Two-dimensional Exchange Spectroscopy Using Pure NQR *

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Exchange between positions with different resonance frequencies can be studied by two-dimensional spectroscopy originally developed for the NMR case. Cross intensity reflects changes of the resonance frequency due to different line shifts or anisotropic interactions. We now present analogous experiments carried out with pure NQR of polycrystalline samples. The specific requirements are discussed in comparison to 2D exchange NMR spectroscopy. The method has been demonstrated with chloroform and p-chlorobenzotrichloride, where the resonances of the ^{35}Cl nuclei were investigated. Isomeric changes taking place in these compounds reveal themselves as cross-peaks provided the right ranges of the temperature and the mixing time are chosen. The corresponding dependences were recorded and are discussed.

1. Introduction

Molecular dynamics can be studied by pure nuclear quadrupole resonance (NQR) methods based on the measurement of spin-lattice relaxation times, lineshape parameters and the temperature dependence of the resonance frequency. As a more direct method, we now propose two-dimensional (2D) exchange NQR spectroscopy in analogy to the known 2D exchange NMR method in liquids [1] or solids [2, 3].

The technique permits the observation of exchange processes between positions with different NQR frequencies. The term "exchange" must be read in a more general sense because it does not only imply "chemical exchange" of atoms or groups but molecular rearrangements such as rotational jumps as well, provided that these motions are accompanied by NQR frequency shifts, i.e. by different electric field gradients, whatever the physical reason is.

2D exchange spectroscopy in principle directly shows the pattern of resonance frequencies among which exchange processes take place in the time scale of the experiment. It is this additional information which makes 2D experiments so attractive compared with one-dimensional spectroscopy, which can specify only the exchange rates at most, but not the specific pathways.

The radio frequency (RF) pulse sequence for 2D exchange experiments consists of three pulses optimized for maximal signal (Figure 1). The first pulse excites the sample assumed to be in equilibrium. The coherences produced in this way evolve in the τ_1 interval prior to the second RF pulse transferring the transverse magnetization isochromats to the "z" direction in part. The magnitude of these z components depends on the phase distribution achieved at the end of the evolution interval τ_1. It also depends on the

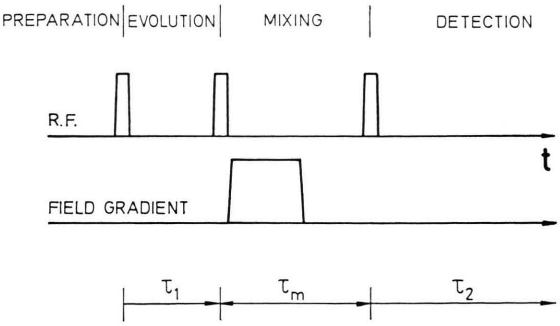

Fig. 1. Basic pulse scheme for 2D exchange spectroscopy [1]. The magnetic field gradient spoiling pulse is optional and can be replaced by appropriate phase cycles [4]. With NQR of powder samples a magnetic field pulse without gradient can also be employed instead. The mixing time τ_m is the interval considered to be relevant for exchange, while τ_1 and τ_2 represent the two dimensions in the time domain. The intervals ideally obey $\tau_1, \tau_2 \ll \tau_m \ll T_1$.

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component of the RF field perpendicular to the local electric field gradient direction. On the other hand, only the magnetization components aligned along the local electric field gradient will be "stored" and will be the potential subject of modification by exchange. Residual coherences, i.e. magnetization components perpendicular to the local electric field gradient direction can be spoiled by a magnetic field pulse applied after the second RF pulse (in the NQR case applied to powder samples no gradient is necessary). Thus echoes of these coherences in the detection interval are avoided. Alternatively, the same effect can be achieved by the aid of appropriate phase cycles [4].

The subsequent "mixing period" τ_m is the interval in which potential exchange processes are to be investigated. The ideal condition therefore is $T_1 \gg \tau_m \gg \tau_1$, where T_1 is the spin-lattice relaxation time. After the mixing interval the longitudinal components are detected by the aid of a read RF pulse producing a free induction decay (FID) signal in the detection period τ_2.

τ_1 and τ_2 represent the two dimensions of the time domain from which the final 2D spectrum is derived. The length of the evolution interval τ_1 therefore must be incremented in a series of repetitions of the experiment. The increment corresponds to the dwell time of the signal acquisition in the τ_2 interval. The desired two-dimensional spectrum is obtained as the two-dimensional Fourier transform, $\tilde{S}(\nu_1, \nu_2)$, of the recorded signal data set, $S(\tau_1, \tau_2)$.

Spurious signal contributions from different coherence pathways are unlikely with NQR in contrast to the NMR case and can be eliminated by the aid of phase cycles [4] if necessary. There may also be the need to suppress the influence of spin-lattice relaxation in the mixing interval and the effects due to the flip-angle distribution in powder samples by a suitable baseline correction in the τ_1-direction after the Fourier transform in the τ_2-direction.

Without exchange, the 2D spectrum consists solely of diagonal peaks. If exchange takes place in the time scale of the mixing period there will be additional cross-peaks at frequency coordinates corresponding to the sites between which the exchange occurs.

2. Special Problems in 2D-exchange NQR

In contrast to NMR, some characteristic problems arise with a 2D-exchange NQR-experiment. For the calculation of the signal intensities of the diagonal peaks and the cross peaks the special situation in NQR has to be considered. 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. Generally the local field gradients have different orientations in space for different positions of the molecule. As a result, only a projection of the polarisation of the old direction on the new direction is contained [5]. For electrical field gradients with cylindrical symmetry, i.e. $\eta = 0$ and a spin of 1 or 3/2 this projection factor is

$$r_1 = 0.5 \cdot (3\cos^2(\theta_{\nu_1 \nu_2}) - 1)\,, \tag{1}$$

where $\theta_{\nu_1 \nu_2}$ is the relative angle between the principal axes of the field gradients.

For a system with tetrahedral angles, i.e. $\theta_{\nu_1 \nu_2} \approx 110^\circ$ this reduction factor is $r_1 = -1/3$.

Additionally, the well-known dependence of flip angle and sensitivity on the angle between the B_1 field and the direction of the electric field gradient [6] must be considered. This influence is different for diagonal and cross peaks. Assuming that the three r.f. pulses are adjusted to give maximum signal intensity, i.e. to a maximum flip angle of 1.774, and for $\eta = 0$, the reduction factor for signal contributions coming from nuclei which were not involved in an exchange process is

$$r_2 = \sqrt{3}/2\pi \cdot \int_0^\pi (\sin^2\theta \cdot \sin^3(1.774 \sin\theta))\,\mathrm{d}\theta \approx 0.386\,. \tag{2}$$

This has to be compared with the influence on the signal intensity of contributions from exchanged nuclei,

$$r_3 = \sqrt{3}/2\pi \cdot \int_0^\pi (\sin\theta \cdot \sin^2(1.774 \sin\theta))\,\mathrm{d}\theta \tag{3}$$

$$\cdot \sqrt{3}/2\pi \cdot \int_0^\pi (\sin^2\theta \cdot \sin(1.774 \sin\theta))\,\mathrm{d}\theta \approx 0.452 \cdot 0.414,$$

which describes the fact that after the second pulse a new independent orientation distribution is established by the exchange process.

The signal reduction due to the powder distribution for exchanged nuclei relative to not exchanged nuclei is

$$r_4 = r_3/r_2 \approx 0.4848\,. \tag{4}$$

The caluclation of the intensities of the diagonal and cross peaks can be done by combination of the calculations by Jeener et al. [1] and Alexander and Tzalmona [5].

The mixing dynamics are described by the differential equation

$$\mathrm{d}/\mathrm{d}t(P-P_0) = L\cdot(P-P_0), \tag{5}$$

where $P-P_0$ is the polarisation vector and L is the exchange matrix. For the special case of our systems, i.e. p-chlorobenzotrichloride and chloroform, where we have three sites but two of them have the same resonance frequency, this matrix can be written as

$$L = \begin{pmatrix} -R_{AA} & -R_{AB} \\ -R_{BA} & -R_{BB} \end{pmatrix}, \tag{6}$$

where

$$R_{AA} = x_A\cdot k\cdot(1-r) + 2x_B\cdot k\,, \tag{7}$$

$$R_{BB} = 2x_B\cdot k, \tag{8}$$

$$R_{AB} = -\,x_A\cdot k\cdot r\,, \tag{9}$$

$$R_{BA} = -2x_B\cdot k\cdot r \tag{10}$$

are the matrix elements,

$$x_A = 2/3, \tag{11}$$

$$x_B = 1/3 \tag{12}$$

are the relative populations of the sites,

$$k = 1/\tau \tag{13}$$

is the exchange or rotation rate constant, and

$$r = 0.5\cdot(3\cos^2(\theta_{\nu_1\nu_2})-1)\cdot r_4 \tag{14}$$

is the intensity reduction factor for signal contributions which are due to the exchange process.

For $\theta_{\nu_1\nu_2}\approx 110^\circ$ this reduction factor is $r\approx -0.16$.

The exchange process is also expected to be the dominant mechanism for spin-lattice relaxation in the temperature range of interest. Other sources of relaxation therefore can be considered to be negligible.

For the mixing coefficients $a_{jl}(\tau_\mathrm{m})$, which describe the exchange process, the following expressions are found [1]:

$$a_{AA}(\tau_\mathrm{m}) = x_A\,e^{-\sigma\tau_m}\cdot(\cosh(D\tau_\mathrm{m}) - \delta/D\,\sinh(D\tau_\mathrm{m})), \tag{15}$$

$$a_{BB}(\tau_\mathrm{m}) = x_B\,e^{-\sigma\tau_m}\cdot(\cosh(D\tau_\mathrm{m}) + \delta/D\,\sinh(D\tau_\mathrm{m})), \tag{16}$$

$$a_{AB}(\tau_\mathrm{m}) = a_{BA}(\tau_\mathrm{m}) = +x_A x_B\cdot k\cdot r/D\cdot e^{-\sigma\tau_m}\cdot\sinh(D\tau_\mathrm{m}) \tag{17}$$

with

$$\sigma = 1/2(R_{AA}+R_{BB}), \tag{18}$$

$$\delta = 1/2(R_{AA}-R_{BB}), \tag{19}$$

$$D = (\delta^2 + 2x_A x_B\cdot k^2\cdot r^2)^{1/2}\,. \tag{20}$$

It is important to note that due to the negative factor r, the cross peaks and diagonal peaks have opposite phases. Diagonal peaks representing two exchange sites with equal resonance frequencies therefore are weakened by the destructive superposition of antiphase signal contributions.

Another important result is that the rate constants σ and δ are of the order of $1/\tau$, which means that also the spin-lattice relaxation time is of the same order of magnitude. This is the reason for the well-known "fading out" which occurs in a lot of compounds at temperatures below the melting point.

In order to obtain significant intensities for the cross peaks it is necessary to optimize the mixing time τ_m. The optimum mixing time, τ_opt, and the intensity ratio of the cross- and diagonal peaks, $\gamma(\tau_\mathrm{opt})$, are given by

$$\tau_\mathrm{opt} \quad = 1/2D\cdot\ln((\sigma+D)/(\sigma-D))\,, \tag{21}$$

$$\gamma(\tau_\mathrm{opt}) = a_{AB}(\tau_\mathrm{opt})/(a_{AA}(\tau_\mathrm{opt})\cdot a_{BB}(\tau_\mathrm{opt}))^{1/2}\,. \tag{22}$$

In our special case we get

$$\tau_\mathrm{opt}\approx\tau \tag{23}$$

and

$$\gamma(\tau_\mathrm{opt})\approx 0.16\,, \tag{24}$$

which means that the relative amplitude of the cross peaks is much lower than is typical in an NMR experiment.

Large frequency differences between the resonance lines of the exchanging nuclei can be also a problem in 2D NQR experiments. Combined with a low magnetogyric ratio this makes it difficult to excite all resonance lines involved in an exchange process simultaneously with a simple RF pulse. A method to overcome this problem by a multipulse sequence is presented later in this article.

Another critical aspect for 2D NQR exchange experiments is the large temperature dependence of the NQR resonance frequencies. The factors discussed for signal reduction generally require measuring times of several hours, which means that during this time the frequency shift due to temperature instabilities must be kept small compared to the linewidth to avoid

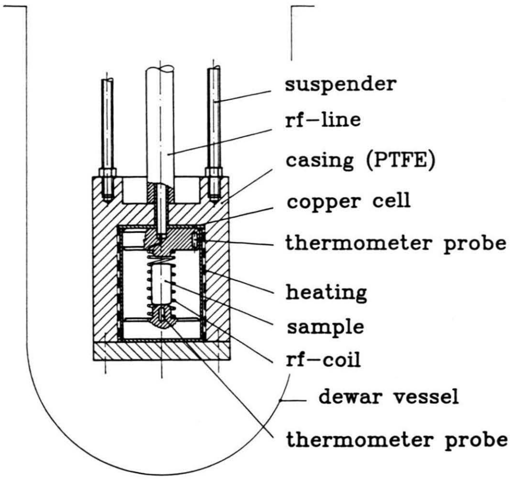


Fig. 2. Cross section of the probehead used for the 2D exchange NQR spectroscopy experiments. The dewar vessel was filled with a cooling agent.

artifacts. In practice this requires a temperature stability of about 0.1 K over the whole experiment.

3. Experimental

NQR Spectrometer

The home built NQR spectrometer has been described elsewhere [7, 8]. For the 2D exchange experiments a special probehead covering a temperature range 77 K to room temperature was built. A cross section is shown in Figure 2.

The RF coil and the sample were located in the center of a closed copper cell coated with Teflon (polytetrafluoroethylene or PTFE). This cell was suspended in a dewar vessel which was filled with liquid nitrogen or dry ice as cooling agents. The interior of the cell was heated by the aid of a heating coil wound bifilarly between the copper cell and the PTFE coating. The PTFE insulation of the copper cell against the cooling bath was designed in such a way that the average heating power virtually corresponds to the cooling power as a crucial condition for a stable temperature control.

Temperatures were measured and controlled with two Pt 100 probes mounted at different positions inside of the copper cell (Figure 2). No temperature difference was detectable. The heating current was stabilized by the aid of a PID feedback control unit. In this way the sample temperatures could be kept constant within 0.1 K over several hours.

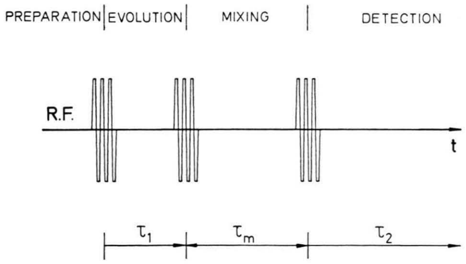


Fig. 3. RF pulse scheme modified for double side-band excitation. Each of the RF pulses in Fig. 1 is replaced by PAEP sequence as described in the text.

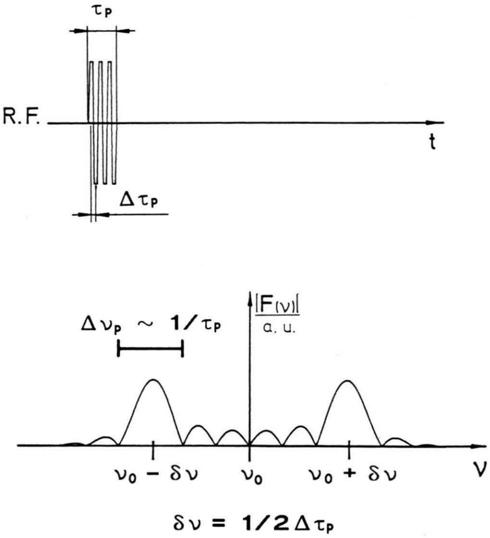


Fig. 4. Phase alternating excitation pulse (PAEP) and its spectrum.

Phase Alternating Excitation Pulses

The typical length of an RF pulse for the optimum ^{35}Cl signal excitation was 2 μs. The corresponding bandwidth often is not sufficient to excite the whole NQR spectrum which can be spread over several MHz.

In the case of two resonance lines the problem can be solved by double frequency band excitation. Each of the RF pulses in Fig. 1 is replaced by a series of phase alternating RF pulses as shown in Figure 3. The spectrum of such a phase alternating excitation pulse (PAEP) is shown in Figure 4.

The net excitation exactly at the transmitter frequency ν_0 is zero, whereas two strong side-bands appear at frequencies $\nu_0 \pm \delta\nu$, with $\delta\nu = 1/(2\Delta\tau_p)$. $\Delta\tau_p$ is the width of one of the single-phase constituents of the PAEP sequence. Choosing $\Delta\tau = 1$ µs, for instance, thus permits the simultaneous excitation of two frequency bands in a separation of 1 MHz. The width of each of these frequency bands is given by $1/\tau_p$, where τ_p is the length of the PAEP sequence (Figure 4).

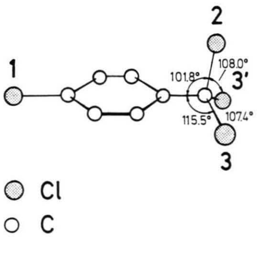
Samples

2D exchange ^{35}Cl NQR experiments were carried out with chloroform and p-chlorobenzotrichloride. The samples were purchased from Merck and Aldrich, respectively. The purity was specified as "pro analysi" (99%).

Chloroform shows two ^{35}Cl NQR lines at 37.295 MHz and 37.540 MHz, measured at a temperature of 207 K. As the NQR line separation is only 245 kHz, there was no need in this case to apply the PAEP sequence. The resonances are observable up to the melting point at $T_m = 210$ K without any "fading out". Relaxation data recorded close to T_m [9, 10, 11] suggest rotational jumps of the molecule.

p-Chlorobenzotrichloride contains four chlorine nuclei (Figure 5). The Cl nuclei 1 and 2 are located in the mirror plane perpendicular to the benzene ring. The nuclei 3 and 3′ have equivalent positions. Rotational jumps of the CCl_3 group, concluded from relaxation data above 200 K [12], interchanges the position of nucleus 2 with one of the nuclei 3 or 3′.

In the interesting temperature range near 210 K the ^{35}Cl NQR frequencies for the different positions are $\nu_1 = 34.58$ MHz, $\nu_2 = 38.07$ MHz, and $\nu_3 = 38.82$ MHz. Therefore at least two lines with a frequency separation of 750 kHz had to be excited. As this is not possible with pulses being 2 µs long, the PAEP sequence described above was used.



p−chlorobenzotrichloride

Fig. 5. Positions of the chlorine atoms in p-chlorobenzotrichloride.

4. Results

Experiments with Chloroform

In this case the simple pulse sequence displayed in Fig. 1 was used. The RF pulse length was 2 µs. The transmitter frequency was 37.390 MHz. In order to avoid the coincidence of mirror signals of diagonal peaks and cross-peaks, the transmitter frequency was chosen somewhat apart from the center frequency between the two resonances. The evolution interval τ_1 was incremented in 128 steps with an increment of 1 µs. The mixing interval τ_m was 768 µs. The temperature was 207 K, i.e. very close to the melting point.

Figure 6 shows the contour plot of a 2D spectrum with its diagonal and cross-peaks, and their mirror images with respect to the horizontal zero line. According to the expectations, the cross-peak intensities are about one order of magnitude smaller than the diagonal peaks. This is demonstrated by the two cross sectional spectra also shown in Figure 6.

Experiments with p-Chlorobenzotrichloride

The PAEP sequence displayed in Fig. 3 was used. Each of the PAEP groups consisted of six RF pulses, 1.2 µs long. The separation of the side-bands therefore was 833 kHz and the bandwidth was about 140 kHz. These values permitted us again to adjust the transmitter frequency somewhat outside of the middle between the two resonance frequencies in order to distinguish between cross-peaks and mirror images of diagonal peaks. An exemplary 2D spectrum recorded at 208 K is shown in Figure 7.

The dependences of the sum of the cross peak intensities and the sum of the diagonal-peak intensities on the mixing time are plotted in Figure 8. The mixing time was varied between 768 µs and 8 ms. At maximum cross peak intensity the cross-peaks are about a factor of seven smaller than the diagonal peaks, in accordance with the expectations for rotational jumps with a rotation angle of $\theta_{\nu_1 \nu_2} = 110°$. The maximum cross-peak intensity was found for a mixing time of $\tau_m = 1.5$ ms.

The diagonal-peak intensities decay with increasing mixing time due to the exchange process and due to spin-lattice relaxation. The ratio of diagonal- and cross-peak intensities is about 2:1 in the limit of long mixing times.

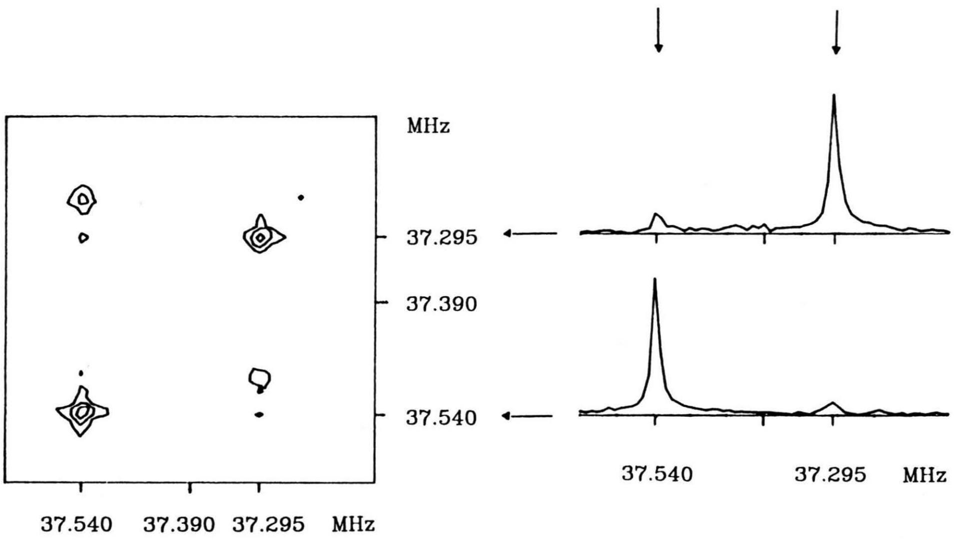


Fig. 6. 2D exchange NQR spectrum of chloroform recorded with ^{35}Cl signals at 207 K using the pulse scheme of Fig. 1 without magnetic field pulse. The mixing time was 768 μs. The contour plot also indicates mirror images of the diagonal peaks adjacent to the cross-peaks. In order to avoid confusion with these artifacts, the transmitter frequency (37.390 MHz) was intentionally shifted from the center frequency. The two cross sectional spectra positioned at the NQR frequencies 37.295 MHz and 37.540 MHz of one of the dimensions in the frequency domain illustrate the large intensity ratio of diagonal (high) and cross-peaks (low).

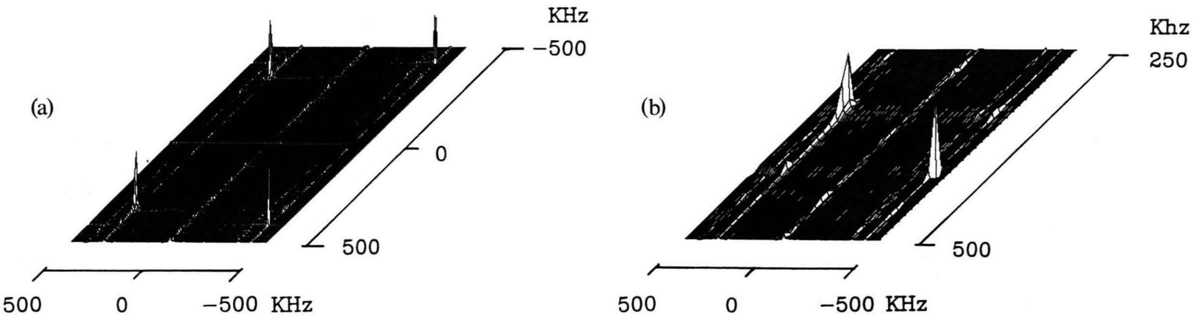


Fig. 7. 2D exchange NQR spectrum of p-chlorobenzotrichloride recorded with ^{35}Cl signals at 208 K using the pulse scheme of Figure 3. The mixing time was 768 μs. τ_1 was incremented in 128 steps with an increment of 1 μs. (a) Whole magnitude spectrum as calculated. (b) Lower part in greater detail.

5. Discussion

It has been demonstrated that two-dimensional exchange NQR spectroscopy is feasible in analogy to the NMR case. The situation is, however, more complicated and a series of difficulties had to be overcome.

The powder geometry of the samples reduces the excitation efficiency of the RF pulses in general. In the present case, a three-pulse sequence is employed for driving the spin states along certain coherence pathways. The reduced RF pulse efficiency enters multiplicatively, and the final signal amplitude is correspondingly low. Changes of the resonance frequency by exchange are normally accompanied by a change of the direction of quantization, so that the cross-peak intensities are reduced additionally.

The exchange processes simultaneously act as efficient spin-lattice relaxation mechanisms. Therefore the T_1 values tend to be of the same order of magnitude as the exchange times. The resulting zero-peak intensity in the two-dimensional spectrum can be much larger than the intensity of the cross- and diag-

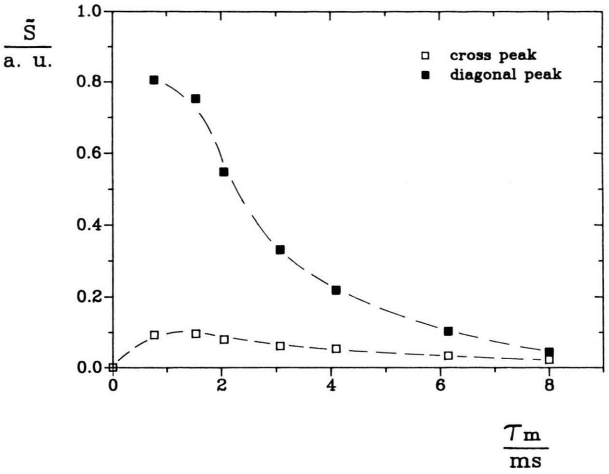


Fig. 8. Intensities of diagonal and cross-peaks of p-chlorobenzotrichloride at 208 K as a function of the mixing time τ_m.

onal peaks, and at the same time the relaxation diminishes the proper cross-peak produced by exchange. Therefore it is recommended to eliminate these relaxation contributions by suitable baseline correction in τ_1 direction after the first Fourier transform in the τ_2 direction.

The problem of large NQR line separations exceeding the excitation-pulse bandwidth achievable for small magnetogyric ratios, can be solved by replacing the pulses by PAEP sequences. Multi-site exchange pathways, however, may require more complicated pulse modulations for the production of a corresponding number of sidebands at the right frequencies.

In spite of these problems it has unambiguously been shown that the technique is suitable for the direct detection of rotational jumps. The one-dimensional methods previously used for this purpose, such as spin-lattice relaxometry, lineshape analysis and the temperature dependence of the NQR frequencies, are comparatively indirect and the interpretation are based on models. 2D exchange NQR spectroscopy in particular provides a means to visualize the exchange pathway pattern of a given compound.

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