NQR Spin Echo in the Effective Fields of Multiple-Pulse Sequences *

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Results of a study, both theoretical and experimental, of a new kind of NQR spin echo technique are reported and discussed.

Key words: NQR, Spin echo, Multiple-pulse sequence.

The action on a spin system by a multiple-pulse sequence may be described in terms of an effective time-independent field, whose ω_e and direction $\boldsymbol{n}(n_x, n_y, n_z)$ are determined via the period t_c, pulse duration t_w, and frequency offset Δ of the sequence [1, 2]. As has been shown [3], a resonant response of the system can be obtained in the effective field. In this paper results, both theoretical and experimental, on the NQR spin echo in the effective field are presented.

We consider a quadrupolar nuclear spin system acted on by two pulsed magnetic fields: a sequence of pulses (frequency ω, amplitude H_1) along the X-axis of the electric field gradient (EFG) tensor and a three-pulse low frequency (l.f.) field (frequency $\Omega \ll \omega$, amplitude H_2) along the Z-axis of the EFG. In the representation used in [3], the equation of motion of the density operator $\varrho(t)$ is

$$i \frac{d\varrho(t)}{dt} = [\Omega_k(n \cdot S) + \omega_2(t) S_z(t) \cos(\Omega t) + H_d(t), \varrho(t)], \quad (1)$$

where

(i) $\Omega_k = \omega_e + 2\pi k/t_c$, t_c is the multiple-pulse sequence period, $k = 0, \pm 1, \pm 2, \pm 3, \dots$,

(ii) $\omega_e = \dfrac{2}{t_c} \cos^{-1}\{\cos(\varphi/2) \cos(\Delta t_c/2)\}$,

(iii) $n_x = \sin(\varphi/2)/\sin(\Omega_0 t_c/2)$, $n_y = 0$,
$n_z = \cos(\varphi/2) \sin(\Delta t_c/2)/\sin(\Omega_0 t_c/2)$, $\varphi = \gamma H_1 t_w$,
γ being the gyromagnetic ratio and t_w the pulse duration of a multiple pulse sequence.

(iv) $\omega_2(t) = \tau H_2(t)$,

$$H_2(t) = \begin{cases} H_2 & \text{for} \quad 0 \le t \le t_{w_1}, \quad \tau_0 \le t \le \tau_0 + t_{w_2}, \\ & \qquad \tau_0 + \tau_1 \le t \le \tau_0 + \tau_1 + t_{w_3} \\ 0 & \text{otherwise}, \end{cases}$$

(see Fig. 1, bottom)

τ_0 and τ_1 are the intervals between the first and second pulse of the three-pulse sequence and between the second and third pulse of this sequence, respectively, and t_{w_1}, t_{w_2}, t_{w_3} are the durations of the first, the second, and the third pulses of the sequence,
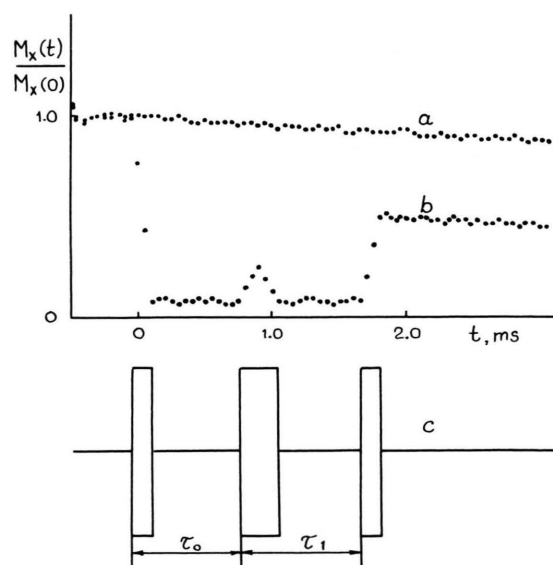

Fig. 1. *Top:* Time dependence of the magnetization M_x, a) in the absence of the l.f. pulse sequence, b) in the presence of this sequence. *Bottom:* The diagram of the l.f. pulse sequence (c).

(v) $S_z(t) = n_z(n \cdot S) + \frac{1}{2} \sum\limits_{m=-\infty}^{\infty} \{a_m \exp(i\,2\pi(m+k)\,t/t_c)$

$\cdot (S_z - (n \cdot S)\,n_z - i\,n_x S_y + \text{C.C.}\}$ with

$a_m = 2(-1)^m \sin(\Omega_0 t_c/2)/(\Omega_m t_c),$

(vi) $H_d(t) = \sum\limits_{m=-\infty}^{\infty} \sum\limits_{p=-2}^{2} b_m^p H_d^p \exp(i\,2\pi(m+p)\,t/t_c);$

here $b_m^p = (-1)^m \sin(p\,\Omega_k t_c)(m\pi + p\,\Omega_k t_c)^{-1}$
(see [2]).

After the unitary transformation

$$\tilde{\varrho}(t) = \exp(-i\theta S_y)\,\varrho(t)\exp(i\theta S_y),\qquad (2)$$

where $\Theta = \tan^{-1}(n_z/n_x)$, (1) takes the form

$i\,\dfrac{d\tilde{\varrho}(t)}{dt} = \Bigl[(\Omega_k + \omega_2(t)\,n_z \cos(\Omega t))\,S_x + \omega_2(t)\,n_x \cos(\Omega t)$

$\cdot \Bigl(S_z \sum\limits_{m=-\infty}^{\infty} a_m \cos(2\pi(m+k)\,t/t_c)$ (3)

$+ S_y \sum\limits_{m=-\infty}^{\infty} a_m \sin(2\pi(m+k)\,t/t_c)\Bigr) + \tilde{H}_d(t,\theta),\varrho(t)\Bigr].$

For the exact solution of (3) it is necessary to consider the infinite harmonic series. Let us restrict ourself to the resonance harmonics, which is correct for the case $\Omega_k \gg \omega_2$ and $n_z \ll n_x \sim 1$. In this case (3) may be rewritten in the form

$$i\,\frac{d\varrho^*(t)}{dt} = [\Delta_k S_x + \frac{1}{2}\omega_2(t)\,S_z + H_d^*(t,\theta),\varrho^*(t)],\quad (4)$$

where

$$\varrho^*(t) = \exp(i\Omega S_x t)\,\tilde{\varrho}(t)\exp(-i\Omega S_x t)\quad (5)$$

with $\Delta_k = \Omega_k - \Omega$. In the experimental situation to be discussed later the case $\omega_2 \gg \|H_d\|$ is realised. In this case the time evolution of ϱ^* is given by

$$i\,\frac{d\varrho^*(t)}{dt} = [H^*(t),\varrho^*(t)]\qquad (6)$$

with the initial condition

$$\varrho^*(0) = 1 - \beta\,\Omega_k S_x,\qquad (7)$$

where β is the inverse temperature of the spin system in the spin-locking state

$$H^*(t) = \Delta_k S_x + H_d^S + \omega_2(t)\,s_z,\qquad (8)$$

and

$$[S_x, H_d^S] = 0.\qquad (9)$$

After three l.f. pulses the solution of (6) with the initial condition (7) may be written in the form

$$\varrho^*(t) = U(t)\,\varrho^*(0)\,U^*(t),\qquad (10)$$

where

$$U(t) = D(t_{w_3})\,P(\tau_1 - t_{w_2})\,D(t_{w_2})\,P(\tau_0 - t_{w_1})\,D(t_{w_1}),\quad (11)$$

$t = \tau_0 + \tau_1 + t_{w_3}$ is the moment of time immediately after the third pulse, and

(i) $\quad D(t_{w_q}) = T\exp\Bigl(-i\int\limits_{\tau_j}^{\tau_j + t_{wq}} dt\,H^*(t)\Bigr),$

$q = 1, 2, 3$ and $\tau_j = 0, \tau_0, \tau_1,$

T is the Dyson ordering operator,

(ii) $\quad P(\tau_j - t_{w_q}) = T\exp\Bigl(-i\int\limits_{\tau_j + t_{wq}}^{\tau_k} dt\,H^B(t)\Bigr),$

$\tau_j = 0,\quad \tau_0\colon \tau_k = \tau_0, \tau_1,$

(iii) $\quad H^B(t) = \Delta_k S_x + H_d^S(t,0).$

Using the solution (10), we obtain the X-component of the macroscopic magnetic moment after the first and immediately after the third l.f. pulses

$M_x(t) = \gamma\hbar\,\text{Sp}\,\varrho^*(t)\,S_x$

$= -\frac{1}{2}\gamma\hbar\,\beta\omega_e \cos(\omega_2 t_{w_1})$ for $t_{w_1} < t < \tau_0,$ (12)

$M_x(t) = \gamma\hbar\,\text{Sp}\,\varrho^*(t)\,S_x$ for $\tau_0 + \tau_1 + t_{w_3} < t.$ (13)

Now we are going to show that in the case of a space inhomogeneity of the applied magnetic fields our results (12) and (13) give

(i) after the first l.f. pulse a zero macroscopic magnetic moment, if $\omega_2 t_{w_1} = \pi/2$,
(ii) after the third l.f. pulse a new kind of NQR spin echo.

We have to use the results (12) and (13) for each spin packet and then to perform the space averaging

$$\bar{M}_x = \int\limits_{-\infty}^{\infty} g(\Omega_k' - \Omega)\,M_x\,d\Omega_k'\qquad (14)$$

for the particular case $\omega_2 \gg \Delta_k \gg \|H_d^S\|$ with $t_{w_2}\omega_2 = \pi$, $t_{w_1}\omega_2 = t_{w_3}\omega_2 = \pi/2$, and the width σ of the Gaussian space distribution. The result is

$$\frac{\bar{M}_x(t_{w_1} < t < \tau_0)}{M_x(0)} = 0,\qquad (15)$$

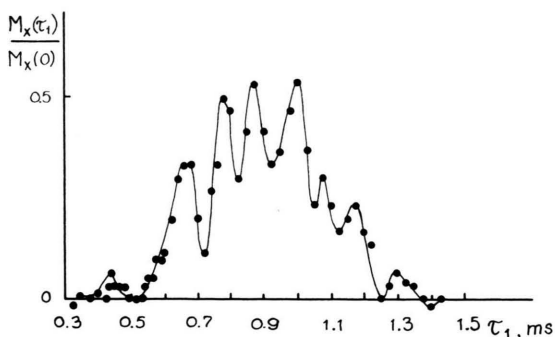$$\frac{\bar{M}_x(\tau_1)}{M_x(0)} = \exp(-(\tau_1 - \tau_0 - t_{w_3})^2\,\sigma^2/2),\qquad (16)$$

Fig. 2. The NQR spin echo in the effective field. M_x versus τ_1.

$M_x(0)$ is the quasi-equilibrium magnetization of the spin system in the spin-locking state.

To verify the theoretical predictions, a set of experiments was performed. With a home-made multiple-pulse NQR spectrometer, the ^{35}Cl NQR in polycrystalline $KClO_3$ was observed at 77 K and $\omega_Q = 28.9538$ MHz. The MW-4 multiple-pulse sequence $90° - (t_c/2 - \varphi - t_c/2)^N$ and the three pulse l.f. sequence $90° - \tau_0 - 180° - \tau_1 - 90°$ were used.

In Figs. 1 and 2 the results obtained are presented. Figure 1 shows $M_x(t)$ for the multiple-pulse sequence with $t_c = 50$ μs, $\varphi = \pi/2$, $\Delta = 0$ both in the absence of l.f. pulses (Fig. 1 a) and in the presence of the three l.f. pulse sequence (Fig. 1 b) with $\Omega_0/2\pi = 5$ kHz, $\tau_0 = 0.8$ ms. The value of the macroscopic magnetic moment after the first l.f. pulse is in satisfactory agreement with (15). It is not zero because a polycrystalline sample was used. Figure 2 shows $\bar{M}_x(\tau_1)$ immediately after the third l.f. pulse. A spin echo appears at $t \approx 2\tau_0 (\tau_1 \simeq \tau_0)$, in agreement with (16), but this expression doe not describe the complicated envelope of the echo. We suppose that this is due to the fact that oscillating terms were not taken into account in (3). The observed modulation of the echo envelope is not excited by dipole-dipole interactions. This was verified by the observation of the NMR spin echo in the effective field of the same multiple-pulse sequence on ^1H nuclei in water, where dipole-dipole interactions are averaged. In these experiments the modulation of the spin echo was also observed.

The method reported here can be used for the study of problems of NQR relaxation and the line widths of the NQR absorption.

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