Pressure Dependence of the Chlorine NQR in Three Solid Chloro Anisoles

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The ^{35}Cl Nuclear Quadrupole Resonance (NQR) frequency (ν_Q) and spin lattice relaxation time (T_1) in the three anisoles 2,3,4-trichloroanisole, 2,3,6-trichloroanisole and 3,5-dichloroanisole have been measured as a function of pressure upto 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, the rate of which is positive and decreases with increasing pressure. In case of 3,5-dichloroanisole the value becomes negative in the higher range of pressure studied. The spin lattice relaxation time T_1 in all the three compounds shows a weak dependence on pressure, indicating that the relaxation is mainly due to the torsional motions.

Key words: NQR; ^{35}Cl; Frequency; Spin-lattice Relaxation Time; Torsional Motion; Pressure and Temperature Dependence; 3,5-dichloroanisole; 2,3,4-trichloroanisole; 2,3,6-trichloroanisole.

Introduction

Anisoles are benzene ring molecules having a methoxy group attached to carbon –1. In contrast to chloroanisoles, phenols have the hydroxyl group. Orthochlorophenols exhibit both inter- and intramolecular hydrogen bonding, the ortho-chlorine playing an important role [1–9]. Chloroanisoles do not exhibit any hydrogen bonding [1–10]. Bayle et al. [9] have studied the effects of inter- and intra-molecular hydrogen bonding in chlorophenols by comparing their ^{35}Cl NQR frequencies, at room temperature and at 77 K, with those of the corresponding chloroanisoles. High pressure NQR studies have been carried out in phenols by Krishnamoorthy et al. [8], but no such investigations are reported in chloroanisoles. Thus a study of anisoles would be interesting as they can be compared with phenols. We have carried out the NQR measurements in three anisoles 3,5-di, 2,3,4- and 2,3,6-trichloroanisoles. While the two chlorines are meta to the methoxy group in 3,5-dichloroanisole, we have in 2,3,4-trichloroanisole all three types of chlorine viz. ortho, meta, and para. In 2,3,6-trichloroanisole, chlorine at 2 and 6 are ortho to the methoxy group. It would be interesting to see how pressure would affect the NQR frequencies and spin lattice relaxation times T_1 in these different types of chlorine. The results of the measurement are reported in this paper.

The temperature dependence of the ^{35}Cl NQR frequency in these anisoles has been studied by Rukmani et al. [11, 12] in the range 77–300 K. The data have been analyzed in the light of the Kushida-Bayer-Brown models. They have evaluated the torsional frequencies and their temperature variation under a two mode approximation using the Bayer model with Tatsuzaki's correction [11, 12]. They have also reported the far infrared and Raman spectra in these anisoles. The compounds used in the present investigations have been procured from Aldrich Chemical Company, U.S.A and used as such. The measurements have been carried out using a home made pulsed NQR spectrometer. Hydrostatic pressure has been generated using a lock-nut type piston-cylinder device [13] and the teflon cell technique [14]. Liquid paraffin was used as the pressure transmitting medium. T_1 has been measured using the inversion recovery sequence ($\pi - \tau - \pi/2$). The width of the π pulse is 20 µs, and that of the $\pi/2$ pulse is 10 µs. τ is varied from 500 µs to 500 ms. The duration of free induction decay (FID) signal is around 200 µs for all the compounds. The NQR frequency and T_1 have been measured with an accuracy of ± 0.0005 MHz and ± 5%, respectively.

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Results

The effect of lattice vibrations on the average value of the electric field gradient (EFG) [15] 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; q_0 is the field gradient of the stationary lattice. From (1) we can obtain

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

The first term in (2) is the 'static term' and represents the effect of pressure on the static lattice (due to compression); the second term, the 'dynamic term', respresents the effect of pressure on the amplitudes of the 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 the changes in the amplitudes of the torsional oscillations. As the amplitudes decrease with pressure, the term $\partial\langle \theta^2 \rangle/\partial p$ is negative. However, in view of the negative sign in (2), the pressure coefficient of the NQR frequency becomes positive. However, as the pressure is progressively increased, the changes in the torsional amplitudes decrease and the static term can become relatively more important and may eventually overcome the dynamic contribution.

Pressure Dependence of NQR Frequency

The pressure dependence of the ^{35}Cl NQR frequencies at 300 K in all the three compounds is shown in Figures 1–3. The variation of the NQR frequency with pressure has been observed to be nonlinear in all the three compounds. The NQR frequencies at 1 bar and 5.1 kbar are shown in Table 1. The experimental data can be expressed in terms of a 2nd order polynomial in pressure of the form

$$\nu(p) = A_0 + A_1 p + A_2 p^2. \tag{3}$$

The best fit parameters are shown in Table 1. From the best fit values it can be seen that A_2 is negative, indicating a decrease of the NQR frequency if the pressure is increased further. A decrease of the NQR frequency at higher pressures is observed in 3,5-dichloroanisole. It is

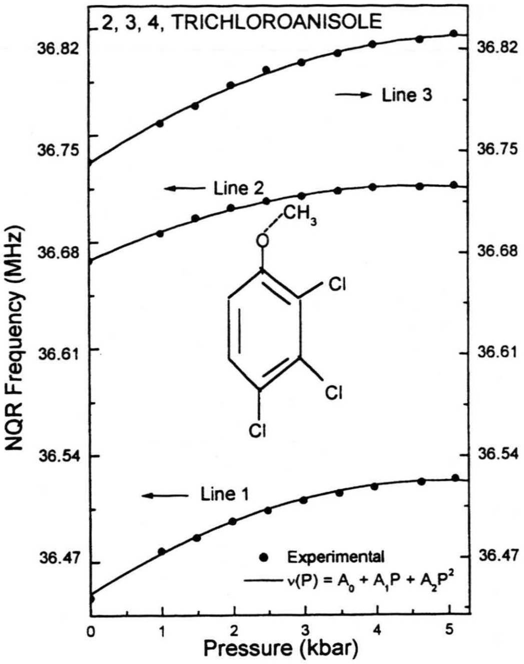

Fig. 1. Variation of ^{35}Cl NQR frequency with pressure in 2,3,4-trichloroanisole.

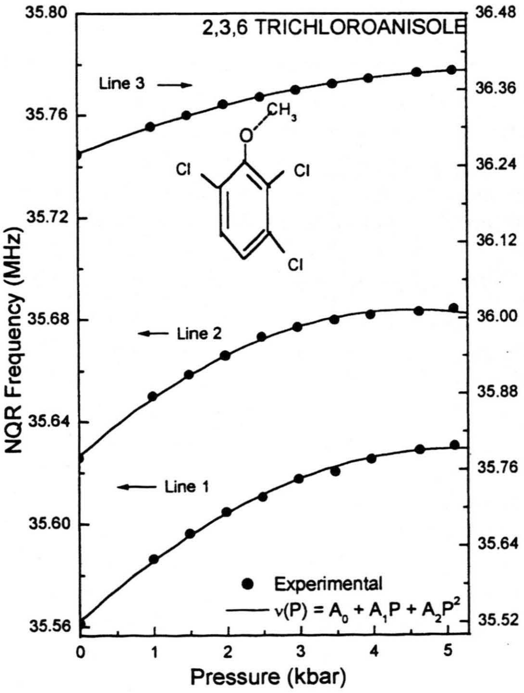

Fig. 2. Variation of ^{35}Cl NQR frequency with pressure in 2,3,6-trichloroanisole.

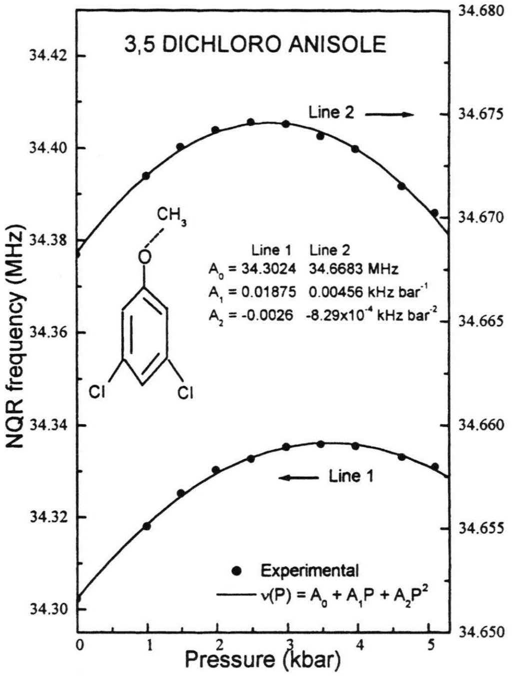

Fig. 3. Variation of ^{35}Cl NQR frequency with pressure in 3,5-dichloroanisole.

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

Compound		NQR frequency (MHz)		A_0 (MHz)	A_1 (kHz bar^{-1})	A_2 (kHz bar^{-2})
		Atm.P.	5.1 kbar			
2,3,4-trichloro-anisole	Line 1	36.2831	36.3388	36.2850	0.02145	–0.00217
	Line 2	36.4299	36.4654	36.4302	0.01538	–0.00167
	Line 3	36.7424	36.8301	36.7415	0.03215	–0.00297
2,3,6-trichloro-anisole	Line 1	35.5605	35.6300	35.5616	0.02591	–0.00248
	Line 2	35.6257	35.6842	35.6266	0.02530	–0.00280
	Line 3	36.2578	36.3908	36.2592	0.04605	–0.00401
3,5-dichloro-anisole	Line 1	34.3023	34.3308	34.3024	0.01875	0.00456
	Line 2	34.6682	34.6702	34.6683	–0.0026	-8.29×10^{-4}

clear from the plot that the static effects are predominant at the higher pressures. A comparison of this plot with that for 2,3,4- and 2,3,6-trichloroanisoles shows that the absence of ortho chlorine to the methoxy group in 3,5-dichloroanisole has resulted in a more prominent pressure effect. Using the best fit values, the pressure coefficients of the NQR frequency $(\partial \nu/\partial p)_T$ are calculated, and their dependence on pressure are shown in Figs. 4–6. A linear variation of the pressure coefficient

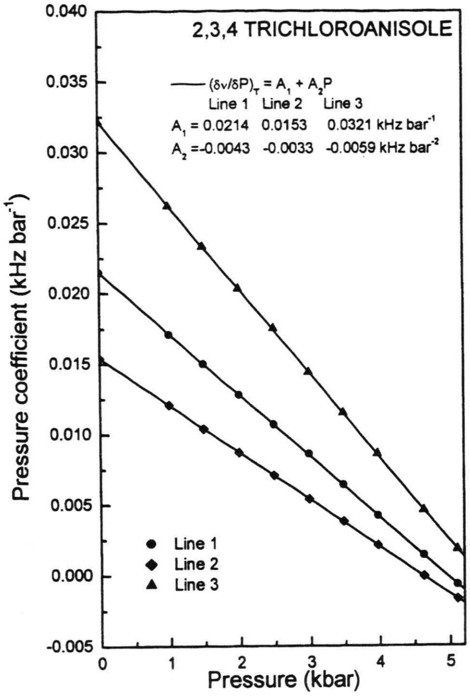

Fig. 4. Variation of pressure coefficient of NQR frequency with pressure in 2,3,4-trichloroanisole.

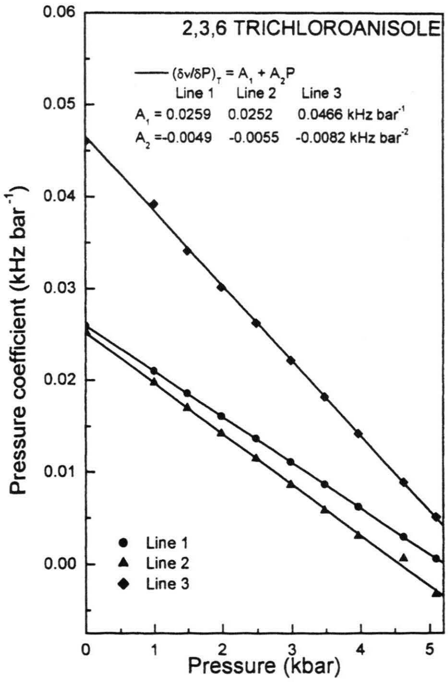

Fig. 5. Variation of pressure coefficient of NQR frequency with pressure in 2,3,6-trichloroanisole.

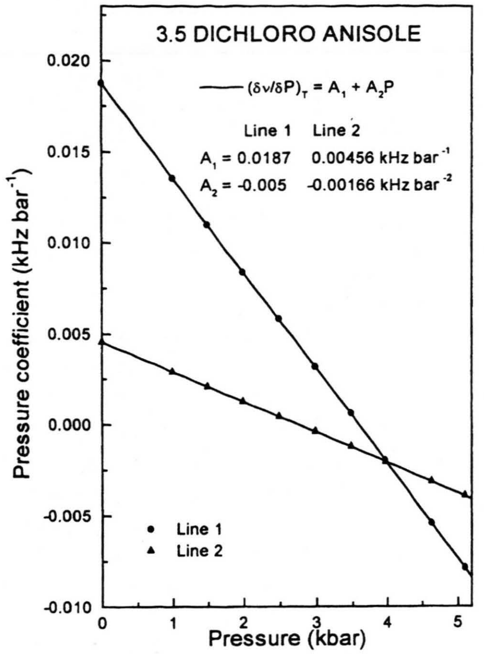

Fig. 6. Variation of pressure coefficient of NQR frequency with pressure in 3,5-dichloroanisole.

with pressure is observed. The non-linearity in $\nu(p)$ 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 compressibility (dynamic effects) of solids at higher pressure.

Thermodynamic Analysis of the NQR Frequency Data

As explained by Bayer [16], the temperature dependence of NQR frequencies arises from the motional averaging of the EFG caused by low lying librational modes. From the observed temperature and pressure derivatives of the NQR frequency, the constant volume temperature derivative $(\partial\nu/\partial T)_V$, i.e. the Bayer term that represents explicit changes in the NQR frequency due to variations in the temperature can be obtained. The following equation, involving the derivatives of the NQR frequency, is used [17]:

$$\left(\frac{\partial\nu}{\partial T}\right)_V = \left(\frac{\partial\nu}{\partial T}\right)_p + \frac{\beta}{\chi}\left(\frac{\partial\nu}{\partial p}\right)_T, \tag{4}$$

where β and χ are the thermal expansion coefficient and isothermal compressibility, respectively. In the high temperature limit, the temperature dependence of the NQR frequency is given by [18]

$$\left(\frac{\partial\nu}{\partial T}\right)_V = \sum_{i=x,y}\left(\frac{3\nu_0 k}{4\pi^2}\right)\frac{1}{I_i f_i^2}, \tag{5}$$

where f_i is the torsional frequency, ν_0 the NQR frequency at 0 K, I_i the moment of inertia of the molecule and k the Boltzmann constant. On the basis of measurements reported for similar substances [17, 19, 20], a value of 25 kg cm^{-1} K^{-1} has been assumed for the ratio β/χ. By substituting the value of constant volume derivative from (4) in (5), the values of f_x and f_y for the two modes are calculated. In this calculation, the value of $(\partial\nu/\partial T)_p$ is taken from the NQR frequency versus temperature data reported in [11]. Table 2 gives the ν_0 and moment of inertia values used to calculate the torsional frequencies, and Table 3 gives the pressure and temperature coefficients and torsional frequencies. They agree well with those reported in [11–12].

Table 2. Values of ν_0 and I_i.

Compound		NQR frequency ν_0 (MHz)	Moment of intertia I_i ($\times 10^{-40}$ kg cm^{-2})	
			I_x	I_y
2,3,4-trichloro-anisole	Line 1	36.8607	1245.28	847.101
	Line 2	37.0489	1245.21	568.717
	Line 3	37.3725	1245.24	527.979
2,3,6-trichloro-anisole	Line 1	36.2478	1285.89	935.822
	Line 2	36.3119	1285.89	935.822
	Line 3	37.1375	1286.97	568.717
3,5 dichloro-anisole	Line 1	34.9680	1069.45	589.428
	Line 2	35.1691	1069.45	589.428

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

Compound		$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial p}\right)_T$ ($\times 10^{-6}$ bar^{-1})		$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial T}\right)_p$ ($\times 10^{-4}$ K^{-1})		f_i (cm^{-1})	
		Atm.P.	5.1 kbar	77 K	300 K	f_x	f_y
2,3,4-trichloro-anisole	Line 1	0.589	–0.0193	–0.395	–0.829	36.2	43.9
	Line 2	0.423	–0.0466	–0.427	–0.875	34.7	51.3
	Line 3	0.876	0.0489	–0.391	–1.026	33.5	51.4
2,3,6-trichloro-anisole	Line 1	0.728	0.0168	–0.503	–0.969	33.5	39.3
	Line 2	0.710	–0.0924	–0.493	–0.982	32.9	38.6
	Line 3	1.271	0.140	–0.666	–1.022	34.7	52.3
3,5-dichloro-anisole	Line 1	0.547	–0.229	–0.460	–1.061	34.2	46.0
	Line 2	0.132	–0.112	–0.344	–0.794	38.0	51.2

The far infrared spectrum of all the three compounds was recorded by Rukmani et al. [11–12] in the range 20–150 cm^{-1}. Bands at 58 cm^{-1} (2,3,4-trichloroanisole), 52 cm^{-1} (2,3,6-trichloroanisole) and 52 cm^{-1} (3,5-dichloroanisole) have been observed at room temperature. They also recorded the Raman spectra in this compound on a Laser-Raman spectrometer ($\lambda = 4880$ Å). Raman lines were observed at 104 cm^{-1}, 132 cm^{-1}, 204 cm^{-1}, 217 cm^{-1}, 338 cm^{-1}, 402 cm^{-1} and 510 cm^{-1} for 2,3,4-trichloroanisole. They could not record Raman spectra below 100 cm^{-1} due to excess noise and drift. They have also recorded the laser Raman spectra at room temperature which have shown peaks at 50 cm^{-1}, 106 cm^{-1}, 206 cm^{-1}, 214 cm^{-1}, 220 cm^{-1}, 307 cm^{-1} and 369 cm^{-1} in case of 2,3,6-trichloroanisole, and peaks at 55 cm^{-1}, 162 cm^{-1}, 189 cm^{-1} and 206 cm^{-1} in case of 3,5-dichloroanisole. The torsional modes evaluated from the NQR results are in good agreement with the infrared spectra results.

The equation of state for the solid, to transform the ν-versus $-\,p$ isotherms to ν-versus $-\,V$ isotherms as given by Kushida, Benedek, and Bloembergen [18] is used in the present analysis. The equation for the compressibility χ of the solid is given by

$$\chi(T,V) = -\frac{1}{V}\frac{\partial V}{\partial p} = \frac{\dfrac{V_0}{V}\,\chi_{00}}{\left[1-\xi\left(\dfrac{V-V_0}{V_0}\right)\right]}. \qquad (6)$$

Here V/V_0 is the volume of the solid at any temperature and pressure relative to the volume at $T = 0$ and $p = 0$. ξ is a constant whose value is about 7.63 [18]. χ_{00}, the compressibility of the solid at $T = 0$ and $p = 0$, was set equal to $14 \times 10^{-6}\ \text{kg}^{-1}\ \text{cm}^{-2}$ [18]. The equation of state obtained from (6) is given as

$$\frac{\xi}{2}\left(\frac{V}{V_0}\right)^2 - (1+\xi)\left(\frac{V}{V_0}\right) - \left[\chi_{00}\,p - (1+\xi)\exp\left(\int_0^T \beta(T)\,\mathrm{d}T\right) + \frac{\xi}{2}\exp\left(2\int_0^T \beta(T)\,\mathrm{d}T\right)\right] = 0. \qquad (7)$$

The equation of state is of the form

$$A\left(\frac{V}{V_0}\right)^2 + B\left(\frac{V}{V_0}\right) + C = 0. \qquad (8)$$

Knowing the values of χ_{00} and the cubical thermal expansion coefficient taken as $336 \times 10^{-6}\ \text{K}^{-1}$ [18] at 300 K, the equation of state can be solved to find (V/V_0) corresponding to each pressure p. Figures 7–9 show plots of the NQR frequency as a function of volume.

In the high temperature approximation ($h\nu \ll kT$) the volume and temperature dependence of the NQR frequency can be written as [18]

$$\nu_T = a\left(\frac{V}{V_0}\right)^n \left[1 + b\left(\frac{V}{V_0}\right)^{-2\gamma} T\right], \qquad (9)$$

where the exponents n and γ represent the volume dependence of the static and dynamic contributions to the NQR frequency. The variation of the NQR frequency with volume is fit to the above equation, assuming $a = \nu_0$ as given in Table 2. The values of the parameters of (9) are shown in Table 4. The value of n gives the static contribution, and the value of γ gives the dynamic contribution to the NQR frequency. From the plots it can be seen that at high volumes, i.e. at low pressures, the dynamic effect dominates and at low volumes, i.e. at high pressures, the static effects dominate, but the value of γ is quite small, suggesting that the contribution from the dynamic term is low.

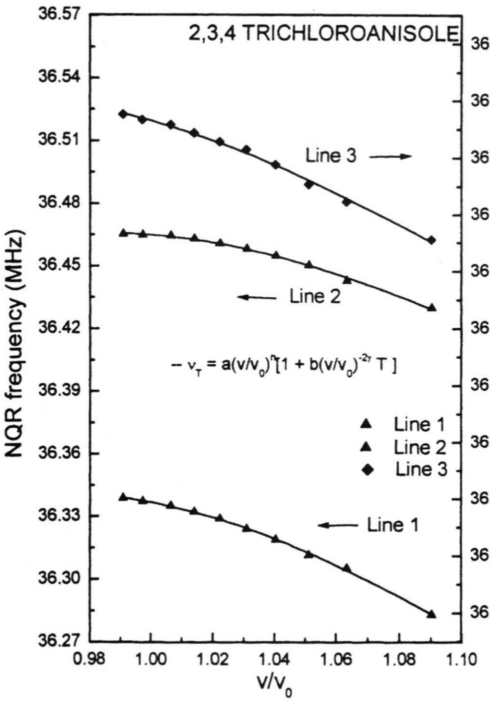

Fig. 7. Variation of ^{35}Cl NQR frequency with volume in 2,3,4-trichloroanisole.

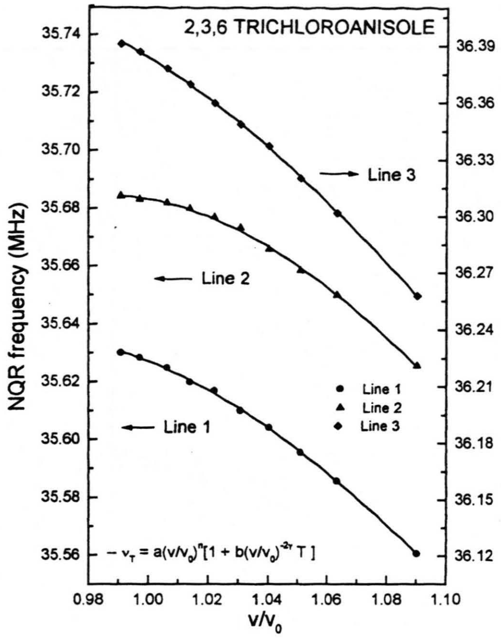

Fig. 8. Variation of ^{35}Cl NQR frequency with volume in 2,3,6-trichloroanisole.

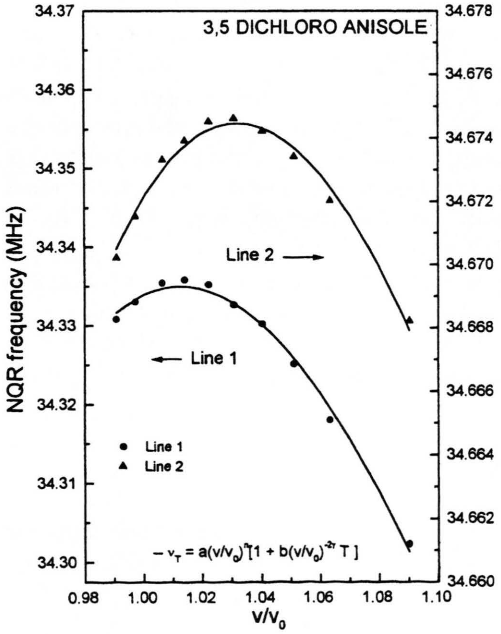

Fig. 9. Variation of ^{35}Cl NQR frequency with volume in 3,5-dichloroanisole.

Table 4. The parameters of (9).

Compound		n	b ($\times 10^{-5}$ K^{-1})	γ
2,3,4-trichloroanisole	Line 1	−0.067	−5	2.04
	Line 2	−0.06	−5	1.78
	Line 3	−0.08	−5	2.12
2,3,6-trichloroanisole	Line 1	−0.079	−6	1.95
	Line 2	−0.084	−6	2.26
	Line 3	−0.113	−7	2.09
3,5 dichloroanisole	Line 1	−0.083	−6	2.39
	Line 2	−0.041	−5	1.59

Pressure Dependence of Spin Lattice Relaxation Time T_1

The spin lattice relaxation time measurements as a function of pressure are carried out at room temperature in all the compounds. T_1 varies nonlinearly (though the variation is small) with pressure for all the lines. Figures 10–12 show plots of T_1 as a function of pressure for all the compounds.

Bayer [16] proposed that the ^{35}Cl quadrupole spin-lattice relaxation in *p*-dichlorobenzene and other chlorine substituted aromatic hydrocarbons where the relaxation is governed by random fluctuations in the EFG is caused by the torsional oscillations of the molecule. This was analysed in detail by Woessner and Gutowsky [21]. Jones et al. [22] have studied the variatoni of T_1 with pressure in *p*-dichlorobenzene and 1,3,5-trichlorobenzene, where they have found a very small nonlinear increase in T_1 with pressure. The pressure coefficients of T_1 for *p*-dichlorobenzene and 1,3,5-trichlorobenzene are found to be 2.026×10^{-9} and 2.2×10^{-9} Pa^{-1}, respectively. Our data have been analyzed using the thermodynamical analysis given by Jones et al. [22].

Thermodynamical Analysis of the Spin Lattice Relaxation Data

Jones et al. [22] have arrived at the following equation, using Bayer's model as developed by Woessner and Gutowsky [21]:

$$\frac{\mathrm{d}\ln T_1}{\mathrm{d}p} = -\frac{\chi}{\beta T}\left(m + \frac{\mathrm{d}\ln T_1}{\mathrm{d}\ln T}\right), \qquad (10)$$

where χ is the volume compressibility given as $\chi = -\,\mathrm{d}\ln V/\mathrm{d}p$ and β is the cubic coefficients of thermal

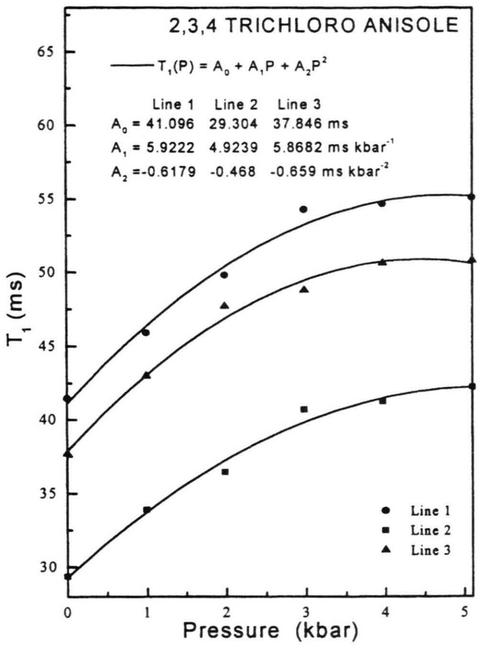

Fig. 10. Variation of spin lattice relaxation time T_1 with pressure in 2,3,4-trichloroanisole.

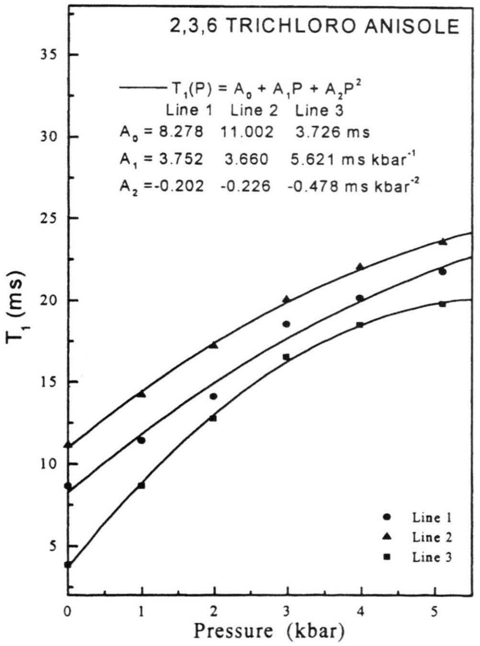

Fig. 11. Variation of spin lattice relaxation time T_1 with pressure in 2,3,6-trichloroanisole.

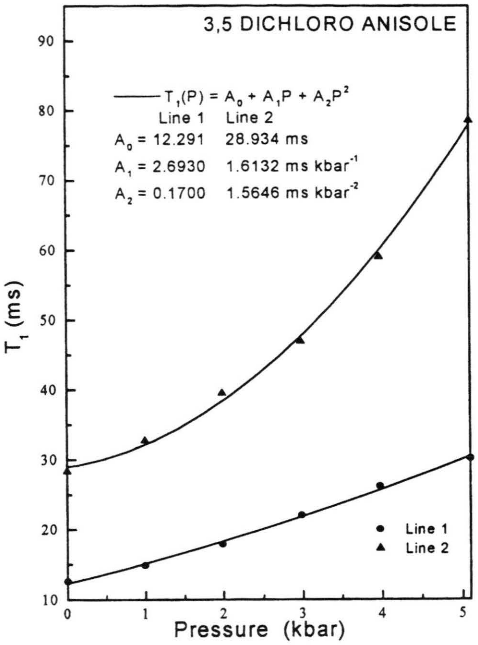

Fig. 12. Variation of spin lattice relaxation time T_1 with pressure in 3,5-dichloroanisole.

expansion given as $\beta = -\,\mathrm{d}\ln V/\mathrm{d}T$. The value of β/χ, as found from the thermodynamical analysis of the NQR frequency data as a function of temperature and pressure, is around 25 kg cm^{-2} K^{-1}. The temperature dependence of T_1 data is not available for this compound, but normally $\mathrm{d}\ln T_1/\mathrm{d}\ln T$ is negative and typically lies in the range -2 to -3 [23]. $\mathrm{d}\ln T_1/\mathrm{d}p$ is positive as found in the present experiment. The signs of these differentials are therefore consistent with (10), if $[m + (\mathrm{d}\ln T_1/\mathrm{d}\ln T)]$ is negative, which means that $m \cong 2$. Woessner and Gutowsky's analysis predicts that T_1^{-1} follows a T^2 law, if torsional motions are responsible for the relaxation. Then $\mathrm{d}\ln T_1/\mathrm{d}p$ will be small, as observed in our experiments.

Discussion

Some of the important observations made regarding the NQR frequencies corresponding to different chlorine positions are discussed briefly below. The two ortho chlorines (2-chlorine and 6-chlorine) show different NQR frequencies, which means that they have different EFG's at their sites. A similar behaviour is observed in chlorophenols, where intramolecular hydrogen bonding between the O–H proton and the 2-chlorine results in the transfer of a lone pair of electrons from the chlorine to the hydrogen bond and thereby reduces the resonance frequency of 2-chlorine. But in case of chloroanisoles no such hydrogen bonding mechanism is present and one would expect the two ortho chlorines to have the same frequency if situated symmetrically in molecule, as in 2,3,6-trichloroanisole. The fact that this is not so, can be attributed either to intermolecular effects due to packing (crystal field effects) or to the methoxy group being a little asymmetric with respect to the two ortho chlorines. The 2-chlorine is assumed to have the higher frequency, and if one takes into account the higher K_i value quoted by Bayle et al. [9] for the ortho chlorine towards which the methoxy group points, it is possible to state that the methoxy group must point a little towards the 2-chlorine.

The two chlorines in the meta position also show different resonance frequencies. The frequency difference in this case is much smaller, and it is reasonable to assume that the reasons for this are the same as in the case of the ortho chlorine. Thus one can assign the higher frequency line to the 3-chlorine. The para position is expected to be affected least by the methoxy group. Thus the chlorine at the para position is observed to have the lowest of the three frequencies in 2,3,4-trichloroanisole.

It is observed that the NQR frequencies increase with the number of chlorine atoms of the molecule, i.e. the NQR frequency observed in case of 3,5-dichloroanisole is less compared to that of 2,3,4- and 2,3,6-trichloroanisole. This reflects an increase in the electrons attractive power of the substituted molecule with respect to the resonant chlorine atom or, in other words, a decrease in the ionic character of the C–Cl bond. The NQR frequencies observed lie in the range 34–38 MHz, indicating a similar chemical environment around the chlorine nuclei.

A comparison of the pressure coefficients in 2,3,4- and 2,3,6-trichloroanisole shows interesting features. The pressure coefficients of line 3 (2-chlorine) in 2,3,4- and 2,3,6-trichloroanisoles are higher compared to line 1 and line 2 in both cases at atmospheric pressure and 5.1 kbar. Line 3 of 2,3,6-trichloroanisole has a higher value of pressure coefficient both at atmospheric pressure and 5.1 kbar. This may be due to the absence of Cl meta to 6-chlorine, resulting in lower static effects and higher dynamic effects. Line 2 (3-chlorine) of 2,3,4-trichloroanisole has two chlorines ortho to 3-chlorine, and it has the lowest pressure coefficient at atmospheric pressure. The pressure coefficients are observed to be very small in case of 3,5-dichloroanisole and becomes negative at higher pressures, showing that the static effects are predominant at higher pressures.

The temperature coefficients are almost similar in all the anisoles, indicating that the internal motions responsible for the motional averaging of the EFG, are similar. This is true, as seen from the torsional frequencies calculated from the thermodynamical analysis, which shows almost the same values for all the compounds studied. The torsional frequencies obtained in the present study agree well with the far infrared and laser Raman spectral results.

As the crystal is compressed, the effects of intermolecular interaction become appreciable, and q_0 is reduced. Thus the exponent $n = \mathrm{d} \ln q_0 / \mathrm{d} \ln V$ may be large and negative for initial changes in pressure. In a series of compounds belonging to a family, if the strength of intermolecular interaction increases, this static term should become more negative; which implies that the measured pressure coefficients of the NQR frequency become progressively less positive and then become negative.

Jones et al. [22] have proposed a model to explain the negative pressure dependence in 1,3,5-trichlorobenzene in terms of an anisotropic polarization of $3\,p_\pi$ orbitals due to an admixture of $3\,d_\pi$ orbitals. The extent of the admixture depends on the relative π-character in the bonds. According to such a model, the lower frequency line has a higher π-character, which leads to a larger distortion of the $3\,p_\pi$ orbitals with pressure. This results in a more negative pressure coefficient for the lower frequency line. Similar observations are made in anisoles also.

The spin lattice relaxation time T_1 was found to be weakly dependent on pressure, implying that the torsional oscillations are responsible for the relaxation.

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