

FLUORINE SPIN-LATTICE RELAXATION IN SOLID CF_2Cl_2 . III*

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The fluorine spin-lattice relaxation time T_1 for solid CF_2Cl_2 has been measured at different magnetic fields in the range from 60 Oe up to 6400 Oe. The observed T_1 increases strongly with increasing field especially in the low field region and then for high magnetic field the increase of T_1 is very slow. The observed field dependence may be explained on the basis of the anisotropy of the chemical shift and the dipole-dipole interaction between the fluorine nuclei.

The fluorine spin-lattice relaxation time T_1 for solid CF_2Cl_2 has been measured at a temperature of 77°K as a function of magnetic field H from 60 Oe up to the maximum value $H_0 = 6430$ Oe which correspond to the resonant frequency $\nu_0 = 25.7$ MHz.

The sample was oxygen-free CF_2Cl_2 (Freon-12) prepared as described in previous papers I and II.

During the measurements of $T_1(H)$ the sample was moved out of the field H_0 and the relaxation process took place at a lower field H . After time t the sample was moved back to the region of high field H_0 , a 90° rf pulse was applied and the amplitude $M(t)$ of the resulting free induction decay signal was observed. The spin-lattice relaxation time may be found from the equation:

$$M(t) = M_H + [M(0) - M_H] \exp(-t/T_1(H)) \quad (1)$$

where M_H is the equilibrium value of the signal (magnetization) at the field H after sufficiently long time, *e.g.*, for $t > 10 T_1$. If one measures T_1 at low field one usually magnetizes the sample at the large field H_0 and starts from $M(0) = M_{H_0} \equiv M_0$. In the case of higher fields $H > H_0/2$ it is better to apply a 90° rf pulse before placing the sample in the field H . In this case $M(0) = 0$.

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The results of the measurements of $T_1(H)$ are presented in Fig. 1. The observed $T_1(H)$ increases strongly with increasing H for low field region and then it seems to approach the asymptotic value $T_1(\infty)$.

To explain the field dependence of T_1 some additional measurements of the fluorine second moment M_2 were performed at 77°K at two different resonant frequencies 30 MHz and 56.4 MHz. The values M_2 calculated from the spectra obtained by a broad line spectrometer are equal to $4.0 \pm 0.1 \text{ Oe}^2$ and $4.5 \pm 0.1 \text{ Oe}^2$, respectively.

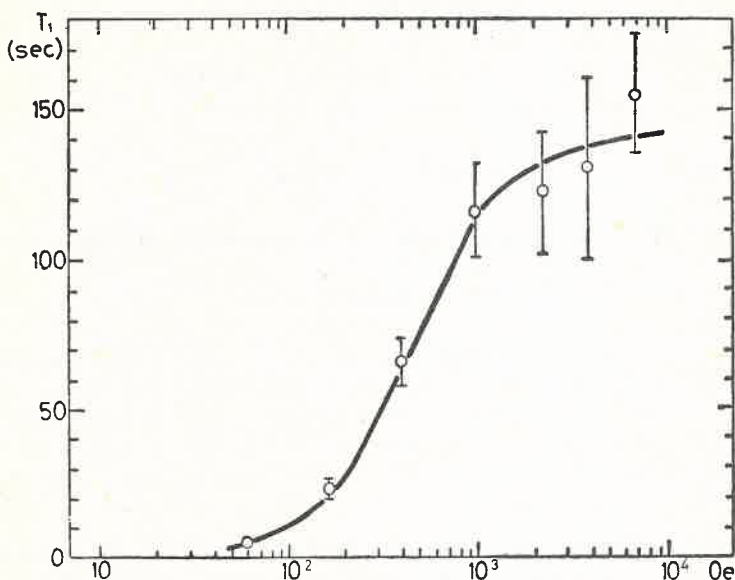


Fig. 1. Field dependence of the fluorine spin-lattice relaxation time in solid CF_2Cl_2 at 77°K

The observed results may be explained taking into account the dipole-dipole interaction between fluorine nuclei and the anisotropy of the chemical shift.

In the case of a rigid lattice the fluorine second moment for polycrystalline substances may be found as follows (Blinic *et al.* 1965, 1966):

$$M_2 = A + BH^2 \quad (2)$$

where constants A and B may be obtained after simple calculations (*e.g.* Aboregen 1961).

$$A = \frac{9}{20} \gamma_F^2 \hbar^2 \sum_j r_{ij}^{-6} \quad (3)$$

$$B = \frac{4}{45} (\Delta\sigma)^2 = \frac{4}{45} [(\sigma_{zz} - \sigma_{xx})^2 + (\sigma_{zz} - \sigma_{yy})(\sigma_{xx} - \sigma_{yy})] \quad (4)$$

γ_F is gyromagnetic ratio for fluorine nucleus, r_{ij} are internuclear distances and σ_{xx} , σ_{yy} , σ_{zz} and $\Delta\sigma$ are principal elements of the screening tensor and anisotropy of the chemical

shift respectively. An additional contribution to the fluorine second moment, produced by the chlorine nuclei in CF_2Cl_2 , viz. $A_{\text{Cl}} = \gamma_{\text{Cl}}^2 \hbar^2 \sum_j r_{ij}^{-6}$ may be neglected because $\gamma_{\text{Cl}}^2 \ll \gamma_{\text{F}}^2$.

From the experimental values of the second moment it follows that $A = (3.8 \pm 0.2) \text{Oe}^2$, $B = (3.5 \pm 1.4) 10^{-9}$ and $\Delta\sigma = 200 \pm 40$ ppm. A similar value of A may be calculated from Eq. (3) if we take into account only the intramolecular dipolar interaction between fluorine nuclei ($r_{ij} = r_{\text{FF}}$). This means that the intermolecular interactions in CF_2Cl_2 are much less important than intramolecular ones. The fluorine spin lattice relaxation time in solid CF_2Cl_2 may be presented as a sum of contributions following from the dipolar interaction and anisotropy of the chemical shift:

$$\frac{1}{T_1} = \left(\frac{1}{T_1} \right)_d + \left(\frac{1}{T_1} \right)_\sigma \quad (5)$$

where $(1/T_1)_d$ may be expressed by formula analogous to that presented by Look and Lowe (1967) for H_2S (the same molecular symmetry — C_{2v} , as for CF_2Cl_2 , Herzberg 1956, Landolt-Börnstein 1955)

$$\left(\frac{1}{T_1} \right)_d = \frac{1}{2} A \gamma_{\text{F}}^2 \text{sech}^2 \left(\frac{\Delta E}{2kT} \right) \left[\frac{\tau c}{1 + \omega_{\text{F}}^2 \tau_c^2} + \frac{4\tau c}{1 + 4\omega_{\text{F}}^2 \tau_c^2} \right] \quad (6)$$

where $\omega_{\text{F}} = \gamma_{\text{F}} H$ is Larmor frequency, τ_c is correlation time for a 90° flip rotation of the vector r_{FF} around the molecular axis and ΔE is the difference of the effective energies for two equilibrium positions of the vector.

The anisotropic part $(1/T_1)_\sigma$ may be presented in a form similar to that of McConnell and Holm (1956)

$$\left(\frac{1}{T_1} \right)_\sigma = \frac{3}{2} B \omega_{\text{F}}^2 f_\sigma \frac{\tau c}{1 + \omega_{\text{F}}^2 \tau_c^2} \quad (7)$$

where a coefficient f_σ is introduced to take into account an eventual quenching effect owing to the molecular flips.

In the case of sufficiently high magnetic field where $\omega_{\text{F}}^2 \tau_c^2 \gg 1$ we have

$$\frac{1}{T_1} = \frac{1}{\tau_c} (a + bH^{-2}) \quad (8)$$

with

$$a = \frac{3}{2} B f_\sigma \quad (9)$$

$$b = A \text{sech}^2 \left(\frac{\Delta E}{2kT} \right). \quad (10)$$

From the experimental results of T_1 it follows that

$$a/\tau_c = (7.4 \pm 1.0) \times 10^{-3} \text{sec}^{-1} \quad \text{and} \quad b/\tau_c = (1.6 \pm 0.4) \times 10^3 \text{Oe}^2 \text{sec}^{-1}.$$

Good agreement between the experimental results and the theoretical values (from

Eqs 5-7) may be obtained if we assume that

$$\frac{1}{T_1} = 7.4 \times 10^{-3} \frac{\alpha^2}{1+\alpha^2} + 0.24 \left(\frac{1}{1+\alpha^2} + \frac{4}{1+4\alpha^2} \right) \quad (11)$$

where $\alpha = \omega_F \tau_c = \gamma_F H \tau_c$, with $\tau_c = (0.7 \pm 0.2) \mu\text{sec}$ and $\gamma_F = 2.5167 \times 10^4 \text{ Oe}^{-1} \text{ sec}^{-1}$.

The field dependence of T_1 described by Eq. (11) is presented in Fig. 1. From the comparison of this dependence with Eqs (5-7) and with second moment data one can find that $f_\sigma \cong 1$ and $\Delta E \cong 1.4 \text{ Kcal/}^\circ\text{K} \cdot \text{mol}$.

To obtain more detailed information about the molecular motion in solid CF_2Cl_2 it will be interesting to do measurements of the temperature dependence of the fluorine second moment and spin-lattice relaxation time.

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