Orientation of Tensorial Interactions Determined from Two-dimensional Nutation Exchange NQR and NMR Powder Spectra

Nicolay Sinyavsky and Mariusz Mackowiak[a]

Baltic State Academy, Molodiozhnaya str. 6, 236029 Kaliningrad, Russia
[a] Institute of Molecular Physics, Polish Academy of Sciences,
Smoluchowskiego 17, 60-179 Poznan, Poland

Reprint requests to Prof. M.M.; Fax: 48-61-8684-524; E-mail: mackow@ifmpan.poznan.pl

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The method for determining the mutual orientation of molecular interaction tensors in powders is described. The technique is based on 2D nutation exchange NQR and NMR spectroscopy. It is shown that the 2D nutation exchange spectra exhibit characteristic ridges, which reflect the motional mechanism in a model-independent fashion. The angles through which the molecule rotates can be read from elliptical ridges in the 2D spectra. The 2D nutation exchange NMR and NQR powder patterns are calculated for spins $I = 1$ and $I = 3/2$ for different symmetry of reorienting molecular groups.

Key words: 2D Spectroscopy; NQR; NMR; Exchange; Nutation.

1. Introduction

The information about rotational motions is provided through angular-dependent spin interactions described by second-rank tensors. Therefore it should be possible to measure angles on a molecular scale directly by magnetic resonance techniques. Whereas this is standard in structural studies on single crystals, this goal is much more difficult to achieve for isotropic or partially ordered samples and, in particular, for obtaining dynamical angular information in such systems. In powders it is no longer possible to relate interaction tensors to a macroscopic frame, but it may still be possible to determine the relative angular orientation of two independent interaction tensors. The information is sufficient to determine an interaction tensor in a molecular frame.

It is the purpose of this paper to propose a new method to obtain angular distributions of reorientational angles. The technique will be applied to provide structural information on molecular groups involved in exchange processes. The method for determining the mutual orientation of molecular interaction tensors is based on 2D-nutation exchange NQR and NMR spectroscopy [1]. The main idea of our proposed experiment is that nutation spectroscopy can be applied to detect exchange processes [2]. Before the exchange jump the nutation frequency is different from the nutation frequency after the jump. These two nutation frequencies (which depend on relative orientations of the molecule before and after the jump) have to be correlated in order to get information on the dynamics of molecular motion. We show that the 2D-nutation exchange spectrum exhibits characteristic ridges, which reflect the motional mechanism in a model-independent fashion. The angles through which the molecule rotates can be read from elliptical ridges in the 2D spectra. The main goal is the development of efficient methodologies for the determination of orientational tensorial interactions in powders and the understanding of the dynamic properties of a quadrupolar spin system.

2. Theory and Methods

The basic scheme of 2D nutation exchange spectroscopy for detecting reorientational motions involves four successive time periods: preparation, evolution, mixing and detection. The preparation period consists of a recycle delay to allow the longitudinal magnetisation to built up by T_1 relaxation, followed by direct single-pulse excitation. The basic three-pulse sequence of Jeener et al. [3] must be suitably modified to allow the detection of exchange processes through nutation spectra. As seen in Fig. 1, the time t_1 = const, and the pulse widths t_w and t'_w are incremented during the cycle of the experiment. The second pulse is phase shifted by 180°. As a matter of fact, the first two pulses could be

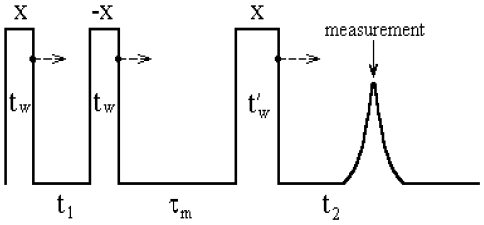

Fig. 1. Principle of 2D nutation exchange spectroscopy for detecting reorientational motion.

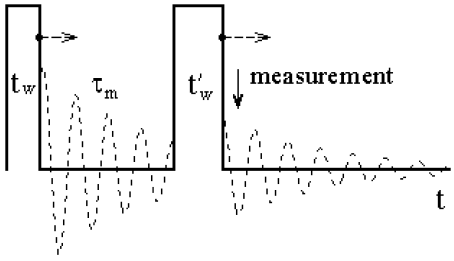

Fig. 2. Two-pulse sequence for a 2D nutation exchange experiment.

replaced by one composite pulse because the length of the evolution period is not relevant for this experiment and may be taken as $t_1 = 0$. The spin "labelling" process occurs during the first-pulse time. Therefore we propose a two-pulse sequence where only two pulses are incremented during the experiment (Fig. 2).

The theory of the transient response of a quadrupolar spin system to the rf pulses was given in [2]. It was shown that the time evolution of the signal created by a pure NQR multipulse sequence is rather complicated. We consider a system with two inequivalent sites A and B of the quadrupolar nuclei in a crystalline environment, with the NQR frequencies ω_0 and ω'_0, respectively, among which the exchange takes place. After the second pulse, for a nuclear spin $I = 3/2$ the intensity of the nondiagonal peak in the 2D exchange spectrum is given by

$$G^{\mathrm{ex}}_{\mathrm{AB}}(t_{\mathrm{w}}, t'_{\mathrm{w}}, t) = \frac{m^2}{4\alpha\xi} e^{-\frac{k}{2}(\tau_m - t_{\mathrm{w}})} \mathrm{sh}\left[\frac{kr}{2}(\tau_m - t_{\mathrm{w}})\right] \quad (1)$$
$$\cdot \left(\cos 2\xi' t_{\mathrm{w}} + \frac{\Delta\omega'^2}{2\xi'^2} \sin^2 \xi' t_{\mathrm{w}}\right)$$
$$\cdot \left[\sin 2\xi t'_{\mathrm{w}} \sin(\omega_0 t + \Delta\omega t'_{\mathrm{w}} + \varphi')\right.$$
$$\left. - \frac{\Delta\omega}{\xi} \sin^2 \xi t'_{\mathrm{w}} \cos(\omega_0 t + \Delta\omega t'_{\mathrm{w}} + \varphi')\right],$$

where $\alpha = \gamma B_1/4$, k is the average exchange rate and r is a reduction factor taking into account the losses

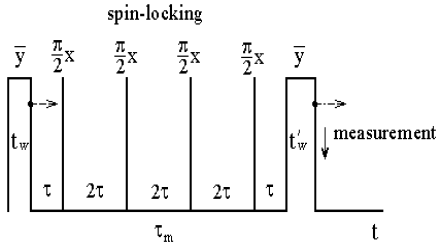

Fig. 3. The spin-locking pulse sequence preventing losses of magnetisation during the mixing period.

of the spin-polarisation projection during the reorientational jumps. The spectrometer frequency ω may be different from the resonance frequency ω_0 by $\Delta\omega = \omega - \omega_0$. Here

$$m = \frac{\alpha[4\eta^2 \cos^2\theta + \sin^2\theta(9 + \eta^2 + 6\eta\cos 2\phi)]^{1/2}}{(3+\eta^2)^{1/2}}.$$

The variable ξ is defined as $\xi = \frac{1}{2}(4m^2 + \Delta\omega^2)^{1/2}$.

The 2D nutation exchange NQR spectrum $S(\omega_{\mathrm{n}}, \omega'_{\mathrm{n}})$ is obtained from the double Fourier transform of $G^{\mathrm{ex}}_{\mathrm{AB}}(t_{\mathrm{w}}, t'_{\mathrm{w}})$ at t = const. The nutation frequency of $I = 3/2$ nuclei is defined by

$$2\xi = \left\{\Delta\omega^2 + \frac{(\gamma B_1)^2}{4(3+\eta^2)}\right. \quad (2)$$
$$\left. \cdot [4\eta^2 \cos^2\theta + \sin^2\theta(9 + \eta^2 + 6\eta\cos 2\varphi)]\right\}^{1/2}.$$

The mixing time τ_{m} is usually long (order of ms). To prevent losses of magnetisation during this period, the pulse sequence must be suitably modified. By using the spin-locking sequence shown in Fig. 3 the magnetisation can be sustained and all information about the nutation process during the mixing time is preserved.

For a spin $I = 1$ there are three different nutation frequencies [4]:

- for the ν_+ line
$$2\xi = [\Delta\omega^2 + (\gamma B_1)^2 \sin^2\theta \cos^2\varphi]^{1/2}, \quad (3)$$
- for the ν_- line
$$2\xi = [\Delta\omega^2 + (\gamma B_1)^2 \sin^2\theta \sin^2\varphi]^{1/2}, \quad (4)$$
- for the ν_0 line
$$2\xi = [\Delta\omega^2 + (\gamma B_1)^2 \cos^2\theta]^{1/2}. \quad (5)$$

The resultant 2D nutation exchange NQR powder spectra for the transitions ν_+, ν_-, and ν_0 are quite

different from that for a spin $I = 3/2$. The corresponding powder patterns are shown in Figs 4 and 5 for comparison. All spectra were calculated for reorientation of a molecular group with two inequivalent positions and the reorientation angle $\theta_s = 106^\circ$(tetrahedral angle).

For a spin $I = 1$ the NQR nutation frequency is independent of the asymmetry parameter η. As shown in Fig. 5, the elliptic singularities in the ridge spectra of powder for $I = 1$ are much more intense than those for $I = 3/2$. It is interesting that the 2D nutation exchange spectrum is not distributed over a frequency plane but lies along the diagonal line for the ν_- transition. 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, in contrast to the $I = 3/2$ case. Corresponding one-dimensional nutation NQR spectra are shown in Figs. 4 and 5 at the top of each spectrum. The form of the elliptical ridges is directly related to the reorientation angle θ_s, which is the angle between the orientations of the unique (z) principal axis of the EFG tensor before and after the reorientation. The high intensity of the elliptical ridge for $I = 1$ allows structural studies of molecules containing ^{14}N (e.g., NO_2-groups). The NQR spectrum is often spread over several hundreds of kHz. Thus the NQR lines are excited under off-resonance conditions. As shown in Figs. 4 and 5, the off-resonance irradiation leads to more "compressed" spectra. However, the dominant features of the off-resonance spectra are preserved.

For quadrupolar nuclei the NMR nutation frequency depends on the strength of the quadrupolar interaction. Consider a nuclear spin system with $I = 1$ or 3/2 experiencing an rf field. The spin Hamiltonian expressed in the rotating frame can be written as [5]

$$\hat{H} = \omega_1 \hat{I}_x + \omega_q (3\hat{I}_z^2 - \hat{I}^2), \tag{6}$$

where

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

$$\omega_{q0} = \frac{3eQq_{zz}}{8I(2I-1)}.$$

The polar angles orienting the magnetic field in the principal axis system of the electric field gradient are θ and φ.

In this paper we analyse the 2D nutation exchange NMR spectra of powders for spins $I = 1$ and 3/2. The influence of the asymmetry parameter η and the rotational angle θ_s on the NMR nutation exchange powder pattern has been considered. The molecular systems investigated here are the AB_2 and AB_3 groups, which show twofold and threefold reorientational jumps, respectively. In order to find the distribution of the NMR powder patterns 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 method of accumulation of partial intensities for various orientations has been used. The obtained spectra are very complex and strongly depend on the molecular group symmetry and the value of the spin. The shape of the spectra and positions of characteristic singularities depend on the jump angle θ_s and the value of the asymmetry parameter η in a rather complex way. The desired parameters can be determined by a computer analysis of the spectrum pattern. Simple analytical formulas do not exist and have to be replaced by a computer modelling.

Characteristic singularities in the spectrum patterns depend on the nutation frequency. For the quadrupolar spin $I = 1$ in the rotating frame the NMR nutation frequencies are given by [4]

$$\begin{aligned} \omega_{H1} &= -r\omega_q + [(r\omega_q)^2 + 1]^{1/2}, \\ \omega_{H2} &= r\omega_q + [(r\omega_q)^2 + 1]^{1/2}. \end{aligned} \tag{7}$$

Here we have introduced the new variable r defined by $r = \omega_{q0}/\omega_1$, where $\omega_1 = \gamma B_1$ is the NMR frequency in the rotating field B_1. Calculated 2D NMR nutation exchange powder patterns for spin $I = 1$ as functions of the asymmetry parameter η and the molecular group symmetry are shown in Figure 6. The cross peaks in the 2D spectrum are widely distributed over all possible nutation frequencies in the powder. The ridge pattern in such a 2D powder spectrum consists of straight lines as well as an elliptical feature that contains information on the geometry of the reorientational process. The 2D nutation exchange spectroscopy provides many advantages, as compared with traditional 2D exchange spectroscopy [6–8].

For a spin $I = 3/2$ the eigenvalues of the Hamiltonian (6) in the rotating frame can be calculated as [5]

$$\begin{aligned} &E_1 = (1/2)\omega_1 + D_-,\ E_2 = (1/2)\omega_1 - D_-, \\ &E_3 = (-1/2)\omega_1 + D_+,\ E_4 = (-1/2)\omega_1 - D_+, \end{aligned} \tag{8}$$

where $D_\pm = (\omega_1^2 \pm \omega_1\omega_q + \omega_q^2)^{1/2}$.

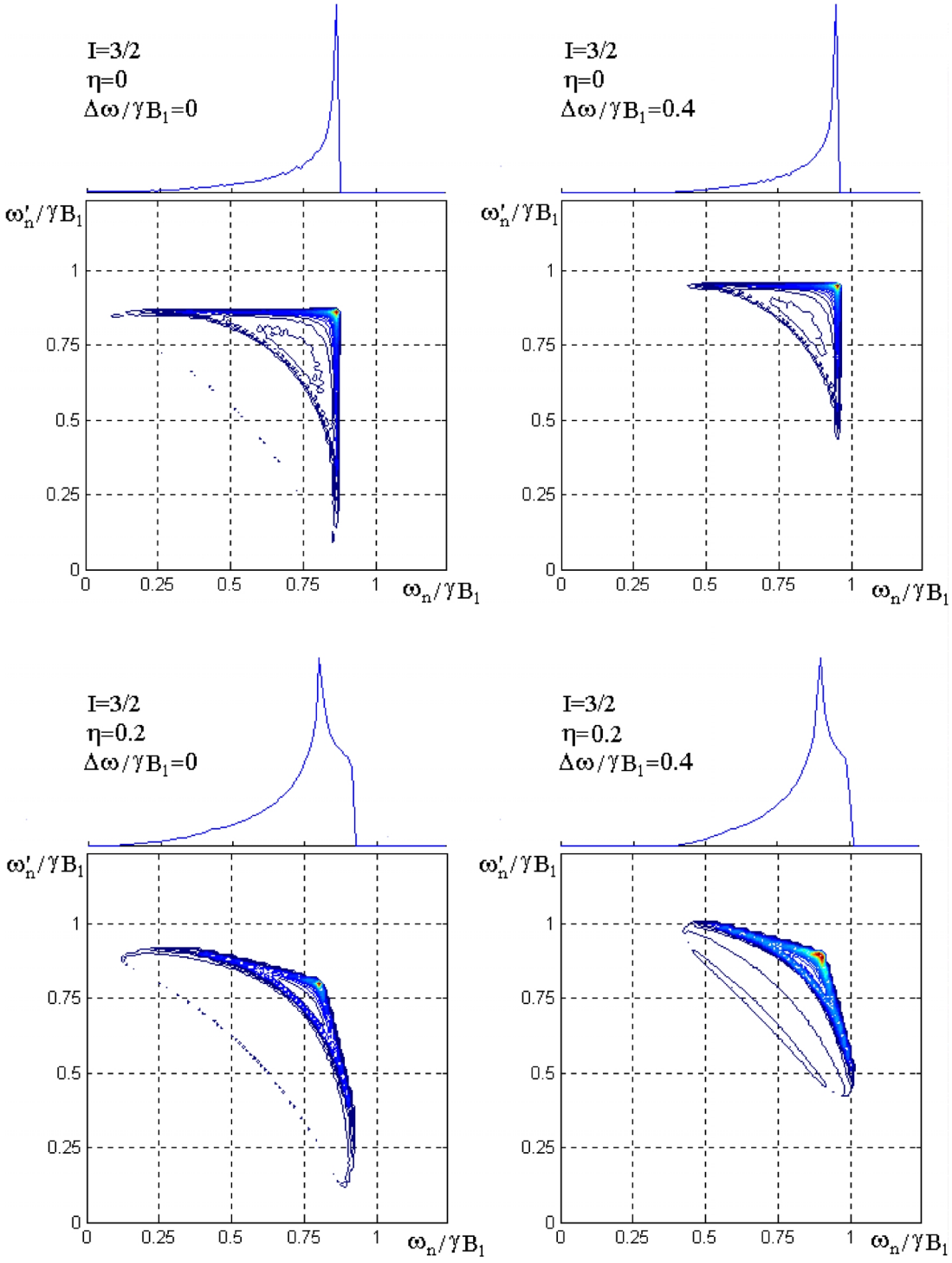

Fig. 4. 2D nutation exchange NQR spectra for $I = 3/2$.

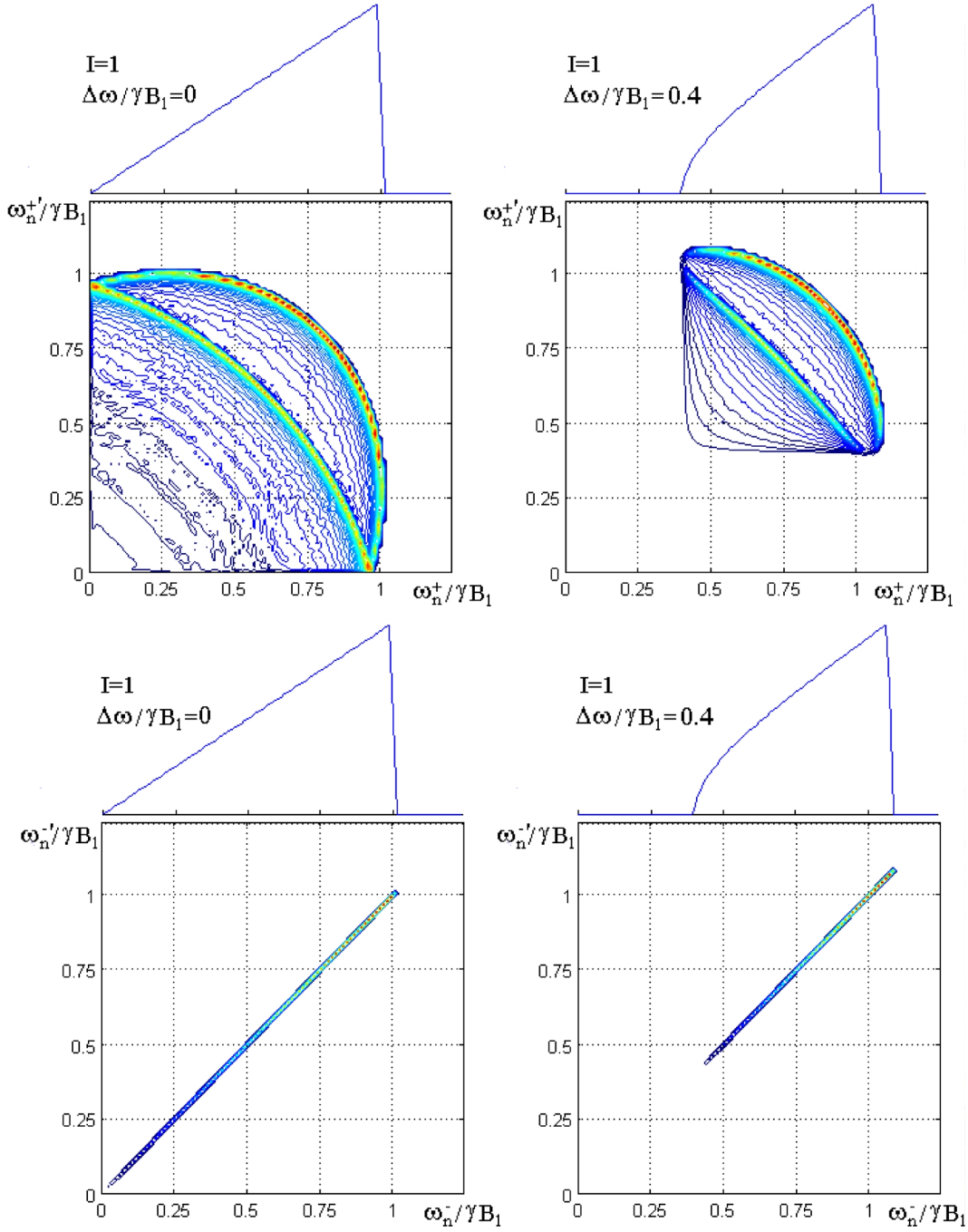

Fig. 5. 2D nutation exchange NQR powder patterns for ν_+ and ν_- lines ($I = 1$).

Since there are three possible transitions between the various energy levels in the rotating frame, the spectrum displays some more complicated features (Figure 7). A simple interpretation of the powder pattern is not possible, and again computer modelling and numerical calculation are necessary. Nevertheless, information on the structural and dynamical properties of the investigated system can be extracted.

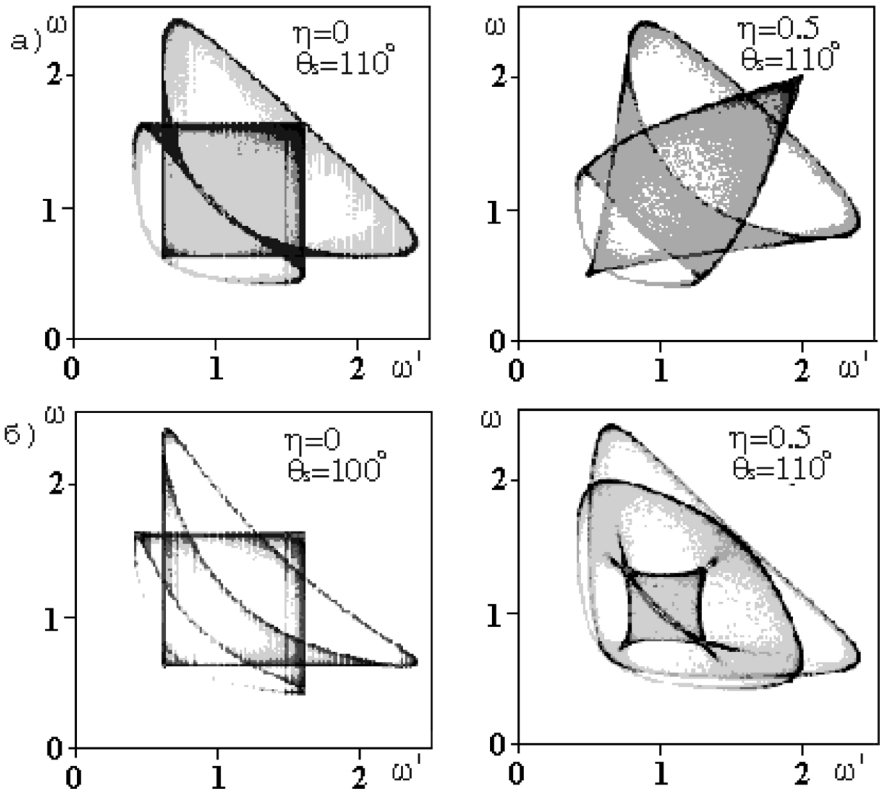

Fig. 6. 2D nutation exchange NMR powder patterns for $I = 1$, $r = 1.5$: a) twofold reorientational jumps (AB_2 molecular group) b) threefold reorientational jumps (AB_3 molecular group).

3. Conclusions

Two-dimensional nutation exchange NQR or NMR can be a convenient means to determine the relative orientation of tensorial interactions in powders. The analysis of 2D NMR and NQR spectra presented here allows the reconstruction of reorientational angles from experimental data without model assumptions, and simultaneous determination of the EFG tensor symmetry. This information, obtained from the characteristic ridges of the spectrum, is inaccessible by other techniques. Drawbacks of the method are the low intensity of the nondiagonal signals. High sensitivity and stability of the spectrometer are necessary to achieve sufficient intensities of the cross peaks in the 2D spectrum.

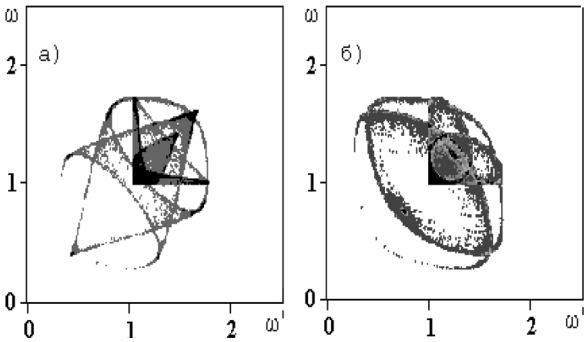

Fig. 7. Characteristic ridges in the 2D nutation exchange NMR powder patterns for $I = 3/2$, $r = 1.5$, $\eta = 0.5$, $\theta_s = 110^\circ$: a) twofold reorientational jumps b) threefold reorientational jumps.

Acknowledgement

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