

EFFECTS OF MOLECULAR REORIENTATIONS BETWEEN UNEQUAL POTENTIAL WELLS IN NQR

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ABSTRACT

The effects of molecular reorientations between three unequal potential wells on the quadrupole relaxation of nuclei, both taking part in this motion directly and being connected with moving atomic groups by the nonvalent interaction have been considered theoretically. The results of this consideration have been used for a quantitative interpretation of the experimental data obtained by the ^{35}Cl NQR techniques for the $\text{Cl}_3\text{P}=\text{NCCl}(\text{CF}_3)_2$ crystal where the motion of the asymmetric $\text{CCl}(\text{CF}_3)_2$ fragment between three unequal wells has been observed.

INTRODUCTION

In the last time some NMR experimental data concerning non-quadrupole nuclei in crystals have been successfully interpreted (refs.1,2) on the basis of models which take in account molecular jumps between equilibrium sites corresponding to unequal minima of the potential energy (refs. 2, 3). It has been shown that such a motion leads to some important peculiarities of the experimental data display in comparison with the equal-well motion (ref. 4). For some crystals containing asymmetric tetrahedral molecular fragments of the type MX_2Y_2 , the nuclear quadrupole resonance (NQR) experimental results exist (refs. 5, 6) which can be considered as connected with reorientational motions between unequal wells, too. The present paper deals with the reorientational motion of the $\text{CCl}(\text{CF}_3)_2$ fragment between three inequivalent positions in the $\text{Cl}_3\text{P}=\text{NCCl}(\text{CF}_3)_2$ crystal. The study of this crystal makes it possible to investigate the influence of the reorientations between unequal wells on the NQR spectrum and the

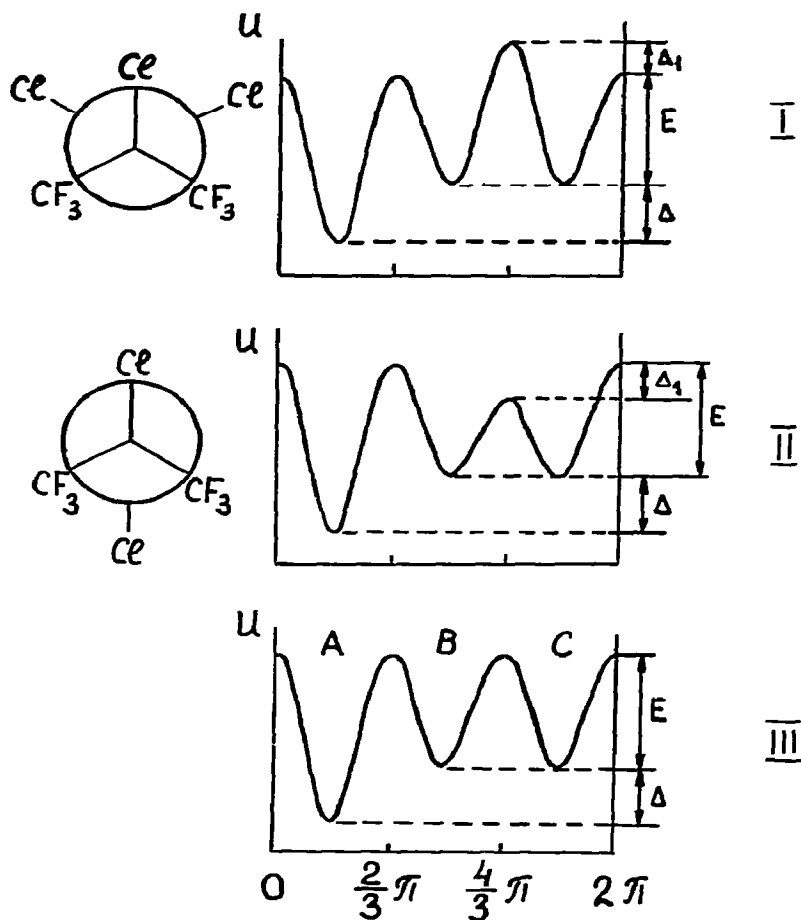


Fig. 1. Three well orientation potential energy profiles for the fragment $\text{CCl}(\text{CF}_3)_2$ in the $\text{Cl}_3\text{P}=\text{NCCl}(\text{CF}_3)_2$ crystal. The forms I and II correspond to different stable conformations of isolated molecule, the form III is accepted to describe the actual reorientational motion in the crystal.

quadrupole spin-lattice relaxation of moving nuclei. Moreover, the effect of the $\text{CCl}(\text{CF}_3)_2$ fragment motion on the quadrupole spin-lattice relaxation of the PCl_3 group chlorine nuclei connected with the moving atomic group by nonvalent interactions has been found. For both situations mentioned the theoretical consideration is given in the next section.

The form of the orientation potential energy function which is to be used to describe the reorientational motion of the $\text{CCl}(\text{CF}_3)_2$ fragment is determined both by its own symmetry and its environment symmetry. For an isolated $\text{Cl}_3\text{P}=\text{NCCl}(\text{CF}_3)_2$ molecule, which has the angle PNC near to 120° , the two potential functions I and II (Fig.1)

would be suitable for two possible molecular conformations; according to that, the reorientational motion in question would be determined by three different barriers. But the molecules are not isolated. The crystal structure and the molecular conformation being not known, we couldn't take into account all the factors determining the form of the potential curve. So, for the experimental data interpretation, the only thing we could do was to accept the most simple model III, which has been used by Anderson (ref. 3) to discuss some NMR data. Owing to the fact that the values of the accepted model parameters obtained from our independent NQR experiments and from the ^{19}F NMR data (see (ref. 7)) are very near to one another, our choice of the model proved to be reasonable.

THEORY

Reorientation mechanism of the quadrupole spin-lattice relaxation for nuclei moving between unequal wells

Theoretical consideration of the direct effect of slow reorientations between unequal wells on the nuclear quadrupole spin-lattice relaxation has been carried out in accordance with the approach developed in (refs. 8, 9).

Consider the reorientations of a MX_2 type fragment in the potential of the form I (Fig. 1). The following notations will be used:

$$w_{AB} = w_{AC} = k \cdot \exp[-(E+\Delta)/RT] \equiv w_1 \quad (1)$$

$$w_{BA} = w_{CA} = k \cdot \exp(-E/RT) \equiv w_2$$

$$w_{BC} = w_{CB} = k \cdot \exp[-(E+\Delta_1)/RT] \equiv w_3$$

with the same constant k that gives

$$\frac{w_2}{w_1} = e^\alpha, \quad \frac{w_3}{w_1} = e^{\alpha_1} \quad \text{with} \quad \alpha \equiv \frac{\Delta}{RT} \quad \text{and} \quad \alpha_1 \equiv \frac{\Delta - \Delta_1}{RT} \quad (2)$$

For the moving nuclei with the spin $3/2$ (for example, ^{35}Cl) in the case of the axially symmetric electric field gradient (EFG) tensor the rate equations are

$$\begin{aligned} \dot{n}^A &= -2w_1 n^A + w_2 P_2 n^B + w_2 P_2 n^C \\ \dot{n}^B &= w_1 P_2 n^A - (w_2 + w_3) n^B + w_3 P_2 n^C \\ \dot{n}^C &= w_1 P_2 n^A + w_3 P_2 n^B - (w_2 + w_3) n^C \end{aligned} \quad (3)$$

Here $n^{\nu} = n_{1/2}^{\nu} + n_{-1/2}^{\nu} - n_{3/2}^{\nu} - n_{-3/2}^{\nu}$ is the population differences between the states $\pm 1/2$ and $\pm 3/2$, and $P_2 = (1/2)(3\cos^2\beta - 1)$ is the second range Legendre polynomial, β being the angle between the principal axes Z and Z' of the EFG tensor in positions ν and ν' respectively. In NQR the observed quantity which describes the time dependence of the quadrupole spin-system longitudinal magnetization due to the spin-lattice relaxation process is $n(t) \equiv \sum_{\nu} n^{\nu}$ (see, for example, ref. 10). So one gets from (3)

$$n(t) \sim a_1 \exp(-t/T_1^{\text{I}}) + a_2 \exp(-t/T_1^{\text{II}}) \quad (4)$$

where the factors a and the relaxation constants T_1 are determined as follows:

$$a_{1,2} = \frac{\sqrt{2} (L + w_2 P_2 \pm \sqrt{L^2 + 2 w_1 w_2 P_2^2})}{[2 w_2^2 P_2^2 + (L \pm \sqrt{L^2 + 2 w_1 w_2 P_2^2})^2]^{1/2}} \quad (5)$$

(6)

$$\frac{1}{T_1^{\text{I,II}}} = \left| L - 2 w_1 \pm \sqrt{L^2 + 2 w_1 w_2 P_2^2} \right|$$

with $L \equiv w_1 - (1/2)w_2 - (1/2)w_3(1 - P_2)$

If β is the tetrahedral angle (which is a practically interesting case), we have $P_2 = -1/3$ and, taking in account (2), we obtain

$$a_{1,2} = \frac{\sqrt{2} (L_1 - \frac{1}{3}e^{\alpha} \pm \sqrt{L_1^2 + \frac{2}{9}e^{\alpha}})}{[\frac{2}{9}e^{2\alpha} + (L_1 \pm \sqrt{L_1^2 + \frac{2}{9}e^{\alpha}})^2]^{1/2}} \quad (7)$$

$$\frac{1}{T_1^{\text{I,II}}} = w_1 \left| L_1 - 2 \pm \sqrt{L_1^2 + \frac{2}{9}e^{\alpha}} \right| \quad (8)$$

where $L_1 \equiv L/w_1 = 1 - (1/2)e^{\alpha} - (2/3)e^{\alpha_1}$.

The expressions (7)-(11) are valid also in the case where $\Delta_1 < 0$ (Fig. 1, the form II).

It may be noted that in the case of equal wells ($\Delta = \Delta_1 = 0$ and $w_1 = w_2 = w_3 \equiv w$) one has $a_1 = 0$ and $n(t)$ becomes a single exponential with $T_1 = (3/8)w^{-1}$ as it is seen from (4) and (8). This result is the same as in ref. 9 where $T_1 = (3/4)\tau$ with $\tau = (1/2)w^{-1}$.

In the case where $\Delta_1 = 0$, that is the potential curve III (Fig. 1) takes place which has been treated by Anderson (ref. 3) for the nuc-

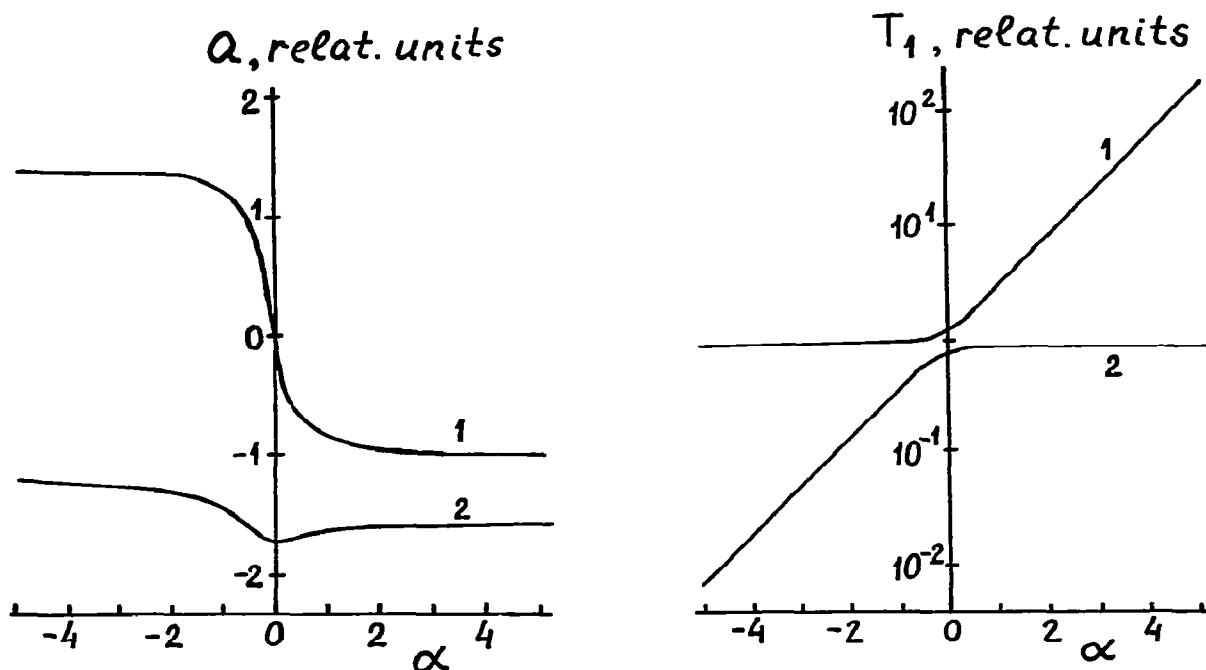


Fig. 2. Plots of the factors Q (Eq.(8)) vs. $\alpha \equiv \Delta/RT$ for the case of the tetrahedral angle β . 1 - Q_1 , 2 - Q_2 .

Fig. 3. Plots of the relaxation constants T_1 (Eq.(9)) vs. $\alpha \equiv \Delta/RT$ for the case of the tetrahedral angle β . T_1^I is expressed in the units of $\tau \equiv (1/2)\omega_2^{-1}$ 1 - T_1^I , 2 - T_1^{II} .

lear magnetic relaxation, the form of Eqs. (7) - (8) remained with $L_1 = 1 - \frac{\tau}{6} e^{-\alpha}$ (ref. 11). Let us consider the factors Q and the relaxation constants T_1 as functions of $\alpha \equiv \Delta/RT$ in this case (Figs. 2 and 3 respectively). On the condition $|\alpha| > 1$ (i.e. $|\Delta| > RT$) one sees (Fig. 2) that the factors Q_1 and Q_2 have the absolute values near to one another and practically do not depend on α . As to the relaxation constants T_1^I and T_1^{II} , they behave very differently (Fig. 3): for the positive Δ and $\alpha > 1$ the value of T_1^I increases exponentially with α but the value of T_1^{II} remains nearly constant. For $\Delta \gg RT$ (that is $\alpha \gg 1$) we obtain from (8)

$$T_1^I = \frac{21}{20} \cdot \frac{1}{2\omega_1} = \frac{21}{20} \cdot e^{\alpha} \tau \quad (9)$$

$$T_1^{II} = \frac{6}{7} \cdot \frac{1}{2\omega_2} = \frac{6}{7} \tau \quad (10)$$

where

$$\tau \equiv \frac{1}{2W_2} \sim \exp(E/RT) \quad (11)$$

Therefore in the case considered on condition $\Delta \gg RT$ (practically $\Delta > RT$ is sufficient) one comes to the following two conclusions:

1) Spin-lattice relaxation process can be described by the single exponential decay curve with the relaxation time T_1^{II} (as in the case of the reorientations between equal wells, that is for $\Delta = 0$).

2) The relaxation time T_1^{II} depends only on the smaller potential barrier E .

It means that in the case of the slow reorientations of an atomic group containing the quadrupole nuclei between three unequal wells of the form III (Fig. 1) with $\Delta \gg RT$, the measurements of the temperature dependence of the quadrupole spin-lattice relaxation of these nuclei give information about the smaller potential barrier value.

Modulation mechanism of quadrupole spin-lattice relaxation due to reorientations of neighbouring atomic groups between unequal wells

The reorientations of an atomic group in a crystal can influence the relaxation of the neighbouring quadrupole nuclei by means of the modulation of magnetic and electric interactions. For the nuclei with the large value of quadrupole interactions (for example, the halogen nuclei in the covalent bonds in contrast with the nitrogen ones (ref. 12)) it can be shown (ref. 13) that the modulation of the electric quadrupole interaction is essentially more effective relaxation mechanism than the magnetic interaction modulation. This relaxation mechanism for equal-well reorientations has been discussed in ref. 14. In the case of the potential curve III (Fig. 1) the contribution of the mechanism in question to the relaxation rate can be expressed as follows (ref. 13):

$$\left(\frac{1}{T_1}\right)_{\text{mod}} = \frac{1}{3} \omega_Q \left(\frac{q'}{q}\right)^2 \left[9P_A P_{B(C)} \frac{\omega_Q \tau_{c_1}}{1 + \omega_Q^2 \tau_{c_1}^2} + 3P_{B(C)} \frac{\omega_Q \tau_{c_2}}{1 + \omega_Q^2 \tau_{c_2}^2} \right] \quad (12)$$

Here q is the ZZ -component of the full EFG tensor on the quadrupole nucleus considered and q' is the ZZ -component of the EFG part on this nucleus due to the moving neighbouring group in question; P_A and $P_{B(C)}$ are the steady-state probabilities to find this group in positions A and B (or C); τ_{c_1} and τ_{c_2} are correlation times; and

$$P_A = (1 + 2e^{-\alpha})^{-1}; \quad P_{B(c)} = e^{-\alpha}(1 + 2e^{-\alpha})^{-1};$$

$$\tau_{c_1} = \tau_0(1 + 2e^{-\alpha})^{-1} \cdot e^{E/RT}; \quad \tau_{c_2} = \frac{1}{3}\tau_0 e^{E/RT} \quad (13)$$

where τ_0 is the pre-exponential Arrhenius' factor.

In the practically interesting case where $\Delta \gg RT$, it follows from (12) and (13):

$$\left(\frac{1}{T_1}\right)_{mod} = \frac{\omega_Q (q'/q)^2}{\exp(\Delta/RT)} \cdot \left\{ \frac{3\omega_Q \tau_0 \exp(E/RT)}{1 + \omega_Q^2 \tau_0^2 \exp(2E/RT)} + \right.$$

$$\left. + \frac{(1/3)\omega_Q \tau_0 \exp(E/RT)}{1 + (1/9)\omega_Q^2 \tau_0^2 \exp(2E/RT)} \right\} \quad (14)$$

where Δ , E , and τ_0 are the parameters of the motion between unequal potential wells. The expression of $(T_1)^{-1}_{mod}$ given by (14) is qualitatively analogous to that in Anderson's magnetic relaxation theory (ref. 3) and gives the curve $T_1(T)$ with the asymmetric minimum.

EXPERIMENTAL RESULTS AND DISCUSSION

The ^{35}Cl NQR spectrum in the crystal $\text{Cl}_3\text{P}=\text{NCCl}(\text{CF}_3)_2$ at 77 K consists of four lines (ref. 15) (29.075, 29.325, 31.045, and 37.482 MHz), the first three of them belonging to the chlorine nuclei in the PCl_3 group and the fourth to the chlorine in the C-Cl bond. Our experimental data show that the spin-lattice relaxation process of the chlorine nuclei in question is described by a single time exponential. The temperature dependences of the resonance frequencies and the relaxation times T_1 , which have been measured for all the chlorine nuclei using the technique (ref. 9), are shown in Figs. 4 and 5.

The exponential temperature dependence of T_1 above 77 K for the chlorine nuclei in the C-Cl bonds (the line 1 in Fig. 5) and the fading out of their resonance signal at $T \approx 125$ K (Fig. 4) point to the existence of a reorientation process which can only be the reorientation of the asymmetric $\text{CCl}(\text{CF}_3)_2$ fragment around the C-N bond between inequivalent positions. This fact is proved by the behaviour of the chlorine NQR signals from the PCl_3 group: the existence of these signals up to $T \sim 190$ K indicates the absence of the whole molecule reorientations in the temperature range considered (77 ÷ 125K).

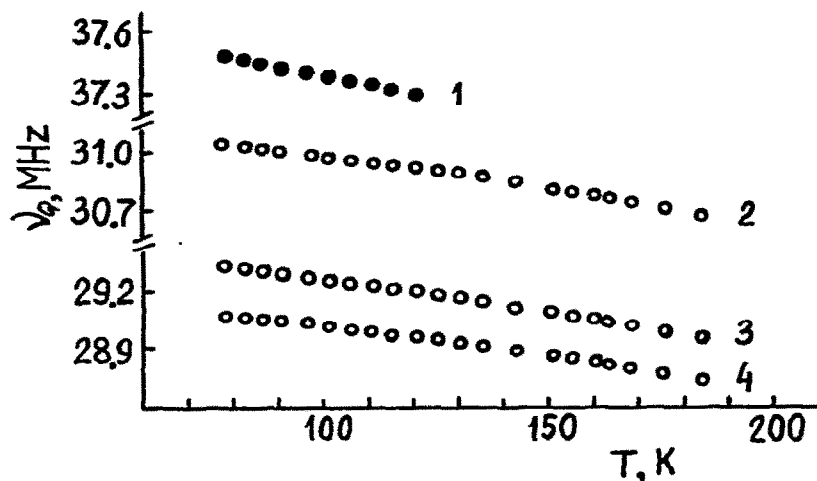


Fig. 4. Temperature dependence of the ^{35}Cl NQR frequencies in the $\text{Cl}_3\text{P}=\text{NCCL}(\text{CF}_3)_2$ crystal: 1- the Cl-C bond; 2,3,4- the Cl-P bonds.

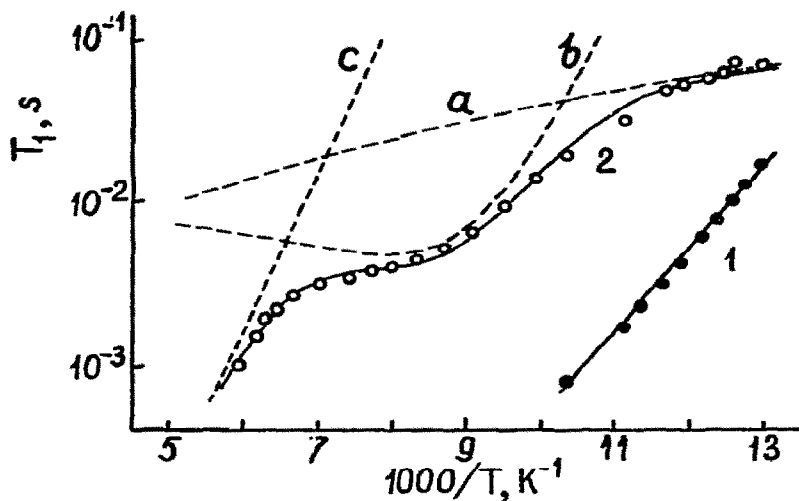


Fig. 5. Temperature dependence of the ^{35}Cl spin-lattice relaxation time T_1 in the $\text{Cl}_3\text{P}=\text{NCCL}(\text{CF}_3)_2$ crystal: 1-the Cl-C bond; 2-the Cl-P bond (see text). The dotted lines represents separate contributions to the ^{35}Cl -P relaxation rate produced by libration (a), modulation (b), and reorientation (c) mechanisms and calculated from Eqs. (16), (14), and (17) respectively. The solid lines 1 and 2 are respectively obtained from Eqs. (10), (11) with $E=2.4$ kcal/mole and Eqs. (15) with the following parameter values:

$$\begin{aligned} \omega_q = 2\pi\nu_q &= 1.95 \cdot 10^8 \text{ s}^{-1}; & q'/q &= 0.05; & \tau_0 &= 1.7 \cdot 10^{-13} \text{ s}; \\ E &= 2.30 \text{ kcal/mole}; & \Delta &= 1.94 \text{ kcal/mole}; & a &= 2.03 \cdot 10^{-3} \text{ s}^{-1}\text{K}^{-n}; \\ n &= 2.05; & b &= 1.1 \cdot 10^9 \text{ s}^{-1}; & V_0 &= 4.8 \text{ kcal/mole}. \end{aligned}$$

According to the ^{19}F NMR experimental data (ref.7), at these temperatures the CF_3 group reorientations, which could influence the relaxation of the chlorine nuclei in the $\text{CCl}(\text{CF}_3)_2$ fragment, are absent too (these reorientations have only been observed above 150 K).

To discuss the experimental data obtained we accept the model III (Fig.1) of the orientation potential curve (see Introduction). Then the single exponential character of the relaxation for the chlorine nuclei in the C-Cl bonds leads to the conclusion that the inequality $\Delta \gg RT$ takes place (see the previous section).

The temperature dependence $T_1(T)$ for one of the chlorine nuclei of the PCl_3 group is shown in Fig.5, curve 2; this curve corresponds to the resonance line 2 in Fig.4. For the other two chlorine nuclei in the PCl_3 group the curves $T_1(T)$ are similar in character and situated near to the curve 2. The character of the $T_1(T)$ function in question is due to the existence of three relaxation mechanisms giving different contributions at different temperatures: the libration mechanism which is most effective at the temperatures below $\sim 85\text{K}$; the modulation mechanism which manifests itself in the temperature range $80 < T < 130\text{K}$; and the reorientation mechanism (reorientations of the symmetric PCl_3 group around P=N bond (ref. 16) with the barrier V_0 which lead to the fading of the NQR signals near 190 K) which becomes predominant at $T > 130\text{K}$. So we have

$$\left(\frac{1}{T_1}\right) = \left(\frac{1}{T_1}\right)_{\text{lib}} + \left(\frac{1}{T_1}\right)_{\text{mod}} + \left(\frac{1}{T_1}\right)_{\text{reor}} \quad (15)$$

where

$$\left(\frac{1}{T_1}\right)_{\text{lib}} = a T^n \quad (16)$$

$$\left(\frac{1}{T_1}\right)_{\text{reor}} = b \exp(-V_0/RT) \quad (17)$$

and $(T_1)_{\text{mod}}^{-1}$ is given by (14).

According to the temperature range in which the modulation mechanism manifests itself, it is due to the reorientations of the asymmetric $\text{CCl}(\text{CF}_3)_2$ fragment. The nonvalent contacts between the fragments which make the modulation effect possible are of the intermolecular origin which is proved by the identical character of the modulation effect for all the chlorine atoms of the PCl_3 group. It may be considered as a confirmation of our decision to use the simple model III (Fig. 1) when processing our experimental results quantitatively. To do it, we apply the theoretical results obtained in the previous section. Equations (10), (11) and (14)-(17) permit to find

the parameters of the observed motion between unequal wells from the independent NQR experimental data. The solid lines 1 and 2 in Fig.5 have been drawn using the best fit motion parameters, the values of which are given in the figure caption. Dotted lines in Fig.5 show the contributions of three relaxation mechanisms (see Eq.(15)) in the case of the chlorine nuclei in the PCl_3 group.

TABLE 1

Activation parameters for the reorientations of the $\text{CCl}(\text{CF}_3)_2$ fragment in the $\text{Cl}_3\text{P}=\text{NCCl}(\text{CF}_3)_2$ crystal

Method of the investigation	Barriers, kcal/mole		τ_0 , s
	E	Δ	
^{35}Cl -C NQR, T_I	2.4		
^{35}Cl -P NQR, T_I	2.3	1.9	$1.7 \cdot 10^{-13}$
^{19}F NMR (ref.7), T_I and M_2	2.2	2.0	$1.7 \cdot 10^{-13}$

The activation parameters of the $\text{CCl}(\text{CF}_3)_2$ group reorientations obtained from our NQR and from NMR (ref.7) data are given in the Table 1. The good coincidence of the independently obtained results shows that the model accepted has been chosen in a reasonable manner.

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