A study of activated molecular motion in 2-nitrobenzene sulphonyl chloride by NQR

A study of activated molecular motion in 2-nitrobenzene sulphonyl chloride by NQR

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Abstract. A comprehensive chlorine nuclear quadrupole resonance study of the temperature and pressure dependences of frequency, line width, and spin–lattice relaxation time in 2-nitrobenzene sulphonyl chloride is reported. The results show that each of the two substituted groups on the benzene ring contributes to the spin–lattice relaxation via a different and independent mechanism. In the high-temperature regime, the data are successfully explained assuming reorientation of the SO_2Cl group between unequal potential wells and field gradient fluctuations resulting from reorientations of nearby NO_2 groups. The activation energy of both motions and the fraction of the electric field gradient influenced by the motion of nitro groups have been estimated, as well as the pressure dependence of the activation enthalpy and the activation volume for these motions.

1. Introduction

Nuclear quadrupolar resonance (NQR) is a widely used technique for studying thermally activated molecular motion in solids. The nuclei being observed can in principle be located either inside or outside the moving molecular fragments. In the latter case it is necessary, in order to detect the molecular motions, that the electric interactions between the moving fragments and the resonant nuclei produces a sufficient modulation of the spin–lattice coupling.

The present study involves chlorine NQR measurements in 2-nitrobenzene sulphonyl chloride. This compound exhibits monoclinic symmetry as described by space group $P2_1/a$ with four equivalent molecules per unit cell [1]. Figure 1 shows the labelling of the atoms in the molecule and indicates the relative orientations of the nitro and sulphonyl chloride groups.

Experimental measurements, as a function of both temperature and applied hydrostatic pressure, have been made. Measurements of the resonance frequency, ν_Q, line width $\Delta\nu$ and spin–lattice relaxation time, T_1, are reported as a function of temperature for the ^{35}Cl and ^{37}Cl isotopes, and of pressure for the ^{35}Cl nuclei.

Section 2 contains a brief overview of experimental procedures. The results are presented in section 3. The analysis and discussion of the data are given in section 4:

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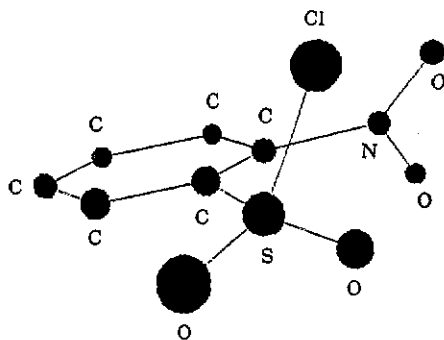
Figure 1. A schematic arrangement of atoms in 2-nitrobenzene sulphonyl chloride.

the spin-lattice relaxation data in section 4.1 and the frequency and line width data in section 4.2.

2. Experimental details

The 2-nitrobenzene sulphonyl chloride used for the experiments was obtained from Aldrich Chemical Co. (#N1,150–7) and used without further purification. The sample container was a cylinder of length 4 cm and diameter 1.1 cm; the amount of sample used was 5 g. The measurements were taken using a Fourier transform (FT) pulse spectrometer [2] with a TECMAG acquisition system. The temperature was controlled to within ±0.1 K using a home-made cryogenic system and a Lakeshore temperature controller. The high-pressure measurements were made using a probe consisting of a RF coil placed inside a cylindrical beryllium–copper pressure vessel [3]. The pressure chamber was connected by means of a high-pressure capillary tube to the helium-gas–mercury–oil compressor system. Pressures were measured using a Harwood manganin gauge in conjunction with a Carey–Foster bridge to an accuracy of better than ±4 kg cm^{-2}. The cryostat [3] provided a temperature stability of better than 0.3 K during the experiment. Copper–constantan thermocouples were employed for the temperature measurements.

The spin–lattice relaxation time was determined from inversion-recovery pulse sequence data and the NQR frequency was obtained from the FFT of the free induction decay after a $\pi/2$ pulse of length 20 μs. The dead time following the pulse was 18 μs. The temperature range covered was between 77 and 300 K and the pressure range between 1 and 2330 kg cm^{-2}.

3. Results

A single NQR line was observed in the temperature range 77–300 K, as expected from the known crystal structure. The temperature dependence of the NQR frequency is plotted in figure 2 and the line width, $\Delta\nu$, in figure 3 as a function of $1000/T$. Note that $\Delta\nu$ decreases slowly in the 77–240 K range but rapidly above 240 K.

The temperature dependences of the ^{35}Cl and ^{37}Cl spin–lattice relaxation times in the 77–220 K range are shown in figure 4. Below 154 K, T_1 is proportional to T^{-2} and the isotopic ratio of T_1 values is equal to the reciprocal of the ratio of squares of the nuclear quadrupole moments. Above 154 K, the T_1 values begin to decrease rapidly and they become isotope independent at the highest temperatures studied.
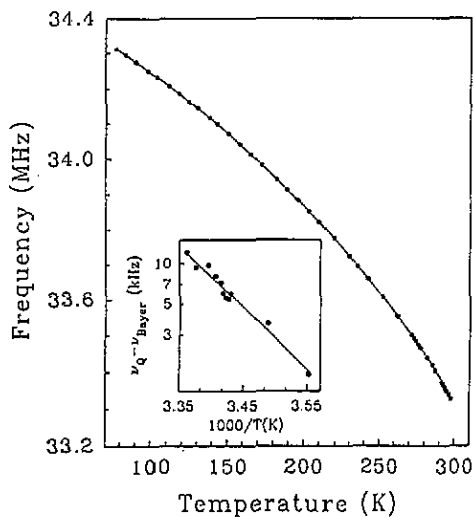
Figure 2. The temperature dependence of the ^{35}Cl NQR frequency in 2-nitrobenzene sulphonyl chloride. The full curve is the fit using equation (12) and the inset shows the difference between the Bayer fit extrapolated for $T > 240$ K and the experimental data.
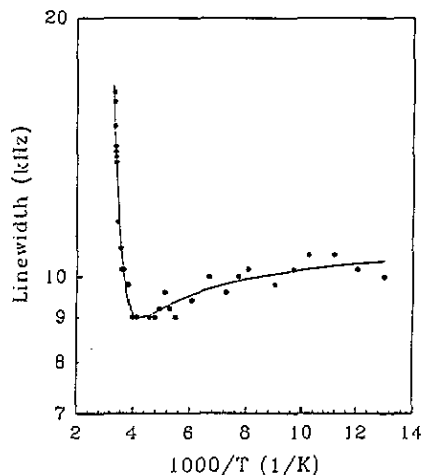
Figure 3. The temperature dependence of the ^{35}Cl line width in 2-nitrobenzene sulphonyl chloride as a function of $1000/T$.
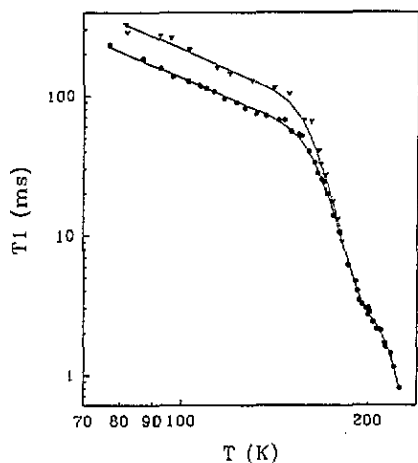

Figure 4. A plot of the temperature variation of T_1 for the ^{35}Cl (●) and ^{37}Cl (▼) isotopes in 2-nitrobenzene sulphonyl chloride. In the low-temperature region $T_1(^{37}$Cl$)/T_1(^{35}$Cl$) \simeq 1.61$; in the high-temperature region $T_1(^{35}$Cl$) \simeq T_1(^{37}$Cl$)$.

Measurements of ν and T_1 as a function of pressure in the range 1–2330 kg cm^{-2}, for nine different temperatures, are shown in figure 5 and 6, respectively. Figure 5 shows that at the lowest temperatures ν increases linearly with pressure, whereas at the highest temperatures the pressure variation in non-linear. From figure 6 we see that the pressure dependence of the logarithm of T_1 obeys a linear relation for all temperatures, but the slope is temperature dependent. Analysis of the pressure dependence of T_1 permits the determination of the nitro group activation volume, ΔV^*, that is, the difference between the molecular group volume at the top of the activation barrier and at a stable state of lower

energy. The data also permit the determination of the pressure dependence of the activation enthalpy.
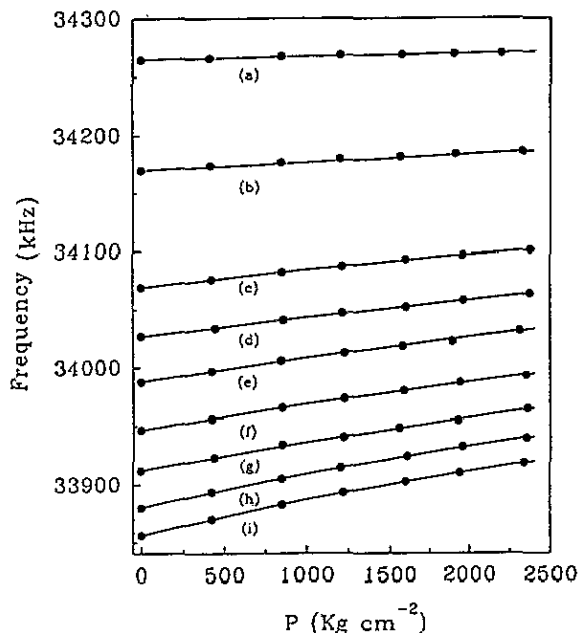

Figure 5. The pressure dependence of the ^{35}Cl NQR frequency at nine different temperatures: (a), 93.2 K; (b), 122.4 K; (c) 150.3 K; (d), 161.2 K; (e), 171 K; (f), 181 K; (g), 189 K; (h), 196.3 K; and (i), 201.3 K.

4. Analysis and discussion

4.1. Spin–lattice relaxation time measurements

The temperature and isotope dependence of the T_1 data for temperatures below 154 K are clear indicators that the relaxation is caused by small-angle molecular librations [4]. For temperatures above 154 K, the temperature and isotope dependences of T_1 are typical of relaxation produced by molecular groups executing large-amplitude motions in relation to the observed nuclei. Such motions create fluctuations which are a significant fraction of the electric field gradient [5]. We will show that such fluctuations, due to the reorientation of neighbouring nitro groups, begin to contribute to T_1 above 154 K and that above 200 K another effective relaxation mechanism, namely the reorientation of the sulphonyl chloride groups, also becomes important.

We will show that T_1 of the chlorine nuclei observed for 2-nitrobenzene sulphonyl chloride can be accounted for in terms of three independent relaxation mechanisms: (i) the libration of the molecule as a whole, $(T_1)_{lib}$; (ii) the modulation of the electric field gradients (EFG) due to reorientations (or inversions) of the neighbouring NO_2 group, $(T_1)_{mod}$; and (iii) the reorientations of sulphonyl groups between unequal potential wells, $(T_1)_{reor}$. The observed T_1 can therefore be written as

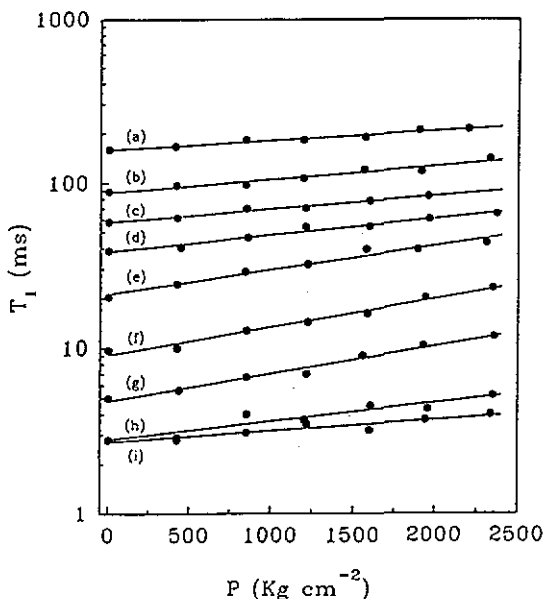$$1/T_1 = (1/T_1)_{lib} + (1/T_1)_{mod} + (1/T_1)_{reor}. \tag{1}$$

Figure 6. The pressure dependence of the ^{35}Cl T_1 values at nine different temperatures: (a), 93.2 K; (b), 122.4 K; (c), 150.3 K; (d) 161.2 K; (e), 171 K; (f), 181 K; (g), 189 K; (h), 196.3 K; and (i), 201.3 K.

For $(T_1)_{lib}$ it is well known that [4]

$$1/T_1 = bT^\lambda \qquad \text{with } \lambda \simeq 2. \tag{2}$$

When the NO_2 groups perform reorientations between potential wells, the relaxation rate $(T_1)^{-1}_{mod}$ due to the modulation of the EFG at the chlorine site can be written as [5]

$$(1/T_1)_{mod} = \tfrac{1}{6}(q'/q)^2 \omega_q^2 \tau / 1 + \omega_q^2 \tau^2 \tag{3}$$

where (q'/q) and τ denote the fluctuating fraction of the EFG and the correlation time for the reorientation of the NO_2 groups, respectively. The correlation time τ follows the Arrhenius law, $\tau = \tau_0 \exp(E/k_B T)$, where E is the activation energy for this motion.

Finally, when the chlorine nuclei perform reorientations between unequal potential wells, such as shown in figure 7, assuming slow reorientations and if $\Delta \gg kT$, it follows that [6, 7]

$$(1/T_1)_{reor} = \tfrac{7}{6}(\tau_r)^{-1} \tag{4}$$

with $\tau_r = \tau_{or} \exp(E_r/k_B T)$. In this case, measurements of the temperature dependence of T_1 give information only about the height of the smaller potential barrier.

Equation (1) was used to fit the observed ^{35}Cl T_1 data, and the following values for the adjustable parameters were obtained: $b = 9.4 \times 10^{-7}$; $\tau_0 = 1.9 \times 10^{-16}$ s; $\tau_{or} = 1 \times 10^{-12}$ s; $\lambda = 1.94$; $E = 28.5$ kJ mol^{-1}; $E_r = 38.5$ kJ mol^{-1}; $(q'/q) = 3.7 \times 10^{-3}$.

The activation energy E obtained for the reorientation of the NO_2 group may seem large compared with the activation energy E_r for the SO_2Cl group, but it should be remembered
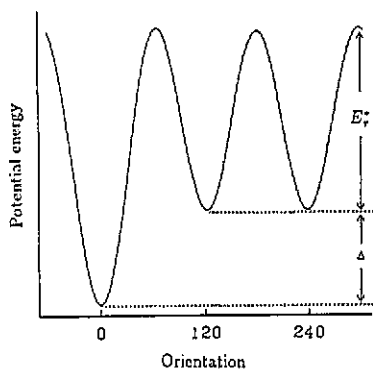
Figure 7. A three-well orientational potential energy profile for the molecular fragment SO_2Cl in a 2-nitrobenzene sulphonyl chloride crystal.

that in the latter case we are referring to the smallest barrier. No measured activation energy for the reorientation of NO_2 has ever been reported. A theoretical calculation for the free molecule of nitrobenzene [8] yielded the value $E = (13 \pm 4)$ kJ mol^{-1}. That this value is lower than the one reported here can be explained by noting that the nitro group is close to the sulphonyl group in the molecule and that intramolecular effects strongly contribute to the barriers in solids. The fluctuation fraction of the EFG, due to this reorientation, represents 0.4% of the total EFG; similar values have been reported elsewhere [9]. The value for E_r obtained for the activation energy of the sulphonyl group is in good agreement with that obtained by Kjuntsel *et al* in $(CCl_3)_2CIP=NSO_2Cl$ [7].

The best fit to the T_1 data for the ^{35}Cl nuclei using the above values of the parameters is shown in figure 4 by the full curve. Also shown is the temperature dependence of T_1 for the ^{37}Cl nuclei, calculated using the best-fit parameters obtained from the ^{35}Cl T_1 fit. In the latter calculation the values for b and ω_q^2 are divided, respectively, by the square of the chlorine quadrupole moment ratio, $(eQ(^{35}Cl)/eQ(^{37}Cl))^2 = 1.61$. The fits are seen to be excellent, indicating that all that is necessary to move from the ^{35}Cl to the ^{37}Cl data is to vary the parameters that depend on eQ in the correct ratio. It can be concluded that the dominant relaxation mechanism for the chlorine nuclei is quadrupolar in nature and results from the time-dependent portion of the EFG at the chlorine nuclear sites.

From figure 6 we note that the pressure dependence of the logarithm of T_1 is linear for all temperatures. For the lowest temperatures (90 to 160 K) the slope is almost constant; it then increases with T for a range of temperatures, and finally decreases again. Considering the temperature range over which the slope changes, we assume that the effect is related to the reorientation of the NO_2 group. We will discuss the relaxation process phenomenologically.

Following the approach of Anderson and Slichter [10], we can derive the rate at which a system transforms from an initial state A_1 to a final state A_2 separated by an excited state A^*

$$A_1 \leftrightarrows A^* \leftrightarrows A_2. \tag{5}$$

In the present case, A_1 and A_2 represent equilibrium orientations of the NO_2 group and A^* is a state whose energy is greater than that of A_1 or A_2 by the energy of the potential barrier to free rotation of the group.

The following proportionalities exist between T_1 and the correlation time τ of the motion causing the modulation:

$$1/T_1 = \tfrac{1}{6}(q'/q)^2/\tau \qquad \omega_q\tau \gg 1 \tag{6a}$$

$$1/T_1 = \tfrac{1}{6}(q'/q)^2 \omega_q^2 \tau \qquad \omega_q \tau \ll 1 \tag{6b}$$

where the correlation time τ for the motion can be written in terms of the difference in the Gibbs function ΔG^* between state A_1 and A^* and τ_0 is taken to be independent of temperature and pressure

$$\tau = \tau_0 \exp(\Delta G^*/RT). \tag{7}$$

On the other hand, we know that pressure changes cause a change in intermolecular distance so (q'/q) will be pressure dependent.

It follows directly from the Gibbs–Helmholtz equation that the enthalpy of activation ΔH^* is given by

$$\Delta H^* = \pm[R\partial \ln T_1/\partial(1/T)]_p. \tag{8}$$

This equation has a plus sign when the conditions of equation (6a) are met and a minus sign when those of equation (6b) are satisfied. The quantity ΔH^* can be obtained from the temperature variation of $\ln T_1$ at constant pressure. It is easily shown that

$$\Delta V^*/RT = \pm[\partial \ln T_1/\partial P]_T + [2/(q'/q)][\partial(q'/q)/\partial P]_T. \tag{9}$$

The term $(1/\omega_q)[\partial\omega_q/\partial P]_T$ has been neglected because its value is approximately 1×10^{-7} cm^2 kg^{-1}. It is easily estimated from the pressure dependence of v and is three orders of magnitude smaller than the first term in equation (9).
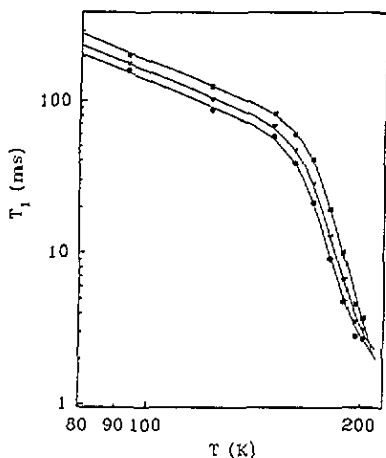

Figure 8. The temperature dependence of T_1 values at three different pressures: ●, 1 kg cm^{-2}; ▼, 849 kg cm^{-2}; and ■, 1931 kg cm^{-2}. The full curves are the fits using equation (1).
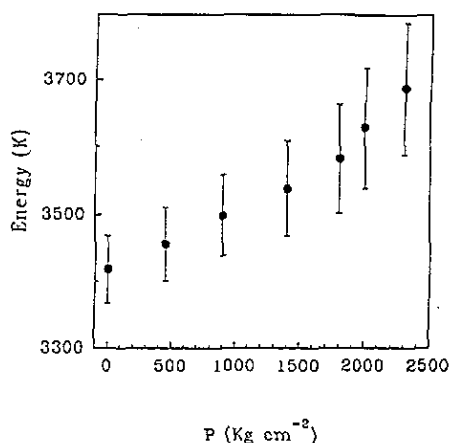
Figure 9. The pressure variation of ΔH^* for the reorientation of NO$_2$ groups.

Figure 8 shows T_1 as a function of T for different pressures. Fitting of these curves using equation (1), with the values of τ_0, τ_{or} and ω_q fixed at the values obtained from

$[T_1(T)]_{p=atm}$, reveals that the pressure dependence of ΔH^* is approximately linear (see figure 9) and that q'/q can be considered to be constant over the pressure range studied. Therefore, the second term in equation (9) can be neglected.

In order to estimate the first term on the right-hand side of equation (9), the contribution of the torsional oscillation relaxation mechanism to the high-temperature T_1 curves in figure 6 was removed using the following procedure. The contribution at atmospheric pressure was obtained by extrapolation of $(1/T_1)_{lib}$. Then, assuming that the pressure dependence of $(1/T_1)_{lib}$ is independent of temperature, the pressure dependence was taken as that observed at the lowest temperatrues, as shown in figure 6. The result of this procedure is shown in figure 10. The slope here is positive, which means that we are in the slow-motion regime, and it is independent of temperature to within the experimental accuracy. It was deduced that $\Delta V^* = 6.9$ cm^3 mol^{-1}. This means that $\Delta V^* \simeq 5\%$ of the molar volume.
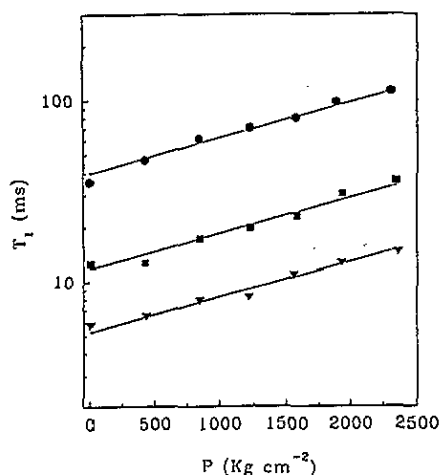

Figure 10. The pressure variation of the ^{35}Cl T_1 values at ●, 171 K; ■, 181 K; and ▼, 189 K. The calculated T_1 values due to the modulation mechanism only are shown.

Anderson and Slichter [10] found an apparent separation of the systems studied into two categories. One category is characterized by small ΔV^* values, in which intramolecular rotation of a group of atoms of the molecule is involved; the other by values of ΔV^* of about 10 to 15% of the molar volume, in which the entire molecule undergoes rotational jumps. Therefore, we conclude that 2-nitrobenzene sulphonyl chloride belongs to the first category.

The activation energy, ΔE^*, for the reorientation process is related to ΔH^* and ΔV^* by the thermodynamic expression

$$\Delta E^* = \Delta H^* - P_t \Delta V^* \tag{10}$$

where P_t, the thermal pressure, is defined as $P_t = T(\alpha/\beta)$. Since we do not have any experimental values for α and β for this compound, it is not possible to substitute directly into equation [10] to obtain a value for ΔE^*.

4.2. NQR frequency and line width measurements

Another experimental fact that supports the assumption of reorientation of the SO$_2$Cl group is the temperature dependence of the NQR line width. In fact, if the SO$_2$Cl group undergoes

reorientations, in order to observe appreciable changes in the line width, it is necessary to satisfy the condition $\Delta\nu \simeq \tau_r^{-1}$, where $\Delta\nu$ is the natural width of the line. The temperature at which we begin to observe broadening is related to the value of τ_r obtained from the analysis of T_1. The expression [12] for the line broadening of quadrupolar nuclei that undergo reorientations is $(\Delta\nu)_{reor} = (\pi\tau_r)^{-1}$ and the best fit is shown by the full curve in figure 3. The fit yields the same activation energy as deduced from the T_1 data.

The NQR frequency was measured for both isotopes. The ratio of frequencies, $\nu(^{35}Cl)/\nu(^{37}Cl)$, has the constant value 1.2688 ± 0.0001 to within experimental error over the entire temperature range studied. This value is in agreement with the ratio of the quadrupole coupling constants, 1.2686 ± 0.0004, found by Jaccarino and King [13]. The temperature dependence of ν shows a normal 'Bayer' behaviour.

Since the broadening of the NQR line begins at 240 K, we assume that below this temperature the frequency data follows the Bayer model [14]:

$$\nu(T) = \nu_0[1 - (3\hbar^2/2Ik\omega)\coth(\hbar\omega/2kT)]. \tag{11}$$

In this expression $\omega = \omega_0(1-gT)$ is an average torsional frequency, ν_0 is the limiting static value of the resonance frequency and I is the averge moment of inertia of the molecule. A least-squares fit of this equation to the experimental data, in the temperature range 77–240 K, using the value of I calculated from the molecular structure, yielded the following parameters: $\nu_0 = 34.524$ MHz; $\omega_0 = 35$ cm^{-1}; and $g = 7.8 \times 10^{-4}$ K^{-1}. These values of ω_0 and g are typical for substituted benzenes [15].

The inset in figure 2 shows the difference between the Bayer fit extrapolated for $T > 240$ and the experimental data plotted as a function of $1000/T$. It is seen that this difference yields an exponential behaviour and agrees with that expected when the frequency is affected by reorientations [16, 17]:

$$\nu - \nu_{\text{Bayer}} \propto -1/\omega_q\tau^2 \tag{12}$$

for $\omega_q\tau \gg 1$. The slope obtained from these data is twice the value of E_r obtained from T_1, as expected from equation (12).

The pressure dependence of the NQR frequency was measured over the same pressure range as for T_1 and at the same temperatures. The data are shown in figure 5. We see that the frequency increases with pressure at each temperature but the change is small. This is reasonable since the pressure primarily causes changes in intermolecular distance, but the dominant contribution to the EFG at a chlorine site is due to the charge distribution in the bond and the pressures used here are not strong enough to significantly change this distribution.

Another observation is that, at the two lowest temperatures, the increase in frequency is linear to within experimental error, whereas at the highest temperatures the increase is non-linear. This change in behaviour is certainly related to the onset of reorientation of the nitro groups. The same behaviour has been found elsewhere [11].

5. Conclusions

NQR data show the existence of three different relaxation mechanisms. At lower temperatures ($T < 154$ K) molecular librations alone dominate the relaxation. Above 154 K, fluctuations of the EFG due to reorientations of nitro groups begin to contribute to T_1 with an activation

energy of $E = 28.5$ kJ mol^{-1}, and a fluctuation fraction of the EFG which represents 0.4% of the total EFG. Above 200 K the reorientation of the sulphonyl chloride group between unequal potential wells becomes important. This mechanism, also responsible for the ^{35}Cl NQR line broadening and the deviation from Bayer behaviour, obeys an Arrhenius law with an activation energy of $E_r = 38.5$ kJ mol^{-1}.

The study of the pressure dependence of the spin–lattice relaxation time permits the determination of an activation volume for the nitro group of $\Delta V^* = 6.9$ cm^3 mol^{-1} and reveals that the pressure dependence of the activation enthalpy is approximately linear.

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