

2D Off-Resonance Nutation NQR Spectroscopy of Spin 3/2 Nuclei*

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The effects of off-resonance irradiation in nutation NQR experiments are demonstrated both experimentally and theoretically. The theoretical description of the off-resonance effects in 2D nutation NQR spectroscopy is given, and general exact formulas for the asymmetry parameter are obtained. It is shown that the outcome of the off-resonance nutation experiments depends on the data acquisition procedure, leading to one- or three-line nutation spectra. To explain this fact and to describe the off-resonance nutation experiment properly, the transient response theory of a quadrupolar spin system to an RF pulse was modified using the wave-function approach. The 2D separation of interactions technique has been applied to separate a static and a randomly time-fluctuating dynamic part of the quadrupole interaction in the antiferroelectric phase of polycrystalline ammonium dihydrogen arsenate.

Two-dimensional off-resonance nutation NQR spectroscopy has been used to determine the full quadrupolar tensor of spin-3/2 nuclei in several molecular crystals containing the ^{35}Cl and ^{75}As nuclei. The off-resonance phenomena in 2D NQR are very important from the practical point of view (determination of η in multiple or broad-line spectrum) and also provide interesting information on the dynamic properties of a quadrupolar spin system.

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

1. Introduction

Two-dimensional nutation NQR spectroscopy allows the determination of the complete set of principal values of the electric field gradient (EFG) tensor at spin-3/2 nuclei in powdered samples without Zeeman perturbation [1, 2]. The 2D-nutation method exploits the fact that the nutation frequency depends on the relative orientation of the RF field vector and the principal axes of the EFG tensor [3]. This method has been originally developed for the conditions that apply to narrow-line solids with an on-resonance irradiation. It correctly describes the cases where the nutation frequency is much larger than the NQR absorption linewidth and the irradiation is exactly on-resonance. In broad-line solids, these conditions are not fulfilled, and consequently the nutation frequency changes over the NQR lineshape with the irradiation

offset [4]. The nutation lineshape varies with offset over the NQR spectrum in a complicated way. The rather simple nutation lineshapes, which can be used for the asymmetry parameter (η) determination, are obtained only in the on-resonance irradiated parts of the NQR spectrum. But very often the observed NQR spectra consist of some closely spaced lines (e. g. due to chemical inequivalence of quadrupolar nuclei); therefore one cannot fulfill the on-resonance condition for all the lines at a time and determine η for each line in a single experiment, where all the lines are excited simultaneously.

The off-resonance phenomena in 2D NQR are very important from the practical point of view (determination of asymmetry parameters in multiple or broad-line spectra) and provide interesting information on dynamic properties of a quadrupolar spin system. An important consequence of off-resonance irradiation is that the modulation of the observed free induction decay changes from amplitude modulation into phase modulation. In this paper we have shown that the outcome of the off-resonance nutation experiments depends on the data acquisition procedure, leading to the one- or three-line nutation spectra. To explain

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this fact and to describe the off-resonance nutation experiment properly, the transient response theory of a quadrupolar spin system to an RF pulse was modified using the wave-function approach. Unlike the earlier theory, where the wave-function coefficients were used in the interaction representation, we write these coefficients in the laboratory frame of reference to obtain an agreement with the experimental results.

The effects of off-resonance irradiation in nutation experiments are demonstrated both experimentally and theoretically. It is shown that off-resonance nutation spectroscopy is a useful extension of the conventional on-resonance experiments, thus facilitating the determination of the quadrupole coupling constant and the asymmetry parameter in multiple spectrum in a single experiment on powder samples. The theoretical description of the off-resonance effects in 2D nutation NQR spectroscopy is given, and general exact formulas for the asymmetry parameter are obtained.

The two-dimensional spin-echo NQR method has been applied for the determination the EFG tensor at the ^{75}As site in the antiferroelectric phase of polycrystalline ammonium dihydrogen arsenate (ADA) where the conventional nutation spectroscopy is useless due to the large NQR linewidth. The 2D separation of the interactions technique has been applied to separate a static and a randomly time-fluctuating dynamic part of the quadrupole interaction [5]. The 2D spectrum displays in the ω_2 -domain the inhomogeneously broadened lineshape which is a convolution of the inhomogeneous static frequency distribution function and the homogeneous lineshape. The ω_1 -domain shows the pure homogeneous lineshape. In such a broad-line crystal the nutation lineshape is considerably distorted by the off-resonance effects. The nutation frequency changes over the NQR lineshape with the irradiation offset.

Two-dimensional off-resonance nutation NQR spectroscopy has been used to determine the full quadrupolar tensor of spin-3/2 nuclei in several molecular crystals containing the ^{35}Cl and ^{75}As nuclei. The unique results obtained by 2D NQR techniques (not available by the conventional 1D NQR spectroscopy) will be discussed.

2. Off-resonance Effects in 2D Nutation NQR Spectroscopy

The response of a system of nuclear spins $I = 3/2$ experiencing electric quadrupole couplings in a zero

externally applied field to a radio-frequency pulse of length t_w was examined using time-dependent perturbation theory [3]. Before considering our experimental results in detail, at this step we must notify that a specific error was made in theoretical calculations published in the paper of Pratt et al. [3]: the expectation values of the operator $\langle I_q \rangle$ were defined in the laboratory frame of reference, but the wave-function expansion coefficients $c_i(t_w)$ were calculated from the Schrodinger equation for the time interval $0 < t < t_w$, where a time-dependent Hamiltonian was defined in a frame rotating with the nuclear quadrupole frequency ω_0 . Therefore, the calculated coefficients $c_i(t_w)$ should be multiplied by the factor $\exp(i\omega_i t_w)$ to transform them to the laboratory frame. Then (11) in Pratt's paper [3] takes the form

$$\begin{aligned} \langle I_q \rangle &= \sum_{i,j} [\overline{c_i(t_w) \exp(i\omega_i t_w)}]^* [c_j(t_w) \exp(i\omega_j t_w)] \\ &\quad \cdot \langle i | I_q | j \rangle \exp[-i(\omega_i - \omega_j)(t - t_w)] \\ &= \sum_{i,j} [\overline{c_i(t_w)}]^* [c_j(t_w) \langle i | I_q | j \rangle \exp[-i(\omega_i - \omega_j)t], \end{aligned} \quad (1)$$

which leads to the following expression for the NQR signal, as required by experimental results:

$$G(t, t_w) = A(t_w) \sin[\omega_0 t + \beta(t_w)], \quad (2)$$

were

$$\begin{aligned} A(t_w) &= \frac{\omega_R}{4\xi^2} R^2(\theta, \varphi) \sin \xi t_w \\ &\quad \cdot \sqrt{4\xi^2 \cos^2 \xi t_w + \Delta\omega^2 \sin^2 \xi t_w}. \end{aligned} \quad (3)$$

The phase factor $\beta(t_w)$ depends on the evolution time t_w and the frequency offset $\Delta\omega$ as

$$\beta(t_w) = \arccos \frac{u}{\sqrt{u^2 + v^2}} \quad (4a)$$

with

$$u = \cos \xi t_w \cos \Delta\omega t_w + \frac{\Delta\omega}{2\xi} \sin \xi t_w \sin \Delta\omega t_w, \quad (4b)$$

$$v = -\cos \xi t_w \sin \Delta\omega t_w + \frac{\Delta\omega}{2\xi} \sin \xi t_w \cos \Delta\omega t_w. \quad (4c)$$

ξ , m and $R(\theta, \varphi)$ are defined as

$$\xi = \frac{1}{2} \sqrt{4m^2 + \Delta\omega^2}, \quad m = \frac{\omega_R R(\theta, \varphi)}{4\sqrt{3 + \eta^2}}, \quad (5)$$

$$R(\theta, \varphi) = \sqrt{4\eta^2 \cos^2 \theta + \sin^2 \theta (9 + \eta^2 + 6\eta \cos 2\varphi)}.$$

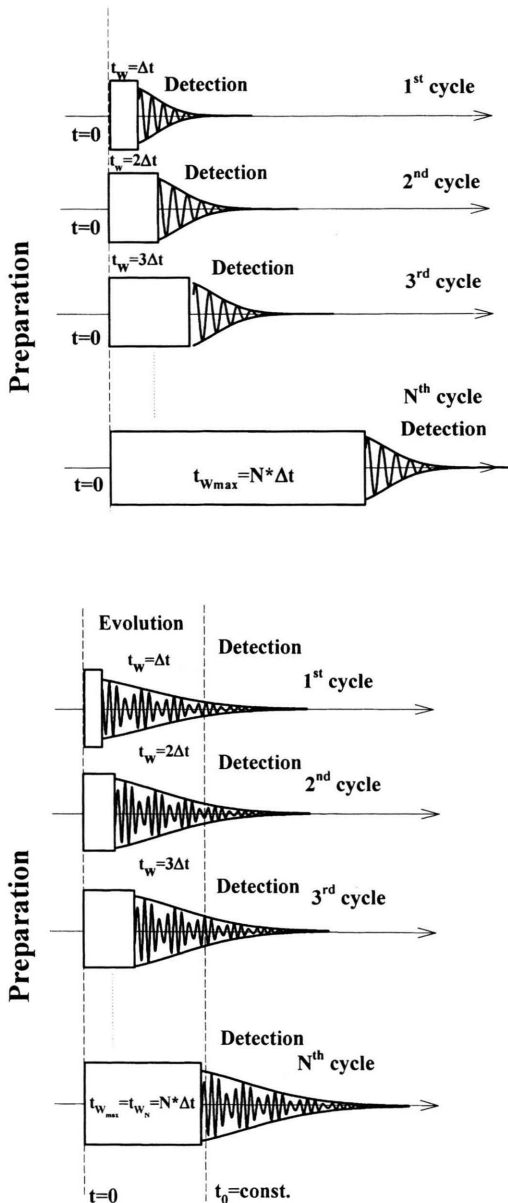


Fig. 1. Different acquisition procedures in 2D nutation experiment. a) the data acquisition is triggered by the end of the RF pulse, b) the data acquisition is triggered by the beginning of the RF pulse with constant delay t_0 .

Here $\Delta\omega = \omega - \omega_0$ is a distance of the RF pulse frequency ω from the NQR frequency ω_0 , $\omega_R = 2\pi\gamma H_1$, θ and φ are polar angles related to the principal axes of the EFG tensor and H_1 is the strength of the RF magnetic field.

The two-dimensional nutation NQR spectrum is obtained from double Fourier transform of (2):

$$S(\omega_2, \omega_1, \theta, \varphi) =$$

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G(t, t_w) \exp(i\omega_2 t) \exp(i\omega_1 t_w) dt dt_w. \quad (6)$$

We have to stress that the uncorrected theory of Pratt [3] leads to false conclusions. Computer simulations published in [6, 4] improperly predict the shape of off-resonance nutation spectra, contrary to experiment.

As follows from (2), an important consequence of off-resonance irradiation is that the modulation of the observed FID changes from amplitude modulation into phase modulation. Moreover, the outcome of off-resonance nutation experiments depends on the data acquisition procedure. The form of the off-resonance 2D-nutation spectrum strongly depends on whether the data acquisition is triggered by the beginning of the RF pulse or its end. Now, let us examine the two cases of NQR data acquisition possible in a pulsed NQR spectrometer.

In the first case (as shown in Fig. 1a) the acquisition of a FID signal starts immediately after the RF pulse is turned off (we neglect the spectrometer dead time for simplicity) and in (2) we have $t = t_w$. Then, after some tedious transformations, the signal induced in the coil is given by

$$G(t_w) = \frac{\omega_R R^2(\theta, \varphi)}{8\xi} \sin(2\xi t_w). \quad (7)$$

Thus, the off-resonance nutation spectrum consists of only one line at the frequency given by

$$\nu_N^{\text{off}} = \frac{\xi}{\pi} = \sqrt{(\nu_N^{\text{on}})^2 + (\Delta\nu)^2}, \quad (8)$$

where ν_N^{on} is the on-resonance nutation frequency and $\Delta\nu$ is the resonance offset. As in case of on-resonance nutation, the asymmetry parameter has a large effect on the evolution of the spin system during the off-resonance RF excitation. After calculation of the two characteristic nutation frequencies corresponding to different crystallite orientations we obtain the following evaluation formula for the asymmetry parameter:

$$\eta = \frac{3 \left[\sqrt{(\nu_3^{\text{off}})^2 - (\Delta\nu)^2} - \sqrt{(\nu_2^{\text{off}})^2 - (\Delta\nu)^2} \right]}{\sqrt{(\nu_3^{\text{off}})^2 - (\Delta\nu)^2} + \sqrt{(\nu_2^{\text{off}})^2 - (\Delta\nu)^2}}. \quad (9)$$

In a powder sample, the characteristic frequencies ν_2 and ν_3 appear as powder pattern singularities [1].

Now let us proceed to the second possible mode of nutation experiment (Fig. 1b), where the acquisition of the FID signal starts at some constant delay t_0 after the RF pulse has been turned on ($t_0 > t_w$). On substitution $t = t_0$, (2) can now be converted to

$$G(t_w) = \frac{R^2(\theta, \varphi)\omega_R}{8\xi} \cdot \left\{ \left[\left(1 + \frac{\Delta\omega}{2\xi}\right) \sin(2\xi - \Delta\omega)t_w + \left(1 - \frac{\Delta\omega}{2\xi}\right) \sin(2\xi + \Delta\omega)t_w + \frac{\Delta\omega}{2\xi} \sin(\Delta\omega t_w) \right] \cos(\Delta\omega t_0) \right. \\ \left. - \left[\left(1 - \frac{\Delta\omega}{2\xi}\right) \cos(2\xi + \Delta\omega)t_w + \left(1 + \frac{\Delta\omega}{2\xi}\right) \cos(2\xi - \Delta\omega)t_w + \frac{\Delta\omega}{2\xi} \cos(\Delta\omega t_w) \right] \sin(\Delta\omega t_0) \right\}. \quad (10)$$

Thus the off-resonance spectrum consists of three-lines. The line at the frequency offset $\Delta\nu$ is independent of the EFG parameters and does not provide any information on the EFG symmetry. The frequencies of two other lines are given by

$$\nu_N^{\text{off}} = \sqrt{(\nu_N^{\text{on}})^2 + (\Delta\nu)^2} \pm \Delta\nu. \quad (11)$$

Thus, the evaluation formula for the asymmetry parameter is of the form

$$\eta = \frac{3 \left[\sqrt{(\nu_3^{\text{off}})^2 \pm 2\nu_3^{\text{off}}\Delta\nu} - \sqrt{(\nu_2^{\text{off}})^2 \pm 2\nu_2^{\text{off}}\Delta\nu} \right]}{\sqrt{(\nu_3^{\text{off}})^2 \pm 2\nu_3^{\text{off}}\Delta\nu} + \sqrt{(\nu_2^{\text{off}})^2 \pm 2\nu_2^{\text{off}}\Delta\nu}}. \quad (12)$$

Let us define the relative decrease of spectral resolution of the off-resonance nutation NQR spectrum by

$$r[\%] = 100 \left(1 - \frac{\nu_3^{\text{off}} - \nu_2^{\text{off}}}{\nu_3^{\text{on}} - \nu_2^{\text{on}}} \right), \quad (13)$$

where $\nu_{2,3}^{\text{on}} = (1/2)\omega_R(3 \pm \eta)/(2\sqrt{3 + \eta^2})$ and $\nu_{2,3}^{\text{off}} = \sqrt{(\nu_{2,3}^{\text{on}})^2 + (\Delta\nu)^2}$ refer to the characteristic nutation frequencies observed in on-resonance and off-resonance experiments, respectively. For a moderate frequency offset, $\Delta\nu = 10$ kHz, the resolution is decreased by less than 10%. However for a frequency offset as high as 100 kHz the nutation spectrum resolution will be decreased by the rather unacceptable value of 80% [7].

Figure 2 shows the outcome of off-resonance nutation experiments using different acquisition procedures. As predicted by the theory, one-line or three-lines off-resonance nutation spectra are observed with the nutation frequencies given by (8) or (11),

depending on whether the data acquisition is triggered by the end of the RF pulse (Fig. 1a) or its beginning (Figure 1b). In both cases, however, using an appropriate formula it is possible to determine the asymmetry parameter of the EFG tensor.

The ^{35}Cl NQR spectrum of $\text{C}_3\text{N}_3\text{Cl}_3$ (cyanuric chloride) exhibits two lines at $\nu_{\text{NQR}}^{(1)} = 36.772$ MHz and $\nu_{\text{NQR}}^{(2)} = 36.740$ MHz at 77 K. By setting the spectrometer frequency at 36.772 MHz a frequency offset of 32 kHz for the second line is obtained. As predicted by (8), the off-resonance line has a higher overall nutation frequency. The off-resonance nutation spectrum reveals less pronounced structure, which might be expected from (13), which predicts that for the

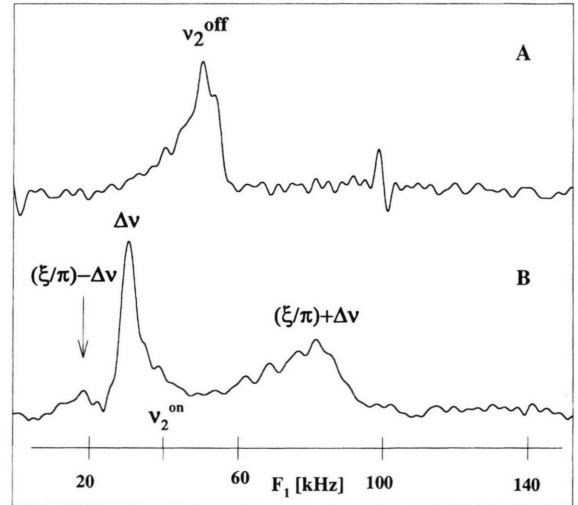


Fig. 2. Effect of different acquisition procedures on the off-resonance nutation spectra in $\text{C}_3\text{N}_3\text{Cl}_3$. The frequency offset is $\Delta\nu = 32$ kHz. a) one-line nutation spectrum with shifted frequency as predicted by (8), b) three-line spectrum with frequency predicted by (11).

frequency offset of 32 kHz the nutation spectrum resolution decreases by about 35 %. Using experimental values of ν_2^{off} and ν_3^{off} , we evaluated the value of the asymmetry parameter in $\text{C}_3\text{N}_3\text{Cl}_3$ from the off-resonance spectrum using (9). The obtained value of 0.222 is identical with that obtained in the on-resonance nutation experiment [8]. Even though the resolution of the off-resonance spectrum decreases with the spectrometer offset, an enhanced resolution can be achieved by using the maximum entropy method (MEM) [9] and an appropriate formula for determination of η .

In inhomogeneously broadened systems the nutation frequency varies for the individual spin packets. In the next section the separation of homogeneous and inhomogeneous interactions is described.

3. Separation of Inhomogeneous and Homogeneous Lineshapes by Two-dimensional Spin-echo NQR Spectroscopy

The 2D separation technique enables a separate spectroscopic observation of a static and a randomly time-fluctuating dynamic part of the quadrupole interaction. The separation is based on the fact that nuclear spin precession under a static quadrupolar Hamiltonian can be time-reversed whereas this can not be achieved under the action of a randomly time-fluctuating Hamiltonian. The 2D spectrum displays in the ω_2 -domain the inhomogeneously broadened lineshape, which is a convolution of the inhomogeneous static frequency distribution function and the homogeneous lineshape. The ω_1 -domain shows the pure homogeneous lineshape. A deconvolution of the inhomogeneous lineshape with the homogeneous one yields a pure static inhomogeneous frequency distribution function that is characteristic for many different models of disordered solids like glasses and incommensurate systems [5].

We have applied the 2D NQR spin-echo technique to study the electric field gradient distribution in polycrystalline samples to draw conclusions concerning the crystal homogeneity and its purity. The 2D spin-echo technique is useful to separate the electric field gradient inhomogeneity associated with imperfections of the crystal lattice, impurities, and internal strains.

In zero field NQR spectroscopy the electric quadrupole interaction is dominant and its static part completely determines the inhomogeneous linewidth.

The homogeneous linewidth is determined by the randomly fluctuating dynamic part of the quadrupole interaction and by the magnetic dipole-dipole interaction that is, however, much weaker and can normally be neglected. The 2D NQR separation technique is suitable for the study of spatially disordered systems as the static and the dynamic disorder are mirrored in the inhomogeneous and homogeneous lineshapes, respectively.

The nuclear spin Hamiltonian in zero magnetic field is determined by the interaction of the nuclear electric quadrupole moment with the local electric field gradient. Due to its electrostatic nature, this interaction is much stronger than the nuclear magnetic dipole-dipole interaction, so we can assume that the Hamiltonian consists only of the quadrupolar term. Thermal motion of the crystal lattice modulates the EFG tensor elements which can be written as a sum of a static part and a time dependent randomly fluctuating part. The quadrupole Hamiltonian can be written as a sum of a static and time dependent term:

$$H_Q = H_Q^0 + \Delta H_Q(t). \quad (14)$$

The motion of the spin system under each term can be studied separately. A two-pulse sequence used in this technique in the notation of 2D spectroscopy consists of three periods (Figure 3). The preparation period consists of a single 90-degree pulse, the evolution period is described by a time variable t_1 and has a refocussing pulse in the middle; the detection period is described by a time variable t_2 (the right half of the spin-echo response which decays with the characteristic time T_2^*). The acquisition of the signal is made in the detection period.

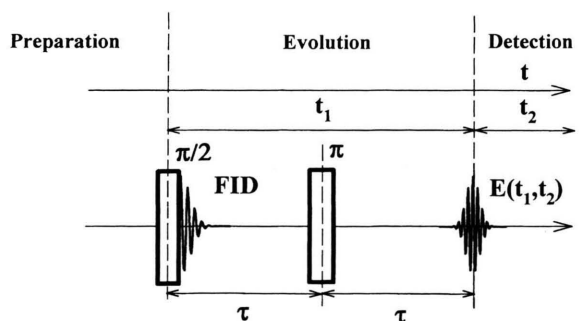


Fig. 3. A two-pulse sequence used in the 2D NQR separation of interactions technique.

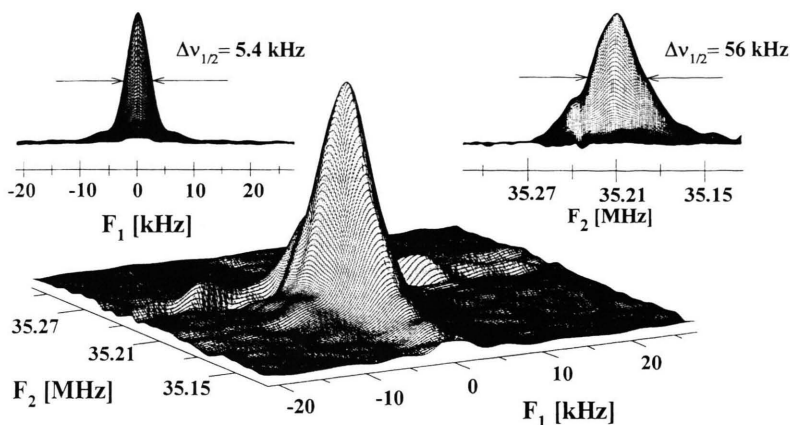


Fig. 4. Two-dimensional ^{75}As NQR separation of inhomogeneous and homogeneous lineshapes in the antiferroelectric phase of $\text{NH}_4\text{H}_2\text{AsO}_4$. The F_2 -domain shows the inhomogeneous lineshape which is a convolution of the static frequency distribution and the homogeneous lineshape. The F_1 -domain shows the homogeneous lineshape only.

The length of the interval t_1 was incremented in a series of the repetition during the experiment. As a result one gets the data set $E(t_1, t_2)$; which is transformed by two-dimensional Fourier transform to give the desired two-dimensional spectra $E(F_1, F_2)$. The line asymmetry in the F_1 and F_2 dimensions is a measure of various factors responsible for transverse relaxation processes in the sample. The half width of this line in the F_1 dimension is inversely proportional to T_2 , whereas in the F_2 dimension the half-width is the reciprocal of T_2^* . Due to relatively long T_2^* times, the spin-echo signal can be distorted for short t_1 intervals by the residual free induction decay (FID). To overcome this serious difficulty, a suitable pulse sequence with alternating phase was used. The phase cycle also eliminates the unwanted signal with the origin at the second pulse, which interferes with the echo. The phase of the pulses was cycled in the following way: $\varphi(90^\circ) = x, -x, x, -x$; $\varphi(180^\circ) = x, y, -x, -y$. The consecutive phases of the FID signals are opposite in this alternating phase experiment and cancelled during the accumulation process, whereas the echo signal is progressively accumulated free of distortion.

In a 2D experiment the inhomogeneous lineshape appears in the ω_2 -domain, whereas the ω_1 -domain displays the homogeneous lineshape, centered around $\omega_1 = 0$. Using the 2D separation technique, the homogeneous lineshape appears as a pure experimental outcome, and it is possible to make a deconvolution of the inhomogeneous lineshape to obtain the pure frequency distribution. The 2D separation experiment in the hydrogen bonded antiferroelectric crystal, ADA, is shown in Figure 4. The 1D NQR lineshape resembles a Gaussian, and the full width at half height of the absorption spectrum is $\Delta\nu_{1/2} = 56 \text{ kHz}$ at 77K.

The ω_2 -domain shows the inhomogeneous lineshape that is a convolution of the static frequency distribution function and the homogeneous lineshape. The latter appears in the ω_1 -domain and is much narrower than the inhomogeneous one. The ratio of the linewidths at 77 K is $(\Delta\nu_{1/2})_{\text{INH}}/(\Delta\nu_{1/2})_{\text{HOM}} = 10$. Since a clear distinction between the static and dynamic disorders can be made with the 2D separation technique, this method might offer valuable contributions to the NQR study of phenomena found in disordered systems where this anisotropy is much higher.

In ordered systems the inhomogeneous broadening is negligible. In a typical molecular crystal like cyanuric chloride our 2D spin-echo experiment gave the ratio $(\Delta\nu_{1/2})_{\text{INH}}/(\Delta\nu_{1/2})_{\text{HOM}} = 1.4$. In ADA, however, the important consequence of the large inhomogeneous broadening is the fact that the nutation frequency is no longer constant over the NQR spectrum, but rather varies for the individual spin packets over the NQR lineshape with the frequency offset.

4. Off-resonance Effects in Inhomogeneously Broadened Nutation Spectra

2D-nutation spectroscopy has been applied for determination the EFG tensor at the ^{75}As site in the antiferroelectric phase of polycrystalline ammonium dihydrogen arsenate (ADA). By determining the asymmetry parameter one can obtain information on the proton arrangement in this class of hydrogen bonded crystals. Due to the large NQR linewidth the conventional nutation spectroscopy is useless and an alternative approach, by introducing a refocussing pulse [2] was used. After the first exciting pulse, we apply

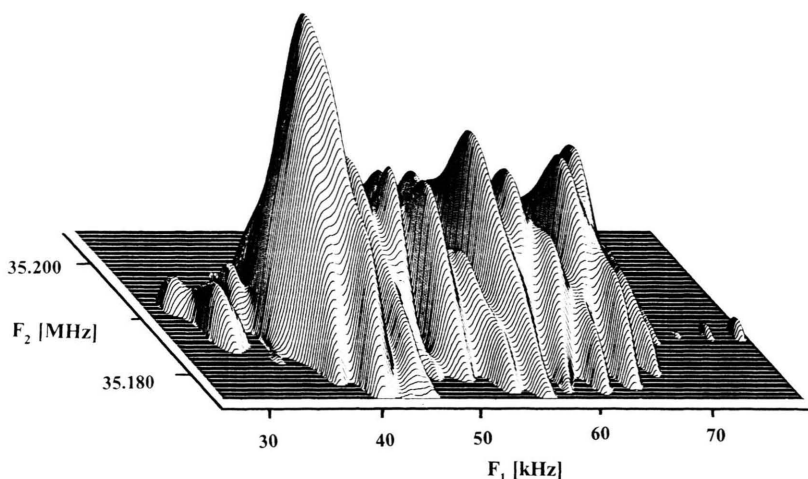
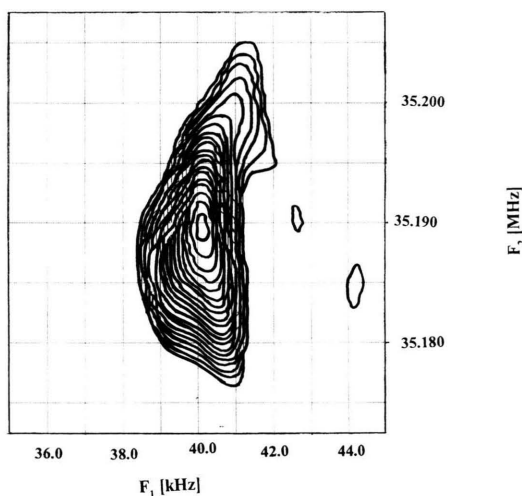


Fig. 5. a) The experimental 2D nutation ^{75}As NQR spectrum in the antiferroelectric phase of polycrystalline ADA at 77 K. b) The top part of the spectrum in Fig. 5a shows more clearly the characteristic curved shape of the contour plots, indicating that irradiation-offset effects are pronounced.



a fixed delay τ , followed by a refocussing pulse denoted by π , which produces a spin-echo after a further period τ . The virtue of this refocussing pulse is that it allows acquisition of nutation spectra from samples with arbitrary inhomogeneous linewidth. Figure 5a shows the 2D spin-echo nutation spectrum obtained as 2D-FT $G(\omega_1, \omega_2)$ of the recorded data set $G(t_1, t_2)$ for ^{75}As in polycrystalline ADA obtained at $\nu_{\text{NQR}} = 35.180$ MHz and 77 K. The nutation spectrum was obtained with a refocussing pulse of 8 μs . Pulse increments of 1 μs were used in the t_1 dimension, 64 transients were accumulated per t_1 value, with a delay

1.5 s between transients, and 273 t_1 values were collected. The delay before the refocussing pulse (τ) was 60 μs . The spectrometer was set on-resonance in the middle of the spectrum. The nutation frequency is thus not constant but rather varies over the lineshape, and this complicates the analysis of the nutation pattern in the 2D spectrum. Characteristic singularities are seen as sharp edges on the low- and high-frequency end of the nutation spectrum. From the positions of the singularities in the MEM spin-echo nutation spectrum we determined the asymmetry parameter $\eta = 1$. This result presents a direct proof that the antiferroelectric proton ordering is correct.

The top part of the spectrum is shown in Fig. 5b, where the characteristic curved shape of the contour plot, indicating that irradiation-offset effects are pronounced, is evident. The fact that the nutation frequency changes with offset, as predicted by (8), must be taken into account in the determination of η . Even though the nutation lineshape is considerably distorted by the off-resonance effects in broad-line solids, the asymmetry parameter can be determined using an appropriate formula (9).

Acknowledgements

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