^{35}Cl NQR Study of Thermoactivated Motions of Nitro Groups in Picryl Chloride *

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The temperature dependences of the ^{35}Cl NQR frequency (ν), spin-lattice relaxation time (T_1), and spin-spin relaxation time (T_2) have been studied in 2,4,6-trinitrochlorobenzene (picryl chloride) from 77 K up to the melting point (354 K). The $T_1(T)$ curve exhibits a pronounced composite mimimum near 300 K which gives evidence for the reorientations of the two *ortho*-NO_2 groups around their two-fold symmetry axes with the activation energies of 27.4 kJ mol^{-1} and 31.2 kJ mol^{-1}. These values can be related to the *ortho*-NO_2 groups having the twist angles of 33° and 81°, respectively (the crystal structure of picryl chloride is known). The $T_2(T)$ dependence exhibits interesting features, too: a deep minimum about 140 K and a new rapid decrease above 270 K.

Key words: NQR, reorientation motion, nitro group.

Introduction

Numerous *ortho*-nitrochlorobenzenes are avialable and of great interest for the systematic study of the reorientation features of nitro groups in solids [1–3]. Specific positioning of the NO_2 groups in such compounds make it possible to use ^{35}Cl NQR. In *ortho*-nitrochlorobenzenes, the chlorine atoms usually have strong steric interactions with the neighbouring nitro groups (see [4]), and so the NO_2 reorientations can be studied by so-called modulation effects on the temperature dependence of the chlorine spin-lattice relaxation time T_1. Indeed, information about such effects on the ^{35}Cl $T_1(T)$ dependence in solid 2,6-dinitrochlorobenzene has been given in [5]. The present paper deals with solid picryl chloride (2,4,6-trinitrochlorobenzene), which exhibits very interesting peculiarities.

Experimental

The ^{35}Cl NQR spectrum of picryl chloride containes one intense line, in accordance with its crystal structure data [6]. The line frequency, 39.366 MHz at 77 K, agrees with the literature value [7]. The temperature dependences of the resonance frequency (ν), the spin-lattice relaxation time (T_1), and the spin-spin relaxation time (T_2) were measured on a polycrystalline sample from 77 K up to the melting point (354 K). The temperature was controlled to within ± 0.5 K using a nitrogen gas flow thermostat. The relative errors of the NQR frequencies and the relaxation times were about 0.005% and 5%, respectively.

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Results and Discussion

NQR Frequency

The temperature dependence of the ^{35}Cl NQR frequency is shown in Figure 1. It has no peculiarities which could be connected with the presence of phase transitions. The temperature coefficient of the frequency, $|\Delta\nu/\Delta T|$, is typical for chlorine nuclei in molecular crystals; its values are ca. 1.5 kHz K^{-1} at 77 K and ca. 5 kHz K^{-1} near T_{mp}, the rate of the increase rising above ca. 280 K.

Spin-Lattice Relaxation Time

The temperature dependence of the spin-lattice relaxation time T_1 reveals two relaxation mechanisms which are effective in different temperature ranges. At low temperatures, from 77 K to ca. 180 K, the relaxation rate is determined by the molecular librations which give a power temperature law (Figure 2):

$$(T_1^{-1})_{libr} = a \cdot T^n, \quad (1)$$

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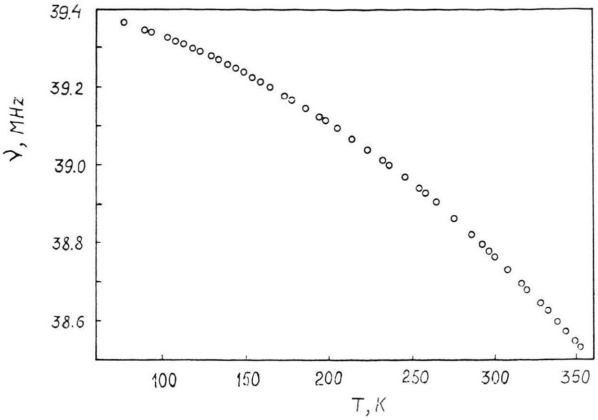

Fig. 1. The temperature dependence of the ^{35}Cl NQR frequency in picryl chloride.

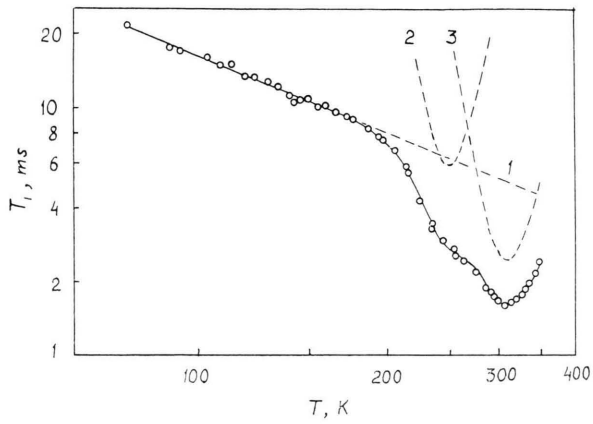

Fig. 2. The temperature dependence of the ^{35}Cl T_1 values in picryl chloride. The solid line is drawn using (4). The dotted lines reflect the separate contributions to the spin-lattice relaxation rate: 1- of librations, 2,3- of low- and high-temperature reorientations, respectively.

where $a = 0.536\ s^{-1}$ and $n = 1.03$ (at 77 K, T_1 value equals ca. 0.0215 s). n is unusually small (in most molecular crystals n is about 2). This indicates that, in solid picryl chloride, there are strong volume effects [8] which influence the chlorine NQR parameters.

Above ca. 180 K, a reorientation mechanism of the modulation type dominates the chlorine relaxation rate (Figure 2). The minimum of the $T_1(T)$ curve, clearly observed near 300 K, shows that the chlorine atom does not take part in reorientations, and the relaxation is due to the motions of neighbouring molecular fragments. In picryl chloride, only the NO_2 groups may be considered as such fragments. Thus, the NQR method gives direct evidence of the NO_2 reorientations in the solid state of this compound.

In picryl chloride, a complete quantitative analysis of the NO_2 reorientations can be carried out. The contribution of this motion to the spin-lattice relaxation rate can be obtained from the equation

$$(T_1^{-1})_{reor} = (T_1^{-1})_{observ} - (T_1^{-1})_{libr} \quad (2)$$

where the second term on the right is (1).

The $T_1(T)$ curve due to the purely reorientational contribution (2) has a pronounced minimum near 300 K and can be described by two terms of the type:

$$(T_1^{-1})_{mod} = C \cdot \frac{\tau_c}{1 + \omega^2 \tau_c^2}, \quad (3)$$

which reflect two modulation motions with different τ_c. In (3) $\omega = 2\pi\nu$, ν is the ^{35}Cl NQR frequency, $\tau_c = \tau_0 \cdot \exp(E_a/RT)$ is the correlation time of the motion (E_a is the activation energy) and C is a measure of interaction between the chlorine nuclei and the moving fragment. Thus, the whole temperature dependence of T_1 can be described by the expression

$$(T_1^{-1})_{observ} = (T_1^{-1})_{libr} + (T_1^{-1})_{mod1} + (T_1^{-1})_{mod2}$$
$$= a \cdot T^n + C_1 \cdot \frac{\tau_{c1}}{1 + \omega^2 \tau_{c1}^2} + C_2 \cdot \frac{\tau_{c2}}{1 + \omega^2 \tau_{c2}^2}. \quad (4)$$

Computer analysis of the data gives the following parameters for the modulation motions:

$T_{min1} = 251$ K, $C_1 = 8.4 \cdot 10^{10}\ s^{-2}$, $\tau_{c1} = 7.94 \cdot 10^{-15}$ s, $E_a = 27.4$ kJ mol^{-1};

$T_{min2} = 307$ K, $C_2 = 2.0 \cdot 10^{11}\ s^{-2}$, $\tau_{c2} = 2.51 \cdot 10^{-14}$ s, $E_a = 31.2$ kJ mol^{-1}.

The best fit to the experimenal data using these values of parameters and those of (1) is shown in Fig. 2 by the full curve; the separate contributions to this curve are shown by the dotted lines. The E_a values found here are comparable with that obtained for the NO_2 group in 2-$NO_2C_6H_4SO_2Cl$ [1] (for the NO_2 group which has no *ortho*-substituents E_a is about 10–12 kJ mol^{-1} [2, 9]). Evident by the reorientational motions in solid picryl chloride are the motions of both *ortho*-NO_2 groups in the molecule.

The crystal structure of picryl chloride is known [6]. In the 2,4,6-$(NO_2)_3C_6H_2Cl$ molecule, the chlorine atom, being rather large, can not be easily located between two NO_2 groups, so these groups become inequivalent: the angle between the planes of the ben-

zene ring and the group (the twist angle) is 33° for one group and 81° for the other group. As a result, the chlorine atom is considerably nearer to the latter [6]. Therefore, one may conclude that the higher potential barrier (31.2 kJ mol^{-1}) characterizes the NO_2 group with the twist angle of 81°.

For the chlorine nuclei, the efficiency of the modulation mechanism (i.e. the depth of the $T_1(T)$ minimum) is usually provided by the change of the electric field gradient (EFG) produced by the moving fragment [10, 11]. Therefore, the coefficients C in (3) are [12]

$$C = \left(\frac{q'}{q}\right)^2 \cdot \frac{\omega^2}{3} \tag{5}$$

where q' is the part of the EFG due to the moving fragment and q is the total value of the EFG at the site of the chlorine nuclei. For $T = T_{min}$ one can write

$$(T_1^{-1})_{min} = \left(\frac{q'}{q}\right)^2 \cdot \frac{\omega}{6}. \tag{6}$$

Equation (6) gives $q'/q = 0.003$ in the case of the "high-temperature" NO_2 group and 0.002 in the case of the "low-temperature" NO_2 group.

Spin-Spin Relaxation Time

The values of T_2, measured by a conventional spin echo method ($90° - \tau - 180°$), are considerably shorter than the values of T_1 and are determined by the magnetic dipole-dipole interactions. The temperature dependence of the spin-spin relaxation time is shown in Figure 3. This dependence is very unusual. The main interesting peculiarities of $T_2(T)$ are its deep minimum at about 140 K and a new rapid decrease above ca. 270 K. The T_2 behaviour seems to be independent of the T_1 behaviour, especially in the low temperature region where the $T_1(T)$ dependence does not show any clear changes.

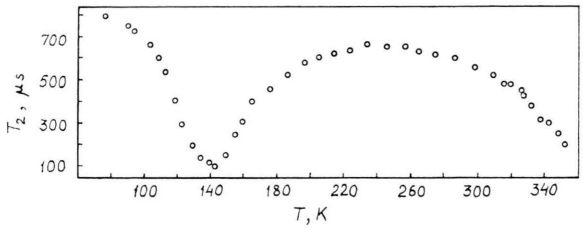

Fig. 3. The temperature dependence of the ^{35}Cl T_2 values in picryl chloride.

Evidently the peculiarities of $T_2(T)$ are not connected with the mechanisms of the $T_1(T)$ changes. In particular, in the region of its minimum, $T_2(T)$ is determined by dynamic processes which are definitely very slow in comparison to the ^{35}Cl NQR frequency. Similar phenomena in the ^{35}Cl NQR $T_2(T)$ have been observed before only for solid $Cl_3CCH(OH)OC_4H_9$ [13].

Conclusion

The present investigation shows once more that in *ortho*-nitrochlorobenzenes the NO_2 reorientations can produce modulation effects on the chlorine T_1 which are large enough to be observed by means of ^{35}Cl NQR. It has to be noted that the modulation minima of the chlorine $T_1(T)$, similar to that found in picryl chloride, are quite rarely observed. So, crystalline *ortho*-nitrochlorobenzenes may be also interesting for the investigation of the modulation mechanism of the quadrupole spin-lattice relaxation due to nonvalent interactions between neighbouring molecular fragments.

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