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An NQR study of thermally activated motions of nitro groups and of the phase transition in 2,6-dinitrochlorobenzene

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Abstract. A study of the temperature dependence of the ^{35}Cl NQR frequency of 2,6-dinitrochlorobenzene is reported. These measurements show the existence of a second-order phase transition at $T \sim 255$ K. The temperature dependence of the spin–lattice relaxation time and the line width between 80 and 300 K is also reported. The splitting of the resonance line in the low-temperature phase (LTP) was shown to behave as an order parameter of the phase transition. The experimental order parameter and the anomalous behaviour of the line width near the transition point were interpreted satisfactorily in terms of the librational soft-mode theory, which assumes anharmonic coupling between molecular librational modes in the crystal. The results also show that the totality of results in the LTP is consistent with the onset of reorientations of nitro groups. The parameters deduced are compared with those obtained in our studies of the *n*-nitrobenzene sulphonyl chloride family of compounds.

1. Introduction

A comprehensive NQR study of thermally activated motions of sulphonyl and nitro groups in the *n*-nitrobenzenesulphonyl chloride family of compounds was reported in previous papers [1–3]. These studies showed that each substituted group in the benzene ring contributes to the spin–lattice relaxation with a different and independent mechanism. The results provided evidence that the presence of the SO_2Cl group close to the NO_2 group strongly contributes to the height of the barrier. The present work, carried out on 2,6-dinitrochlorobenzene (figure 1), was undertaken primarily to investigate how the height of this barrier is affected when a Cl nucleus is close to the NO_2 group, instead of a sulphonyl group or an H nucleus. During these studies, it has emerged that 2,6-dinitrochlorobenzene undergoes an interesting type of phase transition. A study of the temperature dependence of the ^{35}Cl NQR frequency down to liquid nitrogen temperature showed that this compound undergoes a phase transition near 255 K. The single line observed in the high-temperature phase (HTP) splits into two below the transition temperature T_c . It was found that the behaviour of NQR parameters near the phase transition is similar to that observed in chloranil [4]. The results of the NQR experiments will therefore be discussed on the basis of the mechanism used to explain the chloranil phase transition. This is a simple theory that describes a phase transition in terms of the librational soft-phonon mode in molecular crystals [5].

This compound exhibits monoclinic symmetry at room temperature [6,7] with a minimum of two molecules per unit cell.

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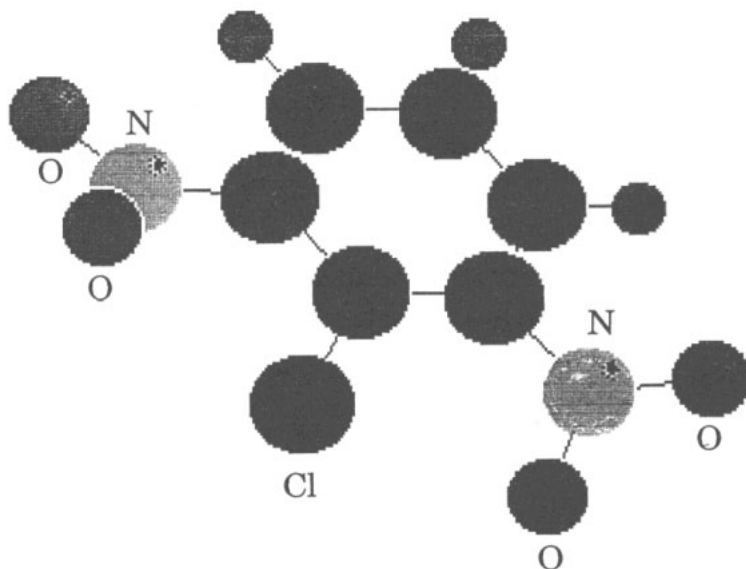


Figure 1. The molecular structure of 2,6-dinitrochlorobenzene.

Experimental measurements of resonance frequency, ν_Q , line width, $\Delta\nu$, and ^{35}Cl spin-lattice relaxation time, T_1 , are reported and analysed as a function of temperature.

A brief overview of experimental procedures is reported in section 2. The results are presented in section 3 and the analysis and discussion of the data are given in section 4.

2. Experimental details

A quantity of polycrystalline 2,6-dinitrochlorobenzene was obtained from the Chemistry Department of Universidad Nacional de Córdoba. Measurements were taken using a Fourier transform pulse spectrometer described elsewhere [8]. The NQR frequency was obtained from the fast Fourier transform (FFT) of the free induction decay after a $\pi/2$ pulse and the spin-lattice relaxation time was determined from a $\pi/2$ - $\pi/2$ pulse sequence. The sample temperature was controlled within ± 0.1 K using a home made cryogenic system. Copper-constantan thermocouples were employed for the temperature measurements. The temperature range covered was between 80 and 300 K.

3. Results

One ^{35}Cl NQR line was observed at high temperature (ν_2). This agrees with the NQR frequency previously reported by Ramanamurthy *et al* [7] at room temperature. This line splits gradually into two lines below the transition point (ν_1 , ν_2), showing that not all Cl nuclei in the crystal are equivalent. The temperature dependence of the resonance frequencies is shown in figure 2. Figure 3 shows the line width, $\Delta\nu$, as a function of temperature. It is observed that $\Delta\nu$, for both lines, increases rapidly with temperature near the phase transition. About T_c the line width decreases until it reaches the value both lines had before the transition point. The temperature dependence of line width in the transition

region is of a 'lambda shape'. This shape is typical for heat capacity when one is dealing with a second-order phase transition. Line 2 shows an extra broadening at $T \sim 175$ K. If only small-angle molecular librations are present, an essentially constant line width is expected far from the phase transition. Since this is not so, we conclude that a second relaxation mechanism must be present and speculate that it is related to reorientations of the NO_2 group.

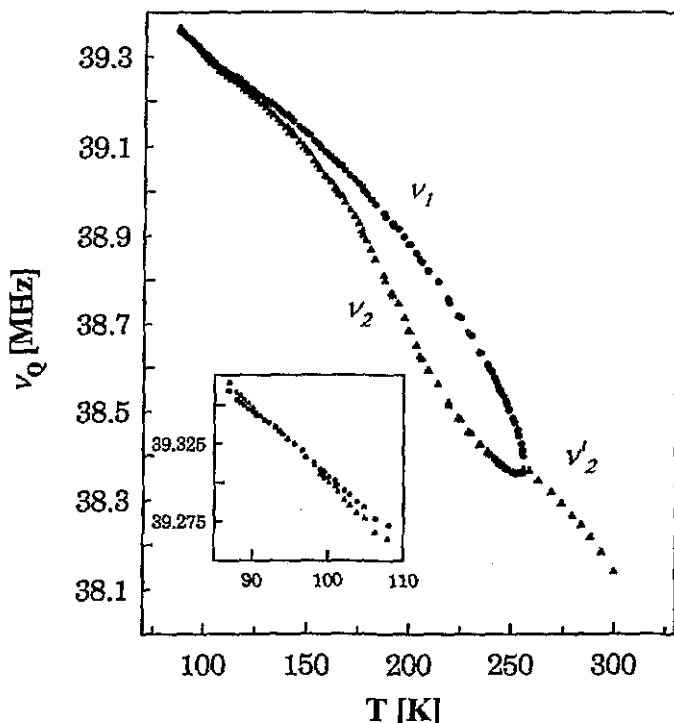


Figure 2. The temperature dependence of the ^{35}Cl NQR frequency in 2,6-dinitrochlorobenzene: ●, line 1; ▲, line 2.

The temperature dependence of the ^{35}Cl spin-lattice relaxation time is shown in figure 4. It is observed, specially for line 1, that T_1 decreases abruptly as the temperature approaches T_c . This phenomenon is due to the critical fluctuations of molecular motions [9–11]. Below the transition region, these data suggest that T_1 is not proportional to $T^{-\lambda}$ in the temperature range measured, as is indicated by a possible straight line fit shown in figure 4. Above 140 K in line 1 and above 130 K in line 2, T_1 values begin to decrease more rapidly, showing a local minimum at about 200 K. This fact, together with the extra broadening of line 2 at $T \sim 175$ K, provide conclusive evidence that a mechanism other than electric field gradient (EFG) modulation by small-angle molecular librations is important for the relaxation.

4. Analysis and discussion

4.1. Nuclear quadrupole resonance frequency

As was mentioned above the temperature dependence of ν_Q and T_1 , in the phase transition

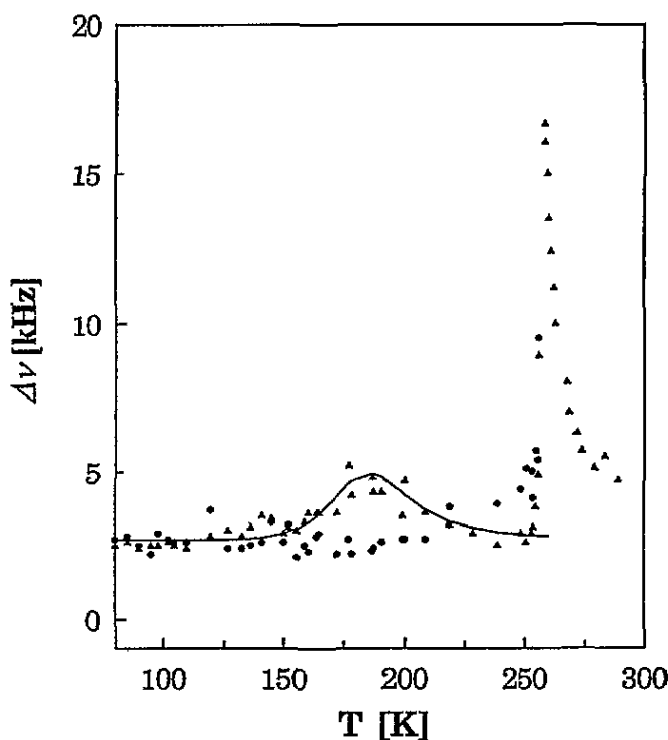


Figure 3. The temperature dependence of the ^{35}Cl line width in 2,6-dinitrochlorobenzene: ●, line 1; ▲, line 2.

region, is similar to that observed in chloranil [4]. We therefore assumed that in 2,6-dinitrochlorobenzene the results can be discussed on the basis of the mechanism that describes the chloranil phase transition. It is assumed that the direction of the C–Cl bond changes gradually in the LTP, implying that a rotation of the molecule as a whole occurs with respect to the crystallographic axes. Thus, the tilt angle θ of the molecule (or to be exact of the Z principal axis of the EFG at the Cl nucleus) from its orientation in the high-temperature phase (HTP) can be regarded as an order parameter. (Order parameter is only a conventional use of the term in analogy with order–disorder transitions. Actually, the crystal is in the ordered state at all temperatures.) It is observed that the average value of ν_1 and ν_2 lies close to the extrapolated curve of ν_2^i in the HTP. Therefore, it may be considered that the splitting of the resonance line originates from loss of some symmetry element or elements due to non-identical intermolecular interactions on the Cl atoms and that is a function of the tilt angle θ . If θ is small, for the two inequivalent sites, the EFG in the nucleus site can be expanded in a series of θ :

$$V_{\mu}^i = a_{\mu}^i + b_{\mu}^i \theta(t) \quad i = 1, 2 \quad (1)$$

then

$$\Delta\nu_{12} = \nu_2 - \nu_1 \propto (b_0^2 - b_0^1) \overline{\theta(t)}. \quad (2)$$

Thus $\Delta\nu_{12}$ can be treated as the order parameter in the system. The model proposed by Chihara and Nakamura [5] assumes that the molecular rotation is brought about by

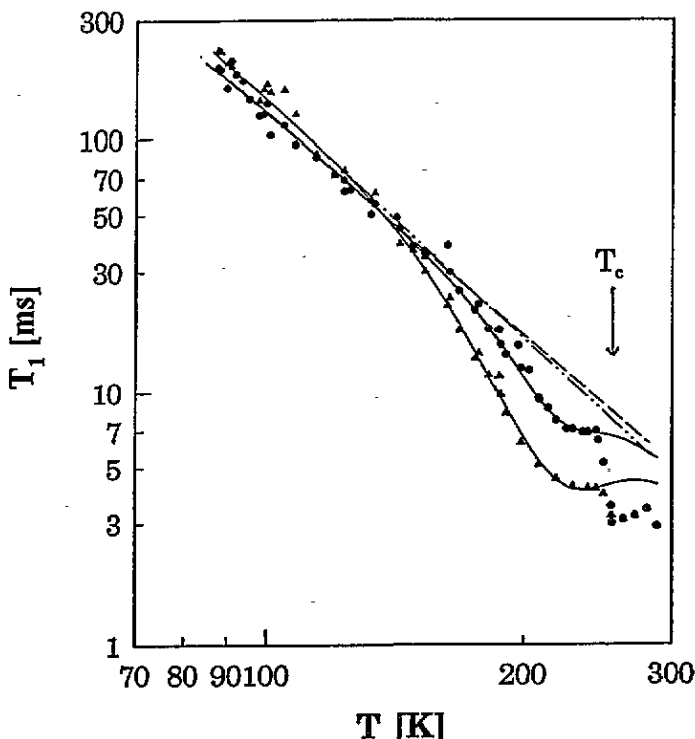


Figure 4. The temperature dependence of T_1 data for ^{35}Cl in 2,6-dinitrochlorobenzene: ●, line 1; ▲, line 2; ---, straight line fit for line 1; - · - · -, straight line fit for line 2.

an anharmonic coupling between librational phonon modes, which produces a uniform librational soft mode at the position of $k = 0$. The potential energy used for the uniform mode is

$$V(\theta) = a(\theta^2 - p\theta^4 - q\theta^6) \quad (3)$$

where θ is the angle of rotation of molecules measured from the equilibrium position in the HTP; a , p and q are constants characteristic of the system under consideration. $V(\theta)$ has its minimum at $\theta = \theta_0$, the equilibrium orientation at 0 K. Above T_c , θ remains zero, corresponding to the maximum of $V(\theta)$. This orientation is not energetically stable, but it becomes stable by anharmonic coupling between the uniform mode for molecular tilt and librational lattice modes whose frequency depends strongly on θ :

$$\hbar\Omega = \hbar\omega + \eta\theta^2. \quad (4)$$

Here ω is the librational frequency in the HTP and Ω is that in the LTP. In other words, the entropy that arises from those librational motions counterbalances the unfavourable increase in the potential energy. Therefore, at any temperature molecules oscillate in a single minimum whose position is determined by making the Helmholtz energy a minimum with respect to θ .

The condition for equilibrium, $\partial A/\partial\theta = 0$, leads to the expression that gives the temperature dependence of the 'order' parameter $s = \theta/\theta_0$:

$$t = (1 + \alpha s^2) / \ln(\alpha/\beta(1 - s^2)[1 + (1 - 2m)s^2] + 1) \quad (5)$$

where

$$\alpha = \eta\theta_0^2/\hbar\omega \quad \beta = (|a|\theta_0^2/\hbar)\omega \quad m = p\theta_0^2 \quad \tau = kT/\hbar\omega.$$

Brunetti [12] has shown that, in molecular crystals where two or more crystalline phases are possible or where two or more chemically inequivalent sites in the unit cell are present, the difference between the resonance frequencies (in the quasiharmonic approximation) changes with temperature in a quadratic way. In the present case, this occurs for temperatures below 200 K as is shown in figure 5(a). Above this temperature there is a change in its behaviour, decreasing with temperature. We assume that this is the region where the phase transition effects begin to be appreciable. The transition temperature T_c was determined to be 255.8 K by extrapolating this curve to zero.

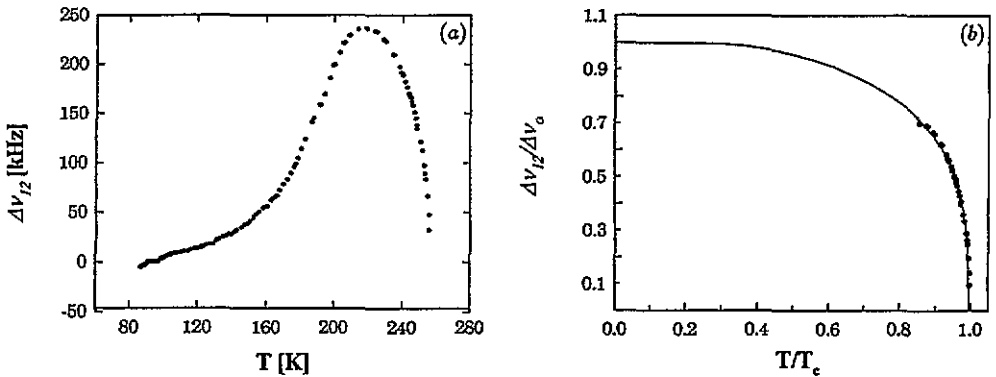


Figure 5. (a) The temperature dependence of the difference between frequencies $\Delta\nu_{12}$ in the LTP. (b) $\Delta\nu_{12}$, reduced by its value at 0 K, is plotted against the reduced temperature T/T_c .

In figure 5(b) $s = \Delta\nu/\Delta\nu_0$ is plotted against the reduced temperature T/T_c for temperatures above 200 K.

Numerical calculations of $s(t)$ (5) were carried out to obtain the best fit of s by assigning reasonable values to α , β and m :

$$\alpha = 0.49 \quad \beta = 0.28 \quad m = 0.44.$$

Figure 5(b) shows the comparison with the experimental $\Delta\nu_{12}$. The same set of parameters values will be used to calculate the generalized susceptibility in the next section.

4.2. Spin-lattice relaxation time and line width

The temperature dependence of the T_1 data for temperatures below 140 K in line 1 and below 130 K in line 2 is a clear indicator that the relaxation is caused by small-angle molecular librations [13]. Above these temperatures and below the transition region, the temperature dependence of T_1 is typical of relaxation produced by molecular groups executing large-amplitude motions in relation to the observed nuclei. Such motions create fluctuations that are a significant fraction of the EFG [14]. In this case we will show that T_1 can be accounted for in terms of the modulation of the EFG due to reorientations of neighbouring NO_2 groups. As a result the observed temperature dependence of the relaxation rate of the Cl nuclei can be written as

$$1/T_1 = (1/T_1)_{\text{lib}} + (1/T_1)_{\text{mod}}. \quad (6)$$

Here the librational contribution obeys a power law temperature dependence [13]:

$$(1/T_1)_{\text{lib}} = bT^\lambda \quad \lambda \simeq 2. \quad (7)$$

The modulation contribution has the form [14]

$$(1/T_1)_{\text{mod}} = \frac{1}{8} (q'/q)^2 \omega_Q^2 \tau / (1 + \omega_Q^2 \tau^2) \quad (8)$$

where q' is the amplitude of moving EFG and q is the full EFG at the nucleus site; $\tau = \tau_0 \exp(E/kT)$ is the correlation time of the modulating motion and E is the activation energy of that motion.

Expression (6) was used to fit the observed ^{35}Cl T_1 data and the following values of the adjustable parameters were obtained:

$$\begin{array}{ll} b = 1.09 \times 10^{-8} & b = 4.8 \times 10^{-9} \\ \lambda = 2.92 & \lambda = 3.08 \\ \tau_0 = 1.5 \times 10^{-13} \text{ s} & \tau_0 = 1.2 \times 10^{-12} \text{ s} \\ E = 19.0 \text{ kJ mol}^{-1} & E = 15.3 \text{ kJ mol}^{-1} \\ (q'/q) = 1.6 \times 10^{-3} & (q'/q) = 2.8 \times 10^{-3}. \end{array}$$

The best fit to the ^{35}Cl T_1 data using the above values of the parameters is shown in figure 4 by a solid line through the data.

Note that the fit gives a value $\lambda \sim 3$ for both lines, showing that this crystal is quite anharmonic [15, 16, 3].

In order to make a comparative study of the activation energy associated with reorientations of the NO_2 group, we show in table 1 the different values obtained in our work.

Table 1.

Compound	E (kJ mol $^{-1}$)
2NO $_2$ - ϕ -SO $_2$ Cl	28.5
3NO $_2$ - ϕ -SO $_2$ Cl	11.7
4NO $_2$ - ϕ -SO $_2$ Cl phase α	6.7
4NO $_2$ - ϕ -SO $_2$ Cl phase β	10.5
2,6-NO $_2$ - ϕ -Cl line 1	19.0
2,6-NO $_2$ - ϕ -Cl line 2	15.3

Note that the values of E obtained in 2,6-dinitrochlorobenzene are smaller than the value deduced for 2NO $_2$ - ϕ -SO $_2$ Cl and bigger than those deduced for 4NO $_2$ - ϕ -SO $_2$ Cl and 3NO $_2$ - ϕ -SO $_2$ Cl. This result illustrates that the volume occupied by the neighbour is important to determine the barrier than an NO $_2$ group has to overcome for reorientation. Further, the fact that the modulation effect is quite strong and that NO $_2$ groups are close to Cl nuclei in the molecule suggests that this effect is intramolecular in origin [1-3].

The temperature dependence of the NQR line width for line 2 supports the assumption of reorientation of the NO $_2$ group. In order to observe appreciable changes in the line width, due to reorientations of the NO $_2$ group, it is necessary that the condition $\Delta\nu \simeq 1/2T_1$ [17]

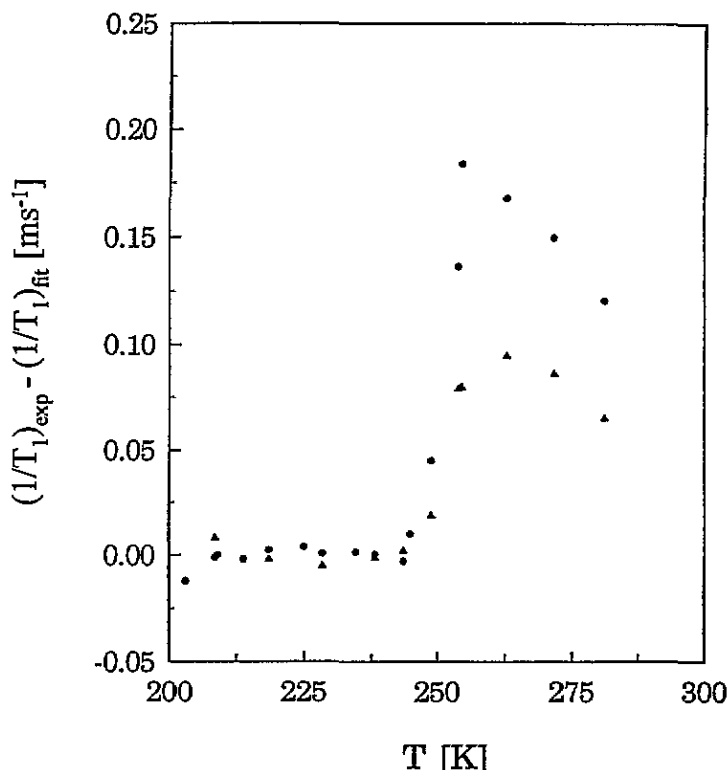


Figure 6. The temperature dependence of $1/T_1$ in the phase transition region.

be satisfied, where $\Delta\nu$ is the natural width of the line. Then, the temperature dependence of the line width is described by the expression

$$\Delta\nu = \Delta\nu_0 + (1/12\pi)(q'/q)^2\omega_Q^2\tau/(1 + \omega_Q^2\tau^2) \quad (9)$$

where $\Delta\nu_0$ is the line width when reorientations are not present. The fit yields an activation energy $E = 19.6 \text{ kJ mol}^{-1}$, in good agreement with the values deduced from the T_1 data. The fit is shown by the solid line in figure 3.

The condition $\Delta\nu \simeq 1/2T_1$ is not satisfied for line 1, where the contribution to $1/T_1$ due to the modulation mechanism is almost half that of the same mechanism in line 2 (see figure 4).

The temperature dependence of $1/T_1$ of line 1 is shown in figure 6 where T_c was taken as 255.8 K. The calculated T_1 values, due to the phase transition mechanism only, are shown. As is seen the transition probability for quadrupole interaction increases anomalously as the temperature approaches T_c . The same phenomenon is observed in the line width (figure 3).

The molecular vibrations generally cause quadrupole relaxation in the crystal, but near the transition temperature the critical fluctuation of the soft librational mode will become so large that only this mode is responsible for the anomaly in T_1 .

For $T < T_c$ Chihara and Nakamura showed that [4]

$$1/T_1 \propto 1/\omega_\theta^2 \quad (10)$$

where ω_θ is the soft-mode frequency

$$\omega_\theta^2 = -A[\alpha x s^x/t(e^x - 1)^2](ds/dt)^{-1} \quad x = (1 + \alpha s^2)/t.$$

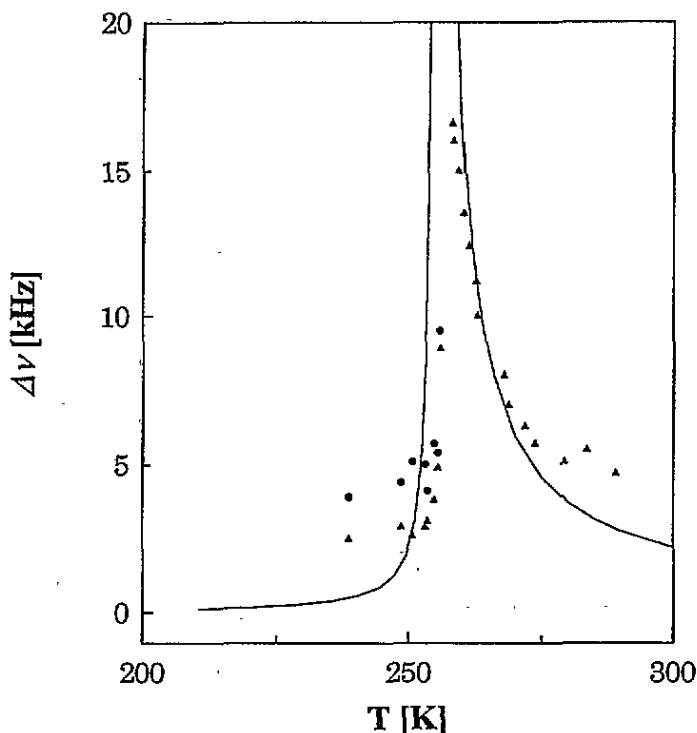


Figure 7. The temperature dependence of the ^{35}Cl line width for both lines in the transition region in 2,6-dinitrochlorobenzene: ●, line 1; ▲, line 2.

When $T > T_c$ ω_θ is zero but the fluctuation of θ remains large enough to affect the transition probability near T_c . The mean square static fluctuation of the Fourier component of s (or θ) at $k = 0$ is given by

$$1/T_1 \propto |\overline{\Delta s}| = (t/v)(e^{-1/t} - 1)/[\alpha - \beta(e^{1/t} - 1)] \quad (11)$$

where v is the volume of the sample.

This model, useful to explain the behaviour of T_1 in the phase transition region, is also useful to explain qualitatively the line width behaviour near the transition. This is so since the most important contribution to $\Delta\nu$ is due to spin-lattice relaxation. By putting $\alpha = 0.49$, $\beta = 0.28$ and $m = 0.44$ as obtained in the preceding section, expression (10) and (11) were calculated. The result is shown in figure 7, the ordinate scale being adjusted to give an agreement with the experimental line width at 250.7 K. It is observed that these expressions qualitatively describe well the experimental data tendency near the phase transition.

5. Conclusions

^{35}Cl NQR frequency data show the existence of a phase transition at about 255 K. In the LTP, Cl NQR measurements of the temperature dependence of T_1 and $\Delta\nu_Q$ data for 2,6-dinitrochlorobenzene are accounted for on the basis of two competing dynamical mechanisms related to small-angle molecular librations and reorientations of the NO_2 group.

The activation energies obtained, $E = 19.0 \text{ kJ mol}^{-1}$ and $E = 15.3 \text{ kJ mol}^{-1}$, are greater than those obtained for $4\text{NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$ and $3\text{NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$ ($E \simeq 10 \text{ kJ mol}^{-1}$) and smaller than that calculated for $2\text{NO}_2\text{-}\phi\text{-SO}_2\text{Cl}$ ($E = 28.5 \text{ kJ mol}^{-1}$). This result provides evidence that the volume of the neighbouring group is important in fixing the height of the barrier.

On the other hand the temperature dependence of experimental data, in the phase transition region, is well explained assuming the transition occurs when molecules in the crystal lattice change their direction uniformly with a change in temperature and the librational modes, coupled in an anharmonic way with the uniform mode, change their frequencies in such a way that entropy compensates the unfavourable potential energy increase due to the uniform angular tilt.

In any case to check the validity of this model it is necessary to perform x-ray spectroscopy below T_c and see whether this compound shows a small broad anomaly in its heat capacity, similar to the case of chloranil.

Acknowledgment

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