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1993 J. Phys.: Condens. Matter 5 5755

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## <sup>35</sup>Cl nuclear quadrupole resonance analysis of the solid 2, 3, 6-trichloroanisole

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Received 1 February 1993

**Abstract.** The temperature dependences of <sup>35</sup>Cl nuclear quadrupole resonance frequencies  $\nu_Q$ , spin–lattice relaxation times  $T_1$ , linewidth  $\Delta\nu$  and spin–spin relaxation time  $T_2$  of the solid 2,3,6-trichloroanisole are reported. Three resonance lines are observed and the experimental measurements of  $\nu_Q(T)$  data are analysed by means of the Bayer–Kushida theory. It appears that only low-frequency lattice modes contribute to the temperature dependence of  $\nu_Q(T)$ . The  $T_1(T)$  relaxation data show a normal behaviour and no thermally activated motion is detected. The linewidth measurements reveal that the electric field gradient affecting the Cl atoms of the molecule undergoes some sort of thermally activated motional narrowing. The  $T_2(T)$  data are somewhat scarce, showing only a normal temperature behaviour for one of the chlorine atoms of the molecule while for the others it is of the order of  $T_2^*$ .

### 1. Introduction

Nuclear quadrupole resonance (NQR) is a very useful technique for studying the static as well as the dynamic properties of a solid (Chihara and Nakamura 1980). The compound studied in this work is 2,3,6-trichloroanisole (2,3,6-TCA) in the solid state. The main motivation for this research was to carry out a comprehensive analysis on the effects of the methoxy group (OCH<sub>3</sub>) motions upon the NQR parameters of the <sup>35</sup>Cl atoms of the 2,3,6-TCA molecule.

In this paper, measurements are reported of the temperature dependence of the <sup>35</sup>Cl NQR frequency  $\nu_Q(T)$ , spin–lattice relaxation time  $T_1(T)$ , linewidth  $\Delta\nu(T)$  and spin–spin relaxation time  $T_2(T)$  belonging to each chlorine nucleus of the molecule. The frequency data as well as all the relaxation times were measured by means of a pulsed fast Fourier transform (FFT) NQR spectrometer. The sample was placed in a cryogenic set-up from 80 K to room temperature. Overall error in the measurements of  $\nu_Q(T)$ , relaxation times and  $T$  are  $\pm 200$  Hz,  $\pm 5\%$  and  $\pm 0.5$  K respectively. All the NQR parameters were collected from 80 to 300 K, the temperature at which the signal-to-noise ratio was so bad that measurements of good-quality data could no longer be obtained.

Most of the analyses discussed later rely upon some assumptions about the molecular structure of the 2,3,6-TCA. These assumptions are based on information provided by previous work on this or similar compounds. Figure 1 depicts the structure of 2,3,6-TCA obtained by means of standard molecule-building software. The interatomic distances obtained fully agree with previously published results. The only remaining ambiguity is the angle formed by the O–C(7) axis and the benzene plane, resulting from torsion of the methoxy group

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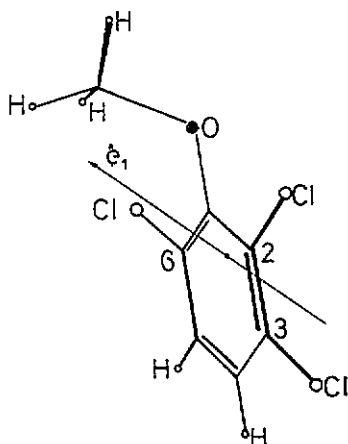


Figure 1. 2,3,6-TCA molecule.

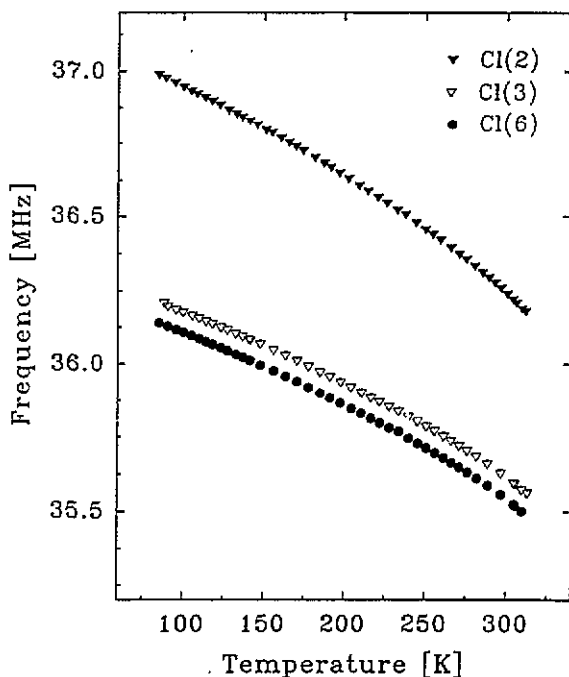


Figure 2.  $^{35}\text{Cl}$  NQR frequency data versus  $T$  of the three observed lines.

around C(1)–O, since it may differ from the value for this compound in either the gaseous phase or the solid phase.

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

Bayle *et al* (1980) and Pertile *et al* (1990) have studied the  $^{35}\text{Cl}$  NQR frequencies of several chloroanisoles which allows us to determine both that the crystalline-field contribution to the EFG at the resonant sites is of the order of 0.3 MHz and the assignment of the resonance lines by means of an additive model of the substituent effects (Biedenkapp and Weiss 1968).

It is generally assumed that chloroanisole molecules possess a planar structure (Owen and Hester 1969), but other workers either by means of different experimental techniques or by theoretical calculations have suggested the possibility of a non-planar geometry of the chloroanisoles (Aroney *et al* 1969, Korschin *et al* 1981).

Our calculated structural parameters for non-planar 2,3,6-TCA compare reasonably well with those calculated for planar anisole (Korschin 1983). In both cases the benzene ring possesses hexagonal symmetry and the methyl group has a threefold symmetry formed by C(7)–O.

From all the considerations listed above, we have assumed that the asymmetry parameter  $\eta \simeq 0$ , the C(2)–C(1)–O angle  $\alpha \simeq 120^\circ$  and the possibility of a non-planar structure for 2,3,6-TCA. Since no crystallographic data are available for 2,3,6-TCA we have assumed that it has two molecules per unit cell as for 2,4,6-TCA (Peneau and Guibe 1968).

## 2. Experimental results

### 2.1. Analysis of the <sup>35</sup>Cl nuclear quadrupole resonance against *T*

Three resonance lines were detected in the temperature range 80–300 K for 2,3,6-TCA; the data are depicted in figure 2. Their temperature behaviours are normal and no phase transitions are observed; this was corroborated by measurements of  $\Delta C_p(T)$  on the compound. Following the Bayer–Kushida theory (see, e.g. Bayer (1951) and Kushida (1955)), and on the assumption that the asymmetry parameter is zero, the temperature dependence of  $\nu_Q$  may be written as

$$\nu_Q(T) = \nu_0(1 - \frac{3}{2}\langle\theta^2(T)\rangle) \quad (1)$$

where  $\nu_0$  is the rigid-lattice NQR frequency value,  $\theta$  is the total angle of rotation of the C–Cl bond and  $\langle\theta^2(T)\rangle$  is given by

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

where  $h$  and  $k_B$  have their usual meanings,  $c$  is the speed of light in centimetres per second,  $\nu_i$  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  $\alpha_i$  is the angle between the EFG  $z$  axis and the axis about which the rotation of the C–Cl bond takes place for the  $i$ th normal mode. If we neglect dispersion of the eigenvectors across the Brillouin zone and take them as those at the zone centre and we also neglect dispersion on the normal mode frequencies and assume that they exhibit a linear temperature dependence (Brown 1960), equation (1) may be written to a good degree of approximation in the form

$$\nu_Q(T) = \nu_0\left\{1 - \frac{3}{2}(h/8\pi^2c)[D/\nu_0(1 - C_1T)] \coth[hc\nu_0(1 - C_1T)/2k_B T]\right\} \quad (3)$$

where  $\nu_1 = \nu_0(1 - C_1T)$  is the average lattice vibrational frequency and

$$D = \sum_i \sin^2 \alpha_i / I_i \quad (4)$$

whose numerical value has been calculated by assuming a standard molecular geometry and point masses. On fitting the experimental data by means of equation (3) the parameters shown in table 1 are obtained.

Table 1. Parameters obtained by means of equation (3).

2,3,6-TCA line frequency	$\nu_0$ (cm <sup>-1</sup> )	$C_1$ (K <sup>-1</sup> ) $\times 10^{-4}$	$\nu_0$ (kHz)
$\nu^{(2)}$	39.60 $\pm$ 0.01	5.59 $\pm$ 0.01	37 190.2 $\pm$ 0.2
$\nu^{(3)}$	37.79 $\pm$ 0.01	6.05 $\pm$ 0.05	36 369.8 $\pm$ 0.2
$\nu^{(6)}$	36.40 $\pm$ 0.01	5.01 $\pm$ 0.05	36 314.2 $\pm$ 0.2

### 2.2. Spin-lattice relaxation time data against $T$

The  $^{35}\text{Cl}$  relaxation times  $T_1(T)$  were measured as a function of the temperature for the resonance line frequencies  $\nu^{(2)}$ ,  $\nu^{(3)}$ , and  $\nu^{(6)}$  (figure 3). In the range  $T < 290$  K the relaxation times behave normally as the relaxation mechanism is driven by torsional oscillations (Woessner and Gutowsky 1963), i.e.

$$[T_{1\text{osc}}(T)]^{-1} = \alpha T^\lambda \quad 80 \text{ K} < T < 290 \text{ K}. \quad (5)$$

As the sample temperature is increased ( $T > 290$  K), a decrease in the relaxation rate is induced by pre-melting effects. A fit of the experimental points by means of equation (5) yields the following parameters:

$$\lambda^{(2)} = 1.91 \pm 0.03$$

$$\lambda^{(3)} = 2.06 \pm 0.05$$

$$\lambda^{(6)} = 1.95 \pm 0.06.$$

It may be seen from the graph that  $T_1(T)$  is almost the same for both Cl(3) and Cl(6), while the relaxation rate approximately doubles for Cl(2).

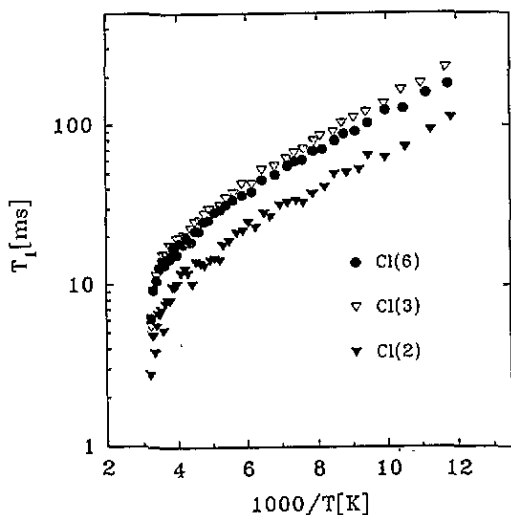


Figure 3. Semilogarithmic graph of the spin-lattice relaxation data versus  $1000/T$ .

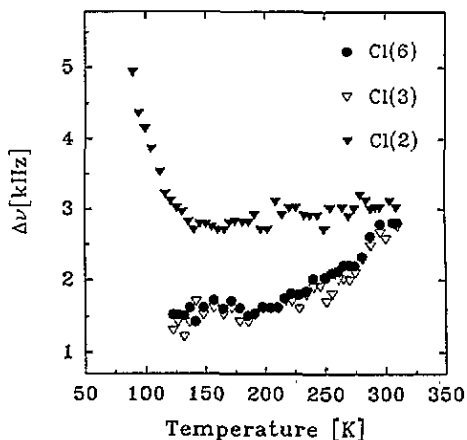


Figure 4. Linewidth data versus  $T$ .

### 2.3. Spin-spin relaxation time data against $T$

It was possible to measure the  $T_2(T)$  data corresponding to only Cl(2) and its temperature behaviour is normal. Its average value over the whole temperature range is  $350 \mu\text{s}$ . For the rest of the Cl atoms in the molecule,  $T_2(T)$  is of the order of  $T_2^*$ . Although the spin-spin relaxation data are scarce, they show no change in the molecular geometry in the whole temperature range. This is because  $T_2^{-1}$  is governed by the static contribution to the resonance linewidth (Abragam 1961).

#### 2.4. Linewidth data against $T$

The linewidths  $\Delta\nu(T)$  for the resonance line frequencies ( $\nu^{(2)}$ ,  $\nu^{(3)}$  and  $\nu^{(6)}$ ) were measured as functions of the temperature (figure 4). At high temperatures the linewidths of the three resonance lines are similar but, as the temperature is lowered,  $\Delta\nu(T)$  for the line frequencies  $\nu^{(3)}$  and  $\nu^{(6)}$  behaves normally while, on the other hand,  $\Delta\nu(T)$  for the line frequency  $\nu^{(2)}$  shows two temperature zones where it behaves differently. From approximately 300 to 140 K it shows almost no change with  $T$ , but below 140 K it increases as  $T$  is lowered. Such an increase in  $\Delta\nu(T)$  with decreasing  $T$  shows a thermally activated process, where the increase with the extrapolated trend of  $\Delta\nu(T)$  at  $T \geq 140$  K against  $T$  follows an Arrhenius law. The points are well fitted, yielding an activation energy of 436 cal mol<sup>-1</sup>. This value falls in the typical range for the height of the rotational potential barrier of methyl groups in organic compounds (Cunliffe 1974).

### 3. Conclusions

Table 1 summarizes the results obtained from the analysis of the <sup>35</sup>Cl NQR line frequencies. The data show a normal behaviour and the fit matches the frequencies with a discrepancy of less than 0.5 kHz, in the temperature range 80–300 K. The values obtained for the average torsional frequencies show that the motions are dominated by low-frequency lattice modes. The differences between the  $\nu_{10}$  corresponding to different resonant nuclei are too small to yield any other physically relevant result. From a qualitative point of view note that the line frequencies  $\nu^{(3)}$  and  $\nu^{(6)}$  behave almost identically as functions of  $T$ ; their average frequency difference with respect to  $\nu^{(2)}$  is about 0.7 MHz which is slightly smaller than the crystalline contribution to the EFG,  $\pm 0.4$  MHz (Pertile *et al* 1990), to the NQR frequency. On the other hand the average frequency difference between  $\nu^{(3)}$  and  $\nu^{(6)}$  is about 0.08 MHz which is approximately an order of magnitude smaller than the latter value. This may indicate that the EFG at Cl(2) has a large contribution from the methoxy group, since the difference between  $\nu^{(3)}$  and  $\nu^{(6)}$  should be zero in the absence of a crystalline contribution to the EFG.

The spin–lattice relaxation data show nothing special but a normal behaviour of  $T_1(T)$  for each resonance line, i.e. the relaxation mechanism is driven by torsional oscillations. Note that, within the experimental errors,  $\lambda^{(2)} = \lambda^{(6)}$  and both are slightly smaller than  $\lambda^{(3)}$ . Also from spin–spin relaxation data it is clear that no change in the molecular geometry takes place in the whole temperature range. However, with respect to the methyl group, it should be taken into account that, since the hydrogen nuclei are somewhat rotating around O–C(7), depending on the sample temperature, the assertion of no molecular geometry change is valid within the radius of rotation of the hydrogen nuclei. This may allow some small temperature-dependent rotations around C(1)–O of the methoxy group, giving rise to a non-planar geometry of the molecule in the solid state and to strong inhomogeneous line broadening. The existence of such an effect may not be detected by  $T_2$  measurements. Considering the frequency and relaxation results together, we may conclude that oscillations about the  $\hat{e}_1$  axis, as shown in figure 1, have the most significant effect on the EFG at the resonant sites.

It is well known from the literature that the methyl group in different organic compounds (Cunliffe 1974) undergoes tunnelling, hindered rotations or rotations about its threefold symmetry axis depending on the sample temperature. For this compound, the onset of methyl rotations from a hindered-rotations regime at temperatures higher than 140 K is thought to be the cause of the motional narrowing effect of the resonance lines.

## Acknowledgments

Partial financial support provided by the Consejo Nacional de Investigaciones Científicas y Técnicas and the Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba is gratefully acknowledged.

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