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PEANUT experiment in NQR spectroscopy for $I=3/2$

Nikolay Sinyavsky [a], Philip Dolinenkov [b], Mariusz Maćkowiak [c,*]

[a] Department of Physics, Baltic State Academy, Molodiozhnaya 6, 236029 Kaliningrad, Russia
[b] Immanuel Kant Baltic Federal University, A. Nevsky St. 14, 236041 Kaliningrad, Russia
[c] Institute of Molecular Physics Polish Academy of Sciences, ul. Smoluchowskiego 17, 60-179 Poznań, Poland

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ABSTRACT

The experiment with phase inversion and phase-inverted echo-amplitude detected nutation (PEANUT) was introduced in the nuclear quadrupole resonance (NQR). Formulas were obtained describing the NQR ($I=3/2$) experiment. Exemplary experiments are provided confirming the predicted particularities of the PEANUT spectra in NQR Cl-35. It is proposed to apply the method for the purpose of determination the asymmetry parameter of the electric field gradient (EFG) tensor in powders with the help of the analysis of PEANUT interferograms. Application of two-dimensional PEANUT experiments, in which the nutation frequencies correlate with the resonance NQR frequencies, can substantially simplify the interpretation of complex spectra.

1. Introduction

The PEANUT experiment [1,2] is based on a measurement of the spin rotary echo. In its pulse scheme shown in Fig. 1, the radio-frequency (rf) excitation and detection of the signal are separated in time and the spread in the nutation frequencies is partially compensated. In comparison with the other known nutation schemes applied in magnetic resonances, PEANUT reveals a number of advantages. The method enables one to obtain and observe high nutation frequencies and compensate the influence of inhomogeneity in the rf field B_1. The range of the spin frequencies contributing to the signal is controlled by the duration of the initial pulse. Finally, no relaxation broadening of spectra is encountered when applying the method. As contrasted to the simplified sequence [3] with the pulse with a high turning angle (HTA) of variable length and registering of the free induction decay (FID), in the PEANUT experiment the rf irradiation and signal detection are separated in time so the dead time of the receiver can be neglected.

The PEANUT experiment is based on a two-pulse spin-echo sequence, in which the π – pulse is replaced with a special composite nutation pulse. The initial pulse represents the rf $\pi/2$ – pulse, the duration of which decides on the range of exciting frequencies in the experiment. Transversal magnetization produced by that pulse evolves in time and dephases during the first free evolution period of length τ. Next, the high-turning-angle (HTA) pulse is switched on with a constant duration T, consisting of two parts of variable duration t'_w and $T-t'_w$ with alternating rf field phases of 0 and π, respectively.

In time t'_w, rf field is directed along the x axis and the magnetization vector of a particular spin packet with resonance frequency offset $\Delta\nu$ nutates with frequency ν_n around an effective axis lying in the xz plane. During time $T-t'_w$, the rf field is applied along the $-x$ axis and the spin packet nutates with the same frequency ν_n around the respective effective axis in the $-xz$ plane. The phase shift at the moment t'_w leads to a partial compensation of the off-resonance contributions and of the field B_1 inhomogeneity at $t'_w=T-t'_w=T/2$. After the HTA pulse, the spins evolve again freely and form the primary echo at the moment τ.

In the two-dimensional (2D) experiment, the PEANUT NQR echo is registered as a function of running time t and t'_w varying from 0 to T. Since total length of the sequence remains constant and does not vary during the experiment, the influence of the relaxation processes on the echo intensity remains the same during the process of measurement. Moreover, there is no need in a special compensatory pulse for sustaining the invariable development of heat.

2. Theory

An action of three rf pulses of arbitrary lengths, frequency offset and arbitrary phases on the spin system in NQR ($I=3/2$) has been discussed in our earlier paper [4]. The method of calculation used in [4], as such, was analogous to that described in Ref. [5]. The response of the system of nuclear spins subdue to

* Corresponding author. Fax: +48 61 8684524.
E-mail address: mackow@ifmpan.poznan.pl (M. Maćkowiak).

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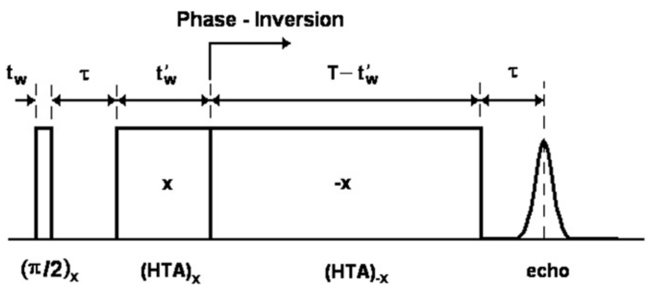

Fig. 1. Pulse sequence for the PEANUT experiment (adapted from [1]). The high-turning-angle (HTA) pulse that nutates the spins is subdivided into two parts that differ in phase by π and create a rotary echo at $t'_w = T/2$.

quadrupolar interactions in zero field to the sequence of three pulses was investigated with use of the non-stationary perturbation theory in the framework of the density matrix formalism.

All the experimental duration is much shorter than the spin-lattice relaxation time. Thus, the spin system can be considered as effectively isolated from the lattice. The axis of the rf coil producing the pulses of field B_1 is oriented in an arbitrary direction (θ, φ) with respect to the main axes of the electric field gradient (EFG) tensor at the nucleus. The durations of all three pulses were considered as much shorter than time $T_{2\rho}$ of establishing a new equilibrium of the system in the presence of rf field $B_1(t)$.

The radiofrequency field interaction is given by

$$B_1(t) = -\gamma\hbar B_1 \cos(\omega t + \varphi_p)[I_x \sin\theta\cos\varphi + I_y \sin\theta\sin\varphi + I_z\cos\theta] \quad (1)$$

where ω is the spectrometer frequency which may be different from the NQR frequency ω_0 by $\Delta\omega = \omega - \omega_0$, and φ_p is the phase of the rf pulse.

By applying general expressions for NQR signals in the case of $I=3/2$ spins obtained in [4], we shall find the formula for the echo signal generated after time τ following the end of the composite signal of the PEANUT sequence (Fig. 1).

Deriving the analytical formulas for the PEANUT experiment is very time-consuming. Details of the calculations can be found in our earlier paper [4] where the response of the quadrupolar nuclei system to the various pulse rf fields is analyzed and the corresponding formulas can be found in the Appendix therein. The complex amplitude of the spin echo signal for the PEANUT experiment in the NQR ($I=3/2$) is defined as

$$S(t'_w) \propto S_0 \left\{ \begin{array}{l} c_0 + c_{2c}\cos 2\omega_n(t'_w - T/2) + \\ + c_{1c}[\cos\omega_n t'_w + \cos\omega_n(t'_w - T)] + \\ + ic_{1s}[\sin\omega_n t'_w - \sin\omega_n(t'_w - T)] \end{array} \right\}, \quad (2)$$

where

$$S_0 = \frac{\omega_1^6}{\alpha\omega_n^5},\; c_{2c} = \sin\omega_n t_w,\; c_{1c} = 2\frac{\Delta\omega^2}{\omega_1^2}\sin\omega_n t_w,$$

$$c_{1s} = 2\frac{\Delta\omega^2}{\omega_1^2}(\cos\omega_n t_w - 1),$$

$$c_0 = \left[\left(\frac{\Delta\omega^2}{\omega_1^2} + 2\frac{\Delta\omega^4}{\omega_1^4}\right)\cos\omega_n T + 1 - \frac{\Delta\omega^2}{\omega_1^2}\right]\sin\omega_n t_w + 2i\frac{\Delta\omega^4}{\omega_1^4}(\cos\omega_n t_w - 1)\sin\omega_n T, \quad (3)$$

$\omega_n = \sqrt{\omega_1^2 + \Delta\omega^2}$ nutation frequency, $\omega_1 = (\gamma B_1/2\sqrt{3}\rho)[4\eta^2 \cos^2\theta + \sin^2\theta(9 + \eta^2 + 6\eta\cos 2\varphi)]^{1/2}$, $\rho = \sqrt{1 + (\eta^2/3)}$, η—asymmetry parameter of the EFG tensor, $\alpha = (\gamma B_1/4)$.

The doubling of the nutation frequency (second term in the expression (2)) is the consequence of the phase inversion of the HTA composite pulse. The signal of the nutation echo is generated by the magnetization components that nutate during the whole HTA pulse and has a maximum at $t'_w = T/2$. The echo amplitude reveals modulations with a nutation frequency ω_n (third and fourth terms in the expression (2)). They originate from the magnetization components that are comprised in time t'_w and nutate during time $T - t'_w$ in the opposite direction. However, their amplitudes depend on the magnitude of the resonance frequency offset of spin packets and these signal components contribute only in the presence of detuning. Signals on the nutation frequency ω_n are maximal at $t'_w = 0$ and $t'_w = T$, and their damping (as well as the width of the nutation echo) is determined by non-resonance contributions of the exciting preparation pulse. In almost all practical cases they can be separated in time from the part of the signal with doubled nutation frequency by a suitable choice of corresponding duration T of the composite pulse. In deriving Eq. (2) the relaxation was not taken into account. Of course in the real experiment this effect exists. In our experiment the value of τ was constant to obtain the best spin-echo.

In real experiments, the amplitude of the signal is influenced by many additional factors, so that the intensity cannot be described by such a simple expression as (2) accurately. In a polycrystalline powder, all values θ and φ occur with equal probability, and the total signal height is then described by a weighted average over all orientations:

$$\langle S(t'_w) \rangle = \int_0^{\pi}\int_0^{2\pi} S(t'_w)\sin\theta\, d\theta\, d\varphi \quad (4)$$

Moreover, to take formally into account the relaxation, the simulated nutation signal was multiplied by the exponent $\exp(-t'_w/T_n)$, where T_n denotes time determining the relaxation damping of the nutation interferogram.

The shapes of the nutation lines depend on the relation between the amplitude of rf field and the inhomogeneous width of the NQR line. In rf fields, for which the frequency ω_1 is low with respect of the inhomogeneous linewidth, the influence of frequency offset is revealed in a very clear manner [1]. In this case, in the absence of other broadening mechanisms, the nutation singularities at ω_n and $2\omega_n$ are not separated from each other and the corresponding peaks in the spectrum are asymmetric showing long tails in their low frequency parts. If ω_1 is higher than the inhomogeneous linewidth, the two kinds of modulations in the nutation interferogram are completely separated.

The minimum asymmetry parameter value that can be determined from a conventional NQR nutation experiment [3], if permitted by the relaxation time T_n, is given by the expression [6]: $\eta_{min} = \sqrt{3}/\nu_r T$, where $\nu_r = \gamma B_1/2\pi$ and T is the duration of the HTA (normal variable length pulse, not composite) . In order to determine $\eta \approx 0.01$ by classical nutation method at a $t_w^{\pi/2} = 1-2\,\mu s$ duration of the 90° pulse, a duration of $T \approx 1$ ms of the HTA pulse is needed. It imposes hard demands on the power of the transmitter of the spectrometer. Contrary to the simple nutation spectroscopy, where the asymmetry parameters are determined from singularities in the FT spectrum, in PEANUT experiment the time nutation interferograms are analyzed. Therefore the smaller asymmetry parameters can be measured. Also the selective excitation is possible for the broad NQR lines and the asymmetry parameters can be determined for different parts of the broad spectrum.

The selectivity of the PEANUT experiment can be controlled with the help of the duration of the initial pulse t_w that excites only the spins within the limits of the $2\pi/t_w$ frequency band. Accordingly, a longer initial pulse will induce a narrower line in the nutation spectrum, since the non-resonance effects contribute to the width of the nutation line.