Two-dimensional Exchange ^{35}Cl NQR Spectroscopy of Chloral Hydrate

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Two-dimensional exchange ^{35}Cl NQR spectroscopy has been applied for studies of the CCl_3-group reorientation processes in chloral hydrate. The experimental results are interpreted on the basis of the 2D-exchange NQR theory, which takes into account the off-resonance irradiation. The pulse-optimisation procedure, which is required by this theory, enabled the detection of the 2D-exchange NQR spectrum and was applied to the quantitative study of the exchange processes in chloral hydrate. A temperature dependent study of the exchange rate revealed two different activation processes in the temperature ranges from 240 to 295 K and from 295 to 310 K, respectively.

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

1. Introduction

Molecular dynamics can be studied by conventional NQR spectroscopy 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 one-dimensional NQR spectroscopy is 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 introduction of the two-dimensional (2D) techniques. 2D exchange NMR spectroscopy was first suggested by Jeener et al. [1]. 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. The term “exchange” implies molecular rearrangements such as rotational jumps, provided that for NQR these motions are accompanied by NQR frequency shifts, i. e. by different electric field gradients.

A rotating molecule or group in a solid usually 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. The direction of quantization changes jumpwise during the exchange process. Moreover, the NQR spectrum is usually spread over several hundred kHz. Thus the NQR lines are excited in off-resonance conditions. As shown in our earlier paper [2], the off-resonance irradiation critically influences the behaviour of the exchanging spin system. This is why the progress in multidimensional NQR has been hampered by experimental and conceptual difficulties. To our knowledge, only two attempts to use the pulse sequence of Jeener for NQR-exchange studies exist in the literature [3, 4].

To explain many unsuccessful attempts we developed a theory, in which the mixing dynamics by exchange and the expected cross-peak intensities are derived as a function of the frequency offset [2]. The theory was illustrated by a study of the optimisation procedure, which is of crucial importance for the detection of the cross- and diagonal-peaks in a 2D-exchange spectrum. We have shown that the harmful off-resonance effects can be compensated for by using short pulses (about 2 μs). The application of this optimisation procedure allows us to obtain 2D-exchange

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spectra in chloral hydrate, which is a subject of the present paper.

2. Experimental

2D exchange ^{35}Cl NQR experiments were carried out with polycrystalline chloral hydrate, $CCl_3CH(OH)_2$. The sample was purchased from Riedel-de Haen. The purity was specified as "pro analysi" (99.5%). The spectra have been recorded with a digital NMR Bruker spectrometer DSX 200 equipped with a special NQR probehead. The temperature was measured and controlled using the Bruker variable temperature unit B-VT 1000. The standard NMR software UXNMR was used. For the 2D exchange experiments two pulse sequences were applied: *hp2d* equivalent to the 2D four-pulse stimulated-echo sequence corresponding to a cosine modulation of the signal, and *noesytp* equivalent to the 2D homonuclear correlation NMR spectroscopy via dipolar couplings. The typical length of an RF pulse for the optimum ^{35}Cl signal excitation was 2.4 μs. As shown in our earlier paper [2], for such a short pulse the off-resonance effects preventing detection of the cross-peaks were compensated for.

3. Results and Discussion

Chloral hydrate crystallises in the monoclinic structure, space group $P2_1/c$ (with $a = 1.150$ nm, $b = 0.604$ nm, $c = 0.960$ nm and $\beta = 120°$), and its elementary cell contains four molecules [5]. In the *ac* plane OH...O type hydrogen bonds between two oxygen atoms of different molecules were found to occur. These bonds are different in length for two crystallographically non-equivalent hydroxyl groups and their H...O lengths being 0.1908 nm and 0.1933 nm, respectively. NQR investigations [6, 7] have shown that the ^{35}Cl spectrum of this compound consists of three lines with equal intensity. The significant splitting ($\Delta\nu = 1.3$ MHz) in the spectrum is explained by the effect of intramolecular interactions. The frequency is significantly lower than those of the other two. This is interpreted as a consequence of hydrogen bond formation between the O-H group and the chlorine atom [5], where the Cl...H length is 0.2643 nm. As follows from the crystallographic data, this chlorine atom is identified as Cl_1; i. e. the atom which makes a hydrogen bond with an OH group of the neighbouring molecule, and occupies the nearest, and symmetrical, position with respect to two oxygen atoms of the same molecule, i. e. it lies in the symmetry plane made by the bonds C_2-C_1, C_1-Cl_1 and the bisector of the angle O_1-C_2-O_2.

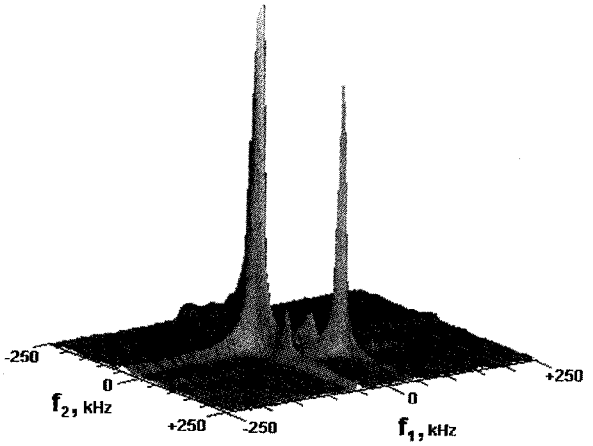

Fig. 1. ^{35}Cl 2D-exchange NQR (magnitude) spectrum of chloral hydrate recorded at 300 K.

At 300 K the NQR frequencies were measured to be $\nu_1 = 37.476$ MHz, $\nu_2 = 38.664$ MHz and $\nu_3 = 38.750$ MHz, and the relaxation time T_1 is 3 ms. With a frequency separation of 86 kHz, both ν_2 and ν_3 lines can be excited simultaneously within the bandwith of conventional RF pulses. An exponential change in the temperature dependence of T_1 above 250 K was interpreted as arising from the hindered rotation of the CCl_3 group [6, 7].

Figure 1 shows the ^{35}Cl 2D exchange NQR magnitude spectrum of chloral hydrate recorded at $T = 300$ K. Cross and diagonal peaks are clearly visible. Without exchange, the 2D spectrum consists solely of diagonal peaks. If exchange takes place at the time scale of the mixing period there are two additional cross-peaks at frequency coordinates corresponding to the sites between which the exchange occurs. The mixing interval was $\tau_m = 3$ ms. The transmitter frequency 38.707 MHz was chosen in the centre frequency between the two NQR resonances at $\nu_2 = 38.664$ MHz and $\nu_3 = 38.750$ MHz. Sometimes it is recommended to choose the transmitter frequency somewhat apart from the centre frequency between the two resonances in order to avoid the coincidence of mirror signals of diagonal peaks and cross-peaks. In our case the mirror signals were avoided by using the *noesytp* pulse program with suitable phase cycling. The evolution period t_1 was incremented in 256 steps. In the t_2 interval 64 data points were taken. The

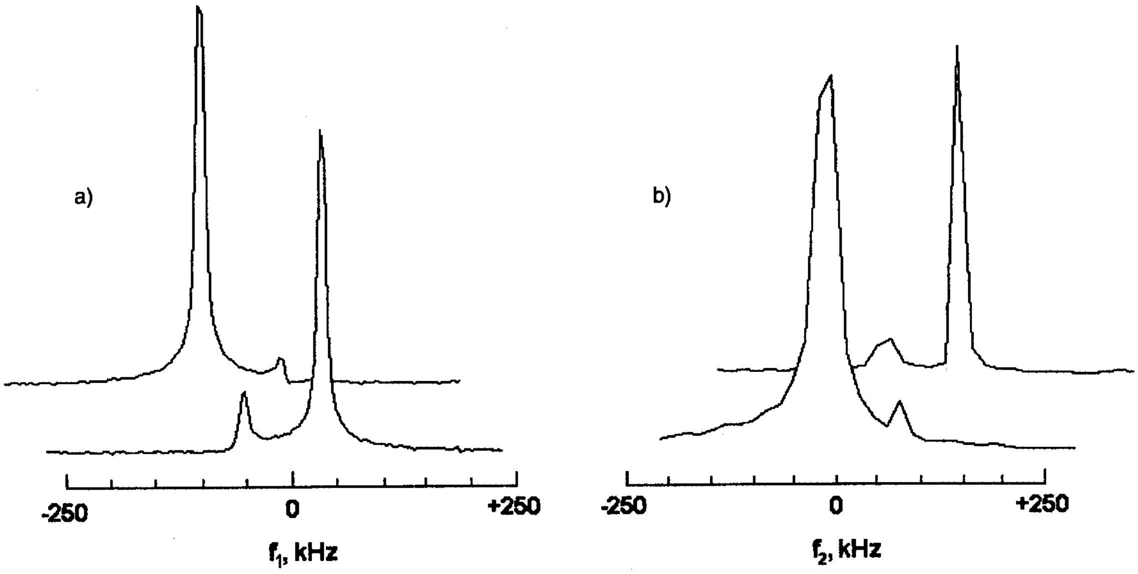

Fig. 2. Cross sectional spectra along the f_1 (a) and f_2 (b) axes for the exchange spectrum of Figure 1.

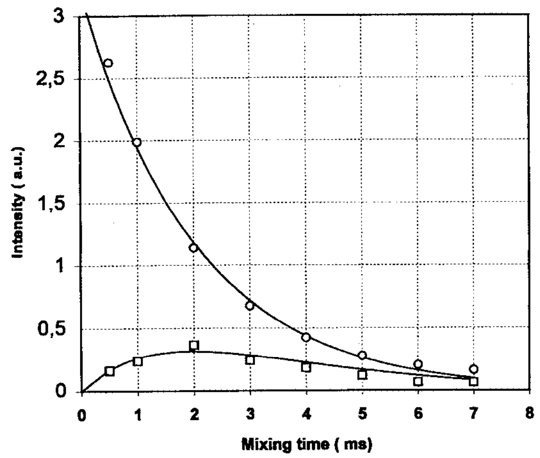

Fig. 3. Intensities I_D (o) and I_C (□) of diagonal and cross-peaks, respectively, of chloral hydrate at 300 K as a function of the mixing time τ_m. The solid lines provide the theoretical dependence calculated for the following model parameters: $k = 250$ s^{-1}, $R = 333$ s^{-1}, $E_a = 14.5$ kcal mol^{-1}, $T = 300$ K, $r = -0.333$, and $\tau_0 = 1.09{*}10^{-13}$ s.

number of accumulations was 32000, the repetition time was 15 ms, and the total time of the experiment was 12 h.

The two cross sectional spectra positioned at the NQR frequencies ν_2 and ν_3 are shown in Figure 2. The sectional spectra at the cross-peak positions are presented in both frequency domains, f_1 and f_2 in Fig. 2(a) and Fig. 2(b), respectively. The spectra demonstrate the large intensity ratio of diagonal peaks (high) and cross-peaks (low). According to the calculation [2], the cross-peak intensities are much lower than those of the diagonal peaks. To avoid the need of extensive phase correction of the broad 2D-spectra, we were analysing the magnitude spectrum. In fact, the cross- and diagonal-peaks have opposite phases, as predicted by theory [2]. We have confirmed this prediction experimentally by careful phasing one of the experimental 2D-exchange spectra (not shown here). Measurements of the cross-peak intensities may be distorted by shoulders and ridges of the diagonal peaks (see Fig. 1). Therefore this harmful contribution must be subtracted in the data analysis to obtain the real values of the cross-peak intensities.

In a series of further experiments, the mixing time was varied. The resulting cross- and diagonal-peak intensities are plotted in Fig. 3 as functions of the mixing time τ_m. As shown in [2], the signal intensities of diagonal- and cross-peaks, obtained for a mixing time τ_m, are described by the mixing coefficients α_{AA} and α_{AB}, respectively. For the exchanging CCl$_3$-group, the mixing coefficient, which describes the intensity of diagonal peaks, is given by

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

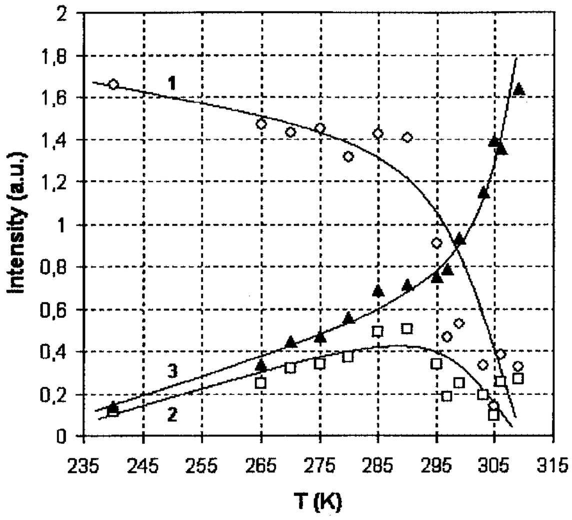

Fig. 4. Temperature dependence of the diagonal signal $I_D/10$ (curve 1) and cross signal I_C (curve 2) intensities of 2D-exchange spectra for chloral hydrate. Curve 3 gives the ratio 20 I_C/I_D. The solid lines are drawn to guide the eye.

For the cross-peaks the mixing coefficient is

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

where k is the average exchange rate, $R = 1/T_1$ is the relaxation rate, and r is a reduction factor taking into account the losses of the spin-polarisation during the reorientational jumps. The value of the reduction factor for the reorienting CCl$_3$-group is $r = -0.333$ [2].

The exchange rate, k, can be expressed by the activation energy, E_a, using the relation

$$k = \tau_0^{-1}\exp\left(-\frac{E_a}{RT}\right), \quad (3)$$

where τ_0 is the extrapolated correlation time. According to Goldman's theory [8] for the reorienting CCl$_3$-group the spin-lattice relaxation time T_1 is related to the correlation time, τ_c, by the simple formula

$$T_1 = \frac{3\tau_c}{4} = \frac{3\tau_0}{4}\exp\left(\frac{E_a}{RT}\right) = \frac{3}{4k}, \quad (4)$$

Thus $R = 4k/3$, and this value was used for fitting the experimental results by (1) and (2). The solid lines in Fig. 3 provide the theoretical dependence calculated for the following model parameters: $k = 250$ s^{-1}, $R = 333$ s^{-1}, $E_a = 14.5$ kcal mol^{-1}, $T = 300$ K, $r = -0.333$, and $\tau_0 = 1.09*10^{-13}$ s. The very good agreement between the experimental results and the theoretical predictions confirms that the motion of the CCl$_3$ group in chloral hydrate is characterized by a three-fold rotational symmetry.

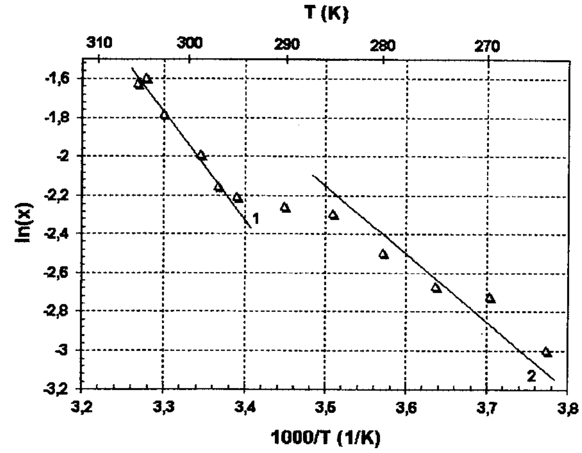

Fig. 5. Temperature dependence of exchange rates in chloral hydrate. The solid lines 1 and 2 are drawn to guide the eye.

In a second series of experiments the temperature was varied. The temperature dependence of the diagonal- and cross-peaks intensities is shown in Figure 4. The measurements were performed in the temperature range 240 - 310 K. Below 240 K the cross-peaks are not visible, because the reorientation is hindered. Above 310 K the NQR spectrum disappears due to the fast rotation of the CCl$_3$ group and shortening of the spin-lattice relaxation time ("fading-out phenomenon"). As follows from (1) and (2), the ratio γ of the mixing coefficients of the cross- and diagonal peaks is given by

$$\gamma = \frac{\alpha_{AB}}{\alpha_{AA}} = \frac{I_C}{I_D} = \frac{2\,\mathrm{sh}(kr\tau_m/2)}{\exp(-kr\tau_m/2) + 2\,\mathrm{ch}(kr\tau_m/2)}. \quad (5)$$

Thus

$$x = kr\tau_m = \ln\frac{1+2I_C/I_D}{1-I_C/I_D}. \quad (6)$$

An activation energy of the exchange process can be determined on assuming an Arrhenius law (see (3)). From the temperature dependence of ln(x) presented in Fig. 5 one can conclude that the activation energy is different in the temperature ranges 240 - 290 K and 290 - 310 K. The results obtained are

E_a = 7.1 kcal mol^{-1} and E_a = 14.5 kcal mol^{-1}, respectively. These values are in accordance with spin-lattice relaxation measurements by Chihara and Nakamura [6] and Kasprzak et al. [7]. This suggests that besides the hindered rotation of the CCl_3 group, activated above 240 K, there is another mechanism of relaxation that is activate above 290 K.

Analysis of the known crystallographic structure of chloral hydrate leads us to the conclusion that this other mechanism is related to an order-disorder transition in which the hydrogen bonds are broken. The energies of hydrogen bonds of the type OH...O, extrapolated on the ground of Newton's results [9] to the lengths H...O = 0.1908 nm and 0.1933 nm, are 7.2 kcal mol^{-1} and 5.8 kcal mol^{-1}, respectively. It seems justified to assume that above 295 K the quadrupole relaxation is a result of the joint influence of correlated rotation of the chloral hydrate molecule as a whole unit and breaking of the hydrogen bonds. This process may be a source of the change in the second moment of the NMR proton line from 12.9 Gs^2 to 7.9 Gs^2 observed above 305 K [10].

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 quadrupolar nuclei. In spite of the fact that the off-resonance irradiation critically influences the spin dynamics, the pulse optimisation procedure allowed us to obtain 2D-exchange spectra. Experimental results for chloral hydrate can be interpreted on the basis of the formalism presented in [2]. The very good agreement of the experimental results with theoretical predictions confirms the validity of the molecular-motion model. 2D-exchange NQR spectroscopy in chloral hydrate has allowed us to measure the activation energy and its temperature dependence. Two different activation processes were detected in the temperature range from 240 to 310 K.

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[1] J. Jeener, B. H. Maier, P. Bachmann, and R. R. Ernst, J. Chem. Phys. **71**, 4546 (1979).
[2] N. Sinyavsky, N. Velikite, and M. Mackowiak, Mol. Phys. **99**, 1653 (2001).
[3] E. Rommel, P. Nickel, F. Rohmer, R. Kimmich, C. Gonzales, and D. Pusiol, Z. Naturforsch. **47a**, 382 (1992).
[4] S. O. Arhunmwunde and G. S. Harbison, XIIIth International Symposium on Nuclear Quadrupole Interactions, Providence, Rhode Island, USA 1995, Abstracts p. 93.
[5] K. Ogawa, Bull. Chem. Soc. Japan **36**, 610 (1963).
[6] H. Chihara and N. Nakamura, Bull. Chem. Soc. Japan **45**, 3530 (1972).
[7] J. Kasprzak, J. Pietrzak, and A. Pietrzak, J. Mol. Struct. **192**, 379 (1989).
[8] M.Goldman, Adv. Magn. Reson. **14**, 59 (1990).
[9] M. D. Newton, Acta Crystallogr. **32**, 116 (1983).
[10] K. Holderna, M. Ostafin, Z. Pajak, and J. Pietrzak, Rep. No. 802/PL, Institute of Nuclear Physics, Cracow 1972, p. 13.