Influence of the rf Field Inhomogeneity on Nutation NQR Spectra of Spin 3/2 Nuclei in Powders

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The influence of the rf field inhomogeneity on the NQR nutation spectra of spin $I = 3/2$ nuclei in powder samples is investigated. To eliminate the rf field inhomogeneity effects, a method of reconstruction of the NQR nutation spectra, based on finding the deconvolution of the Fourier nutation spectrum with a function of the rf field distribution, is used. The method is successfully demonstrated for simulated and experimental NQR nutation spectra of ^{35}Cl in $TiCl_4$. The lineshape analysis of reconstructed nutation spectra allowing the determination of the EFG asymmetry parameter is given. The real advantage of the proposed method is that the high-resolution nutation spectrum may be obtained for a sample filling up the entire coil.

Key words: Nuclear Quadrupole Resonance; 2D Nutation Spectroscopy; Electric Field Gradient Tensor.

1. Introduction

The principal components of the electric field gradient (EFG) tensor at the quadrupolar nucleus are fully determinated by the quadrupolar coupling constant (e^2qQ) and the asymmetry parameter (η). For nuclei with spin $I = 3/2$, the single transition frequency ν_Q depends on both parameters, therefore a conventional 1D zero-field nuclear quadrupole resonance (NQR) experiment is insufficient to determine the full EFG tensor.

Harbison *et al.* [1, 2] have demonstrated that the asymmetry parameter η of the EFG tensor experienced by a quadrupolar nucleus can be determined by analysing the two-dimensional zero-magnetic field nutation NQR spectral data. The nutation method exploits the anisotropic dependence of the relative orientation of the radio-frequency (rf) field direction and quadrupolar axes. The singularities in the powder nutation spectrum, reconstructed by the Fourier transform, determine the asymmetry parameter. However, the accuracy of the method based on the location of singularities in the nutation spectrum is not high, especially for low values of η ($\eta < 0.2$). It should be noted that the resolution in the nutation dimension depends entirely on the homogeneity of the rf field and on the relaxation time of the nucleus in the rotating frame.

Zero-magnetic field nutation spectroscopy relies on two dimensional methodologies where information on the nutation frequency is obtained by incrementing the length of a homogeneous rf pulse. As in other forms of nutation spectroscopy, high radiofrequency field homogeneity over the sample volume is obviously of critical importance. In previous works some authors have tried to circumvent the problem by operating with samples of small volume located in the centre of a long sample coil [1 - 3]. In order to ensure a high rf homogeneity, a compromise between the filling factor and the signal-to-noise ratio has to be achieved. The reduction of a sample volume cannot completely eliminate the distortion and broadening of the nutation spectrum due to the inhomogeneity of the rf field and leads to a further decrease of the already weak NQR signal. Since the rf inhomogeneity is a factor limiting the resolution also in multiple-pulse solid-state NMR, some efforts were undertaken to design a new coil with improved rf homogeneity [4]. The idea for improving the rf homogeneity is to use a coil with continuously varying pitch. However, while the axial homogeneity in the coil with variable pitch can be slightly improved, the radial inhomogeneity still remains [4].

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In this paper we propose a new approach to eliminate the influence of the rf field inhomogeneity on the NQR nutation spectra. The proposed theoretical treatment uses the method of reconstruction of the NQR nutation spectra, based on finding the deconvolution of the Fourier nutation spectrum with a function of the rf field distribution. For a given experimental set-up the rf field distribution may be easily calculated for any helical coil. The method is demonstrated for simulated and experimental NQR nutation spectra of spin $I = 3/2$ nuclei in powder samples. The real advantage of the proposed method is that the high-resolution nutation spectrum may be obtained for a sample filling the entire coil.

2. Theory and Methods

For a helical coil with constant pitch the rf field distribution function $B_1(\rho, z)$ consists of a radial ($B_{1\rho}$) and an axial (B_{1z}) part:

$$B_1(\rho, z) = \sqrt{B_{1\rho}^2 + B_{1z}^2}. \tag{1}$$

The rf field distribution of a helical coil with constant pitch is identical to the field distribution of a coil consisting of a dense stack of parallel rings. This becomes immediately evident by considering the field contributions originating in the currents in infinitesimally short pieces of a helical coil, but can also be seen by considering the formula for the field in the stack of parallel rings derived in, e. g., Purcell's well-known textbook [5]. The field distribution inside a coil can easily be calculated:

$$\begin{aligned} B_{1\rho} &= B_{10} \frac{Rz}{\pi\rho\sqrt{(R+\rho)^2 + z^2}} \cdot \left[-K(k) + \frac{R^2+\rho^2+z^2}{(R-\rho)^2+z^2} \right] E(k), \\ B_{1z} &= B_{10} \frac{R}{\pi\sqrt{(R+\rho)^2 + z^2}} \cdot \left[K(k) + \frac{R^2-\rho^2-z^2}{(R-\rho)^2+z^2} \right] E(k), \end{aligned} \tag{2}$$

where B_{10} is the field value in the centre of a coil, R the radius of a coil, and $K(k)$ and $E(k)$ are the complete elliptic integrals of the first and the second kind, respectively. Here

$$k^2 = \frac{4R\rho}{(R+\rho)^2 + z^2}. \tag{3}$$

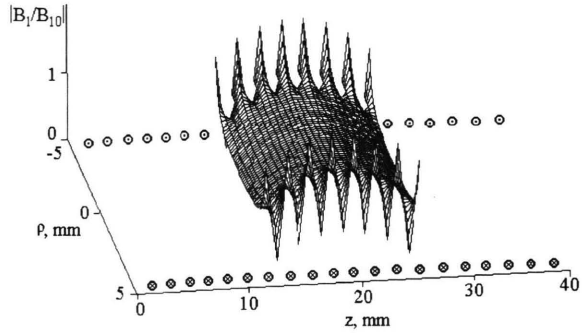

Fig. 1. The rf field distribution across the sample in a typical nutation experiment.

The field distribution $B_1(\rho, z)$ was calculated for a typical experimental set-up used in our spectrometer. The transmitter-receiver coil with $N = 20$ turns, an inner radius $R = 5$ mm, and a length of $L = 40$ mm was used. For these geometrical conditions the field distribution was calculated inside a cylindrical sample volume with a length of $l = 12$ mm and a radius of $r = 4.5$ mm located in the centre of the coil. Results are shown in Figure 1.

The nutation frequency for a particular crystallite of the powder sample is given by [6]

$$\omega = \frac{\gamma B_1}{2\sqrt{3+\eta^2}} \cdot \sqrt{4\eta^2\cos^2\theta + \sin^2\theta(9+\eta^2+6\eta\cos 2\varphi)}, \tag{4}$$

where the polar and azimuthal angles, θ and φ, define the relative orientation between the principal axis of the EFG tensor and the direction of the rf field B_1. We calculated the distribution $f(B_1)$ of the field (as well as the distribution $f(\nu)$ of the nutation frequencies for every component of the nutation spectrum) in the volume of the entire coil and the volume, where only the sample is located (Fig. 2, curves 1 and 2, respectively). These distribution functions were normalised using the maximum intensities of the NQR spectra (not the areas). The vertical axis is in the logarithmic scale. The frequency ν_0 equals $(\sqrt{3}\gamma B_{10})/(4\pi)$, where B_{10} is the amplitude of the rf field in the centre of a cylindrical coil. The essential contribution to the

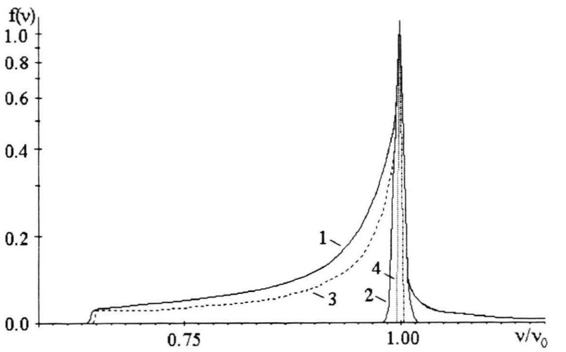

Fig. 2. The distribution of nutation frequencies for a particular crystallite of the powder sample as a function of the rf inhomogeneity in the sample volume. 1: the sample occupies the entire volume of the coil with $N = 20$ turns, an inner radius $R = 5$ mm, and a length of $L = 40$ mm; 2: the sample of a cylindrical form with a length of $l = 12$ mm and a radius $r = 4.5$ mm located in the centre of the coil; 3: the sample occupies the entire volume of the coil, but the radial inhomogeneity is neglected; 4: the sample in a thin-cylinder form of $l = 12$ mm located along an axis of one single turn of $R = 5$ mm (see (5)), in this case only the axial inhomogeneity is considered.

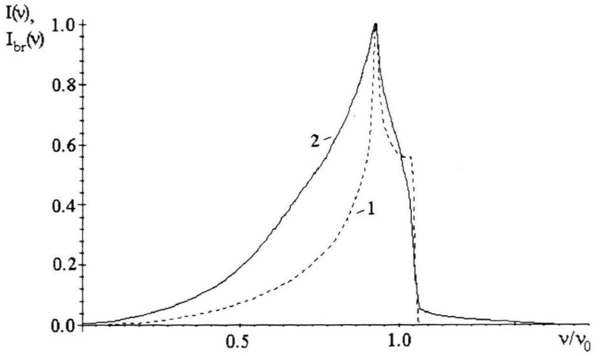

Fig. 3. The broadening of the NQR nutation spectrum as a result of the rf field inhomogeneity. 1: the ideal nutation spectrum for $\eta = 0.19$; 2: the broadened spectrum.

distribution of nutation frequencies is made by the axial inhomogeneity of the $B_1(\rho, z)$ field (as shown by curves 1 and 2 in Fig. 2). For comparison, the distribution of nutation frequencies for the sample filling the entire coil is demonstrated by curve 3 in Fig. 2 (here only the axial inhomogeneity is taken into account). The analytical expression describing the field distribution can be obtained only inside the sample of the thin cylinder form with the length of l located along an axis of one turn with the radius R by

$$f(B_1) = \frac{R}{3lB_{10}}\left(\frac{B_1}{B_{10}}\right)^{-4/3}\left[1-\left(\frac{B_1}{B_{10}}\right)^{2/3}\right]^{-1/2}. \quad (5)$$

Here B_{10} is the field in the centre of the turn. The B_1 field in the sample located at one side of the turn changes according to the relation

$$B_1 = B_{10}\left[1+\left(\frac{z}{R}\right)^2\right]^{-3/2}. \quad (6)$$

This distribution is represented by the curve 4 in Fig. 2 under the assumption that $R = 5$ mm, $l = 20$ mm, and B_{10} is the same as in the centre of a coil with $N = 20$ turns. In other cases (curves 1, 2, and 3), numerical calculations were required.

3. Results and Discussion

The nutation spectrum $I_{\mathrm{br}}(\omega)$, broadened due to the inhomogeneity of the rf field, can be calculated as a convolution of the distribution function $f(\omega)$ with the ideal nutation spectrum $I(\omega)$, determined by (10):

$$I_{\mathrm{br}}(\omega) = I(\omega) \otimes f(\omega). \quad (7)$$

Results of the calculation for $\eta = 0.19$ are shown in Fig. 3 (curve 2). The curve 1 in Fig. 3 is the ideal (nonbroadened) nutation spectrum. The curve 2 is the asymmetrically broadened nutation spectrum for the sample filling up the entire coil.

In order to eliminate the influence of the inhomogeneous rf field from the simulated spectrum (curve 2 in Fig. 3) and from the experimental NQR nutation spectrum of ^{35}Cl in $TiCl_4$ we solved the problem of finding the deconvolution function by transforming the functions $I_{\mathrm{br}}(\nu)$ and $f(\nu)$ into the time domain by the inverse Fourier transform. According to the convolution theorem one has

$$I(\nu) = \mathrm{FT}\left\{\frac{\mathrm{FT}[I_{\mathrm{br}}(\nu)]}{\mathrm{FT}[f(\nu)]}\right\}. \quad (8)$$

In (8) the real and imaginary parts of the functions $I(t)$, $I_{\mathrm{br}}(t)$, and $f(t)$ must be taken into account. Thus

$$\mathrm{Re}[I(t)] = \frac{\mathrm{Re}[I_{\mathrm{br}}(t)]\mathrm{Re}[f(t)] + \mathrm{Im}[I_{\mathrm{br}}(t)]\mathrm{Im}[f(t)]}{\{\mathrm{Re}[f(t)]\}^2 + \{\mathrm{Im}[f(t)]\}^2},$$

$$\mathrm{Im}[I(t)] = \frac{\mathrm{Im}[I_{\mathrm{br}}(t)]\mathrm{Re}[f(t)] - \mathrm{Re}[I_{\mathrm{br}}(t)]\mathrm{Im}[f(t)]}{\{\mathrm{Re}[f(t)]\}^2 + \{\mathrm{Im}[f(t)]\}^2}. \quad (9)$$

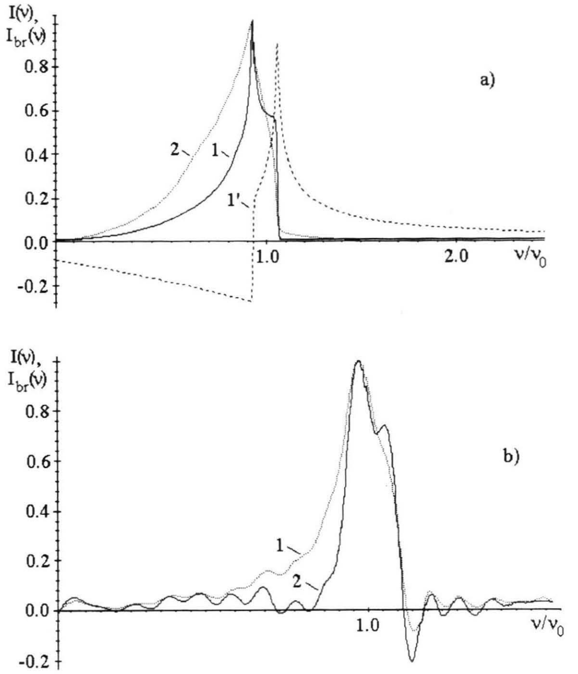

Fig. 4. The reconstructed nutation spectra: a) the computer simulated spectra for $\eta = 0.19$; b) the experimental nutation spectra for ^{35}Cl in $TiCl_4$, $\nu_0 = 26.8$ kHz. Description in the text.

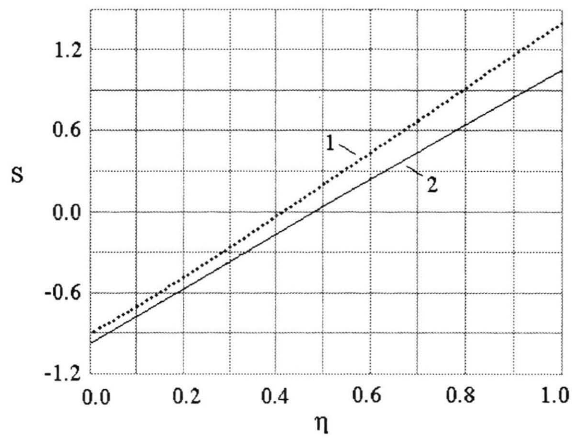

Fig. 5. Dependence of Pearson's asymmetry parameter S for unimodal distribution on the asymmetry parameter η. 1: for the ideal (nonbroadened) nutation spectrum; 2: for the nutation spectrum broadened by the rf field inhomogeneity.

The reconstructed nutation spectra (simulated and experimental) are presented in Figure 4 and effectiveness of the proposed computer analysis is also shown. The curve 2 in Figure 4a is the computer-simulated, broadened due to the rf field inhomogeneity, nutation spectrum ($\eta = 0.19$) for the sample filling up the entire volume of cylindrical coil. The curves 1 and 1' are reconstructed nutation spectra obtained by the deconvolution method (8) from the curve 2 (the real and imaginary parts, respectively). Figure 4b shows the experimental NQR nutation spectrum of ^{35}Cl in $TiCl_4$ (curve 1) and the reconstructed spectrum, where the influence of the rf field inhomogeneity was excluded by the deconvolution method using the calculated distribution function $f(B_1)$ (curve 2). As it can be seen in Fig. 4a, b, now it is not necessary to use a small sample located in the centre of the coil. Therefore the signal-to-noise ratio can be considerably increased and the data acquisition time may be greatly reduced. Note that the reconstructed experimental spectrum (curve 2 in Fig. 4b) reveals distinct singularities, so that the asymmetry parameter can now be determined on this basis.

The other approach that enables one to compensate the rf field inhomogeneity is used in 2D NMR spectroscopy [7]. By using the composite pulses it is possible to obtain any precise rotation angle of nuclear magnetisation. The simplest pulse sequence is $(\pi/2)_\beta(\pi/2)_x$, which is equivalent to $(\beta)_z(\beta_y)$, e. g. phase shift β and rotation of magnetisation β. For the NQR nutation spectroscopy, however, this method can not be applied because the gradual change of the phase β does not lead to the characteristic nutation interferogram (which is necessary to reconstruct the nutation spectrum in a powder sample). As follows from our calculations, the method of compensation of the residual magnetisation component M_z after applying the "$\pi/2$"-pulse ($\sim$ 0,66 π in a case of powder) gives only a partial compensation. The residual magnetisation is a result of the rf field inhomogeneity and cannot be compensated by the composite pulses in case of NQR as well as NMR spectroscopy (for spins $I > 1$). The above mentioned simplest composite pulses $(\beta)_0(\beta)_\pi$ and $(\beta)_0(2\beta)_{2\pi/3}$ at $\beta \approx 0.66\pi$ and the B_1 rf field inhomogeneity of the order of $\pm$ 30% decrease the distribution of the nutation signal intensities from (10 - 11)% to (2 - 8)%. But for spins $I = 3/2$ for any arbitrary angle of rotation of the magnetisation (which depends also on η) the same compensation does not occur. Therefore an effective application of composite pulses for the compensation of the rf field inhomogeneity seems to be impossible in NQR nutation spectroscopy.

On the other hand, the accuracy of nutation frequency singularities determined from the experimental nutation spectrum is not very high (particularly ω_3). Consequently, this can lead to considerable errors in the estimation of the asymmetry parameter η. In [8] we have proposed to use the statistical parameters of the nutation frequency distribution instead of frequency singularities in a powder spectrum. The analytical relation $I(\omega)$, presented by us in [8], for the ideal NQR nutation lineshape of spins I = 3/2 in a powder sample (taking into account the dependence of the intensity of nutation spectrum components on the nutation frequency) has the form

$$I(\omega) = A(\omega_0,\eta)\frac{\omega^2}{\sqrt{(\omega_2^2-\omega_1^2)(\omega_3^2-\omega^2)}}K(k) \quad \text{for } \omega_1 \le \omega \le \omega_2,$$
$$I(\omega) = A(\omega_0,\eta)\frac{\omega^2}{\sqrt{(\omega^2-\omega_1^2)(\omega_3^2-\omega_2^2)}}K\left(\frac{1}{k}\right) \quad \text{for } \omega_2 \le \omega \le \omega_3, \tag{10}$$

where $K(k)$ is a complete normal elliptic integral (the Legendre integral of the first kind):

$$k = \sqrt{\frac{(\omega^2-\omega_1^2)(\omega_3^2-\omega_2^2)}{(\omega_3^2-\omega^2)(\omega_2^2-\omega_1^2)}},$$
$$\omega_1 = \frac{2\eta\omega_0}{\sqrt{3(3+\eta^2)}}, \quad \omega_{2,3} = \frac{(3\mp\eta)\omega_0}{\sqrt{3(3+\eta^2)}}. \tag{11}$$

Here $\omega_0 = \sqrt{3}\gamma B_{10}/2$, and $A(\omega_0,\eta)$ is the normalised constant parameter, which depends weakly on the asymmetry parameter η [8].

The first moment $\langle\omega\rangle$ of the nutation spectrum (the centre of gravity) and the median $\omega_{1/2}$ (that divides the area under the absorption curve into two equal parts) were calculated as a function of η. The obtained functional dependencies of these statistical parameters are rather flat and not highly sensitive to η [8]. Therefore from a practical point of view, for the determination of η in powders we propose to apply Pearson's asymmetry parameter $S(\eta)$ for unimodal distribution [9]. This parameter may be defined as $S = (\xi - \xi_m)/\sigma$, where $\xi = \langle\omega\rangle$ is the centre of distribution, $\xi_m = \omega_2$ the mode of distribution, $\sigma = (\mu_2)^{1/2}$ the mean quadratic deviation, and μ_2 the central second moment. ω_2 is a frequency singularity that appears at the maximum amplitude of the nutation powder pattern. Unlike the singularity at ω_3 used in the conventional method [1], the ω_2-singularity can be accurately determined. The asymmetry parameter can also be determined by analysing the coefficient of the distribution asymmetry $\gamma_1 = \mu_3/(\mu_2)^{3/2}$, where μ_3 is the third central moment of the nutation spectrum. The calculated dependencies of the statistical parameters S and γ_1 of the nutation frequency distribution on the asymmetry parameter η for ideal (nonbroadened) nutation spectra are shown in Figs. 5 and 6, curves 1. The rf field inhomogeneity of the transmitter/receiver coil leads to the asymmetric broadening of the powder nutation spectrum and affects also the dependencies of γ_1 and S on η. The curves 2 in Figs. 5 and 6 show the S and γ_1 dependencies on η for the inhomogeneous rf field (with the sample filling the entire coil). Now it is clearly seen that in order to determine the value of η from experimental values of S or γ_1, it is necessary to take into account the broadening effect due to the rf field inhomogeneity. The broadening effect can be eliminated using the convolution theory. Such a spectrum reconstruction procedure should be applied before using the S and γ_1 analyses.

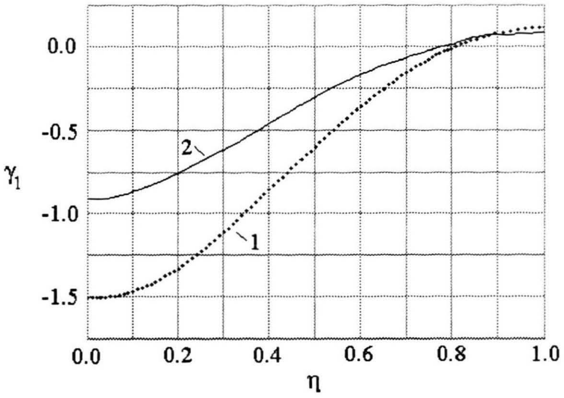

Fig. 6. Dependence of the coefficient of distribution asymmetry γ_1 on the asymmetry parameter η. 1: for the ideal (nonbroadened) nutation spectrum; 2: for the nutation spectrum broadened by the rf field inhomogeneity.

In conclusion we would like to point out that the rf field homogeneity is of critical importance also in NQR imaging experiments [10]. With the ρ NQR imaging technique for powdery solids, the rf amplitudes depending linearly on the spatial coordinates are applied. For a reliable reconstruction of the spatially dependent density of nuclei, the method of spectrum reconstruction used in this paper is highly recommended.

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