An NQR study of thermally activated molecular motion in 4-nitrobenzene sulphonyl chloride

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Abstract. A study of the temperature dependence of the ^{35}Cl NQR frequency and spin–lattice relaxation time in 4-nitrobenzene sulphonyl chloride is reported. The data indicate the existence of four crystalline phases. The observed behaviour of T_1 in two of the phases is explained in terms of molecular librations, modulation effects due to the reorientation of NO_2 groups, and reorientations between unequal potential wells of SO_2Sl groups. Values of the activation energies of these motions in both phases are estimated and compared with those obtained in 2-nitrobenzene sulphonyl chloride.

1. Introduction

In our previous paper [1] we reported a comprehensive nuclear quadrupole resonance (NQR) study of 2-nitrobenzene sulphonyl chloride. It was shown that each of the two substituted groups in the benzene ring contributes to the relaxation through a different mechanism. For the SO_2Cl groups it is the reorientation between unequal wells that is important whereas for the NO_2 groups it is the modulation of the electric field gradients (EFGs) caused by reorientations. The present work represents an extension of the former to another compound of the family, namely 4-nitrobenzene sulphonyl chloride. Figure 1 shows a schematic illustration of the constituent molecules. For this compound the crystal structure is not known.

It is known that the presence of substituted groups in the para- and ortho-positions in the benzene ring affects the bonds in a similar way, which is not the case for a meta-substitution [2]. Therefore, we expected to observe a similar behaviour of the chlorine NQR frequency and spin–lattice relaxation time in 4-nitrobenzene sulphonyl chloride to that found for 2-nitrobenzene sulphonyl chloride. However, for the NO_2 group a lower activation energy and less modulation of the EFG at the Cl site is expected for 4-nitrobenzene sulphonyl chloride, since in this case the NO_2 group is farther from the SO_2Cl group.

The experimental details are given in section 2. The results and their analysis are presented in sections 3 and 4, respectively. Brief conclusions are given in section 5.

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2. Experimental

The specimen of 4-nitrobenzene sulphonyl chloride was obtained from Aldrich Chemical Co. (#17, 092-5). It was divided into two portions, one of which was subjected to a recrystallization (purification) process. Measurements were made on both the purified material (sample 1) and on the 'as provided by the supplier' material (sample 2). The temperature dependences of the NQR parameters in both samples were measured using a Fourier transform pulse spectrometer [3], with a TECMAG acquisition system. The NQR frequency was obtained from the FFT of the free induction decay after a $\pi/2$ pulse. The spin–lattice relaxation time was determined from an inversion-recovery pulse sequence in the low-temperature region. In the high-temperature regime where the signal-to-noise ratio was reduced T_1 was measured from the spin echo following a three-pulse sequence.
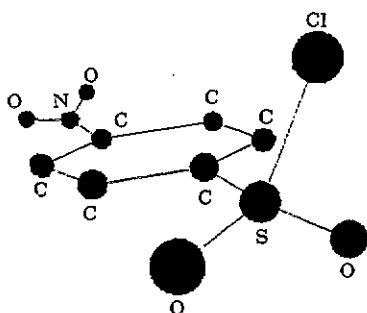

Figure 1. The molecular structure of 4-nitrobenzene sulphonyl chloride.

The temperature was controlled to within ±0.1 K using a home-made cryogenic system and a Lakeshore temperature controller. Copper–constantan thermocouples were used to measure the temperature. The temperature ranges investigated were 77 to 220 K for sample 2, and 77 to 195 K for sample 1.

The NQR frequency previously reported at 77 K [4] agrees with that found in sample 2, but differs by about 150 kHz from that in sample 1. At high temperatures, the results suggest that both samples are in the same phase, but at low temperatures the NQR frequency data indicate that they are in different phases.

3. Results

Four different phases were found in this compound as indicated in figure 2, where the temperature dependence of $\nu(T)$ for the ^{35}Cl nuclei is plotted as a function of temperature. When cooled, sample 1 is found in a phase we call α and it is stable in the range 77 to 195 K. Above 195 K the S/N ratio is very poor and it is not possible to follow the NQR signal. Sample 2 crystallizes at low temperatures in a phase we label δ. As the temperature is increased the sample undergoes a phase transition at about 118.5 K. In this new phase (phase γ), two resonance lines are observed, which indicates two chemically inequivalent positions for the chlorine nuclei in the unit cell. At $T = 131$ K another phase transition to phase β occurs and again a single resonance line is observed. It is important to mention that both samples exhibit signals of similar intensity and line width; this implies that the
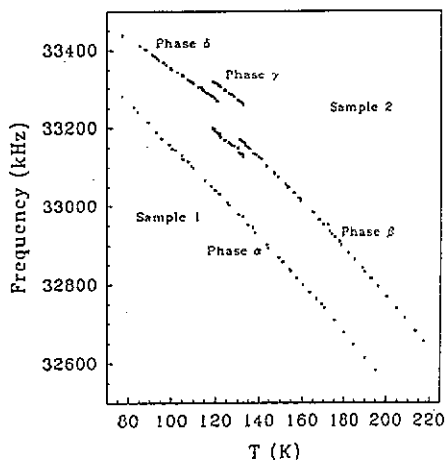
Figure 2. The temperature dependence of the ^{35}Cl NQR frequency in 4-nitrobenzene sulphonyl chloride.

concentration of impurities in the two samples is not sufficiently different to markedly affect the distribution of EFGs.

The temperature dependence of the ^{35}Cl spin–lattice relaxation time, T_1, is shown in figure 3 for both samples. Measurements of the ^{37}Cl T_1 values in the low-temperature regime for sample 1 are shown in figure 4 along with the ^{35}Cl T_1 measurements. These data show that T_1 is not proportional to T^{-2} at the lowest temperatures measured, and that the isotopic ratio of T_1 values is not equal to the reciprocal of the ratio of squares of nuclear quadrupole moments. These two facts suggest the existence of another relaxation mechanism below 135 K. Above 135 K T_1 decreases rapidly. In sample 2, for $T < 119$ K (phase δ), T_1 is proportional to T^{-2}; however, in phase β the behaviour is similar to that in sample 1.

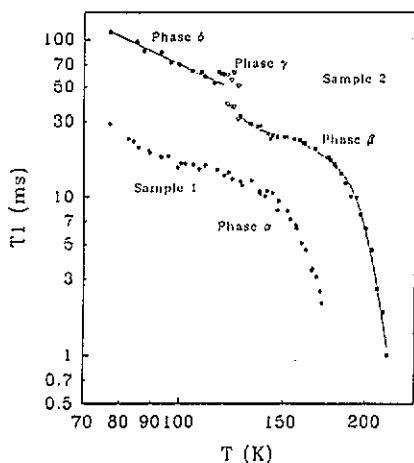
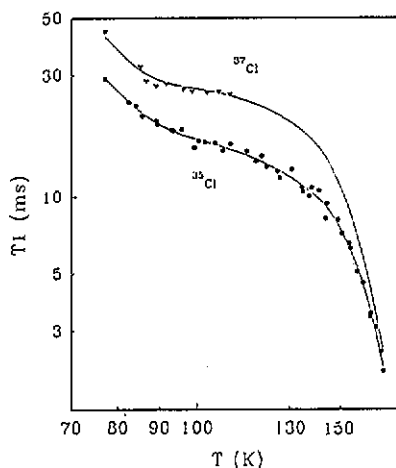**Figure 3.** The temperature dependence of the ^{35}Cl T_1 values in the two samples.

Figure 4. The temperature dependence of T_1 for the ^{35}Cl (●) and ^{37}Cl (▼) isotopes in sample 1 of 4-nitrobenzene sulphonyl chloride.

4. Analysis and discussion

4.1. Frequency and line width measurements

No broadening in the line width related to the reorientation of the SO_2Cl groups was observed in either of the samples. This is as expected since in order to observe appreciable changes in the line width, it is necessary to satisfy the condition $\Delta \nu \simeq \tau_r^{-1}$, and this condition is satisfied only at temperatures above 220 K.

Measurements of the temperature dependence of ν indicate the existence of four different phases in 4-nitrobenzene sulphonyl chloride. When sample 1 is left at room temperature for a long time and then cooled slowly, at around $T = 140$ K the signal is observed in phase β corresponding to the behaviour of sample 2, but if the sample is cooled quickly to 77 K, phase α is obtained. This suggests that the effect of the small change in the amount of impurities between the two samples is to change slightly the stability of the phases.

In sample 2, three different phases are observed. The transitions are first order as indicated by the discontinuities observed in the temperature dependence of ν and the hysteresis (see figure 5) $\sim$ 8 K associated with both transitions. Phase γ is observed in a small temperature interval (118.5–132 K). This phase has lower symmetry than the other two, since two resonance lines are observed. We also note the coexistence of phases in a range $\sim$ 2 K. Figure 6 shows the evolution with temperature of the spectrum through the two-phase transitions. Finally, careful consideration of the data of figure 2 indicates that the temperature dependence of the frequency in phase δ is similar to the behaviour of the higher-frequency line in phase γ, while the behaviour of the lower-frequency line in phase γ is similar to that in phase β.
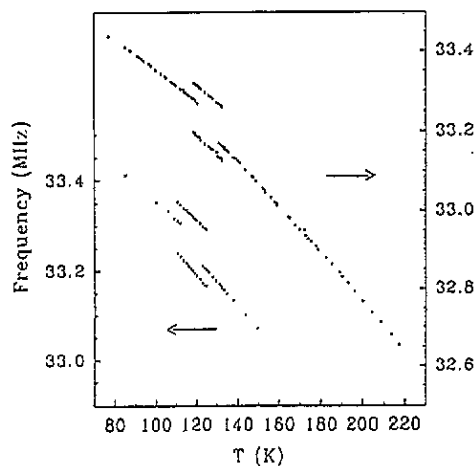

Figure 5. The temperature dependence of ν: ●, warming up; and ▼, cooling down. These data show hysteresis.

Unfortunately, it is not possible to deduce the structural changes that are reflected through the NQR frequency changes from these data alone.

The NQR frequency data in phases α, β and δ can be fit using the Bayer model [5]

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

where $\omega = \omega_0(1 - gT)$ is an average torsional frequency, ν_0 is the limiting static value of the resonance frequency and I is the average moment of inertia of the molecule. A least-squares fit of this equation to the experimental data yielded the following parameters.

	Phase α	Phase β	Phase δ
ν_0 (MHz)	33.694	33.771	33.702
ω_0 (cm^{-1})	27.7	32	36
g	2.9×10^{-4}	6.2×10^{-4}	7.2×10^{-4}

The values of ω_0 and g are typical for substituted benzenes [6].

It is instructive to analyse the temperature behaviour of the differences between the NQR frequency in the various molecular arrangements corresponding to sample 2 and the NQR frequency in sample 1. In this way the effect of the crystalline forces on the molecule can be compared, avoiding the consideration of internal vibration modes, which are removed when the difference is taken. Figure 7 shows these differences; $\Delta \nu$ is plotted as a function of T. Following Brunetti [7] the temperature dependence of $\Delta \nu$ can be written as

$$\Delta \nu = \Delta \nu_e + AT + BT^2 \tag{2}$$

where $\Delta \nu_e$ is the frequency difference between primed and unprimed phases in the rigid lattice, A only depends on the harmonic terms in the intermolecular potential describing the molecular torsional frequencies in the rigid lattice, and B gives the changes due to anharmonicities of the molecular torsional frequencies:

$$A = \nu_0(p' - p) \qquad p = \frac{3k_B}{2} \sum_i^N \left(\frac{1}{I_i \omega_{0i}^2} \right) \tag{3}$$

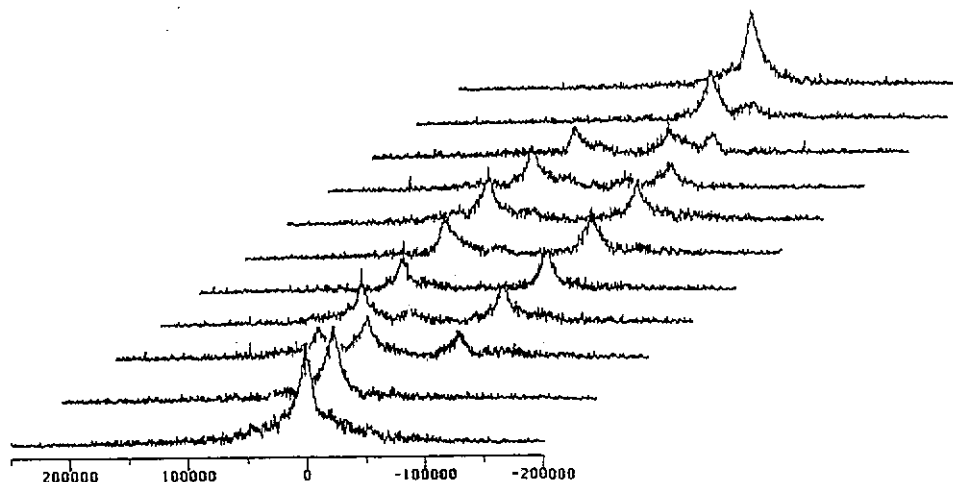$$B = 2\nu_0(q' - q) \qquad q = \frac{3k_B}{2} \sum_i^N \left(\frac{g_i}{I_i \omega_{oi}^2} \right). \tag{4}$$

Figure 6. The temperature evolution of the NQR spectrum through the two-phase transitions.
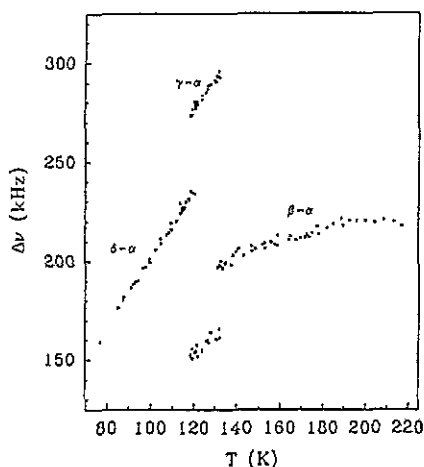
Figure 7. The temperature dependences of the differences $\Delta\nu$ between frequencies corresponding to the various phases.

Using equation (2) to fit the differences between the NQR frequencies in phases δ and α, and in phases β and α, the following values were obtained.

	$\Delta\nu_e$ (kHz)	A (kHz K^{-1})	B (kHz K^{-2})
δ–α	5.4	2.2	-2.5×10^{-3}
β–α	70	1.4	-3.3×10^{-3}

A positive and B negative indicate that on average the torsional frequencies in the unprimed case are higher than those in the primed ones. In the present case, this means that the torsional frequencies corresponding to phase α are lower than those in phase δ and phase β. The same can be said about the thermal volume effect coefficients g_i, which implies that the anharmonic effects are weaker in phase α. This result agrees with that obtained from the fit of NQR frequency data using equation (1). Using the values for the torsional frequencies obtained from the fit of ν in each phase it is possible to obtain estimates of A and B. The values obtained agree with the ones obtained by fitting the differences in both cases. In order to compare $\Delta\nu_e$ values, the difference between the ν_0 frequencies is required, since in our Bayer fit this parameter is related to the intramolecular EFG as well as to the crystalline EFG

4.2. Spin–lattice relaxation time data

In phase α the temperature and isotope dependence of the T_1 data for temperatures below 135 K are clear indicators that the relaxation can not be accounted for by small-angle molecular librations alone. We will show that the observed behaviour is consistent with the existence, for $T < 135$ K, of reorientations of NO_2 groups, in addition to small-angle molecular librations. For temperatures above 135 K reorientations of the SO_2Cl group become important. As a result, the observed temperature dependence of the relaxation rate of the chlorine nuclei is described by the expression

$$1/T_1 = (1/T_1)_{\text{lib}} + (1/T_1)_{\text{mod}} + (1/T_1)_{\text{reor}}. \tag{5}$$

Here the librational contribution obeys a power law temperature dependence [8]:

$$(1/T_1)_{\text{lib}} = bT^\lambda \qquad \lambda \simeq 2. \tag{6}$$

The modulation contribution has the form [9]

$$(1/T_1)_{\text{mod}} = \tfrac{1}{6}(q'/q)^2 \omega_q^2 \tau/1 + \omega_q^2 \tau^2 \tag{7}$$

where q' is the amplitude of the moving EFG and q is the full EFG at the nuclear site; $\tau = \tau_0 \exp(E/k_B T)$ is the correlation time of the modulating motion and E the activation energy of that motion.

The contribution due to the reorientation of the SO$_2$Cl group between unequal wells [10] has the form

$$(1/T_1)_{\text{reor}} = \tfrac{7}{6} 1/\tau' \tag{8}$$

where $\tau' = \tau_0' \exp(E_r/k_B T)$, and E_r is the smaller barrier of the unequal potential well.

The T_1 data in phase β show a qualitatively similar behaviour to those in phase α and are well described by equation (5). Fitting both data sets simultaneously, with the constraint that the τ_0, τ_{0r} and q'/q values are the same in both phases yielded the following values for the parameters.

	b	E (kJ mol^{-1})	E_r (kJ mol^{-1})	λ
Phase α	5.8×10^{-6}	6.7	33.9	1.97
Phase β	8.07×10^{-8}	10.5	41.8	2.59

with $\tau_0 = 4.9 \times 10^{-13}$ s; $\tau_{0r} = 1 \times 10^{-13}$ s, and $(q'/q) = 8 \times 10^{-4}$.

The best fits to the ^{35}Cl T_1 data using these values of the parameters are shown in figures 3 and 4 by the full curves. Also shown in figure 4 is the temperature dependence of T_1 for the ^{37}Cl nuclei, calculated using the above parameters with the values of b and ω_q^2 divided by the square of the Cl quadrupole moment ratio.

The values of E_r are in good agreement with those obtained for the reorientation of the SO$_2$Cl group in (CCl$_3$)$_2$ClP=NSO$_2$Cl and Cl$_3$P=NSO$_2$Cl by Kjuntsel *et al* [11] and in 2-nitrobenzene sulphonyl chloride [1].

The activation energies E obtained for the reorientation of the NO$_2$ groups are comparable to that given by the theoretical calculation for the free molecule of nitrobenzene [12], $E = (13 \pm 4)$ kJ mol^{-1}, but lower than those obtained in 2-nitrobenzene sulphonyl chloride as expected. Also the value of (q'/q) is lower in 4-nitrobenzene sulphonyl chloride than in 2-nitrobenzene sulphonyl chloride indicating that the modulation is intermolecular in the former case.

It may be seen from figure 3 that in sample 2 the temperature dependence of T_1 in phase δ is proportional to T^{-2}. In phase γ, two spin–lattice relaxation times are observed, corresponding to the two non-equivalent chlorine positions in the unit cell. Two additional observations are of interest: (1) just below the phase transition (in phase δ) the T_1 value is equal to the larger T_1 value in phase γ; and (ii) just above the phase transition (in phase β) T_1 has the value of the smaller T_1 in phase γ.

5. Conclusions

^{35}Cl NQR frequency data indicate the existence of four different phases in 4-nitrobenzene sulphonyl chloride. For phases α and β, the temperature dependence of T_1 reveals the existence of three different relaxation mechanisms, as was the case for 2-nitrobenzene sulphonyl chloride. Above 135 K and above 165 K, reorientation of the sulphonyl chloride groups between unequal potential wells provides the dominant mechanism with activation energies $E_r = 33.9$ kJ mol^{-1} and $E_r = 41.8$ kJ mol^{-1} for phases α and β respectively. Below 135 K, molecular librations and reorientations of nitro groups dominate the relaxation. The activation energies obtained for these reorientations are $E = 6.7$ kJ mol^{-1} and $E = 10.5$ kJ mol^{-1} for phases α and β, respectively. In the case of 2-nitrobenzene sulphonyl chloride the modulation effect was due to the reorientation of the neighbouring NO_2 group in the molecule, so the effect was intramolecular. In the present case the modulation effect is not strong. The fact that the two groups are opposite to one another in the benzene ring indicates that the effect is intermolecular in origin.

References

[1]   Pérez S C, Armstrong R L and Brunetti A H 1993 *J. Phys.: Condens. Matter* **5** 4045
[2]   March J 1968 *Advanced Organic Chemistry* (New York: McGraw-Hill)
[3]   Armstrong R L and Ramia M 1985 *J. Phys. C: Solid State Phys.* **18** 2977
[4]   Bray P and Ring R 1953 *J. Chem. Phys.* **21** 2226
[5]   Bayer H 1951 *Z. Phys.* **130** 227
[6]   Moross G G and Story H S 1966 *J. Chem. Phys.* **45** 3370
[7]   Brunetti A H 1980 *J. Mol. Struct.* **58** 513
[8]   Jones L V, Sabir M and Smith J A S 1978 *J. Phys. C: Solid State Phys.* **11** 4077
[9]   Woessner D E and Gutowsky H S 1963 *J. Chem. Phys.* **39** 440
[10] Ainbinder N E, Kjuntsel I A, Mokeeva V A, Osipenko A N, Soifer G B and Shaposhnikov I G 1980 *J. Mol. Struct.* **58** 349
[11] Kjuntsel I A, Mokeeva V A and Soifer G B 1990 *Sov. J. Chem. Phys.* **5** 2148
[12] Lister D, McDonald J and Owen N 1978 *International Rotations and Inversion* (New York: Academic) p 163