Pressure Dependence of the Chlorine NQR in Chloro Pyridines

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The ^{35}Cl NQR frequency (ν_Q) and spin lattice relaxation time (T_1) in 2,6-dichloropyridine, 2 amino 3,5-dichloropyridine and 6 chloro 2-pyridinol have been measured as a function of pressure up to 5.1 kbar at 300 K, and the data have been analysed to estimate the temperature coefficients of the NQR frequency at constant volume. All the three compounds show a non linear variation of the NQR frequency with pressure which can be described by a 2nd order polynomial in pressure. The rate of change of the NQR frequency with pressure is positive and decreases with increasing pressure. The spin lattice relaxation time T_1 in all the three compounds shows a small increase with pressure, indicating that the relaxation is mainly due to the torsional motions.

Key words: Chlorine NQR; Spin-Lattice Relaxation Time; Pressure Dependence; 2,6 dichloropyridine; 2-amino 3,5-dichloropyrine; 6-chloro 2-pyridinol.

Introduction

Our earlier studies on the pressure dependence of the NQR frequency of some solids have shown a nonlinear increase of the NQR frequency with pressure, and also a decrease of the NQR frequency with further increase of pressure in a few cases [1, 2]. We report here the pressure dependence of the ^{35}Cl NQR frequency and spin lattice relaxation time T_1 in 2,6 dichloropyridine, 2 amino 3,5 dichloropyridine and 6 chloro 2-pyridinol.

Earlier Work

The NQR frequency of ^{35}Cl in 2,6-dichloropyridine at 77 K has been reported in [3], and at 300 K in [4, 5]. The variation with temperature of the NQR frequency has been studied in [6], and that of T_1 in [7]. Only a single resonance line was observed in the range 77 to 300 K.

The chlorine NQR of 2 amino 3,5-dichloropyridine and the variation of the NQR frequency and T_1 with temperature (77–300 K) were first reported in [8]. Two resonance lines were observed due to the two inequivalent chlorines in the molecule.

The ^{35}Cl NQR frequency in 6 chloro 2-pyridinol in the range 77 to 300 K was first reported in [9]. The variation of T_1 with temperature in the range 77 to 300 K was studied in [10].

Experimental

The compounds were obtained from Aldrich Co. USA. The pulsed NQR spectrometer was home made. The pressure was transmitted with liquid paraffin, using a lock-nut type piston-cylinder device [11] and the teflon cell technique [12]. T_1 was measured using the inversion recovery sequence ($\pi - \tau - \pi/2$). The duration of the free induction decay (FID) was around 150 μs for all the signals. The NQR frequency and T_1 were measured with an accuracy of ±0.0005 MHz and ±5% respectively.

Results and Discussion

Pressure Dependence of the NQR Frequency

The effect of lattice vibrations on the average value of the electric field gradient (EFG) [13] can be expressed as

$$q = q_0 \left(1 - \frac{3}{2} \langle \theta^2 \rangle \right), \tag{1}$$

where $\langle \theta^2 \rangle$ is the effective mean square amplitude of the torsional oscillations about the axes of the EFG tensor and q_0 is the field gradient in the absence of all lattice vibrations. From (1) one obtains

$$\left(\frac{\partial \ln q}{\partial P}\right) = \left(\frac{\partial \ln q_0}{\partial P}\right)_T - \frac{3}{2}\left(\frac{\partial \langle \theta^2 \rangle}{\partial P}\right)_T . \tag{2}$$

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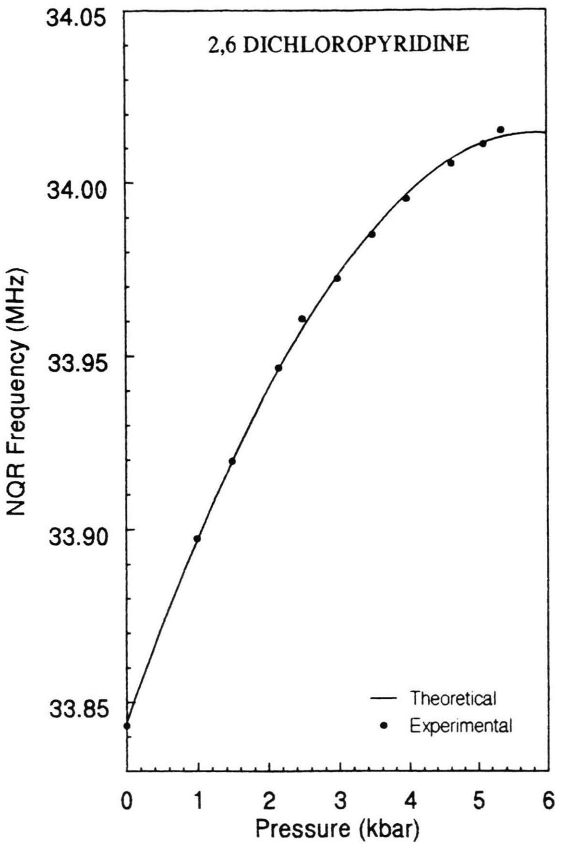

Fig. 1. Pressure dependence of the ^{35}Cl NQR frequency in 2,6 dichloropyridine.

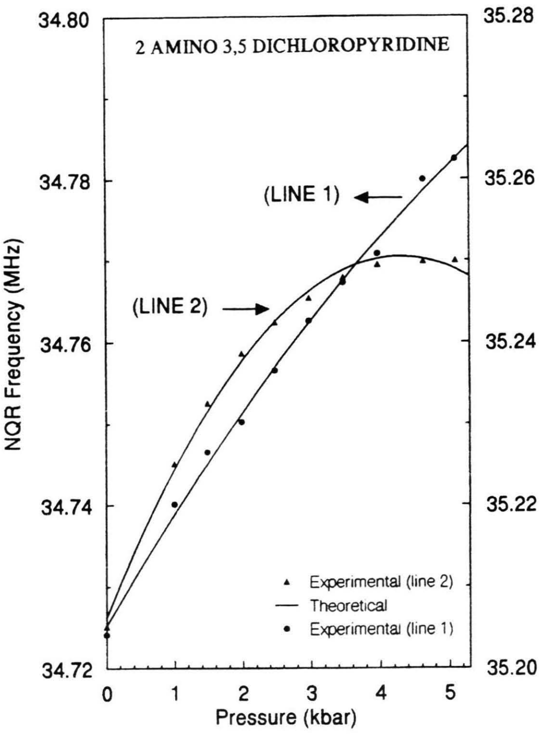

Fig. 2. Pressure dependence of the ^{35}Cl NQR frequency in 2 amino 3,5 dichloropyridine.

The first term in (2) is the "static term" and represents the effect of pressure on the static lattice (due to compression) in the absence of all lattice vibrations; the second term, the "dynamic term", represents the effect of pressure on the amplitude of torsional oscillations.

In molecular solids where the EFG is primarily intramolecular in origin, the main contribution to the pressure variation of NQR frequency comes from changes in the amplitudes of the torsional oscillations. As the amplitudes decrease with pressure, the term $\partial\langle\theta^2\rangle/\partial P$ decreases. Due to the negative sign in (2), the dynamic term results in a positive $(\partial\nu/\partial P)_T$. However, as the pressure is progressively increased, the changes in the torsional amplitudes decrease and the static term becomes more important and may eventually overcome the dynamic contribution.

The pressure dependence of the ^{35}Cl NQR frequencies at 300 K in the three compounds is shown in Figures 1–3. The NQR frequencies of the three substances at one bar and 5.1 kbar are given in the Table 1. The experimental data were fit to a polynomial in pressure:

$$\nu(P)=A_0+A_1P+A_2P^2, \tag{3}$$

Table 1. The best fit values of Equation (3).

Compound		NQR Frequency (MHz)		A_0 (MHz)	A_1 (kHz bar^{-1})	A_2 (kHz bar^{-2})
		Atm. P	5.1 kbar			
2,6-dichloropyridine		33.8432	34.0110	33.8449	0.05668	−0.004634
2 amino 3,5-dichloropyridine	Line 1	34.7241	34.7824	34.7251	0.01427	−0.000599
	Line 2	35.2041	35.2499	35.2051	0.02002	−0.002227
6 chloro 2-pyridinol		34.5030	34.6818	34.5020	0.05007	−0.003014

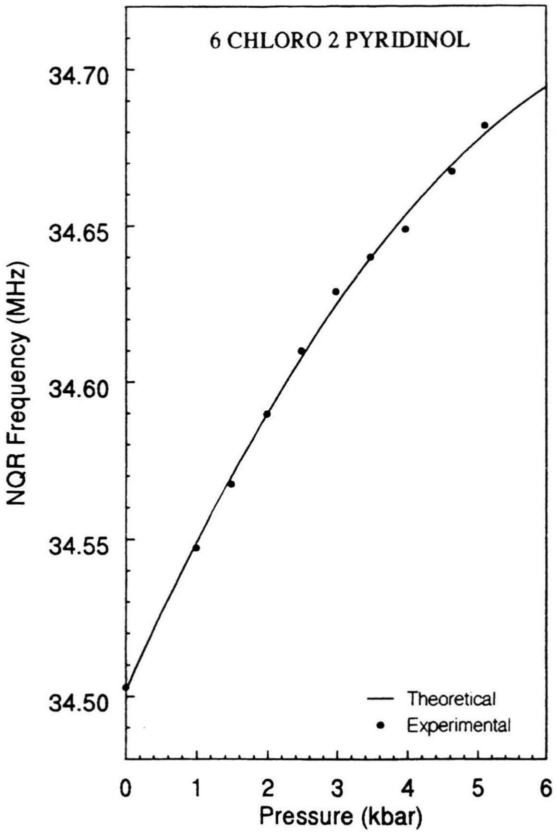

Fig. 3. Pressure dependence of the ^{35}Cl NQR frequency in 6 chloro 2-pyridinol.

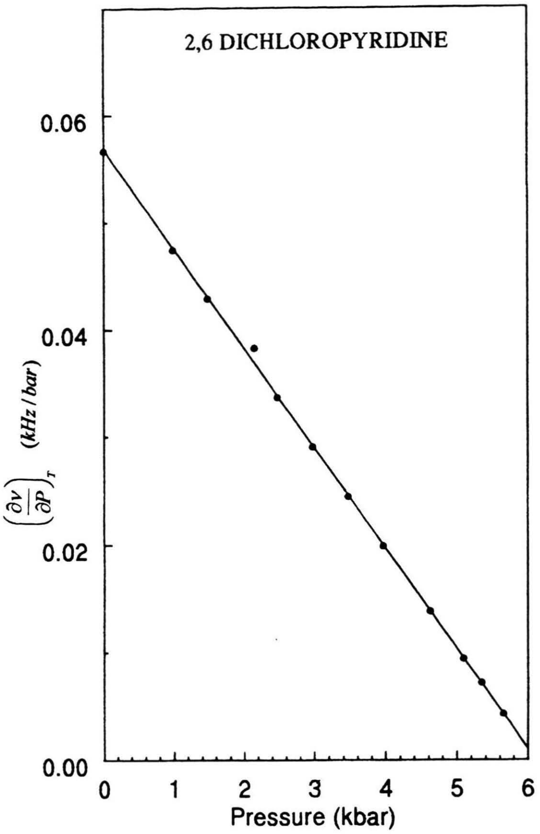

Fig. 4. Variation of $\left(\frac{\partial \nu}{\partial P}\right)_T$ with pressure in 2,6 dichloropyridine.

The best fit parameters of (3) are shown in Table 1. Since A_2 is negative the NQR frequency can decrease if the pressure is increased further. Using the best fit equations, (Figs. 4–6) were obtained $(\partial \nu/\partial P)_T$ is found to be appreciably larger for 2,6-dichloropyridine and 6 chloro 2-pyridinol than for 2 amino 3,5-dichloropyridine. The non-linearity of $\nu(P)$ seems to be due to the opposing nature of the dynamic and static contributions to the pressure dependence and also due to the decrease in the compressibility of solids at higher pressures.

As explained by Bayer [14], the temperature dependence of NQR frequencies arises from the motional averaging of the electric field gradient caused by low-lying librational modes. In the high temperature limit, the temperature dependence of NQR frequencies can be expressed as [15]

$$\left(\frac{\partial \nu}{\partial T}\right)_V = \sum_{i=x,y} \left(\frac{3\nu_0 k}{4\pi^2}\right) \frac{1}{I_i f_i^2}, \tag{4}$$

where f_i is the torsional frequency, I_i the moment of inertia of the molecule, k the Boltzmann constant and ν_0 the NQR frequency at 0 K.

Taking into account the effect of volume change due to temperature and pressure, the constant volume temperature derivative of NQR frequency can also be written as [16]

$$\left(\frac{\partial \nu}{\partial T}\right)_V = \left(\frac{\partial \nu}{\partial T}\right)_P + \frac{\beta}{\chi}\left(\frac{\partial \nu}{\partial P}\right)_T, \tag{5}$$

where β/χ is the ratio of the macroscopic coefficient of thermal expansion to the isothermal compressibility. In a normal temperature dependence experiment, the temperature coefficient of the resonance frequency at constant pressure is measured. Using (5) it is possible to combine $\nu(T)$ and $\nu(P)$ data to estimate the constant volume temperature derivative of the NQR frequency. $(\partial \nu/\partial T)_V$ represents the effect of temperature through molecular motion on the resonance frequency. On the basis of

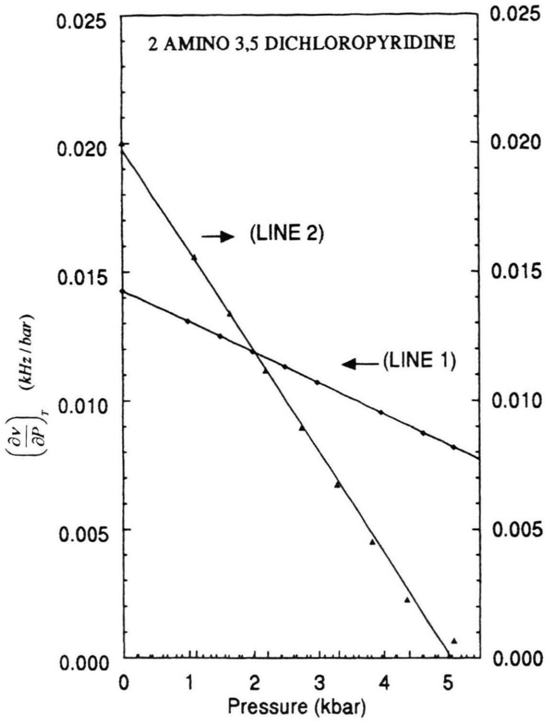

Fig. 5. Variation of $\left(\frac{\partial \nu}{\partial P}\right)_T$ with pressure in 2 amino 3,5 chloropyridine.

measurements reported for similar substances [16–18], a value of 25 kg cm^{-2} K^{-1} has been assumed for the ratio β/χ, and using the experimental values of $(\partial \nu/\partial T)_P$ and $(\partial \nu/\partial P)_T$, (5) was solved to estimate the values of $(\partial \nu/\partial T)_V$. These $(\partial \nu/\partial T)_V$ values were used in (4), along with the values of I_i and ν_0 taken from literature [6, 8, 9] (Table 2), to calculate the torsional frequency for all the compounds, as given in Table 3. The torsional frequencies are in good agreement with those reported [6, 8, 9].

Pressure Dependence of the Spin Lattice Relaxation Time T_1

Bayer [14] proposed a model that the ^{35}Cl quadrupole spin-lattice relaxation in crystalline *p*-dichlorobenzene and other chlorine substituted aromatic hydrocarbons is governed by random fluctuations in the EFG caused by the torsional oscillations of the molecule. This model was further discussed in detail by Woessner and Gutowsky [19]. Jones et al. [20] have studied the variation of T_1 with pressure in *p*-dichlorobenzene and 1,3,5 trichlorobenzene where they have found a nonlinear increase in T_1 with pressure. In the present work, T_1 in all the three compounds is found to increase slowly with pressure. In case of 2,6-dichloropyridine, T_1 was found to be 12.3 ms at atmospheric pressure and 18.1 ms at 5.65 kbar. In 2 amino 3,5-dichloropyridine the values of T_1 for the two lines are 38.3 ms and 42.7 ms at atmospheric pressure and the corresponding values are 53.2 ms and 57.2 ms respectively at 5.1 kbar. In 6 chloro 2-pyridinol the value of T_1 is 9.4 ms at atmospheric pressure and 16.9 ms

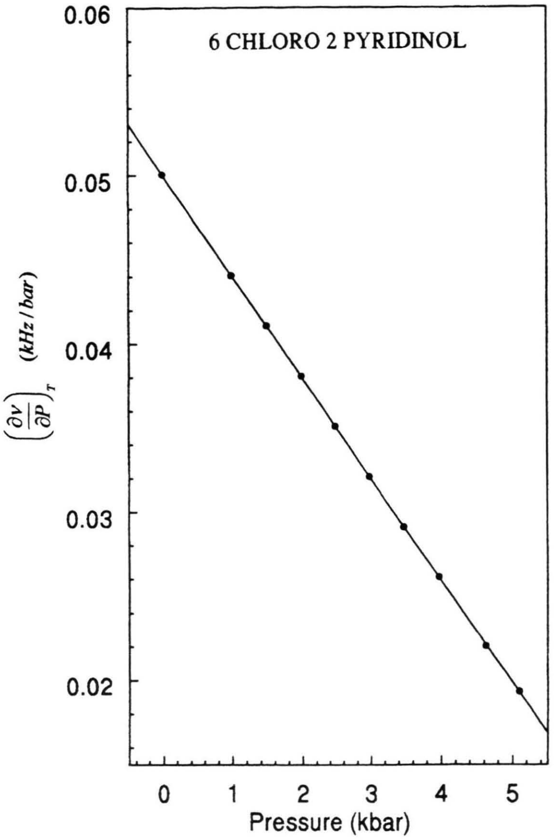

Fig. 6. Variation of $\left(\frac{\partial \nu}{\partial P}\right)_T$ with pressure in 6 chloro 2-pyridinol.

Table 2. Values of ν_0 and I_i.

Compound		NQR frequency ν_0 (MHz)	Moment of inertia I_i (10^{-40} kg cm^{-2})
2,6-dichloropyridine		34.8180	1292.5
2 amino 3,5 dichloropyridine	Line 1	35.3323	1389.2
	Line 2	35.8909	1394.5
6 chloro 2-pyridinol		35.0732	918.0

Table 3. Temperature and Pressure derivatives of ^{35}Cl NQR.

Compound		$(\partial\nu/\partial T)_P$ (kHz K^{-1})	$(\partial\nu/\partial P)_T$ at P=1 bar (Hz bar^{-1})	$(\partial\nu/\partial T)_V$ (kHz K^{-1}) Equation (5)	f_i (cm^{-1})
2,6-dichloropyridine		−4.32	56.68	−2.91	32.8
2 amino 3,5-dichloropyridine	Line 1	−2.93	14.27	−2.57	33.9
	Line 2	−2.98	20.02	−2.48	34.8
6 chloro 2-pyridinol		−2.5	50.07	−1.49	54.5

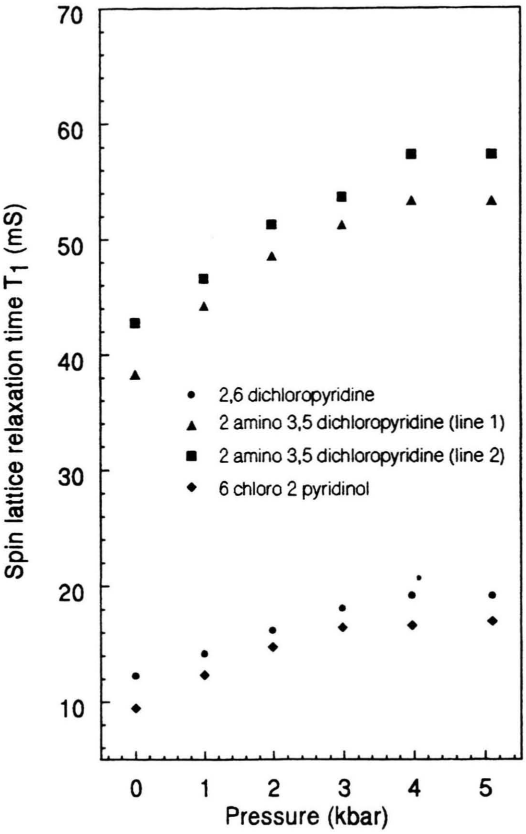

Fig. 7. Pressure dependence of the ^{35}Cl NQR spin lattice relaxation time in the three pyridines.

Table 4. Comparison of pressure and temperature derivatives of T_1.

Compound		$\frac{d\ln T_1}{dP}$ (kbar^{-1})	$\frac{d\ln T_1}{d\ln T}$	m
2,6-dichloropyridine		0.13	−2.38	2.30
2 amino 3,5 dichloropyridine	Line 1	0.23	−2.31	2.29
	Line 2	0.17	−2.18	2.18
6 chloro 2-pyridinol		0.34	−2.16	1.84

at 5.1 kbar. Fig. 7 shows the variation of T_1 with pressure in the three compounds. Jones et al. [20] have arrived at the following equation, using Bayer's model as developed by Woessner and Gutowsky [19]:

$$\frac{d\ln T_1}{dP} = -\frac{\zeta}{\beta T}\left(m + \frac{d\ln T_1}{d\ln T}\right), \tag{6}$$

where ζ is the volume compressibility given as $\zeta = -\,d(\ln V)/dP$ and β is the cubic coefficient of thermal expansion given as $\beta = d(\ln V)/dT$. In molecular crystals in which relaxation is governed by random fluctuations in the EFG due to the torsional modes, $d(\ln T_1)/dP$ is positive and $d(\ln T_1)/d\ln T$ is negative. The values of $d(\ln T_1)/d\ln T$ typically lie in the range −2 to −3 [21]. When the spin lattice relaxation is due to torsional motions, the variation of T_1 with temperature follows the equation [19]

$$T_1^{-1} = a\,T^m. \tag{7}$$

The variation of T_1 with temperature has been studied in [7] for 2,6-dichloropyridine in [8] for 2 amino 3,5-dichloropyridine, and in [10] for 6 chloro 2-pyridinol. Table 4 gives the pressure and temperature derivatives of T_1 for the three compounds along with the m values. The values of m are found to lie within 1.8 and 2.4. The signs of these differentials are consistent with (6), and $d\ln T_1/dP$ is as expected for the case where T_1 is mainly due to torsional oscillations. Thus the torsional motions are responsible for the relaxation, resulting in the weak pressure dependence of T_1.

Conclusion

The NQR frequency in the pyridines studied increases nonlinearly with pressure, which is indicative of an increased contribution from the "static" distortion at higher pressures. Constant volume Bayer terms are calculated, which show good agreement between theoretical and experimental values. The experimental T_1 shows a small increase with pressure, which implies that torsional oscillations are mainly responsible for the relaxation.

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