Nutation Spectra of Nuclear Quadrupole Resonance in Off-Resonance Conditions

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The modes of recording the multidimensional NQR nutation spectra have been analyzed using different off-resonance methods. A method of recording the nutation spectra in off-resonance conditions, based on optimal filtration, has been proposed. For the first time, an experimental spectrum of 3D-^{35}Cl NQR nutation of chloral hydrate is presented.

Key words: 2D Spectroscopy; NQR; Nutation; Exchange:Off-resonance Irradiation.

1. Introduction

Most spectra of NQR nutation for half-integer spins and powdered samples have been obtained at the accurate resonance for $\Delta\omega = 0$. In the 2D exchange NQR nutation spectroscopy [1], several NQR lines coming from different nuclei should be excited at the same time. Hence the experiment should be conducted in off-resonance conditions ($\Delta\omega \neq 0$). When adapting the spectral approach it is possible to assume that in the case of irradiation offset, a step-wise increase in radio frequency (rf) pulse widths in the nutation experiment leads to a narrowing of the spectrum of the exciting pulse and to a decrease in the exciting field B_1 at the nuclei, which significantly distorts the nutation spectrum or even makes it impossible to record it. It is well known that in general, if the interpretation of the effects of the influence of the pulse sequence is totally based on the spectral representation, then the predictions made will be erroneous. The response of a spin nucleus system to the radio frequency of excitation is definitely non-linear, and thus one should be careful when using the spectral model of radio frequency pulses.

2. Theory

To detect the effect of the irradiation offset on the NQR nutation lineshape of a powdered sample in the simplest experiment of one-pulse nutation, we studied a typical case with a 90° pulse of $t_w^{(\mathrm{opt})} = 2.5\ \mu$s, while the pulse duration in the nutation experiment changes from 1 μs to 128 μs at a step of 1 μs (128 points).

For $t_w \gg T_{2\rho}$ and $I = 3/2$ spins and for off-resonance $\Delta\omega \neq 0$, provided that B_1 remains constant in the experiment, the expression describing the signal induction after t_w has the form [2]

$$G(t_w) \sim \frac{m^2}{\alpha\xi} \sin\xi t_w [U \sin\omega_0 t + V \cos\omega_0 t], \quad (1)$$

where

$$U = \cos\xi t_w \cos\Delta\omega t_w + \frac{\Delta\omega}{2\xi} \sin\xi t_w \sin\Delta\omega t_w,$$

$$V = \cos\xi t_w \sin\Delta\omega t_w - \frac{\Delta\omega}{2\xi} \sin\xi t_w \cos\Delta\omega t_w,$$

$$m = \frac{\alpha}{\sqrt{3}\rho} R(\theta,\varphi),$$

$$R(\theta,\varphi) = [4\eta^2 \cos^2\theta + \sin^2\theta(9 + \eta^2 + 6\eta\cos 2\varphi)]^{\frac{1}{2}},$$

$$\alpha = \gamma B_1/4, \quad \xi = \frac{1}{2}\sqrt{4m^2 + \Delta\omega^2}, \quad \rho = \sqrt{1 + \eta^2/3}.$$

Here $\Delta\omega = \omega - \omega_0$ is the distance of an rf pulse frequency ω from NQR frequency ω_0; Θ and ϕ are polar angles related to the principal axes of the EFG tensor, and B_1 is the induction of the rf magnetic field; γ is the magnetogyric ratio and η the asymmetry parameter of the EFG tensor.

At the output of the synchronic detector, the signal (1) may be converted into the form:

$$G(t_w) \sim \frac{m^2}{2\alpha\xi}\left\{-\frac{\Delta\omega}{2\xi}\sin\left[\Delta\omega(t_0-t_w)\right]+\sqrt{\frac{(\Delta\omega)^2}{4\xi^2}\sin^2\left[\Delta\omega(t_0-t_w)\right]+\cos^2\left[\Delta\omega(t_0-t_w)\right]}\cdot\sin(2\xi t_w+\beta)\right\}, \quad (2)$$

where $\mathrm{tg}\beta = \frac{\Delta\omega}{2\xi}\mathrm{tg}\left[\Delta\omega(t_0-t_w)\right]$, and t_0 is the moment of the signal measurement.

As follows from (2), the nutation frequency is equal to $\omega_n = 2\xi$, and in general the nutation spectrum of a powdered sample contains not only a nutation line but also a narrow line at the zero frequency, whose intensity increases with increasing irradiation offset. It has to be noted that the nutation line with "zero" frequency appears only in the imaginary part of the complex signal recorded by a spectrometer. If the time of the signal measurement fulfills the condition $t_0 = t_w + \frac{n\pi}{\Delta\omega}$, where $n = 0,1,2,3\ldots$, then such a line at zero frequency does not appear in the complex signal. It can be concluded from the above that to delete the "zero" line it is enough to select an appropriate slice of the cross-section of the 2D NQR nutation spectrum or use only the real part of the nutation interferogram.

Figure 1 shows the dependence of the 1D-nutation NQR spectrum of a powdered sample on the degree of irradiation offset in the traditional experiment with one-pulse for $I = 3/2$, $\eta = 0.2$, $t_w = 1 \div 128$ μs and for signal measurement at $t_0 = t_w$.

The width of each component of the nutation spectrum was assumed as equal to 3 kHz. NQR nutation spectra for different degrees of detuning were obtained by averaging (2) for a powdered sample and Fourier

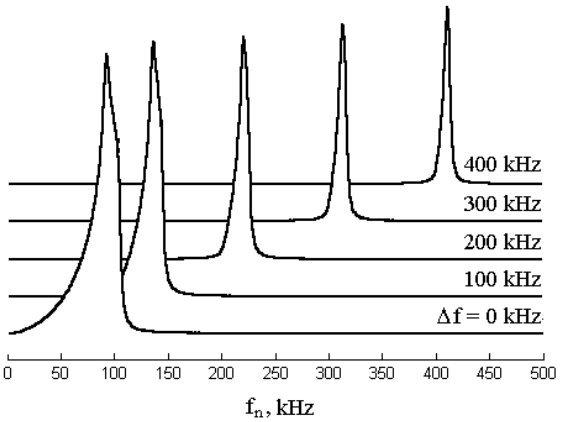

Fig. 1. Dependence on the irradiation offset Δf of the Fourier transformed NQR nutation spectrum.

transformation for variable t_w. With increasing irradiation offset, the nutation line has no longer its characteristic form, the spectral singularities of f_{n2} and f_{n3} can no longer be detected, and the relative frequency bandwidth of a powdered sample nutation on the frequency axis decreases. In the 2D-exchange nutation spectrum this decrease also leads to a diminishing of the range of the observed frequencies and may hinder the detection of exchange singularities. The intensity of the line also decreases with increasing detuning (Fig. 8a), but not to such a degree as it could be expected from the dependence $B_1 = B_{10}\frac{\sin\Delta\omega t_w/2}{\Delta\omega t_w/2}$ on the basis of spectral analysis.

To avoid the nutation frequency offset on the frequency axis and a decrease in the area occupied by the powdered sample nutation frequencies, it is possible to neglect the Fourier transformation and obtain a nutation spectrum using an optimal method of signal filtration from a nutation interferogram. The signal averaged for a powdered sample may be presented in the form

$$\bar{G}(t_w) = \sum_i C_i G(t_w, R_i), \quad (3)$$

where $G(t_w,R_i) = \sum\limits_{\theta_i,\varphi} G(t_w,\theta_i,\varphi_i)\sin\theta_i$ and only those angles are summed up which contribute to the i-th frequency of a powdered sample nutation spectrum. C_i are weighted coefficients. The value of $R_i = \left[4\eta^2\cos^2\theta_i + \sin^2\theta_i(9+\eta^2+6\eta\cos 2\varphi_i)\right]^{1/2}$ indicates the area of the nutation frequency without taking into account a frequency offset caused by detuning.

As follows from the theory of synchronized filtration, the transfer factor of an optimal filter is a complex function of the signal spectrum. The transient characteristics of an optimal filter used for selection of the i-th component of the experimental signal of a powdered sample nutation spectrum (3), have the form

$$H_i(t_w) = AG(t_0 - t_w, R_i), \quad (4)$$

where $A =$ const, $t_0 =$ the signal duration. A signal from the filter output may be found as the convolution

$$S_i(t_w) = \bar{G}(t_w) \otimes H_i(t_w). \quad (5)$$

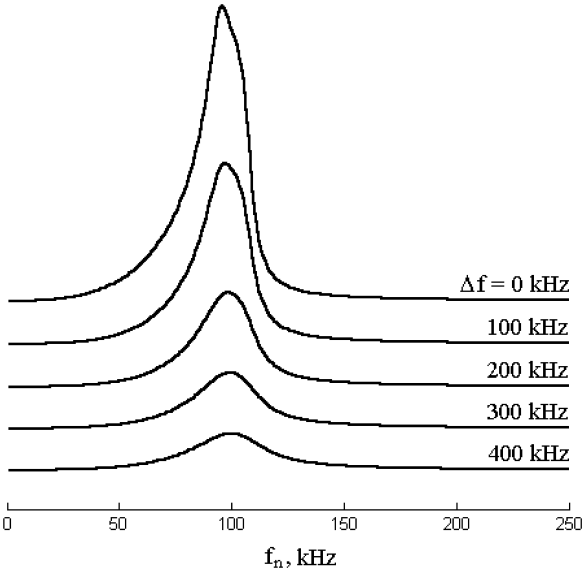

Fig. 2. Dependence on the detuning df of the NQR nutation spectrum obtained via a synchronized filtration method.

The peak value of the output signal is $S_i(t_0)$, which yields for all *i*-th components a complete (energy) spectrum. To perform a synchronized filtration of a complex signal, the output signal (the real part) and the pulse characteristics of the optimal filter are presented in a complex form using the Hilbert transformation.

In this way we have obtained NQR nutation spectra for $I = 3/2$ and $\eta = 0.2$, dependent on the irradiation offset in the form shown in Figure 2. A Henning window was used to eliminate distortions of the base line. In this case the dependence of the signal intensity on the detuning value (Fig. 8b) is stronger than in case of the traditional method. As can be seen on the spectrograms, the nutation frequency range is not getting smaller, nor does it shift with increasing detuning. Besides, the decrease in the signal intensity caused by non-homogeneous frequency characteristics of the filter is not so pronounced as the weakening of the output noise. As a result, the signal to noise ratio will increase at the output of the optimal filter, which is a great asset of the spectral method.

In the spectral approach, the narrowing of the radio frequency spectrum of a pulse, accompanied by an increase in the duration of the pulse t_w can be assumed not to lead to excitation of NQR lines in off-resonance conditions. However, a decrease in the increment (and consequently the duration applied) of the pulse t_w prevents recording of the whole nutation interferogram and significantly reduces the quality of the nutation spectrum. To record the 2D exchange NQR nutation spectra [1], at least two nuclei participating in the exchange process must be excited at the same time. For instance, for chloral hydrate [3] the two closest ^{35}Cl NQR frequencies at 300 K are 38750 and 38664 kHz (the distance between the lines is 86 kHz). Even if the frequency of the spectrometer is found in the middle between the lines (38707 kHz) then the detuning value is $\delta f = 43$ kHz. In view of the above effect it can be concluded that, applying the standard method of obtaining nutation spectra, the 2D exchange NQR nutation spectrum cannot be detected.

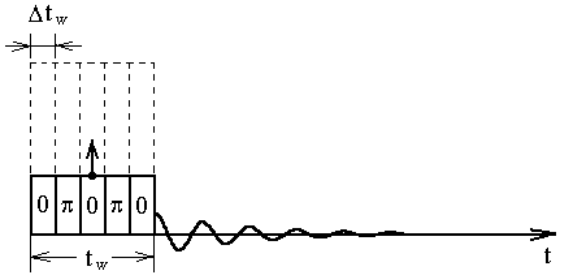

Fig. 3. Radio-frequency pulse with incremented amplitude and coherent phase alternation (PAEP [4]).

Consequently, the only logical solution is to carry out another nutation experiment. Nutation spectra can be obtained by using a complex pulse of a given duration and a coherent phase alternation (phase alternated experimental pulse = PAEP [4]) and by incrementing the amplitude of the irradiation frequency pulse (Figure 3).

In the case of chloral hydrate described above, the pulse carrier frequency is $f_0 = 38707$ kHz, and the durations of component pulses $\Delta t_w = 1/2\delta f = 11.6$ μs. If the complex pulse contains five such pulses Δt_w (the total pulse duration $t_w = 58$ μs), then the width of each of the frequency pulses is $1/t_w = 17$ kHz. The power spectrum of such a PAEP pulse is shown in Figure 4.

It can be assumed that during this nutation experiment both nuclei are excited in resonance and the spectrum of the exciting pulse remains the same throughout the experiment. Every modern spectrometer is equipped with a B_1 field incrementation program. The change in the amplitude of the radio frequency field, i.e. the nutation frequency of the nuclear magnetization $\omega_r = \gamma B_1$, the signal recording $G(\omega_r)$ and the obtaining of the magnetization components of the function $S(t_n)$ of the nutation time after the Fourier transformation are the reverse to those in standard spectroscopy.

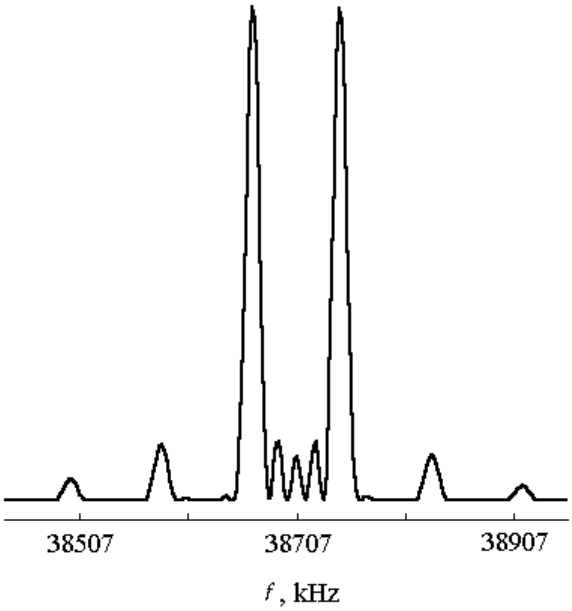

Fig. 4. Power spectrum of the PAEP pulse shown in Figure 3.

However, things are not so simple in reality. As follows from the calculations, in this case the signal, as before, will be defined by (1) in accordance with [5], yet

$$U = \cos\xi t_w \cos\Delta\omega\Delta t_w + \frac{\Delta\omega}{2\xi}\sin\xi t_w \sin\Delta\omega\Delta t_w,$$

$$V = \cos\xi t_w \sin\Delta\omega\Delta t_w - \frac{\Delta\omega}{2\xi}\sin\xi t_w \cos\Delta\omega\Delta t_w,$$

where $t_w = n\Delta t_w$ with $n =$ the number of constituent pulses. Therefore the expression for the nutation frequency remains the same, $\omega_n = 2\xi = \sqrt{4m^2 + \Delta\omega^2}$, i.e. it is dependent on the irradiation offset. For $\Delta f = 0$ the results of the changes in the pulse duration t_w and in the amplitude of the radio frequency of the B_1 field are identical. In the off-resonance conditions a change in the B_1 field induces a frequency modulation of the nutation signal which, after the Fourier transformation, gives a spectrum difficult to interprete. Figure 5 shows the interferogram of such a signal $G(B_1)$, averaged for a powdered sample, with the detuning $\Delta f = 43$ kHz and its Fourier transformation.

The spectrogram in Fig. 6 presents the change in the nutation frequency as a function of B_1 for $\Delta f =$ 100 kHz and $\eta = 0.2$. In fact, the change in B_1 is equivalent to a frequency change $\omega_{rf} = \gamma B_1$. Therefore, after Fourier transformation, a function of t_n, equivalent to the nutation time, is obtained as illustrated in Figure 6. Further on the term "spectrum" will be used.

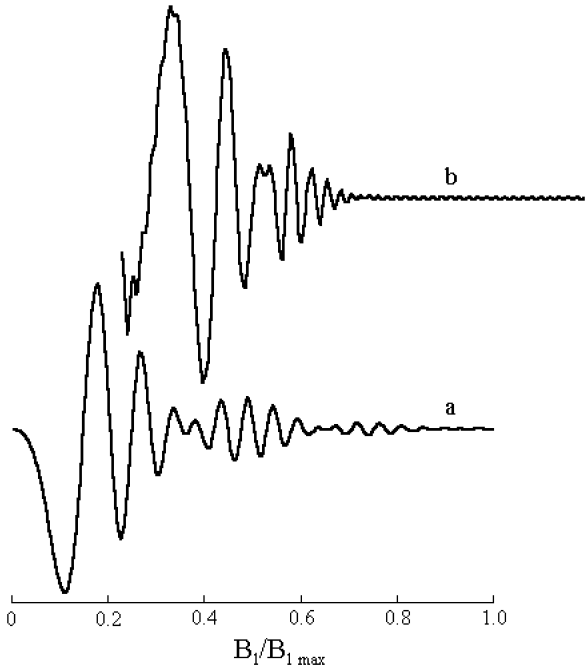

Fig. 5. Interferogram of a $G(B_1)$ signal (a) and its Fourier transformation (b).

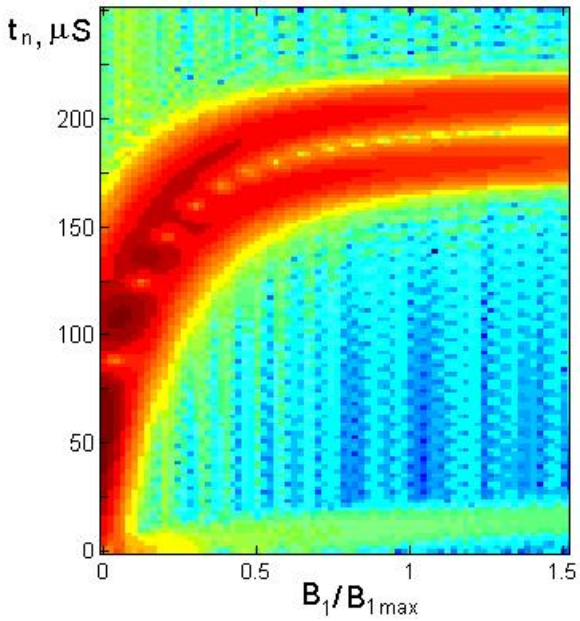

Fig. 6. Nutation spectrogram at change of the B_1 field.

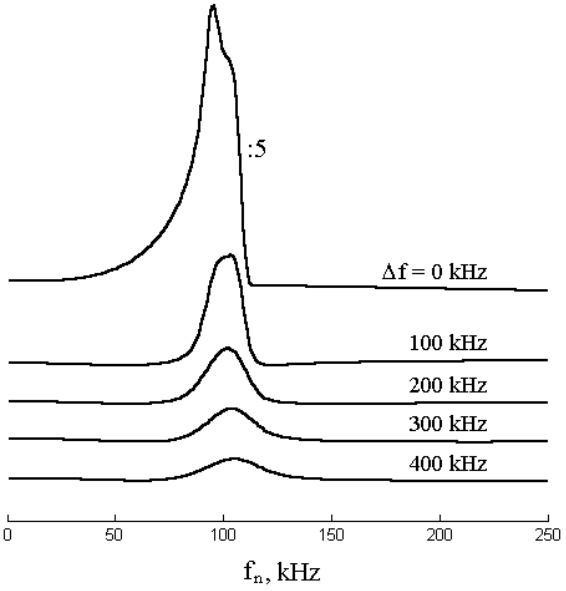

Fig. 7. Dependence on the frequency detuning Δf of an NQR nutation spectrum, recorded with changing radio frequency field f_n.

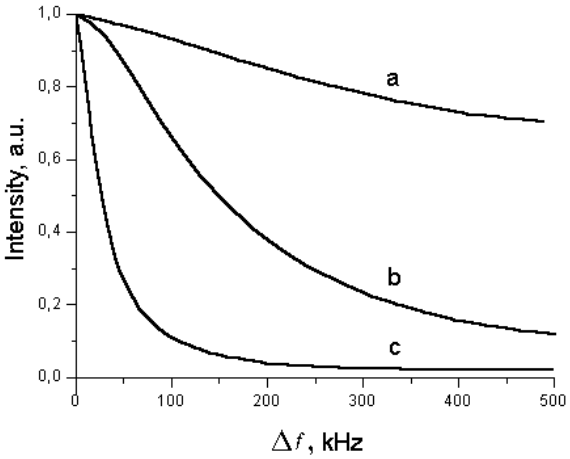

Fig. 8. Decrease in the intensity of the nutation spectrum with increasing detuning Δf: a) traditional method, b) traditional method involving synchronized filtration, c) a method involving change of the r.f. field and synchronized filtration.

To obtain the nutation spectrum on changing B_1, the method of optimal filtration described above was used. For this case ($I = 3/2$, $\eta = 0.2$) the dependence on the frequency detuning Δf of the nutation spectra is shown in Figure 7. The signal intensity rapidly decreases with increasing Δf. This can be explained by the fact that the amplitude of the signal (1) depends not only on the detuning but also on the value of the radio

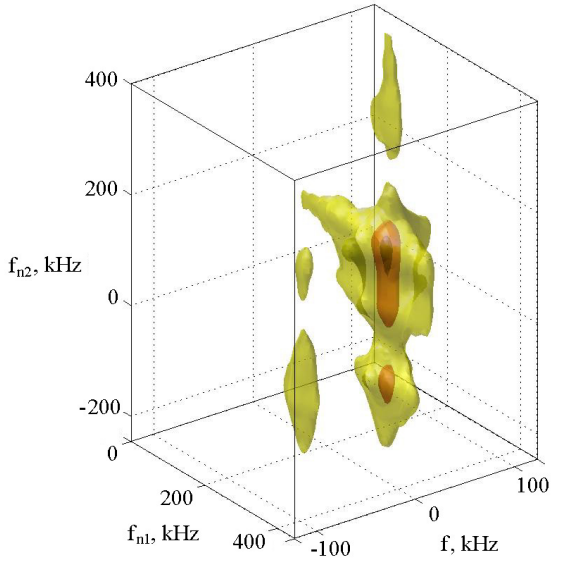

Fig. 9. 3D-NQR nutation spectrum of ^{35}Cl nuclei in chloral hydrate at 300 K.

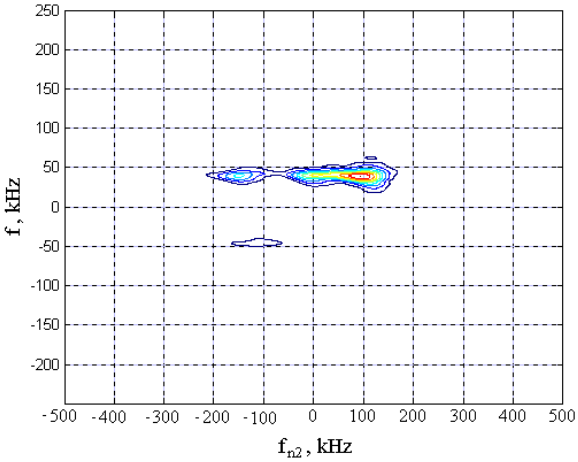

Fig. 10. 2D-nutation spectrum in f, f_{n2} coordinates.

frequency B_1. With increasing detuning the amplitude decreases the faster, the smaller the field B_1. In Fig. 8 the dependencies of the nutation signal intensities on the frequency of detuning Δf for the discussed methods are compared. It follows from the comparison that the method involving a change in the value of the radio frequency field in off-resonance NQR nutation spectroscopy is not attractive in the form described above.

3. Experimental

Experimental studies of nutation in off-resonance conditions were performed using a chloral hydrate

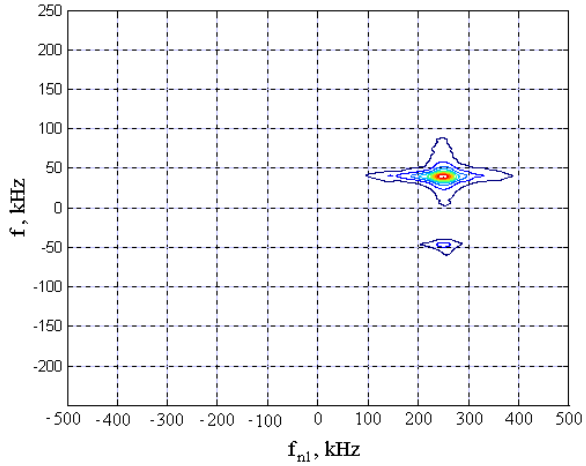

Fig. 11. 2D-nutation spectrum in f, f_{n1} coordinates.

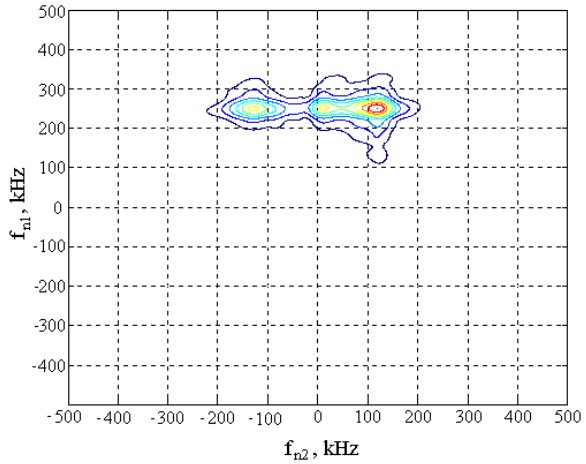

Fig. 12. 2D-nutation spectrum in f_{n1}, f_{n2} coordinates.

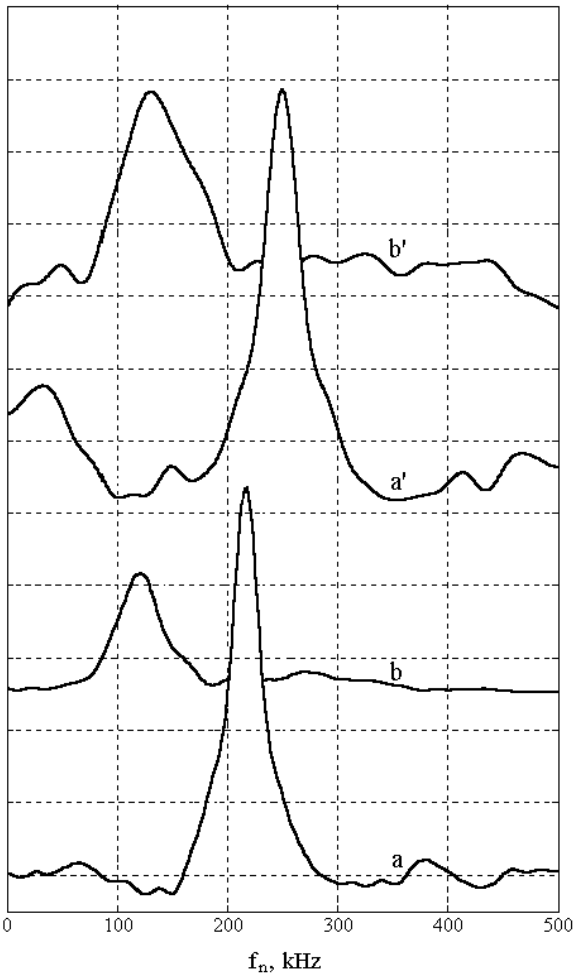

Fig. 13. 1D-nutation spectrum in the coordinates a) f_{n1} and b) f_{n2}.

powdered sample. Figure 9 shows a ^{35}Cl 3D nutation NQR spectrum of $CCl_3CH(OH)_2$ recorded at $T =$ 300 K. In the studies a three-pulse sequence of stimulated echo was used with a given interval between the first and second pulse ($t_1 = 10-30$ μs) and between the second and third interval ($\tau_m = 1-3$ ms). The durations of the first two pulses t_w in the experiment were identical; while the duration of the third pulse (t'_w) changed independently of the duration changes t_w at an increment of 0.5 μs. The number of measurement points with different t_w and t'_w was $32 \cdot 32$. A signal following the third pulse was measured at 256 points with 1 µs interval. As a result, the interferogram $G(t, t_w, t'_w)$ was represented by a data matrix $256 \cdot 32 \cdot 32$. The spectrometer frequency 38.707 MHz was taken between the NQR frequencies $f_2 = 38.664$ MHz and $f_3 = 38.750$ MHz. Chemically pure (99.5%) polycrystalline chloral hydrate was used as sample. The spectra were obtained using a digital NMR Bruker spectrometer DSX 200 equipped with a special NQR probehead. The sample temperature was measured and controlled by a Bruker variable temperature unit B-VT 1000. The standard UXNMR and PV-Wave software was used for the data analysis. For the 3D NQR nutation experiments, two pulse sequences *noesytp* were applied (2D homonuclear correlation NMR spectroscopy via dipolar coupling using a time proportional phase increment – TPPI) modified as described above. The typical duration of a $\pi/2$ pulse for the optimum ^{35}Cl signal excitation was 2.2 μs. The repetition time of the pulse sequence was 15 ms. For the 3D-

measurements, 1024 accumulations at each point were taken.

The 3D-nutation spectrum (absolute values), shown in Fig. 9, has the form of three half-transparent isosurfaces at the level of 0.1, 0.5, and 0.8, respectively. Figures 10 – 13 show the corresponding 2D and 1D-nutation spectra. The asymmetry parameter at ^{35}Cl nuclei in chloral hydrate is $\eta \approx 0$. Thus the nutation spectrum is clear with one nutation frequency singularity f_n.

As can be inferred from the expression for the stimulated-echo sequence [6], for a "zero-frequency" detuning $\Delta f = 0$, the 2D-nutation spectrum will show two lines at the frequencies 0 and $2f_n$ at one nutation frequency and f_n at the other. In the off-resonance conditions, $\Delta f \neq 0$, the spectrum would be much more complex. In the obtained 3D-nutation spectrum there are only the two well visible nutation frequencies f_n and $2f_n$, besides the zero-frequency and the "mirror" signals. By using the synchronized filtration method it is possible to prevent any effect of frequency offset on the detuning value Δf (when compared with Fourier transformation) (Fig. 13a' and b'), and to improve the signal/noise ratio.

4. Conclusions

Results of the present study demonstrate that the proposed method is appropriate for obtaining multidimensional exchange spectra of molecular crystals in powdered samples and for studying their molecular structure and dynamics.

Acknowledgements

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