Rapid Measurement of Nutation NQR Spectra in Powders Using an RF Pulse Train *

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The method of two-dimensional nutation NQR spectroscopy, introduced by Harbison in 1989, has been successfully used for determining of the asymmetry parameter of the EFG tensor for spin-3/2 nuclei in both powdered and monocrystal samples in the absence of an external magnetic field. The inconvenience inherent in the method, however, is the long time required, because data acquisition must be repeated for various RF pulse lengths. We discuss a method to reduce the time of the nutation experiment by using a sequence of identical short RF pulses of length t_w and distance τ. It is shown that for an NQR frequency ω_0, frequency offset $\Delta\omega$, and pulse parameters satisfying the relation $\omega_0 \tau + \Delta\omega\, t_w = 2\pi k$ $(k = 1, 2, 3, \dots, n)$ a synchronism of pulse action takes place and the nutation interferogram can be measured "stroboscopically" between the pulses. The maximum time saving factor that can be obtained as compared to the conventional nutation experiment is of the order of the number of pulses used in a pulse train. The method has been successfully applied for determination of the asymmetry parameter for one of the two ^{35}Cl sites in polycrystalline 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride).

Key words: Nuclear quadrupole resonance; Two-dimensional nutation spectroscopy; Asymmetry parameter.

Introduction

From pure NQR-spectra of spin-3/2 nuclei it is not possible to determine the asymmetry parameter of the EFG tensor, since the NQR frequency depends both on the quadrupolar coupling constant $e^2 qQ/h$ and the asymmetry parameter η. Usual methods which are used to determine η involve application of a small Zeeman field to a monocrystal or powder sample to extract η from the rotation or powder pattern, respectively. A convenient alternative method suggested in [1, 2], however, uses the two-dimensional zero-field nutation NQR technique to determine η for monocrystal or powder samples. The advantage of this technique is that no extra equipment like Helmholtz coils, etc. is required but, instead, the whole experiment can be performed on a commercial pulsed NMR spectrometer using standard 2D-FFT software. In the nutation NQR experiment the two-dimensional time-domain signal is detected during the free induction decay (FID) time t_2 for varying radio frequency (RF) pulse length t_1. Double Fourier transformation of the time-domain signal gives a two-dimensional spectrum $S(\omega_2, \omega_1)$ where the ω_2-dimension corresponds to a pure NQR spectrum and the ω_1-dimension to a nutation NQR spectrum. For powder samples the nutation NQR spectra exhibit three singularities, and η is readily calculated from the positions of two of these singularities alone.

The results of the calculation of off-resonance nutation spectra of spin-1 and spin-3/2 nuclei for powders have been reported in [3]. These results apply to the case when FID data acquisition in a spectrometer starts at some constant delay with respect to the nutation RF pulse turn-on. The more common case, when data acquisition commences just after RF pulse turn-off, has been examined in [4] where exact formulas have been reported for η determined in off-resonance conditions. Very recently the off-resonance effects in nutation NQR spectroscopy have also been reported [5], with particular attention given to broad NQR lines as observed in proton glass samples. Reasonable determination of small η from singularities in nutation

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NQR spectra requires that the signal to noise (S/N) ratio is adequate, as for $\eta < 20\%$ these singularities become markedly less pronounced. In such case the NQR nutation spectra can be obtained by processing of time-domain data with the Maximum Entropy Method (MEM) instead of the Fourier transform algorithm [6, 7] in order to enhance the resolution of nutation singularities. It is also possible to simulate the nutation NQR spectrum by means of a computer with the condition that the mean squares deviation of the simulated spectrum from the experimental one is minimized. For weak NQR lines it may take a long time to complete the nutation experiment, because the possible accumulation of NQR signals per unit of time is restricted by saturation effects, and the data acquisition must be repeated for each RF nutation pulse length. The other drawbacks of the simple method of obtaining nutation NQR spectra are: (i) the RF spectrum of the excitation pulse changes with its length, perhaps causing undesirable effects, (ii) the thermal conditions of the sample change with RF pulse length due to the RF powder absorbed in the sample. To compensate for this effect an additional "dummy" RF pulse of variable length is required in order to "balance" the heat dissipation in the sample.

The essential increase in the speed of collecting data in nutation NQR spectroscopy is possible by means of RF multipulse sequences, in analogy with rapid rotating frame imaging in NMR [8]. In a simple case it may be a sequence of identical, short RF pulses which follow with an interval which is much shorter than the phase memory time of nuclear spins.

1. Theory

Using the wave-function approach described in [9], we obtained for the expectation values of the operators $\langle I_{x,y,z} \rangle$ at the time of turn-off of the n-th RF pulse of a length t_w:

$$\langle I_{x,y,z} \rangle_n = \sum_{i,j} \{[c_i((n-1)\tau + t_w)] \cdot [c_j((n-1)\tau + t_w)] \langle i | I_{x,y,z} | j \rangle \cdot \exp[-i(\omega_i - \omega_j)(t - (n-1)\tau - t_w)]\} . \quad (1)$$

Here $c_i((n-1)\tau + t_w)$ are the expansion coefficients obtained from the solution of the time-dependent Schroedinger equation at the moment of the n-th pulse turn-off. Unlike the paper [9], where coefficients $c_i(t_w)$ were used in the interaction representation, we write these coefficients in the laboratory frame of reference, i.e. with the multiplier $\exp(i\omega_i t_w)$, as $\langle I_{x,y,z} \rangle$ in (1) is also defined in the laboratory frame. In our calculations we neglected the real NQR line width and RF field inhomogeneities in the spectrometer coil. We also neglect relaxation processes ($t_w, \tau \ll T_2, T_1$), although according to [9] they could be introduced phenomenologically. With these assumptions we calculated for spin $I = 3/2$ the NQR signal induced in the RF coil of the spectrometer just after turn-off of the n-th pulse in a sequence of RF pulses which follow with the time interval τ:

$$G(n t_w) = \langle I_x \rangle_n \sin\vartheta \cos\varphi + \langle I_y \rangle_n \sin\vartheta \sin\varphi + \langle I_z \rangle_n \cos\vartheta , \quad (2)$$

where for the expectation values of the magnetization along the coordinate axes we have

$$\langle I_{x,y,z} \rangle_n = i \lambda_{x,y,z} \alpha \cdot \{a_n b_n^* \exp[i(\omega_0(t - (n-1)\tau) - \Delta\omega t_w)] - \mathrm{a}_n^* b_n \exp[-i(\omega_0(t - (n-1)\tau) - \Delta\omega t_w)]\} , \quad (3)$$

where

$$\lambda_x = (3 + \eta)^2 \sin\vartheta \cos\varphi ,$$
$$\lambda_y = (3 - \eta)^2 \sin\vartheta \sin\varphi ,$$
$$\lambda_z = 4\eta^2 \cos\vartheta ,$$

ϑ, φ – polar angles of the RF field $\mathbf{B}_1$ in the EFG principal axis system, $\Delta\omega = \omega - \omega_0$, ω_0 – NQR frequency, $\alpha = \gamma B_1/4$, η-asymmetry parameter of the EFG tensor. The terms a_n and b_n were obtained from the recursion formulas ($n \geq 2$) to be

$$a_n = b_1^* a_{n-1} \exp[i(\omega_0 \tau - \Delta\omega t_w)/2] + a_1 b_{n-1} \exp[-i(\omega_0 \tau - \Delta\omega t_w/2]$$
$$b_n = \{[(\Delta\omega/(2\xi)]^2 - 1\} a_1 a_{n-1} \exp[i(\omega_0 \tau - \Delta\omega t_w)/2] + b_1 b_{n-1} \exp[-i(\omega_0 \tau - \Delta\omega t_w)/2] , \quad (4)$$

where $a_1 = \sin(\xi t_w)$, $b_1 = \cos(\xi t_w) - i\Delta\omega \sin(\xi t_w)/(2\xi)$,

$$2\xi = [(\Delta\omega)^2 + 4m^2]^{1/2} ,$$
$$m = \alpha R(\vartheta, \phi)/(3 + \eta^2)^{1/2} ,$$
$$R(\vartheta, \varphi) = [4\eta^2 \cos^2\vartheta + \sin^2\vartheta (9 + \eta^2 + 6\eta \cos 2\varphi)]^{1/2} .$$

In general case the signal (2) is a complicated sum of signals with various phases. For the case when

$$-\omega_0 \tau + \Delta\omega t_w = 2\pi k , \quad (5)$$

where $k = 0, \pm 1, \pm 2, \pm 3, \ldots$ etc., synchronism of pulse action takes place and the equation for the NQR signal, which is measured "stroboscopically" between pulses of the sequence, has the same form as for a signal measured by means of a conventional method [9] of nutation spectroscopy:

$$\begin{aligned}\langle I_{x,y,z}\rangle = \alpha\,\lambda_{x,y,z}\sin(n\,\xi\,t_\mathrm{w}) \\ \cdot\{U_n\sin[\omega_0(t-(n-1)\tau)] \\ + V_n\cos[\omega_0(t-(n-1)\tau]\}/\xi\,,\end{aligned} \quad (6)$$

where

$$\begin{aligned}U_n &= \cos(n\,\xi\,t_\mathrm{w})\cos(\Delta\omega\,t_\mathrm{w}) \\ &\quad + \Delta\omega\sin(n\,\xi\,t_\mathrm{w})\sin(\Delta\omega\,t_\mathrm{w})/2\,\xi)\,, \\ V_n &= -\cos(n\,\xi\,t_\mathrm{w})\sin(\Delta\omega\,t_\mathrm{w}) \\ &\quad + \Delta\omega\sin(n\,\xi\,t_\mathrm{w})\cos(\Delta\omega\,t_\mathrm{w})/(2\,\xi)\,.\end{aligned}$$

If the NQR signal is measured at some constant delay t_d after turn-off of each pulse in a sequence, then we have for the signal after synchronous detection

$$\begin{aligned}G(n\,t_\mathrm{w}) = \alpha\,R^2(\vartheta,\varphi) \\ \cdot\{\sin(2\,n\,\xi\,t_\mathrm{w})\cos(\Delta\omega\,t_\mathrm{d}+\Psi) \\ + \Delta\omega\,[1-\cos(2\,n\,\xi\,t_\mathrm{w})] \\ \cdot\sin(\Delta\omega\,t_\mathrm{d}+\Psi)/(2\,\xi)\}/(2\,\xi)\,,\end{aligned} \quad (7)$$

where Ψ is a constant phase shift of the reference signal for the synchronous detector. Expression (7) describes the "discrete interferogram" of a single nutation line at the frequency $2\,\xi$ and contains a constant term, dependent on the frequency offset $\Delta\omega$. Note that this result is analogous to the case when the off-resonance nutation NQR spectrum of single crystal is obtained by the conventional method [4, 5]. For powder samples integration of (7) over the angles ϑ and φ yields, therefore, a powder pattern (in ω_1 dimension) analogous to that obtained in [1, 2]. For a completely coherent spectrometer, at which all the time intervals in a pulse sequence are formed from the same RF generator, the values t_w and τ can be made divisible by the period of the spectrometer frequency $T = 2\pi/\omega$, thus for the on-resonance case ($\Delta\omega = 0$) the condition given by (5) is automatically satisfied. The form of the nutation curve for the spectrometer frequency set on-resonance is shown in Figure 1 a. The entire curve consists of FID data sampled once after each pulse. Thus, the number of data points in ω_1 dimension is equal to the number of pulses in a sequence, and for n data points the spectral resolution in ω_1 is equal to $1/(n\,t_\mathrm{w})$. For $\Delta\omega \neq 0$ the condition (5) can still be satisfied by proper tuning of the spectrometer frequency, however, in this case the restrictions imposed by off-resonance effects in the nutation NQR spectra [4, 5] should be considered. The limitation of the method presented here is that for obtaining a sufficient number of points of the nutation curve (before it decays to the noise), the NQR line should not be too broad, as the minimum spacings possible between the pulses are limited by dead-time problems. To avoid this limitation, the spin echo instead of FID signal is usually recorded [2]. For the two-pulse sequence, with the neglect of the FID signal after the first and second RF pulse, we obtain for the echo signal after synchronous detection

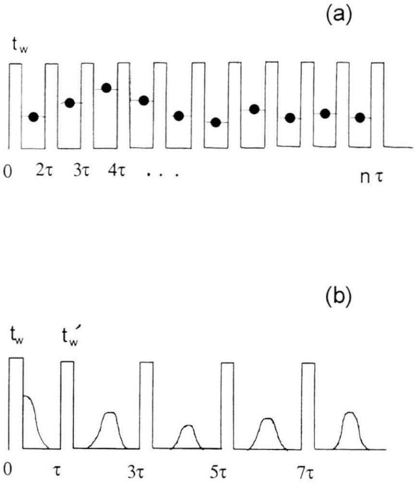

Fig. 1. A schematic representation of the nutation NQR experiment: (a) the method of rapid measurement of the nutation interferogram using an RF pulse train, (b) the method using coherent accumulation of spin echoes in a CPMG sequence. The length of refocusing pulses is incremented for each point of the nutation interferogram.

$$\begin{aligned}G(t_\mathrm{w},t_\mathrm{w}') = \alpha\,R^2(\vartheta,\varphi)\{1-[\Delta\omega/(2\,\xi)]^2\} \\ \cdot[1-\cos(2\,\xi\,t_\mathrm{w}')]\{-\sin(2\,\xi\,t_\mathrm{w})\cos\Psi \\ + \Delta\omega\,[1-\cos(2\,\xi\,t_\mathrm{w})]\sin\Psi/(4\,\xi)\}/(4\,\xi)\,.\end{aligned} \quad (8)$$

This expression describes the interferogram which consists of a single nutation frequency at $2\,\xi$ and a constant term dependent on $\Delta\omega$. From the form of this expression it is also evident that for obtaining the entire nutation interferogram one can change the length of the second pulse t_w' at a fixed length of the first pulse t_w. In this case the total time of the nutation experiment can be reduced to some extent by repeated refocusing and coherent coaddition of echo signals in a CPMG pulse sequence shown in Figure 1 b.

2. Experimental

A nutation experiment using the pulse train method was carried out using a home-built pulsed FT NQR spectrometer with a full computer control of the measuring process, including tuning of the NQR probe head. The RF coil was 40 mm long and had 10 mm inner diameter, evenly wound with 10 turns of double wire (bifilar winding) to increase the RF homogeneity without increasing the coil inductance. The $\pi/2$ pulse length measured at 36 MHz was 10 μs. The sample was packed in a 9 mm i.d. and 13 mm long glass tube container and was placed in the center of the RF coil. A sequence of 100 identical RF pulses of length 2–7 μs and of intervals 249–254 μs was used. Typically 256 transients of 4096 data points with a 3000 ms recycle time and 6.4 μs sampling period were accumulated. It is convenient that the sum of intervals $t_w + \tau$ in the pulse train is set to be an integer multiple of the data sampling period. This enables reconstruction of the nutation interferogram $D(i)$ by rearranging of data table in a computer memory according to the simple algorithm

$$D(i) = D(c + (i-1)(p\backslash n))\,, \tag{9}$$

where $i = 1, 2, \ldots, n$, n is the number of pulses, p the number of data points, "\" denotes the integer division and c is a constant responsible for the "phase shift" of the entire interferogram with respect to the first pulse of the pulse train. The method has been applied to the ^{35}Cl NQR in 2,4,6-trichloro-1,3,5-triazine (cyanuric chloride – $C_3Cl_3N_3$). The mesurements were carried out at 77 K by immersing the RF coil in a liquid nitrogen bath. This helped in maintaining good thermal stability of the sample, because significant heating of the sample by a long RF pulse train would otherwise cause an undesirable drift of the NQR frequency. It is worth mentioning that we did not encounter probe arcing problems, as opposed to the conventional method of nutation NQR spectroscopy [1] using very long RF pulses towards the end of the nutation experiment.

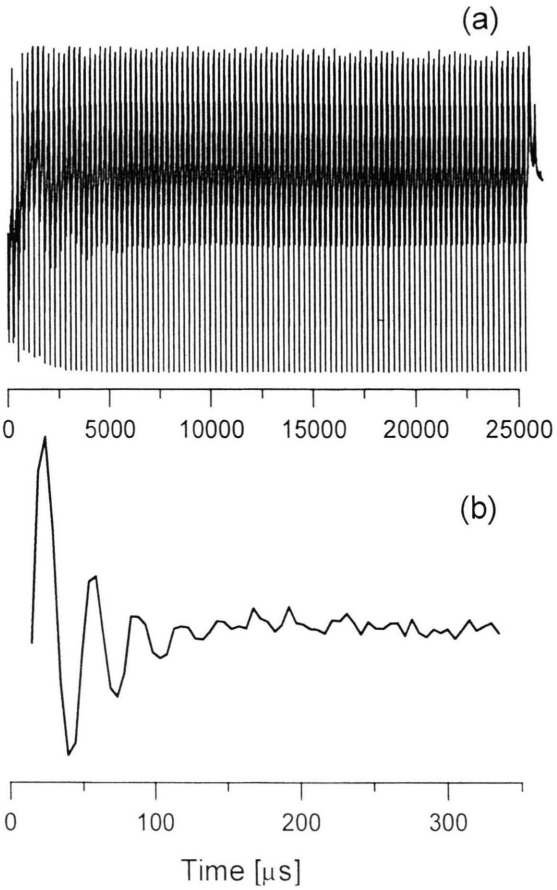

Fig. 2. Experimental nutation ^{35}Cl NQR interferogram obtained for cyanuric chloride: (a) raw data after accumulation of 256 transients showing the spectrometer response to the RF pulse train composed of 100 pulses of length 5 μs and interval 251 μs, (b) nutation interferogram obtained by taking one data point after each pulse according to the algorithm given by (9) in the text.

3. Results and Discussion

As reported in [7], the ^{35}Cl NQR spectrum of cyanuric chloride exhibits two NQR lines. At 77 K their frequencies are $\nu_1 = 36.772$ MHz and $\nu_2 = 36.740$ MHz. Using the pulse train method, the nutation spectrum was obtained only for the upper frequency line with spectrometer frequency set exactly on-resonance. We did not attempt a detailed examination of the off-resonance behaviour of the nutation interferogram as predicted by (5). Nevertheless, we observed that the amplitude of the nutation curve was strongly diminished when the spectrometer frequency has been set several kilohertz off-resonance. Figure 2a shows the NQR signal after 256 accumulations together with spectrometer response to the RF pulse train. Figure 2b shows the nutation curve (interferogram) obtained from the data shown in Fig. 2a using the algorithm (9) with $p\backslash n = 40$ and $c = 12$. The latter value has been determined experimentally by trial and error

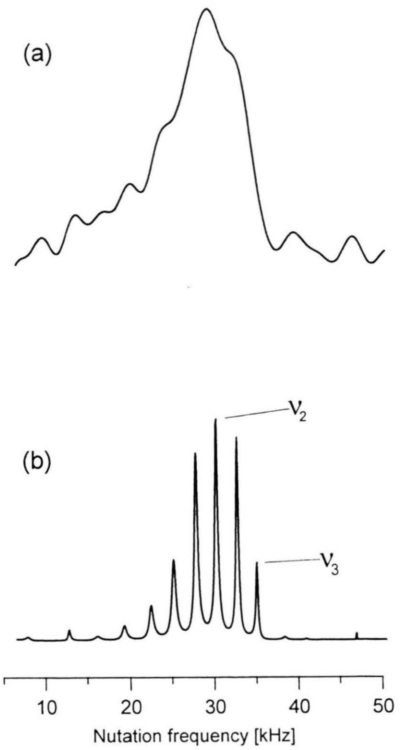

Fig. 3. ^{35}Cl NQR nutation spectra of cyanuric chloride obtained by processing of the nutation interferogram shown in Fig. 2b by (a) the FFT and (b) the MEM algorithm, also showing distinct positions of ν_2 and ν_3 singularities.

method in order to obtain the minimum distortion which was pronounced towards the end portion of the interferogram. For an arbitrary value of *c*, this distortion appeared as drift on the interferogram baseline and probably arose from interference from the lower off-resonance NQR line. A nutation spectrum obtained as Fourier transformation of the interferogram is shown in Figure 3a. It has the typical powder pattern shape described in [1] with a pronounced shoulder on its right side, indicating a significant asymmetry parameter. The exact positions of the ν_2 and ν_3 singularities were determined by processing the nutation interferogram with a Maximum Entropy Method (MEM) instead of the FFT algorithm [7], and the asymmetry parameter was calculated from the expression $\eta = 3(\nu_3 - \nu_2)/(\nu_3 + \nu_2)$ derived in [1] to be 0.23 ± 0.005, in good accordance with the result obtained by the conventional method [7]. The maximum time saving factor possible with this experiment as compared to the conventional method of nutation NQR spectroscopy can be roughly estimated as equal to the number of pulses contained in a pulse train, as all *n* data points of the nutation interferogram are collected from a single transient instead of *n* transients repeated for varying RF pulse length. However, further study is required, including relaxation and off-resonance effects, to get more physical insight into this method.

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