Influence of Thermoactivated Molecular Motions on the ^{35}Cl Quadrupole Relaxation *

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The effect on the ^{35}Cl quadrupole relaxation of modulations of the electric field gradient by thermally activated motions of nearby nonbonding symmetric and asymmetric atomic groups has been investigated. This way the activation energy of the motions has been determined and the fraction of the electric field gradient influenced by the motions has been estimated. This fraction can be taken as a measure of the intensity of nonbonding interactions in solids.

Key words: Molecular motion; Modulation effect; Nuclear quadrupole relaxation.

Introduction

Thermally activated molecular motions in solids obeying the Arrhenius law can be studied by nuclear quadrupole resonance (NQR) spectroscopy of nuclei situated outside the moving molecular fragments, provided the electric or magnetic interactions between the moving fragments and the resonant nuclei ensure a sufficient modulation of the spin-lattice relaxation. So far this has been studied in detail only for ^{14}N nuclei [1].

In this paper we report on analogous observations for ^{35}Cl nuclei. Moving atomic groups around the chlorine nuclei create fluctuations of a fraction of the electric field gradient (EFG) at these nuclei [2]. This mechanism leads to the observed V-form of the temperature dependence of the spin-lattice relaxation time T_1. In fact, the mechanism is most effective when the rate of the thermally activated motion becomes comparable with the NQR frequencies. In what follows, we shall consider the reorientations of both symmetric and asymmetric atomic groups and the permutational motions of ligands (pseudo-rotation).

Theoretical

A theory of the modulation effect on the quadrupole spin-lattice relaxation of nuclei of spin $I=3/2$ (e.g. the chlorine nuclei) has been developed by Woessner and Gurowsky [2]. The theory describes the relaxation process which is caused by a fluctuating EFG component at a nucleus due to a nearby moving group.

The experimentally observed relaxation rate $(T_1^{-1})_{\text{obs}}$ contains two contributions: the contribution from the modulation effect and the librational one. Both contributions are independent and additive:

$$(T_1^{-1})_{\text{obs}} = (T_1^{-1})_{\text{lib}} + (T_1^{-1})_{\text{mod}} \,. \tag{1}$$

Here the librational contribution obeys a temperature power law

$$(T_1^{-1})_{\text{lib}} = a \cdot T^n , \tag{2}$$

and the modulation contribution has the form [2]

$$\begin{aligned}(T_1^{-1})_{\text{mod}} &= \frac{(e^2 Q\, q'/\hbar)^2}{12} \frac{\tau_c}{1+\omega^2 \tau_c^2} \\ &= \frac{1}{3} (q'/q)^2 \frac{\omega^2 \tau_c}{1+\omega^2 \tau_c^2} \,. \end{aligned} \tag{3}$$

Here q' is the amplitude of the moving EFG and q is the full EFG at the nucleus; $\omega = 2\pi\nu$ (ν is the NQR frequency); $\tau_c = \tau_0 \exp(E_a/RT)$, where τ_c is the correlation time of the modulating motion and E_a the activation energy of the motion. At the temperatures where the rates of the modulating motion are very large or very small (as compared with the NQR frequency), the librational relaxation mechanism becomes dominating.

The significant quantity in (3) is the fraction q'/q of the full EFG at the quadrupolar nucleus. q'/q can be obtained from the minimum of the modulation curve

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$T_1(T)_{\text{mod}}$, this minimum characterizing the efficiency of the modulation mechanism:

$$(T_{1\,\text{min}}^{-1})_{\text{mod}} = (q'/q)^2\,\omega/6. \tag{4}$$

q'/q is a characteristic of the nonbonding interactions in solids; so the NQR method gives a simple and effective means of discovering and studying these interactions.

Experimental

We studied the following substances as powdered solids:
$p\text{-ClC}_6H_4SO_2N{=}PCl_3$,
$Cl_2C{=}CHC(COCH_3)_2CH_2SCH_3$,
$Cl_3P{=}NCCl(CF_3)_2$,
$(CCl_3)_2ClP{=}NR$ ($R = POCl_2$, SO_2Cl, SOCl),
$CCl_3CCl_2N{=}CClCCl_3$ and $(o\text{-ClC}_6H_4NPCl_3)_2$.
These compounds have been prepared with known methods. The temperature dependence of the ^{35}Cl NQR frequencies ν and of the relaxation times T_1 was measured for all chlorine nuclei in the molecules. The ^{35}Cl NQR spectra of the compounds were detected with a homemade pulsed NQR spectrometer from 77 K up to the respective melting points. The temperatures were obtained by means vapour from liquid N_2. Stabilization and measurement of temperature were made with an accuracy of ± 0.5 K. The values of T_1 were measured using the "progressive saturation" pulsed method with an error of about 10%.

Results and Discussion

The compounds used for the investigation exhibit molecular motions of different effectiveness. We consider modulation effects due to reorientations of PCl_3, CH_3, and CCl_3 in an equal-well potential, reorientations of $CCl(CF_3)_2$ between unequal potential wells and the intramolecular position exchange of the chlorine atoms (pseudo-rotation).

$p\text{-ClC}_6H_4SO_2N{=}PCl_3$ (I)

The effect of modulation on chlorine relaxation was very striking in crystal I, for the chlorine nuclei in the C–Cl bonds (Figure 1). As shown in [3], the modulation is due to the nonbonding interaction of the chlorine nuclei in the benzene ring with the reorienting PCl_3 groups belonging to nearby molecules. The temperature dependence of T_1 shows a deep minimum. T_1 in the region of the minimum was too small to measure ($T_{1\,\text{min}} \approx 1 \cdot 10^{-5}$ s). NQR in this region was observed only through the free induction decay after the 90° pulse. The curve $T_1^{-1}(T)$ observed experimentally for the chlorine atom in the benzene ring is described in this case by (1)–(3). The data give an activation energy of the PCl_3 group reorientations E_a of 5.4 kcal mol^{-1}, the same as $E_a = 5.4 \pm 0.2$ kcal mol^{-1} given directly by the curve $T_1(T)$ for the chlorine nuclei belonging to the PCl_3 group. The measurement of a T_1 minimum allows the other parameters of (3) to be estimated as well: $\tau_0 = 1.2 \cdot 10^{-14}$ s, $q'/q = 0.04$.

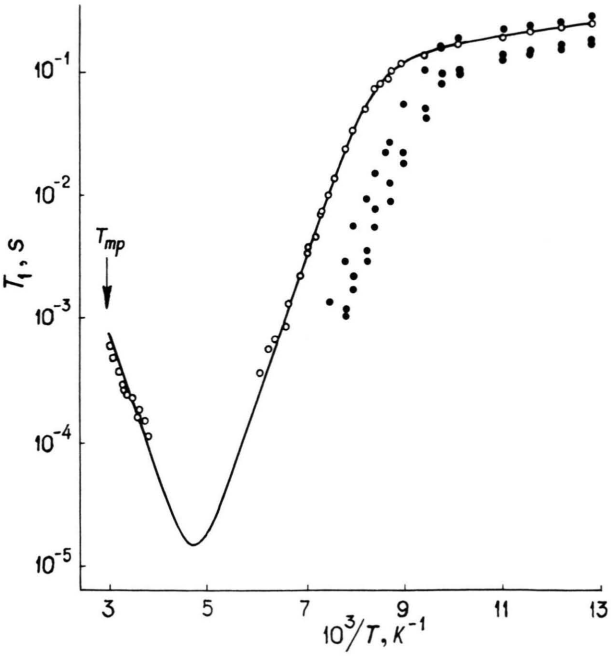


Fig. 1. Temperature dependence of the ^{35}Cl T_1 in crystalline $p\text{-ClC}_6H_4SO_2N{=}PCl_3$. Open circles: CCl; filled circles: PCl_3; solid line: computed curve. T_{mp} is the melting temperature.

We recall that an attempt to explain the modulation minimum in crystal I as the effect of the modulation of the magnetic dipolar interactions of the chlorine nuclei failed because it led to unreasonably short distances between chlorine atoms belonging to different fragments (tenth parts of Å) [3]. The same is true for all the other compounds considered here.

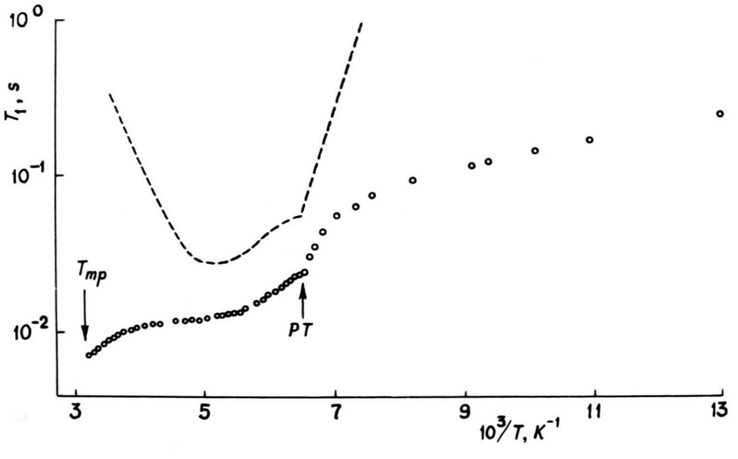


Fig. 2. Temperature dependence of the ^{35}Cl T_1 in two phases of crystalline $Cl_2C{=}CHC(COCH_3)_2CH_2SCH_3$. Circles: $T_1(T)_{obs}$; dashed lines: $T_1(T)_{mod}$. T_{mp} is the melting temperature and PT the phase transition point. The relaxation time is the same for both chlorines in the molecule.

$Cl_2C{=}CHC(COCH_3)_2CH_2SCH_3$ (II)

Another example of the modulation curve for chlorine nuclei was recently observed for the high-temperature phase of crystal II (Figure 2). In this case the modulation effect is due to the interaction of the chlorine atoms of the dichlorovinyl group with one of the three CH_3 groups of the molecule [4]. However, here the effect of this interaction is much smaller than in crystal I. From the modulation contribution $T_1(T)_{mod}$, which can be separated from the observed curve $T_1(T)_{obs}$ on the basis of (1), the value of $(T_{1\,min})_{mod}$ is obtained as $2.8 \cdot 10^{-2}$ s (see Fig. 2), which gives $q'/q \approx 0.001$. This value of q'/q seems to be the smallest one found so far (see also $q'/q \approx 0.013$ in [5] and $q'/q \approx 0.02$ in [6]). This illustrates the sensitivity of the chlorine NQR method in detecting such effects. Of course, this sensitivity depends on the relative contribution of the librational relaxation mechanism as well. The nonbonding electric interactions of the chlorine atoms with the CH_3 group lead to a rather large value of E_a associated with CH_3 reorientation: $E_a = 4.2 \pm 0.2$ kcal mol^{-1} ($\tau_c = 1 \cdot 10^{-13}$ s, $T_{min} = 197$ K). The value of E_a is still larger in the low-temperature phase of this crystal (Fig. 2), where the above-mentioned interactions are evidently stronger.

$Cl_3P{=}NCCl(CF_3)_2$ (III)

In the above cases the modulation effect was due to the reorientations of symmetric atomic groups around a three-fold axis. In crystal III this effect is produced by the reorientational motion of an asymmetric molecular fragment. According to experimental data obtained by means of the ^{35}Cl NQR and ^{19}F NMR methods [7], it seems probable that in crystal III reorientations of the $CCl(CF_3)_2$ fragment in an unequal-well potential take place, thus affecting the relaxation of the chlorine nuclei of the PCl_3 groups. The activation energy of the $CCl(CF_3)_2$ reorientations in crystal III is rather small, and this motion is activated at low temperatures. In fact, T_1 of the chlorine nuclei belonging to the $CCl(CF_3)_2$ fragments is about 1 ms at $T < 100$ K. Therefore, a full modulation curve of type (3) with $T_{min} \approx 125$ K was observed for the ^{35}Cl nuclei of the PCl_3 group. The unequal-well character of the reorientations leads to an asymmetry of the V-form modulation curve (the slope of the high-temperature branch is smaller than that of the low-temperature one).

By means of a theoretical consideration of a three-well potential analogous to that used by Anderson in NMR [8] (the depth of the two equal potential wells is smaller than that of the third one at the same altitude), one can obtain the temperature law for the relaxation time [7]. In particular, the following result holds for $(T_{1\,min})_{mod}$:

$$(T_{1\,min}^{-1})_{mod} \propto \frac{(q'/q)^2\,\omega}{\exp(\Delta/RT)}, \tag{5}$$

where Δ is the difference between the two above mentioned depths. So, unequal-well character of the reorientations reduces the effect of the modulation mechanism. The quantitative analysis of the ^{35}Cl NQR data in crystal III gives $q'/q \approx 0.05$, which shows the presence of considerable nonbonding interactions between two molecular fragments. However, the big value of Δ (1.94 kcal mol^{-1}) increases $T_{1\,\mathrm{min}}$ up to about $6 \cdot 10^{-3}$ s (i.e. by more than a factor of $2 \cdot 10^3$ compared with the case of $\Delta = 0$).

$(CCl_3)_2ClP=NR$ (R = $POCl_2$, SO_2Cl, SOCl) (IV), $CCl_3CCl_2N=CClCCl_3$ (V)

In crystals IV both the CCl_3 groups bonded to the tetracoordinated phosphorus atom perform reorientations [9–11]. The analysis of the $\nu(T)$ and $T_1(T)$ curves for the ^{35}Cl nuclei entering the CCl_3 groups shows that these groups are dynamically distinguishable: the fade out temperatures of the ^{35}Cl NQR signals and the activation energies of reorientations for the two groups are different ($E_a = 7.9 \pm 0.4$ and 9.2 ± 0.2 kcal mol^{-1} when R = $POCl_2$ [9], $E_a = 8.1 \pm 0.5$ and 11.1 ± 0.2 kcal mol^{-1} when R = SO_2Cl [10], $E_a = 8 \pm 1$ and 11 ± 1 kcal mol^{-1} when R = SOCl [11]. The more strongly hindered CCl_3 group in all three compounds seems to interact with the chlorine atom of the P–Cl bond. This assumption is based on the modulation character of the $T_1(T)$ curve for the chlorine nuclei in the P–Cl bonds: at high temperatures this curve falls exponentially almost up to the melting points T_{mp} of the compounds; moreover, in the compounds with R = $POCl_2$ and SO_2Cl, the $T_1(T)$ dependence slopes towards a minimum (see Figure 3). The activation energy E_a obtained for the three compounds from the P–Cl chlorine data confirms this interpretation too ($E_a = 9.4 \pm 0.3$, 11.1 ± 0.3 and 12 ± 1 kcal mol^{-1} when R = $POCl_2$, SO_2Cl and SOCl respectively). A reasonable estimate of $T_{1\,\mathrm{min}}$ ($< 3 \cdot 10^{-4}$ s) gives $q'/q > 0.01$. This indicates that the nonbonding interactions are rather effective.

Similar results were observed for one of the ^{35}Cl nuclei of the strongly hindered CCl_3 group in the CCl_3CCl_2N fragment of crystal V [12]. This nucleus feels the modulating action of another CCl_3 group of the $CClCCl_3$ fragment which reorients with an activation energy of 10.4 kcal mol^{-1}: the $T_1(T)$ curve of the above mentioned chlorine nucleus contains the low-temperature branch of the modulation curve (3), which falls near T_{mp} (it is reasonable to consider this fall as the tendency to have a minimum [12]). The energy E_a found from this branch is 10.9 kcal mol^{-1}. The estimated value of $T_{1\,\mathrm{min}} < 10^{-3}$ s gives $q'/q > 0.005$ in this crystal. Obviously the interaction of the two CCl_3 groups has intermolecular character.

$(o\text{-}ClC_6H_4NPCl_3)_2$ (VI)

In the crystals of the $(Cl_3PNAr)_2$ type we have observed [13] a new kind of thermally activated motions in solids – the position exchange of chlorine atoms bonded to the penta-coordinated phosphorus atom (the pseudo-rotation). In crystal VI we have observed the modulation effect of such a motion of the chlorine atoms Cl (1), Cl (2), and Cl (3) on the relaxation of the o-Cl nuclei taking no part in the motion (the intramolecular effect). The pseudo-rotation in crystal VI

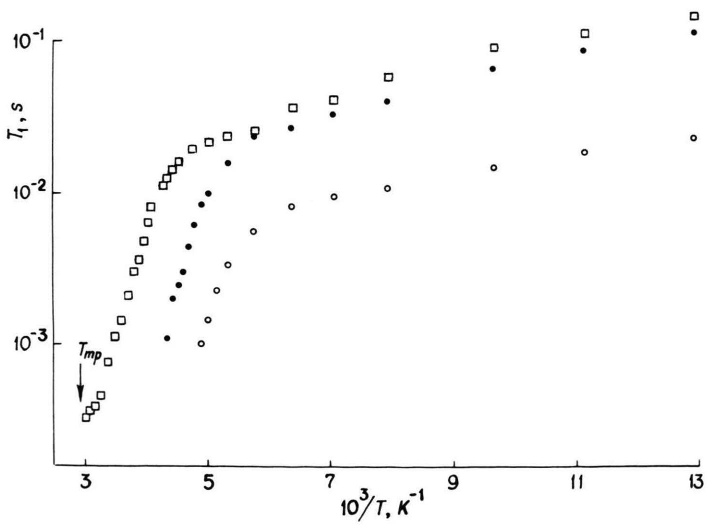
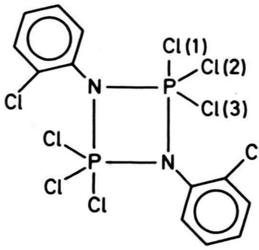


Fig. 3. Temperature dependence of the ^{35}Cl T_1 in crystalline $(CCl_3)_2ClP=NPOCl_2$. Squares: = PCl, open and filled circles: CCl_3 (the data are shown for one of the three chlorines of the CCl_3 group). T_{mp} is the melting temperature.

has the high activation energy $E_a = 11.2 \pm 0.4$ kcal mol^{-1} as determined from the $T_1(T)$ data of the Cl(1), Cl(2), Cl(3) nuclei. Therefore, only the low-temperature branch of the curve (3) can be observed in the $T_1(T)$ curve of the o-Cl nuclei (the energy E_a found from the observed branch is 11.0 ± 0.5 kcal mol^{-1}). The slope towards a minimum near T_{mp} (situation looks like that shown in Fig. 3) gives for $T_{1\,min}$ an upper limit of $5 \cdot 10^{-4}$ s, so the lower limit of q'/q, according to (4), is 0.02. The value of τ_0 which can be estimated from (3) in this case (about 10^{-14} s) agrees satisfactorily with that found by means of ^{1}H NMR [13] in the same compound ($\tau_0 = 5.5 \cdot 10^{-13}$ s, $E_a = 12.7$ kcal mol^{-1}).



Conclusion

In this paper experimental data on the modulation influence of some kinds of thermal motions on the ^{35}Cl quadrupole relaxation are reported. These data may be used as a means to study thermally activated motions of atomic groups, including those containing no quadrupolar nuclei. On the other hand, they may be useful for the investigation of the nonbonding electric interactions in solids, the efficiency of these interactions being characterized by the fraction of the electric field gradient on the chlorine nuclei affected by the thermal motion of the outside molecular fragments.

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