I_{p,3})I_E + I_E(I_{q,3} - I_{p,3})] = -\tfrac{2}{3}E + (I_EI_{p,e} + I_{p,e}I_E) = -\tfrac{2}{3}E + L_e + M_e + 4N_1,$$
$$E = I_EI_E,\ I_{p,e} = 2I_{p,i}^2$$

Table 2
The commutation, anticommutation, and trace relations

$$[K_1^p,K_1^q] = -[K_2^p,K_2^q] = \tfrac{1}{2}iK_1^r,\ [K_1^p,K_2^q] = -[K_2^p,K_1^q] = -\tfrac{1}{2}iK_2^r,$$
$$[K_1^p,K_1^q]^+ = -[K_2^p,K_2^q]^+ = \tfrac{1}{2}K_2^r,\ [K_1^p,K_2^q]^+ = [K_2^p,K_1^q]^+ = \tfrac{1}{2}K_1^r,$$
$$[K_1^p,K_3^q] = [K_1^p,K_3^r] = [K_1^p,K_e^q] = -[K_1^p,K_e^r] = \tfrac{1}{2}iK_2^p,$$
$$[K_1^p,K_3^q]^+ = [K_1^p,K_3^r]^+ = [K_1^p,K_e^q]^+ = [K_1^p,K_e^r]^+ = \tfrac{1}{2}K_1^p,$$
$$[K_2^p,K_3^q] = [K_2^p,K_3^r] = [K_2^p,K_e^q] = -[K_2^p,K_e^r] = -\tfrac{1}{2}iK_1^p,$$
$$[K_2^p,K_3^q]^+ = -[K_2^p,K_3^r]^+ = [K_2^p,K_e^q]^+ = [K_2^p,K_e^r]^+ = \tfrac{1}{2}K_2^p,$$
$$[K_3^p,K_3^q] = [K_e^p,K_e^q] = [K_3^p,K_e^q] = [K_e^p,K_3^q] = [K_e^p,K_a^p] = [K_a^p,K_b^p]^+ = 0,$$
$$[K_e^p,K_3^q]^+ = [K_e^p,K_e^q]^+ = -[K_3^p,K_3^q]^+ = -[K_3^p,K_3^q]^+ = \tfrac{1}{2}(K_E - 2K_e^r),$$
$$[K_a^p,K_a^p]^+ = [K_e^p,K_e^p]^+ = K_e^p,\ [K_a^p,K_e^p]^+ = K_a^p,\ [K_a^p,K_b^p] = iK_c^p,$$
$$[K_E,K] = 0,\ [K_E,K]^+ = 2K,\ \mathrm{Tr}(K_E,K) = \mathrm{Tr}(K);$$

The linear relations

$$K_e^p = \tfrac{1}{2}(K_E - K_e^q + K_3^q) = \tfrac{1}{2}(K_E - K_e^r - K_3^r) = K_E - K_e^q - K_e^r = \tfrac{1}{3}(K_E + K_3^q - K_3^r),$$
$$K_3^p = \tfrac{1}{2}(K_E - 3K_e^q - K_3^q) = \tfrac{1}{2}(-K_E + 3K_e^r - K_3^r) = -K_e^q + K_e^r = -K_3^q - K_3^r,$$
$$K_3^p + K_3^q + K_3^r = 0,\ K_e^p + K_e^q + K_e^r = K_E;$$

The trace relations

$$\mathrm{Tr}(K_E) = 3,\ \mathrm{Tr}(K_e^p) = 1,\ \mathrm{Tr}(K_a^p) = 0,\ \mathrm{Tr}[(K_E)^2] = 3,$$
$$\mathrm{Tr}[(K_a^p)^2] = \mathrm{Tr}[(K_e^p)^2] = \tfrac{1}{2},$$
$$\mathrm{Tr}(K_a^pK_b^p) = \mathrm{Tr}(K_a^pK_e^p) = \mathrm{Tr}(K_a^pK_b^q) = \mathrm{Tr}(K_1^pK_1^q) = \mathrm{Tr}(K_2^pK_2^q) = 0,$$
$$\mathrm{Tr}(K_e^pK_3^p) = \mathrm{Tr}(K_e^pK_e^q) = -\mathrm{Tr}(K_3^pK_3^q) = -\mathrm{Tr}(K_3^pK_3^q) = -\mathrm{Tr}(K_3^pK_e^q) = \tfrac{1}{4},$$

Here, a, b, $c = x, y, z$, and K denotes any operators of the set; these relations hold also after cyclic permutations of p, q, r, and/or a, b, c.

Table 3
The relations among two-particle operators

$$[K,L] = [K,L]^+ = [K,M] = [K,M]^+ = [L,M] = [L,M]^+ = 0,$$
$$[N,K] = [N,L] = [N,M] = [N_1,N_2] = [N_2,N_3] = 0,$$
$$\mathrm{Tr}(KL) = \mathrm{Tr}(KM) = \mathrm{Tr}(LM) = 0,$$
$$[L_a,L_b] = iL_c,\ [L_a,L_b]^+ = 0,\ [L_a,L_b]^+ = [L_e,L_e]^+ = L,\ [L_a,L_e] = L_a,$$
$$\mathrm{Tr}(L_a) = 0,\ \mathrm{Tr}(L_e) = 1,\ \mathrm{Tr}(L_a,L_b) = 0,\ \mathrm{Tr}[(L_a)^2] = \tfrac{1}{2},$$

Here, $a, b, c = x, y, z$ or cyclic permutations; K, L, M or N denote any operator of the K, L, M or N sets, respectively.

Similarly to [19] we use the following system of notations. The place of the operator in the product of two one-particle fictitious spin-1/2 operators corresponds to the number of the spin to which this operator refers. Thus, if we are considering a system consisting of two spins 1 and 2, than for example operator $I_{p,1}$ for spin 1 can be presented as $I_{p,1}^{(1)} = I_{p,1}^{(1)}I_E^{(2)} = I_{p,1}I_E$ (I_E is a unit operator for spin 2).

Further on we will also use the ordinary notation of operators of a fictitious spin-1/2 for designating the sum of the corresponding one-particle operators:

$$I_{p,1} = I_{p,1}^{(1)} + I_{p,1}^{(2)} = I_{p,1}I_E + I_EI_{p,1} = 2K_1^p + L_1 + M_1;$$
$$I_{p,2} = I_{p,2}^{(1)} + I_{p,2}^{(2)} = I_{p,2}I_E + I_EI_{p,2} = 2K_1^q + L_2 + M_2;$$
$$I_{p,3} = I_{p,3}^{(1)} + I_{p,3}^{(2)} = I_{p,3}I_E + I_EI_{p,3} = 2K_1^r + L_3 + M_3. \qquad (6)$$

The total quadrupole Hamiltonian of the two-spin system in terms of two-particle operators looks as follows: