Lineshape Analysis of 2D NMR and NQR Nutation Spectra of Integer and Half-Integer Quadrupolar Nuclei

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A lineshape analysis of the NMR and NQR powder nutation spectra of integer and half-integer quadrupolar nuclei is presented. Simulated NMR nutation spectra of spin I = 1 and 3 nuclei are reported. For I = 1 the formulas for the singularities of the NMR nutation powder patterns as a functions of η, e^2Qq and γB_1 are given. The NQR nutation powder patterns for spin I = 3/2, 5/2, 7/2, and 9/2 for different induced transitions are calculated, and some experimental aspects of the method are discussed. A universal empirical formula to facilitate the determination of the asymmetry parameter from the NQR nutation frequency singularities for any arbitrary spin or transition is found. The NQR nutation spectra for half-integer and integer spins are compared. For integer spins the two-frequency excitation of the nutation spectrum is analysed. Application of the 2D-nutation lineshape analysis for the determination of the quadrupole interaction parameters is emphasised.

Key words: 2D Nutation Spectroscopy; NQR; NMR; Electric Field Gradient Tensor.

1. Introduction

The quadrupole coupling constant e^2Qq and asymmetry parameter η of the electric field gradient (EFG) tensor at the site of the nucleus give information about the local electronic environment of the nucleus and are therefore valuable for the exploration of molecular structure and dynamics. The description of the NMR spectra of quadrupolar spins depends strongly on the spin quantum number I and the relative magnitude of the Zeeman and quadrupole interactions. When the quadrupole interaction is small with respect to the Zeeman interaction, the anisotropic contribution of the quadrupole term to the NMR transition frequencies can be calculated by perturbation theory. In high magnetic fields, all Zeeman transitions shift in first order because of the quadrupole interaction except the 1/2, –1/2 transition which experiences a much smaller second-order shift. As a result of this, typical spectra of polycrystalline samples containing quadrupolar spins give characteristic powder patterns for the 1/2, –1/2 transition, whereas all other transitions are usually broadened beyond detection [1]. Because the magic angle is not effective for the second-order quadrupolar interaction, MAS will not average this interaction but yields powder patterns for the 1/2, –1/2 transition which are approximately four times narrower than for static samples. Although, in principle, it is possible to extract information about the electric field gradient from the spectra of static or spinning polycrystalline samples, in practice the powder patterns are often blurred.

To overcome this problem, Samoson and Lippmaa [2] introduced the two-dimensional NMR nutation experiment. The basic idea of the nutation experiment is to study the evolution of the spin system in a small radiofrequency field in the rotating frame. This technique is similar to the transient nutation method suggested by Torrey [3]. The nutation spectroscopy relies on two-dimensional methodologies where the nutation frequency ω_{1n} information (contained in the first dimension) is obtained by incrementing the length of a homogeneous rf pulse, while the second dimension corresponds to the conventional NMR spectra (for the central transition). The projection of the 2D spectrum $I(\omega_{1n}, \omega_2)$ along the spectroscopic axis ω_{1n} results in the nutation line. The characteristic singularities in the powder nutation spectrum, reconstructed by the

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Fourier transform, determine the parameters of the EFG tensor.

Traditionally, quadrupole interaction parameters can be determined by NQR. Harbison *et al.* [4] 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 rf field direction and quadrupolar axes. This method has originally been developed for nuclei with spins $I = 3/2$, because a conventional 1D NQR experiment is insufficient to determine the full EFG tensor. In previous works the 2D NQR nutation spectroscopy has been extensively applied, but only for a spin $I = 3/2$. As shown in [5], the 2D-nutation NQR lineshape and frequency are considerably modified by the offset of the spectrometer frequency from resonance. The influence of relaxation processes [6] and the rf field inhomogeneity [7] on the form of nutation line and on location of characteristic singularities in the powder pattern have also been considered. The analytical formulas for the lineshape of the powder nutation spectrum are given in [8]. The multiple-pulse sequences to study the NQR transient nutation for spins $I = 3/2$ in powders [9] and $I = 1$ in single-crystal [10] were also investigated.

In this paper the lineshape analysis of 2D NQR and NMR nutation spectra will be extended to the nuclear spins not considered before. NQR nutation powder patterns for spin $I = 3/2$, 5/2, 7/2, and 9/2 for different induced transitions will be calculated. 2D NMR and NQR nutation powder patterns for integer spins $I = 1$ and $I = 3$ and some experimental aspects of the method will be discussed. The main goal is the development of efficient methodologies for the determination of quadrupole interaction parameters, e^2Qq and η, and the understanding of the dynamic properties of a quadrupolar spin system.

2. Theory

For quadrupolar nuclei the NMR nutation frequency depends on the strength of the quadrupolar interaction. The quadrupole frequency is given by [1, 11]

$$\omega_q = \omega_{q0}(3\cos^2\theta - 1 + \eta\cos 2\varphi\sin^2\theta), \quad (1)$$

where $\omega_{q0} = e^2qQ/8I(2I-1)$. The polar angles orienting the magnetic field in the principal axis system of the electric field gradient are θ and φ.

Solid-state 2D-NMR nutation spectroscopy has been extensively studied with applications to half-integer quadrupolar nuclei [2, 12]. It has been shown that the characteristics of the NMR nutation patterns in these systems are useful for the determination of quadrupolar coupling constants. The majority of elements in the periodic table have nuclei with half-integer quadrupole spins. However, the theories and experiments have to be extended to nuclear systems with integer spins for $I = 1$ (^2H, ^6Li, ^{14}N) and $I = 3$ (^{10}B).

In this paper we analyse the NMR nutation spectra of powders for integer spins. However, the possible multiquantum transitions between the various energy levels in the rotating frame are neglected. In a conventional one-pulse nutation sequence these multiquantum transitions cannot distort the obtained nutation pattern.

Consider a nuclear spin system with $I = 1$ experiences an rf field. Analysis of the spin Hamiltonian expressed in the rotating frame gives three energy levels:

$$E_1 = \omega_q, E_{2,3} == -\omega_q/2 \pm [(3\omega_q/2)^2 + \omega_1^2]^{1/2}, \quad (2)$$

where $\omega_1 = \gamma B_1$ and the corresponding frequencies of the one-quantum nutation transitions are

$$\begin{aligned} \omega_{12} &= -3\omega_q/2 + [(3\omega_q/2)^2 + \omega_1^2]^{1/2}, \\ \omega_{13} &= \ \ 3\omega_q/2 + [(3\omega_q/2)^2 + \omega_1^2]^{1/2}. \end{aligned} \quad (3)$$

Characteristics of the NMR nutation patterns for spin $I = 1$ are presented in Table 1. The shape of 2D nutation spectra depends on the ratio of the quadrupole frequency ω_{q0} and the strength of the radiofrequency field ω_1. Here we introduced the new variable r defined as $r = 3\omega_{q0}/(2\omega_1)$. The frequency distance

Table 1. Characteristics of the NMR nutation spectra for spin $I = 1$.

Nutation frequency singularities	ω_{12}	ω_{13}
$\theta = 0$	$-2r + (4r^2 + 1)^{1/2}$	$2r + (4r^2 + 1)^{1/2}$
$\theta = \pi/2, \varphi = 0$	$r(1-\eta) + [r^2(1-\eta)^2 + 1]^{1/2}$	$-r(1-\eta) + [r^2(1-\eta)^2 + 1]^{1/2}$
$\theta = \pi/2, \varphi = \pi/2$	$r(1+\eta) + [r^2(1+\eta)^2 + 1]^{1/2}$	$-r(1+\eta) + [r^2(1+\eta)^2 + 1]^{1/2}$

between the most intensive singularities (presented in Table 1) is given by $\Delta\omega = 2r(1-\eta)$. In principle, this quantity can be used for the determination of the asymmetry parameter η. However, by measuring only the frequency distance $\Delta\omega$ it is impossible to determine both η and e^2Qq, as the r parameter depends on the ratio of e^2Qq and ω_1.

For a nuclear spin $I = 3$ the analytical solutions of the spin Hamiltonian in the rotating frame do not exist. The nuclear energy levels, corresponding NMR nutation frequencies, and the NMR nutation powder pattern for all induced transitions should be computed numerically.

In case of NQR nutation spectroscopy, the analytical formulas for the lineshape of the powder nutation spectrum of spin $I = 3/2$ nuclei are given in our previous work [8]. It should be noted, however, that for spins $I = 1, 3/2, 5/2, 7/2$ some attempts have been made to determine the NQR nutation frequencies, but only for some specific monocrystal orientations [13, 14].

For a spin $I = 1$ system with the one-frequency excitation of the NQR nutation spectrum the powder averaging leads to the characteristic "triangle" lineshape of the powder pattern. When the off-resonance effects are neglected, the analytical expression describing the nutation lineshape function is given by [8, 15]

$$I(\omega) = \begin{cases} 2\omega/\omega_1^2 & \text{for } 0 < \omega < \omega_1 \\ 0 & \text{for } \omega_1 < \omega < \infty \end{cases} \qquad (4)$$

In order to find the distribution of the NQR nutation frequencies in powder for spins $I = 5/2, 3, 7/2, 9/2$ and various induced transitions it is necessary to consider an average over all equally probable orientations θ and φ of the principal axes of the EFG tensor with respect to the linearly polarised rf magnetic induction B_1 (the resonance offset is assumed to be zero).

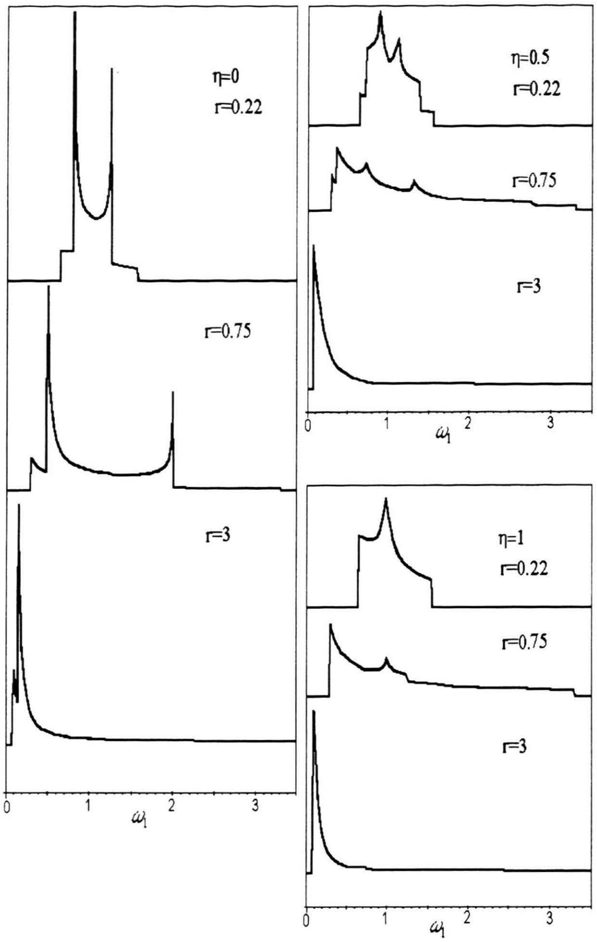

Fig. 1. Series of calculated NMR nutation powder patterns for a spin $I = 1$ and different values of η and r.

3. Results and Discussion

A) 2D NMR Nutation Spectroscopy

The characteristics of the NMR nutation powder patterns for half-integer nuclear spins were discussed in [1, 11, 12]. It was shown that in the extreme cases $\omega_{q0} \ll \omega_1$ ($r \approx 0$), and $\omega_{q0} \gg 10\omega_1$ ($r \gg 10$), the nutation spectrum consists of a single line. In the first situation ω_{q0} may be neglected with respect to ω_1, the evolution of the nuclear transverse magnetisation following the rf pulse is analogous to that of spin $I = 1/2$, and the nutation frequency is simply $\omega = \omega_1$. In the second situation straightforward perturbation theory shows that the nutation frequency becomes $\omega = (I + 1/2)\omega_1$, because the central transition may be treated as the transition between the simple two-level system. In intermediate cases, $0.1 < r < 100$, the spectra are complicated and several peaks can occur because many transition frequencies ω_{ij} in the rotating frame exist. In addition the nutation spectra will be powder patterns because of the anisotropic nature of the quadrupole interaction. Therefore for intermediate cases the experimentally obtained nutation spectra have to be compared with simulated spectra. For the spins $I = 3/2, 5/2$ the $(I + 1/2)^2$ possible nutation frequencies of the central transitions are

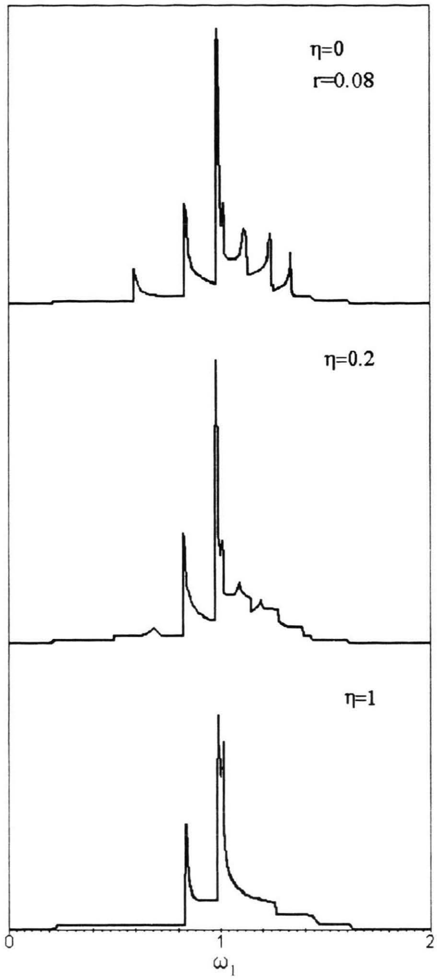

Fig. 2. Calculated NMR nutation powder patterns for a spin $I = 3$ as a function of η (at a constant value of r).

allowed. In powder samples only $2I$ of them are dominant. The weaker components may be explained by multiquantum coherences.

For a spin $I = 1$ the NMR nutation spectrum is the simplest one. In Fig. 1 the NMR nutation powder patterns for a spin $I = 1$ at various values of η and r parameters are shown. For the intermediate values of η and r the nutation spectrum displays some more complicated features. In the extreme cases $r = 0$ (corresponding to $e^2Qq = 0$) and $r > 10$ (at low values of the rf field) the nutation spectrum consists of a single narrow line at frequencies $\omega = \omega_1$ and $\omega = 0$, respectively. In general case the powder pattern for $I = 1$ may exhibit up to six singularities, as follows from a Table 1.

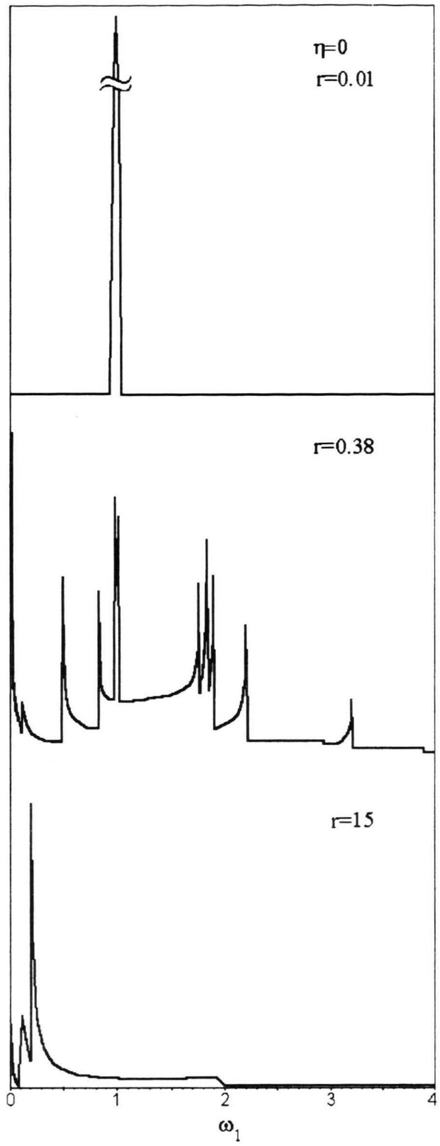

Fig. 3. Calculated NMR nutation powder patterns for a spin $I = 3$ as a function of r, with $\eta = 0$.

Calculated NMR nutation powder patterns for a spin $I = 3$ as a function of η and r parameters are shown in Figs. 2 and 3, respectively. Here again, the most complex pattern is obtained for the intermediate values of η and r. In the extreme cases $r \approx 0$ and $r > 10$, as for a spin $I = 1$, the NMR nutation pattern exhibits one narrow line at $\omega = \omega_1$ and $\omega = 0$, respectively. As was mentioned above, for half-integer spins at the extreme case $r > 10$, where $\omega = (I + 1/2)\omega_1$, the nutation pattern is quite different.

By comparing an experimental NMR nutation spectrum to a set of simulated spectra for a spin $I = 3$ one can determine the quadrupole coupling constant e^2Qq and the asymmetry parameter η of the EFG tensor. The distance between the nutation pattern singularities increases with increasing r, but this resolution enhancement effect is compensated by the drastic loss of signal intensity, and the spectrum is reduced to a single line for large values of r. This imposes great restrictions on the range of quadrupolar coupling constants that can be studied by the nutation experiment.

For the determination of the quadrupole parameters e^2Qq and η the method of centre of gravity instead of nutation lineshape analyses has been proposed in [2]. However, due to the very broad nutation spectrum involved, this method leads to a large error and cannot be recommended. An important cause for nutation spectrum broadening is the inhomogeneity of the rf field [7]. The effect of rf inhomogeneity cannot simply be described with a Lorentzian broadening because a spread in ω_1 will also cause a spread in the r parameter, and will thus change the whole nutation spectrum. The other approach that enables one to compensate the rf field inhomogeneity is by using composite pulses, instead of a conventional one-pulse sequence [1]. This method utilises the X, $-X$ composite pulse. Although in some cases the spectral broadening due to rf field inhomogeneity may be slightly reduced [16], the excited even-multiquantum transitions may obscure the powder nutation spectrum. Another important experimental aspect in the nutation experiment is that one has to ensure that the recycle delay is long enough for the system to return to equilibrium before the next pulse arrives. If the recycle delay is short with respect to T_1, the nutation spectrum will consist a number of ω_1-harmonics which can easily be mistaken for components with a large quadrupole frequency. The nutation spectra are also very sensitive to the resonance offset. A serious consequence of off-resonance irradiation is that the modulation of the observed free induction decay changes from amplitude modulation into phase modulation. Therefore, there will be dispersive contributions to the nutation lineshapes. The other experimental drawback is that the rf spectrum of the excitation pulse changes with its length, causing undesirable distortions of the nutation lineshape. The magic angle spinning (MAS), as shown by Nielsen [17], can also influence the nutation lineshape by introducing spurious echo signals at certain frequencies of sample rotation.

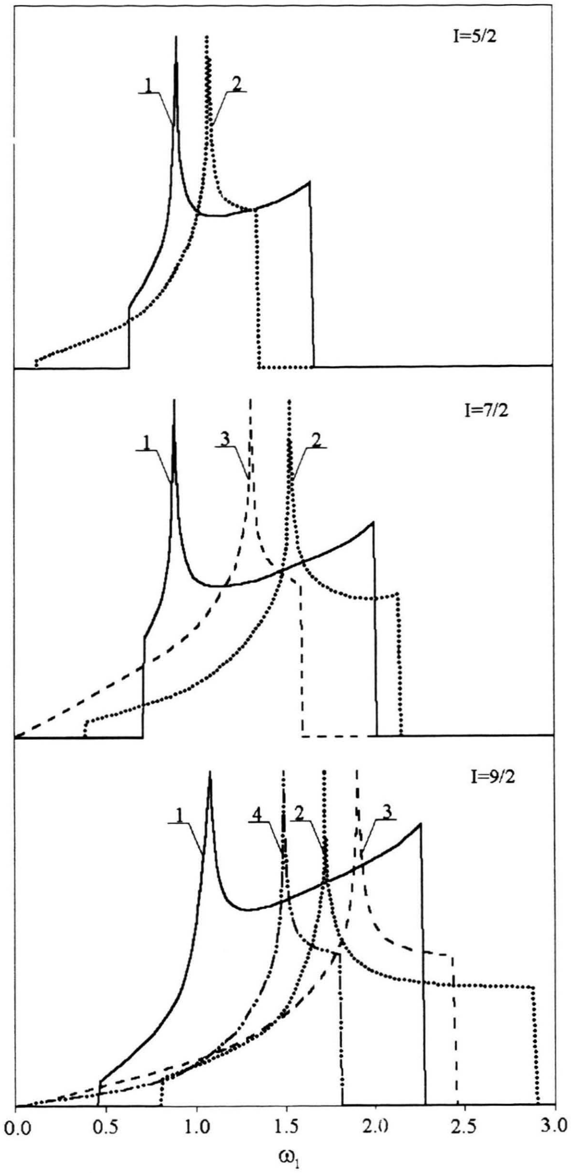

Fig. 4. NQR nutation powder patterns for different spins as functions of the induced transition. The maximum intensities of the nutation spectra are normalised, $\eta = 0.5$ (1: $\pm 1/2 \rightarrow \pm 3/2$, 2: $\pm 3/2 \rightarrow \pm 5/2$, 3: $\pm 5/2 \rightarrow \pm 7/2$, 4: $\pm 7/2 \rightarrow \pm 9/2$).

B) 2D NQR Nutation Spectroscopy

The two-dimensional zero-field nutation NQR powder spectra for a spin $I = 3/2$ were studied by Harbison *et al.* [4]. It was shown that the asymmetry parameter η could be determined from two of the three singularities ω_{n1}, ω_{n2} and ω_{n3} appearing in the

Table 2. Values of a and b for different nuclear spins and transitions.

Spin	Transition	a	b
$J = 3/2$	±1/2→±3/2	1.0000	1.0000
$J = 5/2$	±1/2→±3/2	1.5849	2.2017
	±3/2→±5/2	0.9984	0.2898
$J = 7/2$	±1/2→±3/2	2.2350	4.4430
	±3/2→±5/2	1.5597	0.2265
	±5/2→±7/2	0.7857	0.3867
$J = 9/2$	±1/2→±3/2	2.8101	8.6859
	±3/2→±5/2	2.0688	0.5994
	±5/2→±7/2	1.2606	0.1002
	±7/2→±9/2	0.7209	0.3987

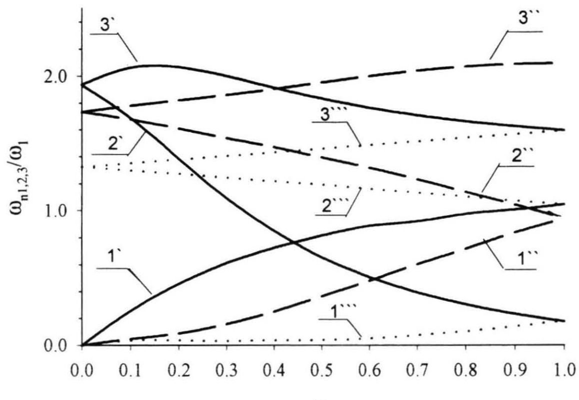

Fig. 5. Dependence of the NQR nutation frequency singularities on the asymmetry parameter η for different induced transitions. $I = 7/2$ (': ±1/2→±3/2, '': ±3/2→±5/2, ''': ±5/2→±7/2).

powder nutation spectrum. For a spin $I = 5/2$ the NQR nutation lineshape was studied only for one transition (±1/2→±3/2) [18]. In Fig. 4 we present the calculated NQR nutation powder patterns for spins I = 5/2, 7/2, 9/2 as functions of the all-possible induced transitions. It can be seen that the nutation pattern strongly depends on the excited transition as well as the asymmetry parameter. Figure 5 shows the dependence of the NQR nutation frequency singularities on the asymmetry parameter η for different induced transitions. After calculation of the two characteristic nutation frequencies corresponding to different crystallite orientations we obtain the following evaluation formula for the asymmetry parameter:

$$\eta = 3\frac{\omega_{n3} - \omega_{n2}}{a\omega_{n3} + b\omega_{n2}}, \quad (5)$$

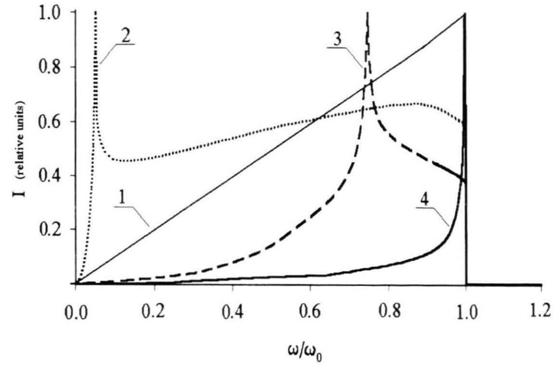

Fig. 6. NQR nutation powder patterns for a spin I =1 (for any arbitrary value of η. 1: one-frequency excitation of any possible transition (ν_+, ν_-, or ν_0), 2: two-frequency excitation (ν_- and ν_+) for the relative intensities of the rf fields 0.05:1, 3 and 4: as in 2, but for the relative intensities of the rf fields 0.75:1 and 1:1, respectively.

where the coefficients a and b depend on the nuclear spin and the transition involved. Thus (5) has universal character and can be applied for any arbitrary spin or transition. The values of a and b are given in a Table 2 for different nuclear spins and transitions. Although for $I > 3/2$ from the pure NQR spectra it is possible to extract both the quadrupole coupling constant and the asymmetry parameter, very often only one (usually the lowest) NQR transition is available. The frequencies corresponding to the higher transitions may be outside the spectrometer range. The advantage of the nutation experiment is that only one NQR transition is required to determine the complete set of principal values of the EFG tensor.

For a spin I = 1 the NQR nutation powder pattern for one-frequency excitation has a pure "triangle"-shape for each of the transition (ν_+, ν_-, ν_0), independently of the η value. The nutation lineshape is shown in Fig. 6 (curve 1). In the extreme cases $\eta \cong 0$ or $\eta \cong 1$ the rf pulse may excite the two NQR transitions simultaneously, i. e. (ν_+ and ν_- or ν_- and ν_0, respectively). In this case the lineshape is different (as shown in Fig. 6, curves 2, 3, and 4) and depends on the relative intensities of the rf fields exciting the two transitions. Here again the nutation spectrum is independent of η. If the spectrometer frequency is set exactly in the middle between the excited NQR frequencies, the same rf amplitude excites both transitions. The resultant spectrum is depicted in Fig. 6 (curve 4). As it can be concluded, for a spin I = 1 with the two-frequency excitation the characteristic singularity of the powder nutation spectrum provides

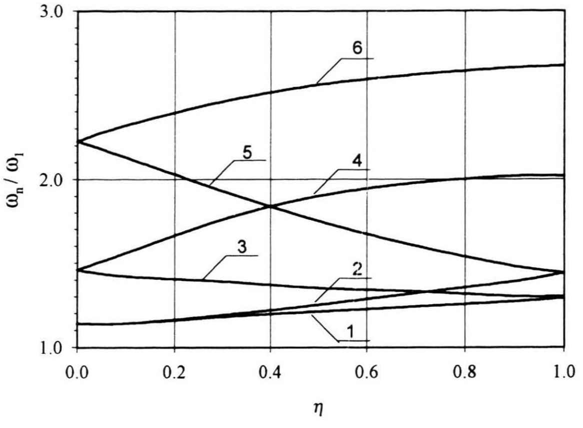

Fig. 7. NQR nutation frequency singularity ω_n/ω_1 (corresponding to the maximum amplitude of the nutation spectrum) as a function of the asymmetry parameter η for the one-frequency excitation of different transitions. I = 3. 1: (−3 → −2), 2: (+3 → +2), 3: (−2 → −1), 4: (+2 → +1), 5: (+1 → 0), 6: (−1 → 0).

information on the relative intensities of the rf fields, but not on the asymmetry parameter.

For a spin $I = 3$ with the one-frequency excitation the NQR nutation powder pattern is also characterised by the "triangle"-shape. But, unlike the $I = 1$ case, the position of the nutation frequency singularity depends on the asymmetry parameter η. Figure 7 shows the NQR nutation frequency singularity (corresponding to the maximum amplitude of the nutation spectrum) as a function of the asymmetry parameter η for different allowed transitions. All functional dependencies shown in Fig. 7 are rather flat and not highly sensitive to η. Therefore, from a practical point of view for the determination of η it may be not enough to study only one transition. Moreover, the knowledge of $\omega_1 = \gamma B_1$ is also necessary. Here, as in the case of spin $I = 1$, for some values of asymmetry parameter the two-frequency transitions are also possible. The corresponding lineshape depends on the relative intensities of the rf fields.

In conclusion, we may emphasise the important role of 2D NMR/NQR nutation spectroscopy for the determination of quadrupole interaction parameters for any arbitrary nuclear spin or transition. As follows from the simulated nutation spectra, the transient nutation processes are different for integer and half-integer nuclear spins.

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