Two-dimensional Exchange and Nutation Exchange Nuclear Quadrupole Resonance Spectroscopy

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A theoretical treatment of the 2D exchange NQR pulse sequence is presented and applied to a quantitative study of exchange processes in molecular crystals. It takes into account the off-resonance irradiation, which critically influences the spin dynamics. The response to the three-pulse sequence of a system of spins $I = 3/2$ in zero applied field, experiencing electric quadrupole couplings, is analysed. The mixing dynamics by exchange and the expected cross-peak intensities as a function of the frequency offset have been derived. The theory is illustrated by a study of the optimization procedure, which is of crucial importance for the detection of the cross- and diagonal-peaks in a 2D-exchange spectrum. The systems investigated are hexachloroethane and tetrachloroethylene. They show threefold and twofold reorientational jumps about the carbon-carbon axis, respectively.

A new method of direct determination of rotational angles based on two-dimensional nutation exchange NQR spectroscopy is proposed. The method involves the detection of exchange processes through NQR nutation spectra recorded after the mixing interval. The response of a system of spins $I = 3/2$ to the three-pulse sequence with increasing pulse widths is analyzed. It is shown that the 2D-nutation exchange NQR spectrum exhibits characteristic ridges, which manifest the motional mechanism in a model-independent fashion. The angles through which the molecule rotates can be read directly from elliptical ridges in the 2D spectrum, which are also sensitive to the asymmetry parameter of the electric field gradient tensor.

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

1. Introduction

Molecular dynamics can be studied by pure NQR methods based on the measurement of spin-lattice relaxation times, lineshape parameters and the temperature dependence of the resonance frequency. However, the amount of information provided by conventional one-dimensional NQR spectroscopy is very often limited. The 1D NQR method is unable to assign the specific lines of the multiline NQR spectrum to the particular reorienting molecular groups and to provide information on exchange-pathways.

Important improvements were achieved by introducing two-dimensional (2D) techniques that offer fundamental advantages. 2D-exchange spectroscopy involves a combined study of the distribution of nuclear environments, exchange rates, and pathways between the sites, which are distinguishable because of different resonance frequencies. 2D NMR exchange spectroscopy was first suggested by Jeener et al. [1]. Progress in multidimensional NQR has been hampered by experimental and conceptual difficulties, which we try to overcome in this paper. In contrast to NMR, some characteristic problems arise with a 2D-exchange NQR-experiment. The quantization axis is defined by the local direction of the EFG tensor. The direction of quantization changes jumpwise during the exchange process. With powder geometry, corresponding averages must be considered. Moreover, the NQR spectrum is usually spread over several hun-

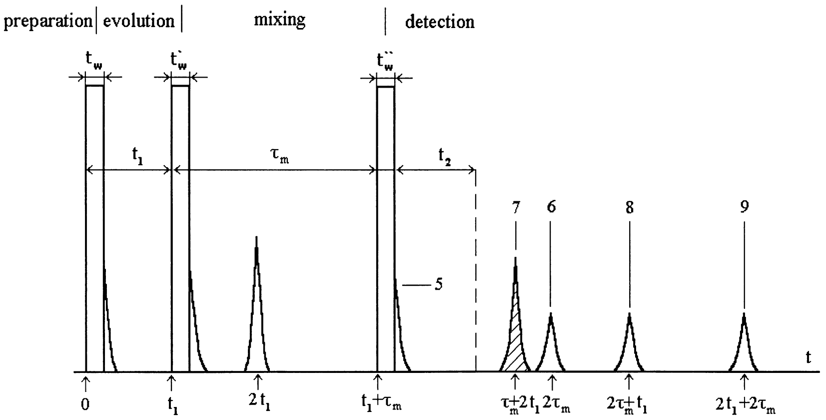

Fig. 1. Basic pulse scheme of 2D-exchange spectroscopy. Schematic representation of the response of a system of quadrupolar spins to the three-pulse sequence. The subsequent NQR signals after the third pulse are denoted by numbers.

dreds kHz. Thus the NQR lines are excited in off-resonance conditions. We show in this paper that the off-resonance irradiation critically influences the behaviour of the spin-exchange system. To our knowledge, only two attempts to use the pulse sequence of Jeener for NQR-exchange studies exist in the literature [2, 3]. Both research groups have used the conventional NMR approach without taking into account the off-resonance phenomena.

Due to lack of the external quantization axis, 2D-exchange NQR spectroscopy is less informative than 2D-exchange NMR, where the angles of reorientation of the electric field gradient tensors can be determined directly, thus yielding information about the type of motion [4] . In this paper we propose a new type of experiment to overcome this serious limitation: 2D-nutation exchange NQR spectroscopy. The 2D-nutation method exploits the fact that the nutation frequency depends on the induction B_1 of the RF field, the asymmetry parameter, and the relative orientation of the principal axes of the EFG tensor and the coil axis [5]. In the 2D-nutation experiment, a single excitation pulse of increasing length is applied to the spin system to encode information in one frequency dimension (leading to nutation spectra). From the powder-pattern singularities of the NQR spectrum the complete set of principal values of the EFG tensor can be determined. However, information on molecular dynamics is not available in the conventional nutation experiment.

Usually a rotating molecule or group in a solid has a number of discrete positions with relatively high potential barriers between them. Therefore the rotational correlation time is essentially the residence time of the molecule or group in a definite potential minimum, whereas the transition between the minima is very rapid. Generally the local field gradients have different orientations in space for different positions of the molecule. As a result, before the jump at the time t_1, the NQR nutation frequency (which is determined by the angles θ_1 and φ_1 of the largest EFG tensor principal axis with respect to the coil axis) is different from the nutation frequency after the jump at the time t_2 (determined by the angles θ_2 and φ_2). These two nutation frequencies have to be correlated in order to get information on the dynamics of molecular motion. This is the main idea of our proposed experiment: 2D-nutation spectroscopy can be applied for detection of exchange processes. We show that the 2D-nutation exchange NQR spectrum exhibits characteristic ridges, which manifest the motional mechanism in a model-independent fashion. The angles through which the molecule rotates can be read directly from the elliptical ridges in the 2D spectrum.

2. 2D-exchange NQR Spectroscopy

The transient response theory of a quadrupolar spin system to the three RF pulses (based on the solution of the time-dependent Schrödinger equation) has been given in [6], where it was shown that the time evolution of the signal created by a pure NQR multi-pulse sequences is rather complicated. The basic pulse scheme of 2D-exchange spectroscopy is given in Figure 1. A schematic representation of the response of a system of quadrupolar spins to the three-pulse sequence is denoted by numbers which correspond to the different subsequent signals. However, the most relevant term describing the exchange interactions is the stimulated echo signal (denoted by 7 in Fig. 1). This is consequently the only term that gives rise to cross and diagonal peaks. 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. For a nuclear spin $I = 3/2$ the intensity of diagonal (AA) and cross (AB) peaks of the exchange spectrum is given [6] by

$$G_{\mathrm{SE}}^{\mathrm{ex}} = \frac{\alpha}{6\rho^2} R^2(\theta,\varphi) \exp\{-\frac{k}{2}(\tau_m - t_w')\}\big(P_{(\mathrm{AA})} + P_{(\mathrm{AB})}\big), \tag{1}$$

$$\begin{aligned}
P_{(\mathrm{AA})} = {} & \frac{\sin\xi t_w \sin\xi t_w' \sin\xi t_w''}{\xi^3}\big(K_1^2 + K_2K_2^*\big)\,\mathrm{ch}\Big(\frac{kr}{2}\big(\tau_m - t_w'\big)\Big) \\
& \cdot \left[\frac{\Delta\omega}{2\xi}\left[\sin\xi t_w''\big(\frac{\Delta\omega^2}{4\xi^2}\sin\xi t_w \sin\xi t_w' - \cos\xi t_w \cos\xi t_w'\big) - \cos\xi t_w'' \sin\xi(t_w + t_w')\right]\right. \\
& \qquad \cdot \cos\Big[\omega_0\big(t_2 - t_1\big) + \Delta\omega\big(t_w + t_w''\big) + \varphi_1 + \varphi_3 - \varphi_2\Big] \\
& \quad + \Big[\cos\xi t_w''\big(-\frac{\Delta\omega^2}{4\xi^2}\sin\xi t_w \sin\xi t_w' + \cos\xi t_w \cos\xi t_w'\big) - \frac{\Delta\omega^2}{4\xi^2}\sin\xi t_w'' \sin\xi\big(t_w + t_w'\big)\Big] \\
& \qquad \left.\cdot \sin\Big[\omega_0\big(t_2 - t_1\big) + \Delta\omega\big(t_w + t_w''\big) + \varphi_1 + \varphi_3 - \varphi_2\Big]\right],
\end{aligned}$$

$$\begin{aligned}
P_{(\mathrm{AB})} = {} & \frac{\sin\xi' t_w \sin\xi' t_w' \sin\xi t_w''}{\xi'^2\xi}\big(K_1'^2 + K_2'K_2'^*\big)\,\mathrm{sh}\Big(\frac{kr}{2}\big(\tau_m - t_w'\big)\Big) \\
& \cdot \left[\left[\frac{\Delta\omega}{2\xi}\sin\xi t_w''\big(\frac{\Delta\omega'^2}{4\xi'^2}\sin\xi' t_w \sin\xi' t_w' - \cos\xi' t_w \cos\xi' t_w'\big) - \frac{\Delta\omega'}{2\xi'}\cos\xi t_w'' \sin\xi'(t_w + t_w')\right]\right. \\
& \qquad \cdot \cos\Big[\omega_0 t_2 - \omega_0' t_1 + \Delta\omega'\big(t_w + t_w''\big) + \varphi_1 + \varphi_3 - \varphi_2\Big] \\
& \quad + \Big[\cos\xi t_w''\big(-\frac{\Delta\omega'^2}{4\xi'^2}\sin\xi' t_w \sin\xi' t_w' + \cos\xi' t_w \cos\xi' t_w'\big) - \frac{\Delta\omega\Delta\omega'}{4\xi\xi'}\sin\xi t_w'' \sin\xi'\big(t_w + t_w'\big)\Big] \\
& \qquad \left.\cdot \sin\Big[\omega_0 t_2 - \omega_0' t_1 + \Delta\omega'\big(t_w + t_w''\big) + \varphi_1 + \varphi_3 - \varphi_2\Big]\right],
\end{aligned}$$

where $\alpha = \gamma B_1/4$, $\rho = \big(1 + \eta^2/3\big)^{1/2}$, $R(\theta,\varphi) = \big[4\eta^2\cos^2\theta + \sin^2\theta(9 + \eta^2 + 6\eta\cos 2\varphi)\big]^{1/2}$, k is the average exchange rate, and r is a reduction factor taking into account the losses of the spin-polarization projection during the reorientational jumps. The spectrometer frequency ω may be different from the resonance frequency ω_0 by $\Delta\omega = \omega - \omega_0$; φ_1, φ_2, and φ_3 are the phases of the pulses, respectively. Here $K_1 = \frac{2\alpha\eta}{\sqrt{3}\rho}\cos\theta$ and $K_2 = -\frac{\alpha\sin\theta}{\sqrt{3}\rho}(3e^{-i\varphi} + \eta e^{i\varphi})$. The variables ξ are defined as $\xi = \frac{1}{2}\sqrt{4m^2 + \Delta\omega^2}$, where $m = \frac{\alpha R(\theta,\varphi)}{\sqrt{3}\rho}$.

The part $P_{(\mathrm{AA})}$ in (1) describes the diagonal peak with coordinates $[\omega_0, \omega_0]$ whereas $P_{(\mathrm{AB})}$ refers to the cross-peak with coordinates $[\omega_0, \omega_0']$ in the 2D NQR spectrum.

As follows from (1), the cross-peak (AB) intensity for the pulses $t_w^{\mathrm{opt}} = \frac{1}{\xi'}\arcsin\big(\frac{\xi'}{\sqrt{2}m}\big)$ and $t_w''^{\mathrm{opt}} = \frac{1}{\xi}\arcsin\big(\frac{\xi}{\sqrt{2}m}\big)$ reaches its maximum value,

$$G_{\mathrm{AB}} = \frac{\sqrt{3}\rho'^2(k_1'^2 + k_2'k_2'^* R(\theta,\varphi)}{16\alpha^2\rho R'^2(\theta,\varphi)}\alpha_{\mathrm{AB}}, \tag{2}$$

where the mixing coefficients, which describe the exchange process, are given by

$$\begin{pmatrix} \alpha_{\mathrm{AA}} & \alpha_{\mathrm{AB}} \\ \alpha_{\mathrm{BA}} & \alpha_{\mathrm{BB}} \end{pmatrix} = e^{-\frac{k}{2}t} \begin{pmatrix} \mathrm{ch}\left(\frac{kr}{2}t\right) & \mathrm{sh}\left(\frac{kr}{2}t\right) \\ \mathrm{sh}\left(\frac{kr}{2}t\right) & \mathrm{ch}\left(\frac{kr}{2}t\right) \end{pmatrix}. \tag{3}$$

The maximum intensity of the diagonal peak (AA) is achieved for the pulses $t_w^{\mathrm{opt}} = t_w'^{\mathrm{opt}} = t_w''^{\mathrm{opt}} = \frac{1}{\xi}\arcsin\left(\frac{\xi}{\sqrt{2}m}\right)$. The observed intensity in this case is

$$G_{\mathrm{AA}} = \frac{\sqrt{3}\rho^2(k_1^2 + k_2 k_2^* R(\theta,\varphi)}{16\alpha^2\rho R'^2(\theta,\varphi)}\alpha_{\mathrm{AA}}. \tag{4}$$

In powder samples the problem of computing a powder average reduces to the numerical integration of (1) over all crystallite orientations.

Molecular dynamics of solid hexachloroethane (C_2Cl_6) and tetrachloroethylene (C_2Cl_4) has been studied by several authors [7] using NQR methods. The crystal structure of C_2Cl_6 is orthorhombic, space group $D_{2n}^{16} = P_{nma}$, with four molecules per unit cell [8]. Figure 2 shows the molecular structure of hexachloroethane. Here, pure tetrahedral symmetry of the CCl_3 groups is assumed for simplicity. The chlorine nuclei are located at the three corners of the tetrahedra. Thus the rotational jump of the CCl_3 group, concluded from relaxation data [7], interchanges the position of chlorine nuclei. This reorientation is equivalent to the rotation along the C-C bond axis by an angle $\delta = \pm 120°$ ($\alpha = \arcsin(4/3\sqrt{2})$, $\beta = 2\arcsin(2/\sqrt{6})$. For the mixing coefficients, which describe the intensity of diagonal peaks ($\alpha_{\mathrm{AA}}, \alpha_{\mathrm{BB}}, \alpha_{\mathrm{CC}}$), the following formula is found:

$$\alpha_{\mathrm{AA}} = \frac{1}{3}\exp\left(\frac{-6R - 4k + kr}{6}\tau_m\right) \tag{5}$$
$$\cdot \left[\exp\left(-\frac{kr}{2}\tau_m\right) 2\,\mathrm{ch}\left(\frac{kr}{2}\tau_m\right)\right].$$

For the cross-peaks ($\alpha_{\mathrm{AB}}, \alpha_{\mathrm{BA}}, \alpha_{\mathrm{AC}}, \alpha_{\mathrm{CA}}, \alpha_{\mathrm{BC}}, \alpha_{\mathrm{CB}}$), the mixing coefficient is given by

$$\alpha_{\mathrm{AA}} = \frac{2}{3}\exp\left(\frac{-6R - 4k + kr}{6}\tau_m\right) \mathrm{sh}\left(\frac{kr}{2}\tau_m\right). \tag{6}$$

The relative amplitude of the cross peaks is much lower than is typical in an NMR experiment. The signal intensities of the diagonal and cross peaks in powders were analysed as functions of the pulse length and the relative frequency offset of the spectrometer

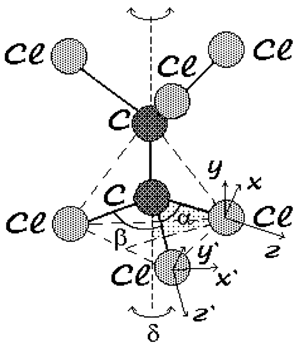

Fig. 2. Molecular structure of hexachloroethane.

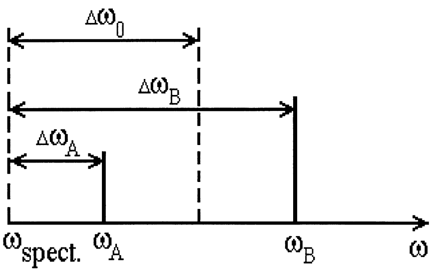

Fig. 3. The spectrometer frequency offset with respect to the NQR lines at the frequencies ω_{A} and ω_{B}.

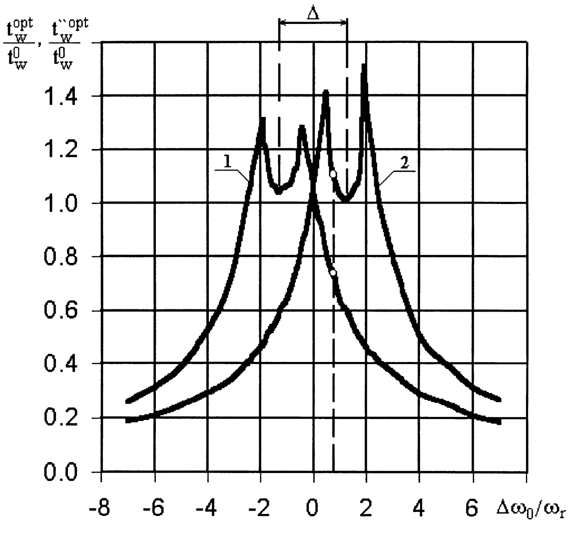

Fig. 4. Calculated optimum pulse length for observation of the AB cross-peak in the 2D-exchange NQR spectra as a function of the relative frequency offset: curve 1: t_w^{opt}/t_w^0, curve 2: $t_w^{n\mathrm{opt}}/t_w^0$, ($t_w^{\mathrm{opt}} = t_w'^{\mathrm{opt}}$). The analysis was performed for the relative frequency distance $\Delta = 2.45$ between the lines corresponding to sites A and B.

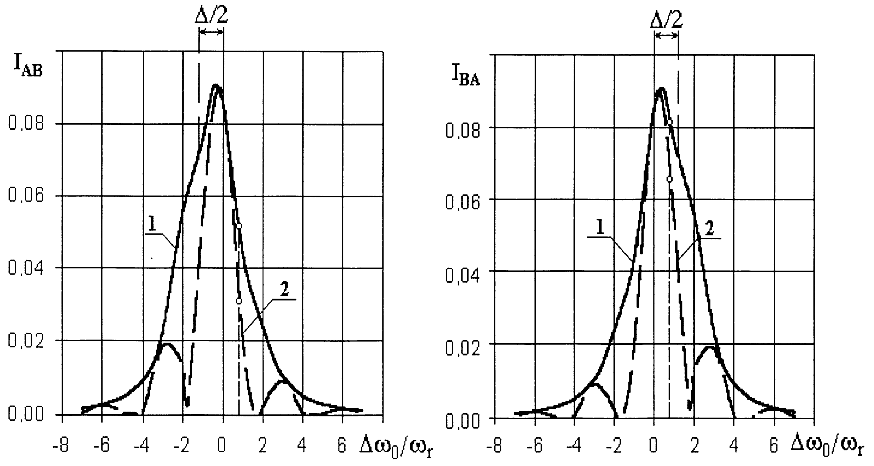

Fig. 5. Intensities of cross peaks of the 2D-exchange NQR spectra as a functions of the relative frequency offset: 1: $t_w = t'_w = t_w^{\mathrm{opt}} = t_w^{\prime\mathrm{opt}}$, $t''_w = t_w^{\prime\prime\mathrm{opt}}$, 2: $t_\mathrm{w} = t''_\mathrm{w} = t''_w = t_w^0$ ($\Delta = 2.45$).

frequency $\Delta\omega_0/\omega_\mathrm{r}$. The analysis was performed for various parameters $\Delta = (\Delta\omega_\mathrm{B} - \Delta\omega_\mathrm{A})\omega_r$, where $\omega_r = \gamma B_1$ (see Figure 3).

Figure 4 shows the calculated dependence of the optimum pulse length on the relative frequency offset for $\Delta = 2.45$. Here t_w^0 denotes the optimum length of the three pulses for a limit case $\Delta\omega_0/\Delta\omega_r \approx 0$ and $\Delta \approx 0$. The $\pi/2$-pulse length was assumed to be 10 µs, that corresponds to $\omega_r = 2\pi * 32.6$ kHz. As shown in Fig. 4, the optimum values of the pulse length depend strongly on the relative resonance offset. Usually the whole NQR spectrum is spread over several hundreds kHz, so the specific NQR lines are always excited in the off-resonance condition. Thus the length of pulses $t_w = t''_w$ and t''_w must be optimized in order to achieve cross-peaks with sufficient intensity. As follows from Fig. 5, for the unoptimized pulses at certain values of the resonance offset the cross-peaks may not be visible. Therefore the optimization procedure of the pulse length is of crucial importance for detection of the cross- and diagonal-peaks in the 2D-exchange NQR spectrum.

For obtaining 2D NQR exchange spectra, some special requirements have to be fulfilled. Here are some practical hints describing necessary steps of data acquisition:

1. Determine the relative frequency distance Δ between the NQR lines ω_A and ω_B for nuclei taking part in the exchange process.
2. Calculate the function $I_\mathrm{AB}(\Delta\omega_0/\omega_r)$ for obtained Δ and determine the spectrometer frequency offset $(\Delta\omega_0/\omega_r)_\mathrm{opt}$ to get the maximum possible intensity of the cross-peak.
3. Adjust the spectrometer frequency, trying to keep close to the values of $(\Delta\omega_0/\omega_r)_\mathrm{opt}$. In order to avoid the coincidence of mirror signals of diagonal peaks and cross- peaks, the transmitter frequency should be set somewhat apart from the centre frequency between the two resonances.
4. Optimize the pulse lengths $t_W^{\mathrm{opt}} = t_W^{\prime\mathrm{opt}}$ and $t_W^{\prime\prime\mathrm{opt}}$.

In the case of a multiple NQR spectrum we recommended looking for various possible cross-peaks separately, because the optimum conditions depend strongly on the frequency offset. The off-resonance phenomena are responsible for this effect. We have shown that the off-resonance irradiation critically influences the behaviour of the spin-exchange system. It is interesting to note that the off-resonance effects are less pronounced for very strong and short RF pulses. The relative frequency offset is inversely proportional to the RF field strength, and thus the off-resonance effects can be compensated to some extent by working with short pulses (about 2 µ s). As we have already mentioned, there are only two reports in literature on the detection of 2D-exchange NQR cross-peaks [2, 3]. In both cases the authors applied 2 µs-pulses. They did not give any reason for that, but now it is clear that the off-resonance effects preventing detection of the cross-peaks were compensated for.

3. 2D-nutation Exchange NQR Spectroscopy

The basic three-pulse sequence of Jeener [1] must be suitably modified to allow the detection of exchange processes through nutation spectra. As seen in Fig. 6, the time t_1 = const, and the pulse widths

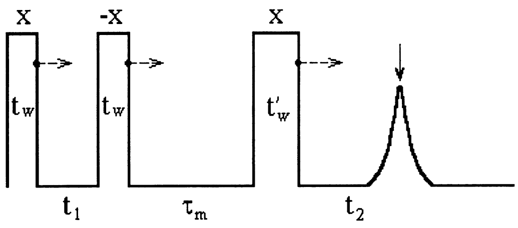

Fig. 6. Principle of 2D-exchange nutation NQR spectroscopy for detecting reorientational motion.

t_w and t'_w are incremented during the experimental cycle. The second pulse is phase-shifted by 180°. The direction of the RF field introduces an external quantization axis as the effective RF field, seen by a given nucleus, which depends on the relative orientation of the EFG tensor eigenframe with respect to the direction of the RF coil. After the first pulse the nuclear magnetization becomes "phase-coded", where the resultant phase depends on the nutation frequency. The second pulse with the same length but the opposite phase produces the longitudinal magnetization with the amplitude depending on the t_w value. The exchange process predominantly takes place during the mixing period τ_m while the magnetization is longitudinal. The molecular reorientation during the mixing time τ_m involves changes of (θ, φ), which are detected as changes of the nutation frequency. A third pulse rotates the longitudinal magnetization after exchange into the transverse component for detection. As the nutation frequency of the nuclei during the mixing time may change by a reorientational jump, the nutation frequencies before and after the jump correlate with each other. The resultant 2D-nutation exchange NQR spectrum contains information about the type of molecular motion.

The two-dimensional nutation NQR spectrum is obtained from the double Fourier transform of $G^{\mathrm{ex}}_{\mathrm{SE}}(t_w, t''_w)$ (as follows from (1)). Let us consider the reorientational motion of the $\mathrm{CCl_2}$-group in tetrachloroethylene $\mathrm{C_2Cl_4}$ (Fig. 7). The nutation frequencies of $^{35}\mathrm{Cl}$ nuclei ($I = 3/2$) in two inequivalent sites A and B are determined [9] by

$$\omega = \left\{\Delta\omega_1^2 + \frac{(\gamma B_1)^2}{4(3+\eta_1^2)} \cdot \left[4\eta_1^2\cos^2\theta + \sin^2\theta(9+\eta_1^2+6\eta_1\cos 2\varphi)\right]\right\}^{1/2},$$

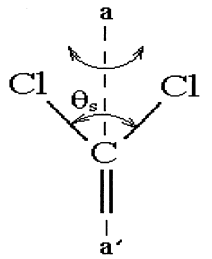

Fig. 7. Schematic representation of the reorientational motion for the $\mathrm{CCl_2}$-group. θ_S is the NQR-relevant reorientation angle (jump angle), that is well-defined by the orientation of the C-Cl bond before and after the jump.

$$\omega = \left\{\Delta\omega_2^2 + \frac{(\gamma B_1)^2}{4(3+\eta_2^2)} \cdot \left[4\eta_2^2\cos^2\theta + \sin^2\theta'(9+\eta_2^2+6\eta_2\cos 2\varphi')\right]\right\}^{1/2}. \tag{7}$$

The θ' and φ' coordinates after the jump can be expressed by the angles θ, φ and the angle θ_{s} between the C-Cl bonds, see Figure 7. Let us assume for simplicity that $\eta_2 = \eta_1 = \eta$. Defining the new dimensionless variable δ as the square of the nutation frequency

$$\delta = \frac{4(\omega^2 - \Delta\omega^2)}{3(\gamma B_1)^2},$$

we find that (7) may be rewritten as

$$\delta_1 = \frac{1}{3(3+\eta^2)}\left[4\eta^2\cos^2\theta + \sin^2\theta(9+\eta^2+6\eta\cos 2\varphi)\right],$$
$$\delta_2 = \frac{1}{3(3+\eta^2)}\left[4\eta^2\cos^2\theta' + \sin^2\theta'(9+\eta^2+6\eta\cos 2\varphi')\right]. \tag{8}$$

The frequencies of the nutation singularities in the powder pattern correspond to different relative orientations of the quadrupolar tensor and the coil axis:

$$\begin{aligned}
\delta_{\mathrm{S1}} &= \frac{4\eta^2}{3(3+\eta^2)} \quad \text{for}\,\theta = 0\ (\theta' = 0),\\
\delta_{\mathrm{S2}} &= \frac{(\eta-3)^2}{3(3+\eta^2)} \quad \text{for}\,\theta = \varphi = \frac{\pi}{2}\ \left(\theta' = \varphi' = \frac{\pi}{2}\right),\\
\delta_{\mathrm{S3}} &= \frac{(\eta+3)^2}{3(3+\eta^2)} \quad \text{for}\,\theta = \frac{\pi}{2},\ \left(\theta' = \frac{\pi}{2}, \varphi = \varphi' = 0\right).
\end{aligned} \tag{9}$$

For the singularity $\varphi = 0$ of the 2D-nutation exchange spectrum (3) can be recognized as the parameter representation of an ellipse. The ellipse is characterized by its center $[(\delta_{S1} + \delta_{S3})/2, (\delta_{S1} + \delta_{S3})/2]$ and by its semiaxes

$$a = \frac{\cos\theta_S}{\sqrt{2}}(\delta_{S3} - \delta_{S1}), \qquad b = \frac{\sin\theta_S}{\sqrt{2}}(\delta_{S3} - \delta_{S1}). \tag{10}$$

The ratio b/a of the semi-axes a and b of the ellipse is directly related to the motional jump angle θ_s by

$$\frac{a}{b} = |\mathrm{tg}\,\theta_S|, \tag{11}$$

where a and b are the principal axes of the ellipse, parallel and perpendicular to the diagonal, respectively.

Since the EFG is an irreducible second-rank tensor, the jump angles θ_S and $180° - \theta_S$ cannot be distinguished in the spectrum. The two angles can be discriminated on the basis of the known molecular structure. For the nutation-frequency singularities $\varphi = \pi/2$ and $\theta = \pi/2$ the set of (8) describes two lines. The straight lines start at the singularities of the 2D-nutation exchange spectrum on the diagonal at the point $[\delta_{S2}, \delta_{S2}]$ and extend until they touch the ellipse at points determined by a square with $(\delta_{S3} - \delta_{S1})$ side. The length of the square sides is determined by the distribution of all possible nutation frequencies. Thus, for example, for the $\varphi = \pi/2$ singularity the straight line is determined by

$$\frac{\delta_1 - \delta_{S2}}{\delta_{S2} - \delta_{S1}} = \frac{\delta_2 - \delta_{S2}}{\delta_{S2} - \delta_{S3}\sin^2\theta_S - \delta_{S1}\cos^2\theta_S}. \tag{12}$$

The cross peaks in the 2D-nutation exchange NQR spectrum are widely distributed over all possible nutation frequencies of the powder. The ridge pattern in such a 2D power spectrum consists of straight lines as well as an elliptical feature that contains information on the geometry of the reorientation process. In fact, the form of the ellipse is directly related to the reorientation or 'jump' angle θ_S, which is the angle between the orientations of the unique (z) principal axis (for CCl_2, the C-Cl bond) before and after the reorientation. Figure 8 shows contour plots of the exchange intensities for different θ_S values. The spectrum pattern is very sensitive to the value of asymmetry parameter η, as shown in Figure 8b).

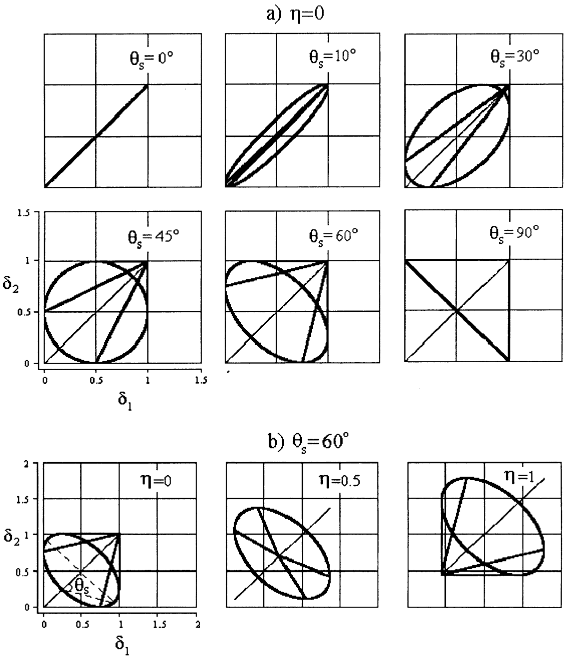

Fig. 8. The relation between the exchange ridges and the jump angle for the CCl_2-group: a) Theoretical ridge spectra of powder singularities for chlorines exchanging between two sites by different jump angles ($\eta = 0$) b) 2D-nutation exchange patterns at fixed jump angle $\theta_S = 60°$ as a function of the asymmetry parameter.

The computer-simulated 2D-nutation exchange NQR powder spectra were obtained by numerical integration of (1) and the total signal height is then described by a weighted average over all crystallite orientations with θ and φ taken with 1°-steps. The analytical expression describing the signal strength of the stimulated echo $G_{SE}(t_w, t'_w)$ in the presence of exchange was derived in our previous paper [6]. It was shown that the cross-peak intensity optimized for maximal signal for the C_2Cl_4 molecule can reach only about 0.09 intensity of the diagonal peak. The intensity of the cross-peaks is intrinsically weak. The relative amplitude of the cross-peaks is much lower than is typical in an NMR experiment. Nevertheless, the exchange pathways are detectable and the intensities follow the theoretical expectation. The calculated 2D-nutation exchange NQR spectrum (power spectrum) for C_2Cl_4 under assumption of $\eta = 0$ and a jump angle $\theta_S = 60°$ is shown in Figure 9. The jump angle θ_S can be read directly from the geometry of the ridge pattern, as shown in Figure 9b).

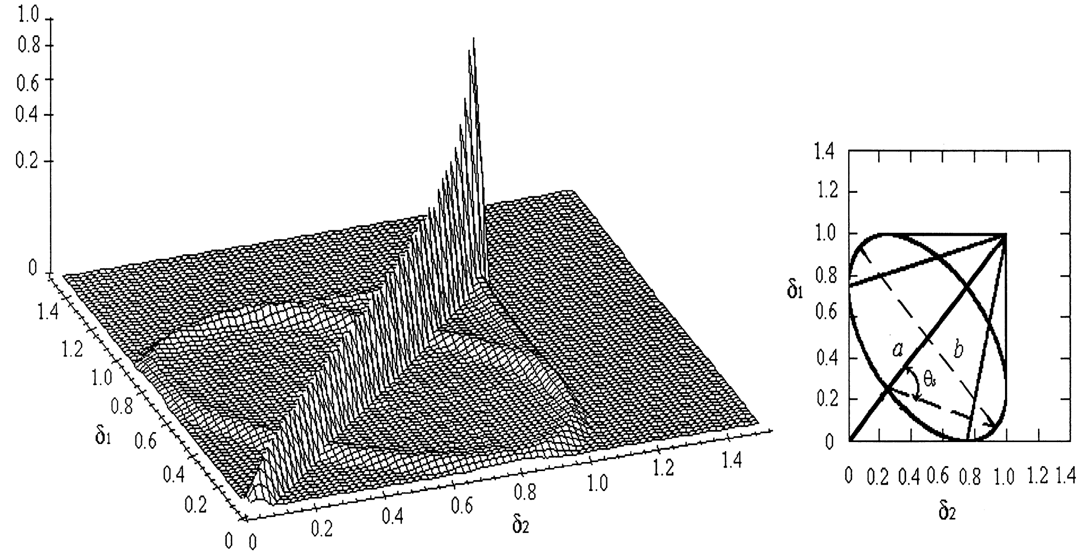

Fig. 9. Calculated 2D-nutation exchange NQR spectra for C_2Cl_4 under the assumption of $\eta_1 = \eta_2 = 0$ and a jump angle $\theta_S = 60°$ (a); calculated ridge patterns (b). The jump angle θ_S can be read directly from the geometry of the ridge pattern.

4. Conclusions

In the present study it has been demonstrated that 2D NQR exchange spectroscopy is appropriate for quantitative studies of exchange processes in molecular crystals containing quadrupole nuclei. The method is of particular value for the detection of exchange networks in systems with many sites. We have shown that the off-resonance irradiation critically influences the spin dynamics. To our knowledge, this is the first time such an approach has been applied to NQR and that such analytical expressions have been given. The mixing dynamics by exchange and the expected cross-peak intensities as a function of the frequency offset have been derived. The results make it possible to plan future experiments on spin-exchange in quadrupolar systems, and we plan to make these the subject of another paper.

It has been demonstrated that two-dimensional nutation exchange NQR spectroscopy is suitable for the direct determination of rotational angles as well as the asymmetry parameter. The characteristic ridges of the spectrum manifest the motional mechanism in a model-independent fashion. The major obstacle of the proposed method is the relatively low intensity of the 2D NQR spectrum. For obtaining 2D nutation exchange spectra, some special experimental requirements have to be fulfilled. High sensitivity and stability of the spectrometer are necessary to achieve sufficient intensities of the cross-peaks in the 2D spectrum.

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