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A nuclear quadrupole resonance study of the solids 2,3,6-trichloroanisole, 2,4,6-trichloroanisole and p-chloroanisole

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Abstract. The temperature dependence of the ^{35}Cl nuclear quadrupole resonance frequencies ν_Q of the solids 2,3,6-trichloroanisole, 2,4,6-trichloroanisole and p-chloroanisole are reported. The experimental measurements are analysed by means of the Bayer–Kushida theory. It appears that only low-frequency lattice modes contribute to the temperature dependence of $\nu_Q(T)$. A comprehensive study of the frequency data allows us qualitatively to identify the motion responsible for the electric field gradient averaging mechanism at the resonant sites. Additionally, an unreported phase was found in p-chloroanisole, which turns out to be that corresponding to the stable phase.

1. Introduction

Nuclear quadrupole resonance (NQR) is a widely used technique to study the electronic distribution, to analyse substituent effects on the resonant nuclei, to search for phase transitions, etc, in solid state physics. In this work, measurements of the temperature dependence of the ^{35}Cl NQR transition frequency $\nu_Q(T)$ in 2,3,6-trichloroanisole (2,3,6-TCA), 2,4,6-trichloroanisole (2,4,6-TCA) and p-chloroanisole (PCA) are reported. The main motivation of this research was to study the motions of the methoxy group ($-\text{OCH}_3$), to determine the influence of the substituents on the NQR parameters and to search for phase transitions. This latter aspect was additionally checked through the detection of anomalies ΔC_p in the specific heat by means of differential thermal analysis (DTA). The $\nu_Q(T)$ data were measured by means of a super-regenerative spectrometer and the $\Delta C_p(T)$ data by means of a DTA apparatus. Overall error in the measurements of $\nu_Q(T)$ and T are ± 500 Hz and ± 0.2 K, respectively. Frequency measurements were gathered at closely and evenly spaced temperatures (0.5 K) for each line. The 2,3,6-TCA frequency data were collected from 77 to 270 K, a temperature at which the signal-to-noise ratio was sufficiently poor to prevent measurements of good-quality data; the 2,4,6-TCA frequency data were collected from 77 to 300 K.

Previous work on similar compounds has been reported; Rukmani and Ramakrisna (1986) measured the temperature dependence of the ^{35}Cl $\nu_Q(T)$ for 3,5- and 2,3-dichloroanisole. Both compounds show two resonance lines each, and these have been assigned to the two chlorine atoms in the same molecule with the help of the additive model for the substituent effect (Biedenkapp and Weiss 1968). Their analyses of the

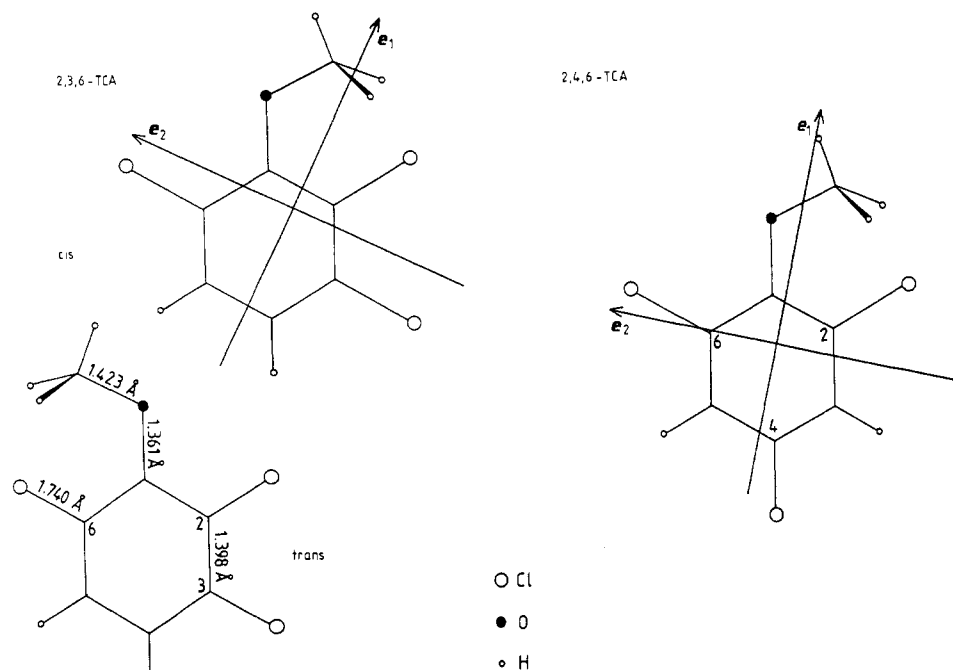


Figure 1. Molecular conformation of 2,3,6-TCA and 2,4,6-TCA and principal inertia axes.

NQR transition frequencies suggest that only normal mode frequencies of low value, e.g. those associated with lattice modes, dominate the temperature dependences. Unfortunately their experimental data does not allow us to pursue a more detailed analysis.

Peneau and Guibe (1968) studied the Zeeman splitting of the ^{35}Cl NQR lines on a 2,4,6-TCA single crystal at liquid nitrogen temperature. A value for the electric field gradient (EFG) asymmetry parameter, $\eta \approx 0.1$, and two relative directions of the EFG principal axis forming an angle of 55° approximately were found. This confirms the existence of two crystalline sites.

Bayle *et al* (1980) have studied the ^{35}Cl NQR frequencies of four different chloroanisoles which allows one to estimate that the crystalline-field contribution to the EFG at the resonant sites is of the order of 0.3 MHz. The assignment of the resonance lines is supported by both an additive model of the substituent effect and a derivation of resonance frequencies from INDO calculations of molecular orbital populations.

It is generally assumed that the chloroanisole molecule possesses a planar structure (Owen and Hester 1969), but other workers by means of different experimental techniques have suggested the possibility of a non-planar geometry. Aroney *et al* (1969) measured the electric dipole moment of anisole and other *para*-substituted anisoles and concluded that the non-planar conformation of the molecule is due to a torsion of the methoxy group around the C(1)–O bond by an angle of approximately 18° . Measurements of methyl torsional transitions on solid anisole by means of Raman spectroscopy (Konschin *et al* 1981) support evidence of the coexistence of two stable conformers: the locally stable orthogonal conformer and the globally stable planar conformer. The orthogonal conformation is one having the C(1)–O bond perpendicular to the benzene plane ring. The planar conformation was found to be energetically more favourable than the orthogonal conformation.

Calculated structural parameters for planar anisole (Konschin 1983) compare reasonably well with electron diffraction measurements reported by Seip and Seip (1973). These workers find that for planar conformation the benzene ring possesses hexagonal symmetry and the methyl group has a threefold symmetry axis coinciding with the C(7)–O bond. In addition the C(2)–C(1)–O angle α is found to be of the order of 124°.

From all the above considerations we have decided to assume the planar conformation for 2,3,6-TCA, 2,4,6-TCA and PCA compounds taking the angle $\alpha = 120^\circ$, although the coexistence of two configurations, namely *cis* or *trans*, for 2,3,6-TCA might be possible (figure 1). Since no crystallographic data are available for the trichloroanisoles we have also assumed that 2,3,6-TCA has two molecules per unit cell as for 2,4,6-TCA (Peneau and Guibe 1968).

2. Experimental results

2.1. ^{35}Cl nuclear quadrupole resonance assignments

The NQR frequencies for several chloroanisoles (2,3-, 2,4- and 3,5-dichloroanisole, 2,3,6-trichloroanisole and 2,4,6-trichloroanisole) which were measured at liquid nitrogen temperature and the frequency data for pentachloroanisole and 2,3,5,6-tetrachloroanisole taken from the literature (Bayle *et al* 1980) are given in tables 1 and 2. The frequency assignments were done by means of the additive model of the substituent effect (Biedenkapp and Weiss 1968):

$$\nu_{\text{cl}}^{\text{c}} = \nu_{\text{cl}}^0 + \sum_i K_i \quad (1)$$

where $\nu_{\text{cl}}^0 = 34.695$ MHz corresponds to the chlorobenzene NQR frequency and the K_i coefficients are the frequency shifts due to the i substituent (—Cl or —OCH₃ in the present case) at the position ortho, meta or para with respect to the resonant nucleus. The numerical values of the K_i , for both *cis* and *trans* configurations, were obtained from the literature (Bayle *et al* 1980). Figure 2 shows the experimental ν_{O} -values against the $\nu_{\text{cl}}^{\text{c}}$ calculated by means of equation (1). The points are situated along a line of positive slope over a band of about ± 0.4 MHz. Therefore the crystalline field in the anisoles is estimated to contribute ± 0.4 MHz to the NQR frequencies.

2.2. Analysis of the ^{35}Cl nuclear quadrupole resonance against T

Three resonance lines were detected in the temperature range 80–270 K for both 2,3,6-TCA and 2,4,6-TCA; the data are depicted in figures 3 and 4. Their temperature behaviours are normal and no phase transitions are observed; this was corroborated by measurements of $\Delta C_p(T)$ for both compounds. Following the Bayer–Kushida theory (see e.g. Kushida 1955) and on the assumption that the asymmetry parameter is negligible, the temperature dependence of ν_{O} may be written as

$$\nu_{\text{O}}(T) = \nu_0 [1 - \frac{2}{3} \langle \theta^2(T) \rangle] \quad (2)$$

where ν_0 is the rigid-lattice NQR frequency value, θ is the total angle of rotation of the C–Cl bond and $\langle \theta^2(T) \rangle$ is given by

$$\langle \theta^2(T) \rangle = \frac{h}{8\pi^2 c} \sum_i (I_i \nu_i)^{-1} \sin^2 \alpha_i \coth \left(\frac{h c \nu_i}{2 k_B T} \right) \quad (3)$$

where h and k_B have their usual meanings, c is the speed of light in centimetres per

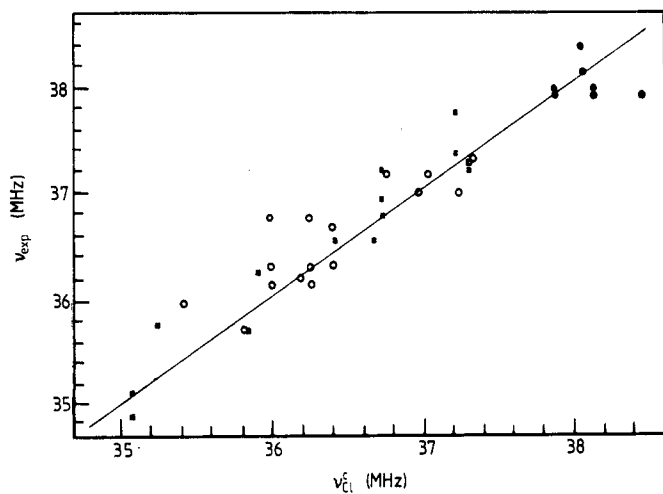


Figure 2. Correlation between the experimental NQR frequency data (measured at 77 K) and the calculated frequency data for the chloroanisole family: ■, dichloroanisoles; ○, trichloroanisoles; □, tetrachloroanisoles (Bayle *et al* 1980); ●, pentachloroanisole (Bayle *et al* 1980).

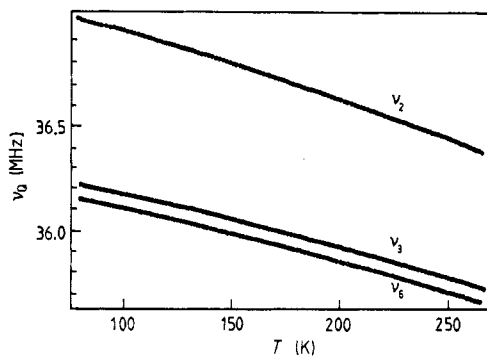


Figure 3. ^{35}Cl NQR frequency data versus T for the three observed lines ν_2 , ν_3 and ν_6 in 2,3,6-TCA.

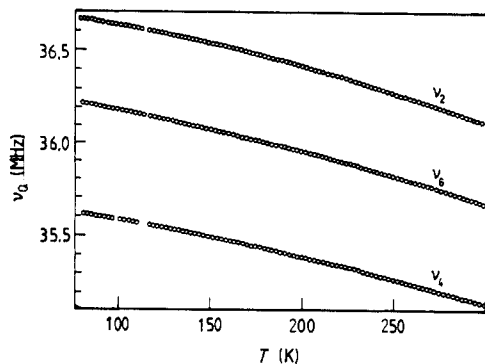


Figure 4. ^{35}Cl NQR frequency data versus T of the three observed lines ν_2 , ν_4 and ν_6 in 2,4,6-TCA.

Table 1. K_i -values for the chloroanisole family obtained from Bayle *et al* (1980).

Substituent	K_i (MHz)		
	Ortho	Meta	Para
—OCH ₃	0.668 ^a 0.410	-0.175	0.000
—Cl	1.335	0.566	0.345

^a The —OCH₃ group points towards the resonant Cl.

Table 2. Calculated values of the NQR frequency obtained by means of equation (1).

Compound	$\nu_{\text{Cl}}^{\text{c}}$ (MHz)	ν_{exp} (MHz)	Assignment
2,3,5,6-tetrachloroanisole	37.629	37.749 37.363	2
	37.351	37.278 37.203	6
	36.766	36.928 36.772	3, 5
	36.766	37.203 36.928	3, 5
Pentachloroanisole	38.175 ^a	37.985	2, 6
	37.917	37.926	
	38.101	38.367	3, 5
	38.101	38.133	
	38.497	37.904	4
2,3-dichloroanisole	36.698 ^a	36.551	2
	36.440		
	35.855	35.701	3
2,4-dichloroanisole	35.929 ^a	36.252	2
	35.671		
	35.261	35.751	4
3,5-dichloroanisole	35.086	35.092	3, 5
	35.086	34.867	
2,3,5-trichloroanisole	37.063 ^a	37.177	2
	36.785		
	36.421	36.676	3
	35.431	35.976	5
2,3,6-trichloroanisole	37.264 ^a	36.996	2
	37.006		
	36.200	36.213	3
	36.274 ^a	36.149	6
	36.016		
2,4,6-trichloroanisole	36.274 ^a	36.763	2
	36.016		
	36.274 ^a	36.319	6
	36.016		
	35.827	35.706	4
3,4,5-trichloroanisole	36.421	36.685	3, 5
	36.421	36.339	
	37.827	35.314	

^a Value of $\nu_{\text{Cl}}^{\text{c}}$ calculated when the —OCH₃ group points towards the resonant Cl.

second, ν_i is the i th normal mode frequency expressed in reciprocal centimetres, I_i is a moment of inertia associated with the i th normal mode and α_i is a angle between the EFG z axis and the axis about which the rotation of the C—Cl bond takes place for the i th

Table 3. Parameters obtained by means of equation (4).

Line	ν_{10} (cm ⁻¹)	C_1 (10 ⁻⁴ K ⁻¹)	ν_0 (kHz)
2,3,6-TCA			
ν_2	39.95 ± 0.01	6.04 ± 0.01	37 195.2 ± 0.5
ν_3	38.03 ± 0.05	6.21 ± 0.03	36 370.8 ± 0.4
ν_6	37.03 ± 0.01	5.69 ± 0.01	36 313.2 ± 0.5
2,4,6-TCA			
ν_2	48.56 ± 0.01	8.09 ± 0.01	36 892.6 ± 0.6
ν_4	43.96 ± 0.07	6.95 ± 0.04	35 827.3 ± 0.5
ν_6	40.94 ± 0.05	5.42 ± 0.02	36 474.3 ± 0.3

normal mode. Neglecting dispersion of the eigenvectors across the Brillouin zone and taking them as those at the zone centre, and also neglecting dispersion on the normal mode frequencies and assuming that they exhibit a linear temperature dependence (Brown 1960), equation (1) may be written to a good degree of approximation in the form

$$\nu_0(T) = \nu_0 \left[1 - \frac{3}{2} \frac{h}{8\pi^2 c} \frac{D}{\nu_{10}(1 - C_1 T)} \coth\left(\frac{h c \nu_{10}(1 - C_1 T)}{2k_B T}\right) \right] \quad (4)$$

where $\nu_1 = \nu_{10}(1 - C_1 T)$ is the average vibrational frequency and

$$D = \sum_i \frac{\sin^2 \alpha_i}{I_i} \quad (5)$$

whose numerical value has been calculated by assuming a standard molecular geometry and point masses. Fitting the experimental data by means of equation (4) the parameters shown in table 3 are obtained. The fit matches the frequency data with a discrepancy of less than 0.5 kHz, in the temperature range 80–270 K. The values obtained for the average torsional frequencies show that the motions are dominated by low-frequency lattice modes. The difference between some of the parameters, namely ν_{10} , corresponding to different resonant nuclei are too small to yield any other physical relevant result. From a qualitative point of view the values of ν_{10} for 2,3,6-TCA and 2,4,6-TCA indicate that the intermolecular forces are stronger in 2,4,6-TCA than in 2,3,6-TCA. This conclusion is in agreement with the fact that the melting point of 2,4,6-TCA (334.3 K) is higher than that of 2,3,6-TCA (316.3 K) as obtained from our DTA measurements.

Figures 5(a) and 5(b) show the differences $\Delta\nu_{3,6}(T) = \nu_3(T) - \nu_6(T)$ and $\Delta\nu_{2,6}(T) = \nu_2(T) - \nu_6(T)$, respectively, for 2,3,6-TCA as functions of temperature. Similarly figures 6(a) and 6(b) show $\Delta\nu_{2,6}(T) = \nu_2(T) - \nu_6(T)$ and $\Delta\nu_{6,4}(T) = \nu_6(T) - \nu_4(T)$, respectively, for 2,4,6-TCA.

Note from figure 5(a) that lines 3 and 6 behave almost identically with respect to T , their difference being of the order of 70 kHz over the whole temperature range. $\Delta\nu_{3,6}(T)$ increases almost linearly up to 70 kHz from 80 to 200 K and remains almost constant from 200 to 250 K. Note from figure 5(b) that $\Delta\nu_{2,6}(T)$ is on the average an order of magnitude larger than $\Delta\nu_{3,6}(T)$ and behaves almost linearly from 80 to 250 K. It appears that the NQR of Cl(3) and Cl(6) is affected mostly by the same motions in the whole temperature range with a dominant mode taking place above 200 K. $\langle\theta^2(T)\rangle$ behaves differently for Cl(2). Under the assumption that the molecular conformation of 2,3,6-TCA

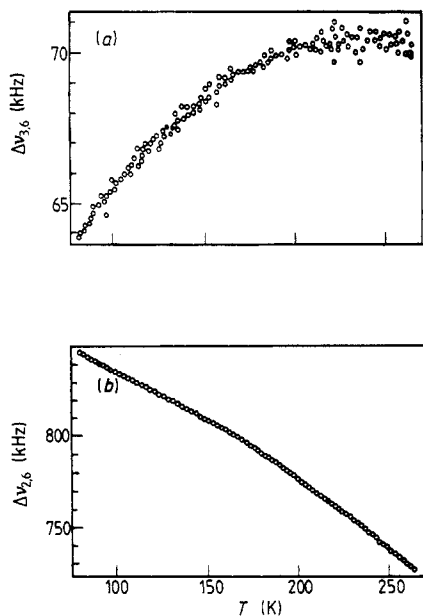


Figure 5. NQR frequency differences $\Delta\nu_{3,6}(T) = \nu_3(T) - \nu_6(T)$ and $\Delta\nu_{2,6}(T) = \nu_2(T) - \nu_6(T)$ versus T for 2,3,6-TCA.

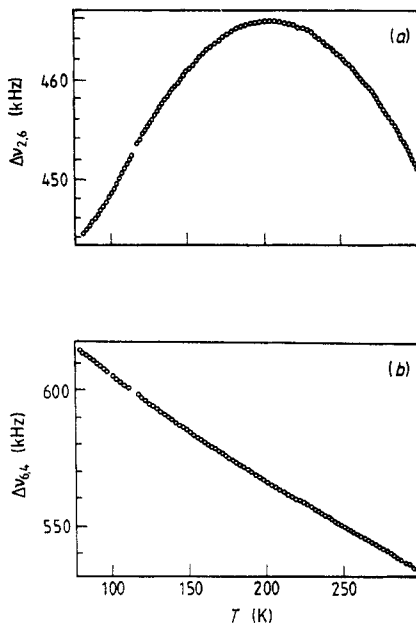


Figure 6. NQR frequency differences $\Delta\nu_{2,6}(T) = \nu_2(T) - \nu_6(T)$ and $\Delta\nu_{6,4}(T) = \nu_6(T) - \nu_4(T)$ versus T for 2,4,6-TCA.

is *cis* and taking into account that the calculation of the principal axis of inertia shows that one of the axes is almost parallel to the C(3)–Cl(3) and C(6)–Cl(6) directions (figure 1). The mode that most affects the EFG, namely oscillations about the \hat{e}_1 axis, may account for the same temperature dependence of $\langle\theta^2(T)\rangle$ for Cl(3) and Cl(6) nuclei.

Figure 6(a) shows that $\Delta\nu_{2,6}(T)$ increases up to 463 kHz from 80 to 200 K and decreases from 200 K to higher temperatures, while $\Delta\nu_{6,4}(T)$ increases almost linearly in the whole temperature range (figure 6(b)).

The change in behaviour of ν_3 for 2,3,6-TCA at about 200 K, shown in figure 5(a), that of ν_2 for 2,4,6-TCA also at about 200 K, shown in figures 6(a) and 7, and that of ν_Q for both phases of PCA, shown in figure 8, may indicate the onset of an additional motion affecting $\langle\theta^2(T)\rangle$, probably related to the —OCH₃ group.

Figure 7 shows the temperature dependence of the derivatives $d\nu_Q(T)/dT$ of the NQR frequencies with respect to the temperature for every resonant nucleus in both 2,3,6-TCA and 2,4,6-TCA. The graphs show that $d\nu_Q(T)/dT$ varies almost linearly with T for every resonant nucleus. Two groups of different resonant nuclei may be distinguished by the rate of change in $d\nu_Q(T)/dT$ with T . These are Cl(2) in 2,3,6-TCA and 2,4,6-TCA, Cl(6), Cl(3) in 2,3,6-TCA and, Cl(4), Cl(6) in 2,4,6-TCA. In addition, $d\nu_Q(T)/dT$ for Cl(2) in 2,4,6-TCA shows a slight change in slope beyond approximately 210 K.

The temperature dependence of $d\nu_Q(T)/dT$ could be analysed in terms of the Bayer–Kushida (see Kushida 1955) and Brown (1960) model. Introducing a linear temperature dependence for the torsional frequencies in equation (3) and differentiating equation (4) we can write in the high-temperature approximation

$$(1/\nu_0)[d\nu_Q(T)/dT]_T = b_0(1 + 2T\langle c_1 \rangle) \quad (6)$$

$$(1/\nu_0)[d^2\nu_Q(T)/dT^2]_T = b_0(4\langle c_1 \rangle + 6T\langle c_1^2 \rangle) \quad (7)$$

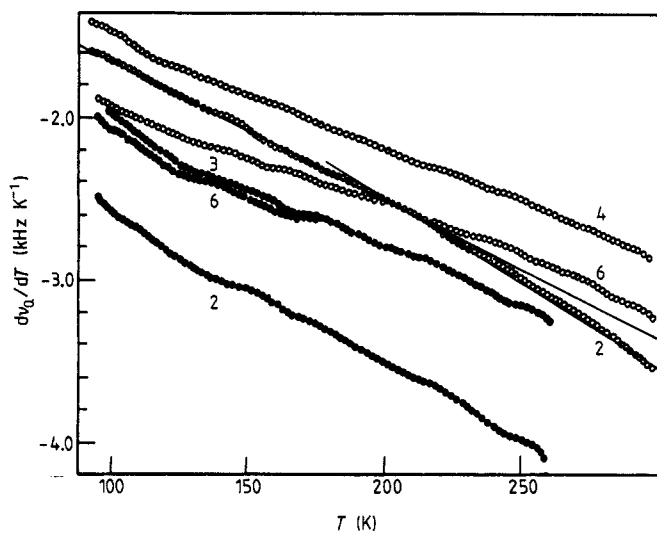


Figure 7. Derivative of the NQR frequencies, with respect to T , versus T : ●, $d\nu_Q(T)/dT$ for the 2.3,6-TCA lines; ○, $d\nu_Q(T)/dT$ for the 2.4,6-TCA lines.

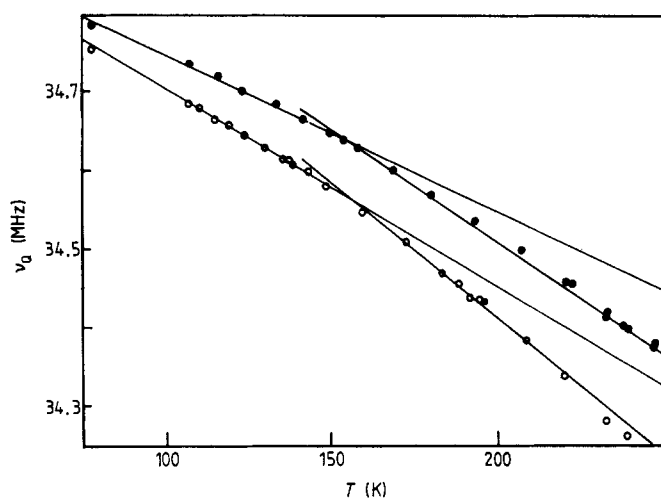


Figure 8. ^{35}Cl NQR frequency data versus T of the two observed phases in PCA: ●, stable phase; ○, unstable phase.

where

$$b_0 = -\frac{k_B}{h} \sum_i \frac{A_i}{\nu_{0i}^2} \quad (8)$$

and

$$\langle c_1 \rangle = \frac{\sum_i \frac{A_i c_i}{\nu_{0i}^2}}{\sum_i \frac{A_i}{\nu_{0i}^2}} \quad (9)$$

Table 4. Values of $(\sin^2 \alpha_i)/I_i$

	$(\sin^2 \alpha_i)/I_i (10^4)$					
	2,3,6-TCA			2,4,6-TCA		
	Cl(2)	Cl(3)	Cl(6)	Cl(2)	Cl(4)	Cl(6)
\hat{e}_1	2.87	11.3	11.3	5.34	1.02	11.02
\hat{e}_2	1.65	0.00	0.00	8.83	14.95	0.80
\hat{e}_3	7.47	7.47	7.47	6.85	6.85	6.85

and

$$A_i = (3h/8\pi^2)[(\sin^2 \alpha_i)/I_i]. \quad (10)$$

Equation (6) shows that $d\nu_Q(T)/dT$ behaves linearly with T , with a slope given by $2b_0\langle c_1 \rangle$ and intercept equal to b_0 . At temperatures of the order of 100 K the second term on the right-hand side of equation (7) is much smaller than the first term; then the slope of $d\nu_Q(T)/dT$ is independent of T . This is in agreement with the obtained experimental values of c_{10} and the data in figure 7. Therefore to a good degree of approximation it could be assumed that $\langle c_i^2 \rangle = \langle c_i \rangle^2$; then

$$\frac{1}{\nu_0} \left(\frac{d^2 \nu_Q(T)}{dT^2} \right)_T \approx 4b_0 \langle c_1 \rangle = -4 \frac{k_B}{h} \sum_i \frac{A_i}{\nu_{0i}^2} c_i \quad (11)$$

for each resonant Cl in both compounds. On the grounds that $\langle \theta^2(T) \rangle$ is governed by lattice modes, namely oscillations about the principal axis of inertia, equation (11) explains the experimental results of figure 7 as follows. The resonance lines belonging to the same compound are affected by the same motions and the ratio $(\sin^2 \alpha_i)/I_i$ (table 4), the factor that weighs the effect of the i th mode on the data. Thus, we see that oscillations about the \hat{e}_1 axis dominates $\langle \theta^2(T) \rangle$ for Cl(3) and Cl(6) in 2,3,6-TCA. Also note that $d\nu_Q(T)/dT$ for Cl(2) possesses a larger slope and intercept, showing that other modes corresponding to oscillations about \hat{e}_2 and \hat{e}_3 are significant. A similar conclusion is achieved for the data of 2,4,6-TCA.

The observed change in slope of $d\nu_Q(T)/dT$ beyond 210 K for Cl(2) in 2,4,6-TCA is associated with the onset of an extra motion of the methoxy group which affects this resonant nucleus more.

In order to compare with the previous results, measurements of $\nu_Q(T)$ for PCA were performed. Figure 8 depicts the frequency measurements. The data show the existence of a single resonance line and a phase transition. Irrespective of how the sample is cooled, it always solidifies in the unstable phase, which is the phase reported in the literature. As the sample is warmed from liquid-nitrogen temperature, there is a phase transition at about 235 K to a stable phase, which has not been previously reported. Once the solid PCA is in the stable phase, it will always remain there, irrespective of whether the sample is either cooled or warmed in the range 77–250 K. Also, the frequency data in both phases show two zones of almost linear behaviour separated at approximately 160 K. This may indicate the onset of an extra motion affecting $\langle \theta^2(T) \rangle$.

3. Conclusions

The frequency data show that the resonance lines for both 2,3,6-TCA and 2,4,6-TCA behave normally. The largest average frequency difference is of the order of 780 and 570 kHz

respectively for the two compounds. These differences are relatively larger than the crystalline field in the anisole family, which was estimated to be of the order of 400 kHz. This validates the frequency assignments previously obtained. A comprehensive analysis of the behaviour of the NQR frequencies against T allows qualitative identification of the modes that affect the EFG at the resonant sites. Oscillation about the \hat{e}_1 axis is thought to be the most significant motion that affects the EFG at the resonant sites in 2,3,6-TCA. The other motions are also present in both compounds. There is also evidence that an extra motion internal to the methoxy group takes place above 210 K in 2,4,6-TCA. The measurements on the PCA reveals the existence of a phase transition from an unstable phase to a stable phase. The first phase is that reported in the literature. This compound also shows evidence of the onset of an extra motion above 160 K. The next step on the study of the NQR in this family of compounds will be to measure the relaxation times and lineshapes.

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