

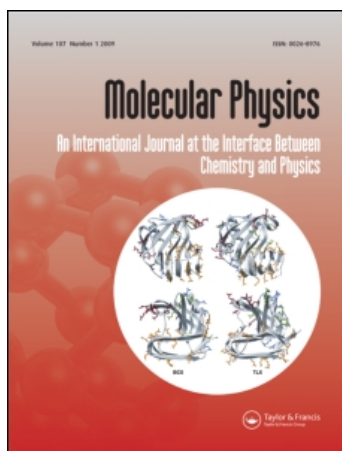
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RESEARCH ARTICLE

Study of dynamics in pentachlorophenol in the solid state by 1D Nuclear Quadrupole Resonance exchange spectroscopy

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The paper reports studies of the dynamic process in pentachlorophenol (PCP) in the solid state by one-dimensional Nuclear Quadrupole Resonance (NQR) exchange spectroscopy employing shaped rf pulses. Pentachlorophenol exhibits intramolecular hydrogen bonding between the hydroxyl proton and one of the *o*-chlorines. Reorientation of the hydrogen bond with migration of the hydroxyl proton from one *o*-chlorine to the other is possible in a wide temperature range. In this process the two *o*-chlorines are exchanged; at the same time this implies the exchange of the two *m*-chlorines as well, which we have chosen to monitor, modeling it as a two-site exchange process. A detailed analysis of the appropriate Bloch-McConnell equation is performed to formulate the relevant kinetic matrix. The exchange pulse sequence implemented by us involves suitably modulated shaped RF pulses to achieve simultaneous on-resonance excitation of the two exchanging sites. This approach results in a clear definition of the exchange time window and requires only a short experiment time. Kinetic parameters, namely, the spin-lattice relaxation rate and the exchange rate are deduced from the experimental signal intensities. Variable temperature measurements in the range 213 K–318 K have been carried out to extract the activation parameters as well.

Keywords: proton migration; quadrupolar nuclei; NQR spectroscopy; modulated shaped pulses; simultaneous excitation

1. Introduction

Molecular dynamics involving quadrupolar nuclei in the solid state may be studied by 1D Nuclear Quadrupole Resonance (NQR) measurements of the temperature dependence of spectral frequencies and T_1 s [1,2]. Further, two-dimensional NQR exchange spectroscopy [3–7] has also been employed to monitor molecular motion in the solid state. Both these methods have their own merits and demerits. While the 1D version is unable to provide direct information on the exchange pathways, the 2D version based on the work by Jeener *et al.* three pulse sequence [8] suffers from excitation efficiency issues, off-resonance effects as well as lack of a well defined exchange time window under certain conditions. Besides these, a major concern in a 2D experiment is the experiment duration.

In this context, we have recently developed two 1D approaches [9] and applied them to three-site exchange; one of our approaches achieves selective excitation of one of the exchanging sites and the other results in simultaneous on-resonance excitation of multiple exchanging sites. As described in our earlier work, these approaches, *viz.*, the selective inversion recovery

and bi-selective inversion recovery experiments, provide a clear definition of the exchange time window, besides reducing the experiment time and eliminating off-resonance effects. In the present work, we investigate theoretically the behaviour of the selective inversion recovery as well as the bi-selective inversion recovery experiment in the case of a two-site exchange process; we establish experimentally the suitability of the bi-selective sequence for the present system, *viz.*, pentachlorophenol. The pulse sequences in question involve selective and bi-selective shaped pulses [10,11]. The selective shaped pulses have been chosen to be Gaussian pulses, whereas the bi-selective shaped pulses are generated by cosine modulation of the Gaussian envelope to achieve simultaneous on-resonance excitation of both the exchanging sites. The pulse sequences are given below:

$$1. (\Theta)_{\text{selective}} - \tau_m - (\Theta')_{\text{bi-selective}}$$

$$2. (\Theta)_{\text{bi-selective}} - \tau_m - (\Theta')_{\text{bi-selective}}$$

Following the appropriate first pulse, the sequences involve a mixing time (τ_m) and finally a cosine modulated Gaussian pulse as the read pulse.

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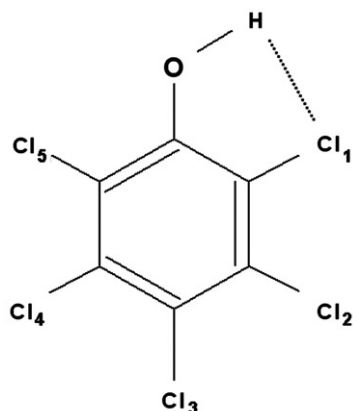


Figure 1. Structure of pentachlorophenol.

The effect of the pulse sequences on the spin system has been described in detail in earlier work [9]. In the present work we report and analyse experimental results on molecular dynamics in pentachlorophenol (PCP), applying the 1D bi-selective inversion recovery experiment.

PCP exhibits five different NQR frequencies and asymmetry parameters corresponding to five ^{35}Cl nuclei at room temperature [12]. The structure of the molecule is given in Figure 1. The NQR frequencies along with the corresponding asymmetry parameters are given in Table 1. It is reported in the literature [13] that in the solid state at low temperature PCP exhibits intermolecular hydrogen bonding to form chains giving rise to a ‘solid polymer’, whereas at higher temperatures it shows intramolecular hydrogen bonding between the $-\text{OH}$ group and one of the two *o*-chlorine atoms, behaving as a monomeric species. This is commonly observed in *o*-halophenols [14–16]. It may be noted that a structure involving an intramolecular hydrogen bond would allow the hydroxyl group to undergo rapid reorientation with migration of the hydroxyl proton from one *o*-halogen atom to another in the crystalline state [13]. This process exchanges the position of the two *o*-chlorines and the two *m*-chlorines – and may therefore be considered a two site exchange process. We note here that the presence of the ^{37}Cl isotope in the PCP molecule is not expected to have a measurable impact on the exchange process cited, as measured by ^{35}Cl NQR. Since we are basically tracking indirectly the process of proton migration from one *o*-chlorine to the other, the presence of the ^{37}Cl isotope at either of the *meta* positions or at the *para* position would clearly not have any effect; nor would a ^{37}Cl isotope at one or both of the *ortho* positions be expected to influence the hydrogen bond exchange dynamics. In the following we therefore analyse the dynamics in terms of the

Table 1. Frequencies and asymmetry parameters of quadrupolar resonance for PCP at 300 K.

Position	Frequency (MHz)	Asymmetry parameter
ν_3	38.02	0.167 ± 0.010
ν_4	37.75	0.185 ± 0.018
ν_2	37.71	0.164 ± 0.013
ν_1	36.98	0.163 ± 0.017
ν_5	36.67	0.100 ± 0.007

two-site exchange model of the *meta* chlorines by ^{35}Cl NQR, which has higher detection sensitivity.

2. Theoretical description

In earlier work [9], we have given a detailed analysis of the Bloch–McConnell equation [17] for three site exchange, as well as the density matrix calculation for the pulse sequences, employing Goldman’s fictitious spin-1/2 formalism [18]. Here, we briefly summarize the corresponding results for two site exchange.

2.1. Formulation of kinetic matrix

The two-site exchange network is defined in Figure 2. The Bloch–McConnell equations for such a system may be written as follows:

$$\frac{dz_{1A}(t)}{dt} = \begin{bmatrix} -\frac{(z_{1A}(t) - z_{1A})}{T_{1A}} - k_{AB}z_{1A}(t) \\ +r_B k_{BA}z_{1B}(t) \end{bmatrix} \quad (1)$$

$$\frac{dz_{1B}(t)}{dt} = \begin{bmatrix} -\frac{(z_{1B}(t) - z_{1B})}{T_{1B}} - k_{BA}z_{1B}(t) \\ +r_A k_{AB}z_{1A}(t) \end{bmatrix}. \quad (2)$$

Here, z_1 denotes the equilibrium polarization in terms of Goldman’s formalism. The above equations are formulated with the considerations that the two exchanging sites (A, B) have two different spin-lattice relaxation times (T_{1A}, T_{1B}) and two different reduction factors (r_A, r_B). It may be recalled that the reduction factors denote the ‘projection loss’ of polarization [3,19] due to exchange in NQR. Here k_{ij} indicates the rate constant for the transfer of polarization from site i to site j . Invoking microscopic reversibility at dynamic equilibrium [3], the above set of differential equations may be formulated in terms of the following matrix representation:

$$\frac{d}{dt} \begin{bmatrix} L \\ M \end{bmatrix} = \begin{bmatrix} -\frac{1}{T_{1A}} - \frac{1}{2}k & \frac{1}{2}r_B k \\ \frac{1}{2}r_A k & -\frac{1}{T_{1B}} - \frac{1}{2}k \end{bmatrix} \begin{bmatrix} L \\ M \end{bmatrix}. \quad (3)$$

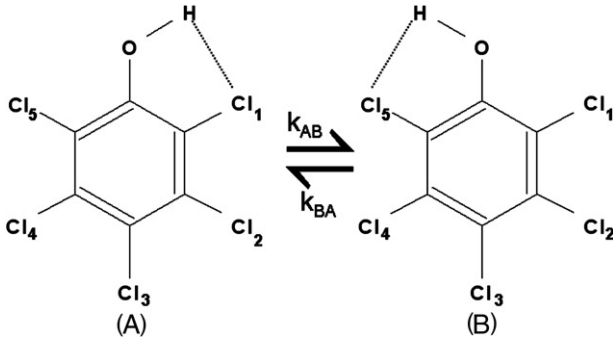


Figure 2. Two-site exchange process in crystalline pentachlorophenol.

L and M are defined as follows:

$$L(t) = z_{1A}(t) - z_{1A} \quad (4a)$$

$$M(t) = z_{1B}(t) - z_{1B}. \quad (4b)$$

In Equation (3), the individual rate constants have been replaced by $k_{ij} = k[x_j]$ (with $i, j = A, B$) where k is an average rate constant, $[x_j]$ being the fractional population of site j , set to $1/2$ above to describe the case of equal populations.

The solution of the above set of coupled homogeneous differential equations may be given as:

$$L(t) = \left(\frac{eu - 2bf}{2p} \right) \exp\left(-\frac{gt}{2}\right) + \left(\frac{ev + 2bf}{2p} \right) \exp\left(-\frac{ht}{2}\right) \quad (5)$$

$$M(t) = \left(\frac{fv - 2de}{2p} \right) \exp\left(-\frac{gt}{2}\right) + \left(\frac{fu + 2de}{2p} \right) \exp\left(-\frac{ht}{2}\right). \quad (6)$$

Here e, f define the initial conditions:

$$e = L(0) = z_{1A}(0) - z_{1A} \quad (7a)$$

$$f = M(0) = z_{1B}(0) - z_{1B}. \quad (7b)$$

Further, we have:

$$a = \frac{1}{T_{1A}} + \frac{k}{2}; d = \frac{1}{T_{1B}} + \frac{k}{2} \quad (8a)$$

$$b = \frac{r_B k}{2}; c = \frac{r_A k}{2} \quad (8b)$$

$$p = \sqrt{(a-d)^2 + 4bc} \quad (8c)$$

$$a + d + p = g; a + d - p = h \quad (9a)$$

$$a - d + p = u; -a + d + p = v. \quad (9b)$$

2.2. The signal of interest

The final signal of interest in the case of the singly selective experiment (sequence 1) is given in

the following. We have assumed that the carrier is set at the mean frequency of the two NQR signals corresponding to the two exchanging sites A and B; site A is inverted by the first shaped pulse of the sequence, set to the appropriate offset frequency.

The final density matrix at the end of the read pulse for the inverted site as well as for the un-inverted site in the case of sequence 1 is given as follows:

$$\begin{aligned} \sigma_A(\tau_{m,+}) &= R[z_{1A} \cos \lambda_A \Theta' - y_{1A} z'_{2A} \sin \lambda_A \Theta'] \\ \sigma_B(\tau_{m,+}) &= S[z_{1B} \cos \lambda_B \Theta' - y_{1B} z'_{2B} \sin \lambda_B \Theta']. \end{aligned} \quad (10)$$

Here, we have:

$$R = 1 + \frac{q_A}{2p} \left[u \exp\left(-\frac{gt}{2}\right) + v \exp\left(-\frac{ht}{2}\right) \right] \quad (11)$$

$$S = 1 - \frac{q_{Ac}}{p} \left[\exp\left(-\frac{gt}{2}\right) - \exp\left(-\frac{ht}{2}\right) \right]. \quad (12)$$

Here, the initial conditions are as follows:

$$e = z_{1A}(0) - z_{1A} = z_{1A}(\cos \lambda_A \Theta - 1) = q_A z_{1A} \quad (13a)$$

$$f = z_{1B}(0) - z_{1B} = 0. \quad (13b)$$

λ is the orientation factor, which depends on the asymmetry parameter (η) as well as the orientation of the RF coil with respect to the QPAS [17]. Since the two sites under investigation have two different asymmetry parameters, the orientation factors are also different, denoted λ_A, λ_B . Hence the signal of interest for both the inverted site (A) and the un-inverted site (B) are expressed as:

$$S_{\text{Inv,crystal}}^A(t) \propto \frac{\sqrt{3}}{2} \lambda_A R \sin \lambda_A \Theta' \quad (14a)$$

$$S_{\text{Uninv,crystal}}^B(t) \propto \frac{\sqrt{3}}{2} \lambda_B S \sin \lambda_B \Theta'. \quad (14b)$$

Similarly for the bi-selective inversion recovery experiment (sequence 2), with the carrier placed at the mean frequency of the two signals of interest, the signals are given by:

$$S_{\text{Inv,crystal}}^A(t) \propto \frac{\sqrt{3}}{2} \lambda_A C \sin \lambda_A \Theta' \quad (15a)$$

$$S_{\text{Inv,crystal}}^B(t) \propto \frac{\sqrt{3}}{2} \lambda_B D \sin \lambda_B \Theta'. \quad (15b)$$

Here,

$$\begin{aligned} C &= 1 + \left(\frac{q_A u - 2q_B b}{2p} \right) \exp\left(-\frac{gt}{2}\right) \\ &\quad + \left(\frac{q_A v + 2q_B b}{2p} \right) \exp\left(-\frac{ht}{2}\right) \end{aligned} \quad (16)$$

$$\begin{aligned} D &= 1 + \left(\frac{q_B v - 2q_A c}{2p} \right) \exp\left(-\frac{gt}{2}\right) \\ &\quad + \left(\frac{q_B u + 2q_A c}{2p} \right) \exp\left(-\frac{ht}{2}\right). \end{aligned} \quad (17)$$

The above expressions are obtained with the assumption that the two sites are equally populated (i.e. $z_{1A} = z_{1B}$), the initial conditions being given by:

$$e = z_{1A}(\cos \lambda_A \Theta - 1) = q_A z_{1A} \quad (18a)$$

$$f = z_{1B}(\cos \lambda_B \Theta - 1) = q_B z_{1B}. \quad (18b)$$

For both experiments, we need to take powder averages of the terms containing λ to describe the signal from a polycrystalline sample.

3. Experimental

In the present work we report the application of the bi-selective inversion recovery experiment to monitor the dynamic process in polycrystalline pentachlorophenol [$C_6Cl_5(OH)$]. The experiments were carried out at a series of temperatures. The spectra were recorded with a Bruker Avance 400 NMR spectrometer (5.4 cm vertical magnet bore) using a Bruker 5 mm BBO probehead. The probe arrangement was described earlier [9]. The sample temperature was measured and regulated using the Bruker variable temperature unit BVT-3200.

From Table 1, the two *m*-chlorine NQR signals, $\nu_2 = 37.71$ MHz and $\nu_4 = 37.75$ MHz are almost 44 kHz apart. These two frequencies may be readily excited and monitored simultaneously with the hardware at our disposal. The transmitter frequency was placed at the middle of these two lines. The amplitude modulation of the soft pulse was carried out as described earlier [9]. The $\pi/2$ pulse (Θ') was calibrated for maximum signal intensity whereas the π pulse (Θ) was calibrated for null signal. Table 2 gives the pulse parameters used in these experiments.

Several series of experiments were carried out for various mixing periods ranging from 0–1000 ms and at different temperatures ranging from 213–318 K to extract the activation parameters. 128 data points were collected during the acquisition period. The number of scans was 128 and the repetition time was 250 ms. The total time of a single experiment is 33 s.

4. Results and discussion

Rapid reorientation of the hydroxyl group with migration of a proton from one *o*-halogen atom to another for 2,4-dihalo- and 2,4,6-trihalo-phenols in the crystalline state has been discussed in the literature [14,15]. Measurement of the temperature dependence of ^{35}Cl -NQR frequencies reveals the presence of such a reorientation process. With increase of temperature the frequency difference between the two NQR lines

Table 2. Pulse duration and corresponding power levels.

Pulse name	Pulse width	Power level
Bi-selective 90°	70 μ s	~ -3.2 dB
Bi-selective 180°	150 μ s	~ -4.0 dB
Selective 180°	150 μ s	~ 2.2 dB

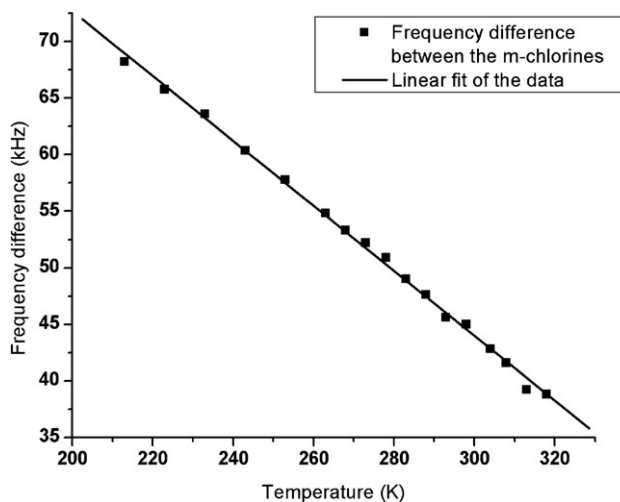


Figure 3. Plot of frequency difference between the two *m*-chlorine NQR lines against temperature. (The linear fit of the data does not have any theoretical significance.)

due to the two *o*-halogen atoms decreases and at a particular temperature they merge with each other [14]. In the case of PCP if such a reorientation process were to occur, the frequency difference between the two *m*-chlorines would also be affected. We have measured the temperature dependence of the two NQR lines due to the *m*-chlorines from 213 K to 318 K. Figure 3 shows the plot of frequency difference against temperature for the two *m*-chlorines which strongly suggests an ongoing exchange process.

A rapid reorientation of the hydroxyl group above the phase transition temperature of 62°C has been reported for PCP [13]. Since all our experiments are performed well below the phase transition, we are monitoring the slow exchange regime.

To quantitate the process we need to find the correct fitting equations. We first calculate the reduction factors for the two sites using the following equation as given in [6].

$$r = \frac{1}{2} [3 \cos^2 \beta - 1 + \eta \sin^2 \beta]. \quad (19)$$

Here, β is the angle between the principal axes of the electric field gradient tensors (EFG) of the two exchanging chlorine atoms. In accordance with the

X-ray structure reported for PCP [12], we find $\beta=120.4^\circ$ and hence the reduction factors are $r_A=-0.055$ and $r_B=-0.047$. The fitting equations are then derived by taking the powder average of the terms containing $\lambda\Theta$ for these values of r . The relevant fitting equations are given in the following.

Selective experiment: Signal from the low frequency line (inverted site A , ν_2):

$$S_{\text{Inv.powder}}^A = 0.72 - \frac{1.161}{2p} \left[\begin{array}{l} u \exp(-\frac{gt}{2}) \\ +v \exp(-\frac{ht}{2}) \end{array} \right]. \quad (20)$$

Signal from the high frequency line (uninverted site B , ν_4):

$$S_{\text{Uninv.powder}}^B = 0.75 + 1.161 \frac{c}{p} \left[\begin{array}{l} \exp(-\frac{gt}{2}) \\ -\exp(-\frac{ht}{2}) \end{array} \right]. \quad (21)$$

Bi-selective experiment: Signal from the low frequency line (ν_2) or site A :

$$S_{\text{Inv.powder}}^A = 0.72 - \frac{1.161}{2p} \left[\begin{array}{l} (u - 2b) \exp(-\frac{gt}{2}) \\ +(v + 2b) \exp(-\frac{ht}{2}) \end{array} \right]. \quad (22)$$

Signal from the high frequency line (ν_4) or site B :

$$S_{\text{Inv.powder}}^B = 0.75 - \frac{1.205}{2p} \left[\begin{array}{l} (v - 2c) \exp(-\frac{gt}{2}) \\ +(u + 2c) \exp(-\frac{ht}{2}) \end{array} \right]. \quad (23)$$

Here, we have set the following integrals equal, since in fact they differ by only *ca.* 1%:

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta (s_A q_A) \approx \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta (s_A q_B) \quad (24)$$

$$\int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta (s_B q_A) \approx \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta (s_B q_B) \quad (25)$$

with

$$s_A = \frac{\sqrt{3}}{2} \lambda_A \sin \lambda_A \Theta'; \quad s_B = \frac{\sqrt{3}}{2} \lambda_B \sin \lambda_B \Theta'; \quad (26)$$

$$q_A = (\cos \lambda_A \Theta - 1); \quad q_B = (\cos \lambda_B \Theta - 1).$$

In general the signal intensities of both the exchanging sites depend on both the reduction factors irrespective of the type of experiment. Furthermore the average exchange rate (k) may be directly extracted by fitting the experimental signal intensities of the un-inverted site in the case of the singly selective experiment provided the reduction factors and the asymmetry parameters of the two sites are known. As a model of the mixing time dependence of the signal, we have

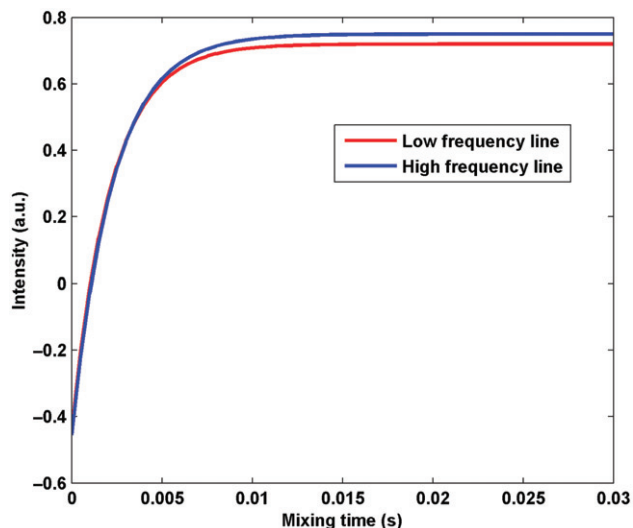


Figure 4. Theoretical plot of signal intensity against mixing time (τ_m) for the inverted sites at $T=313$ K for the bi-selective experiment.

plotted all the fitting equations against mixing time (0–40 ms) for PCP at $T=313$ K, employing the following model parameters for the fitting equations: $k=240 \text{ s}^{-1}$, $T_{1A}=3$ ms, $T_{1B}=3.2$ ms, $r_A=-0.055$, $r_B=-0.047$. Figure 4 provides the theoretical plot of the signal intensities of both the inverted sites against mixing time (τ_m) at $T=313$ K for PCP for the bi-selective experiment. Owing to the fact that the two relaxation times (T_1) as well as the two reduction factors (r) are different in the case of PCP, we need to monitor the mixing time dependence of signal intensities of both the exchanging lines irrespective of the type of the experiment. This is unlike the case of chloral hydrate [9] where the reduction factors and T_1 s are equal at all the sites involved. Figure 5 depicts the theoretical plot of the signal intensity of the un-inverted site at $T=313$ K against mixing time for the selective inversion recovery experiment at various r values for the inverted site. Since the change in signal intensity of the un-inverted site in case of PCP is predicted to be hardly detectable from the theoretical plot, we did not perform the selective inversion recovery experiment for PCP. In the case of the bi-selective experiment we need to plot signal intensities of both the exchanging lines against mixing time as stated earlier. In this case various possible combinations of the fitting parameters of the two fitting equations help unravel the required kinetic parameters.

The experimental data for the bi-selective experiment at eleven chosen temperatures are then fitted with the appropriate fitting equations. The plot of the signal intensities of the low frequency line is given in Figure 6 for two different temperatures. Similar plots are

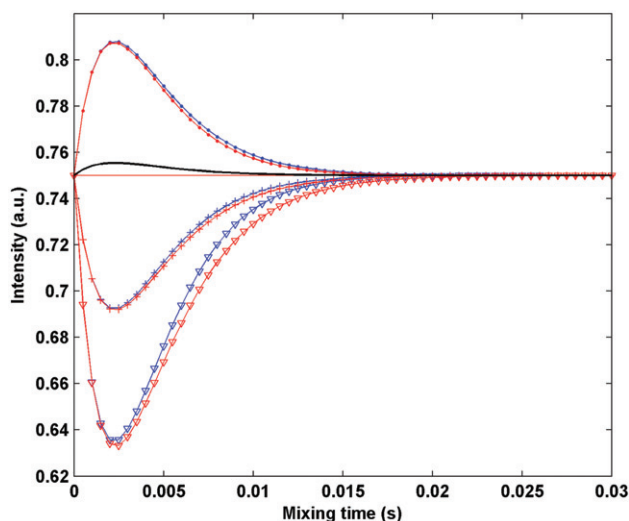


Figure 5. Theoretical plot of un-inverted site signal intensity against τ_m for the selective experiment at $T=313$ K for various r_A and r_B values. Blue curves: $r_A = -0.5$; red curves: $r_A = 1$. (\bullet) $r_B = -0.5$; ($+$) $r_B = 0.5$; (∇) $r_B = 1$; (horizontal trace with no symbol, and with intensity 0.75) $r_B = 0$. The black curve corresponds to $r_A = -0.055$, $r_B = -0.047$ (i.e. the present case). The model parameters used to generate the plot are as follows: $T_{1A} = 3$ ms, $T_{1B} = 3.2$ ms, $k = 240$ s $^{-1}$.

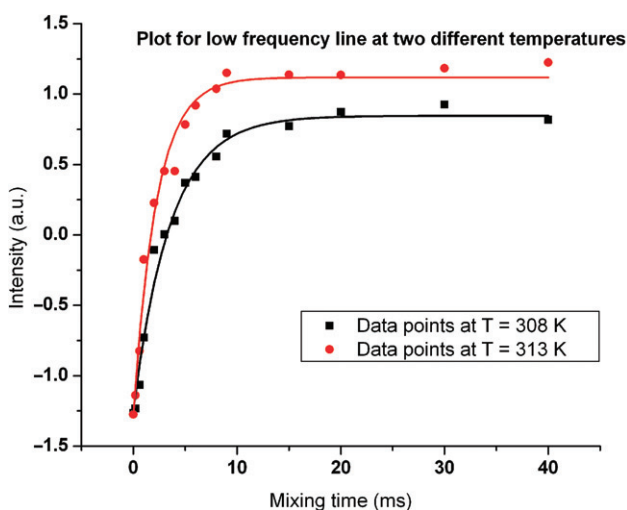


Figure 6. Plot of experimental signal intensity of the low frequency line against τ_m for bi-selective experiment at two different temperatures.

obtained for the high frequency line also. The kinetic parameters are then determined by taking various possible combinations of the fitting parameters. They are tabulated in Table 3¹. A closer look at the relaxation data reveals that the T_1 values for both the sites decreases gradually in the temperature range 213 K–298 K, whereas a sharp change is observed in the T_1 values for both the sites above 300K. This may

Table 3. Kinetic parameters calculated from the plot of signal intensity against τ_m at various temperatures.

Temperature (T) (K)	Bi-selective experiment		
	T_{1A} (ms)	T_{1B} (ms)	k (s $^{-1}$)
213	119.656	139.894	0.092
233	111.593	131.717	0.971
243	110.391	126.347	2.225
268	105.107	117.720	11.114
278	93.428	111.572	20.841
288	69.870	81.511	37.260
298	28.674	36.339	78.128
308	4.927	5.553	150.414
311	3.294	3.584	183.067
313	2.958	3.243	234.251
318	1.891	2.063	291.765

be due to the presence of an ongoing exchange process which becomes prominent in the higher temperature range. The exchange rates thus measured are used to extract the activation energy assuming an Arrhenius law. It may be recalled that the Arrhenius equation is given by:

$$k = A \exp\left(-\frac{E_a}{RT}\right). \quad (27)$$

Here, k is the exchange rate constant, T is the absolute temperature and E_a , the activation energy, A being the frequency factor. Further the Eyring equation, given in Equation (28), is used to calculate the relevant activation parameters.

$$\begin{aligned} k &= \frac{k_B T}{h} \exp\left(-\frac{\Delta G^*}{RT}\right) \\ &= \frac{k_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right). \end{aligned} \quad (28)$$

Equivalently, we have:

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT}. \quad (29)$$

Here, k_B is the Boltzmann constant, h is Planck's constant, while ΔH^* is the enthalpy of activation and ΔS^* , the entropy of activation. Other symbols have the same significance as in Equation (27). The relevant activation parameters thus determined are given in Table 4. For the particular temperature range of 213–318 K the system exhibits a single activation energy which we consider as being due to the exchange of hydroxyl hydrogen from one *o*-chlorine to the other in the crystalline state.

Table 4. Activation parameters obtained for the reorientation process.

Arrhenius plot		Eyring plot	
Activation energy E_a (kJ mol ⁻¹)	Frequency factor A (s ⁻¹)	Enthalpy of activation ΔH^* (kJ mol ⁻¹)	Entropy of Activation ΔS^* (J mol ⁻¹ K ⁻¹)
42.841	2.665×10^9	40.624	-8.647

5. Conclusion

In this report, we have demonstrated the application of the 1D 'bi-selective inversion recovery experiment' for the quantitative study of a two site exchange process in the solid state by pulsed NQR spectroscopy. Unlike the three site case already studied in [9], the rate parameters are extracted by plotting experimental signal intensities of both the exchanging sites. According to the fitting equations obtained by solving the appropriate Bloch–McConnell type equations, signal intensities of both the exchanging sites contain information about the exchange process. Suitable combinations of the various fitting parameters from the exponents and the amplitude factors allow us to extract the required kinetic parameters, *viz.*, the two spin-lattice relaxation rates and the exchange rate. We have also reported the activation energy and the other relevant activation parameters related to the two site exchange process in PCP.

Acknowledgements

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Note

1. It is to be noted that the actual values are a strong function of the molecular structural parameters owing to the β dependence of r : β being determined in turn from the relevant bond angles.

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