

FLUORINE SPIN RELAXATION IN LIQUID  $\text{CF}_2\text{Cl}_2$ . II

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The temperature dependence of fluorine relaxation times  $T_1$  and  $T_2$  and the field dependence of  $T_1$  were measured for liquid  $\text{CF}_2\text{Cl}_2$ . The coupling constant for indirect scalar interaction between the fluorine and chlorine nuclei was found to be  $|J_{\text{FCL}}|/2\pi = (12 \pm 3)$  Hz.

In the previous publication (paper I) the fluorine spin-lattice relaxation time was measured at the frequency of 28 MHz for pure liquid  $\text{CF}_2\text{Cl}_2$  from  $-90^\circ\text{C}$  up to the critical temperature  $112^\circ\text{C}$ . The decrease of  $T_1$  with increasing temperature was observed. This behaviour was explained as being due to the spin-rotational interaction.

The present paper reports measurements of the fluorine spin-lattice relaxation time  $T_1$  and spin-spin relaxation time  $T_2$  for liquid  $\text{CF}_2\text{Cl}_2$  (Freon 12) in the range above  $0^\circ\text{C}$  up to  $80^\circ\text{C}$  at a resonant frequency of 14 MHz. Moreover the field dependence of  $T_1$  at  $20^\circ\text{C}$  in the range from 1 Oe up to 24 kOe is presented. The sample was prepared using anhydrous and oxygen-free Freon 12 degassed (below  $10^{-2}\text{Tr}$ ) by a freeze-pump-thaw technique.

The fluorine relaxation times  $T_1$  and  $T_2$  at 14 MHz (3.5 kOe) and  $T_1$  at higher frequencies were measured by spin-echo technique using the methods proposed by Carr and Purcell (1954) and Meiboom and Gill (1958). The method of  $T_1$  measurement at low magnetic fields (from 1 Oe to 500 Oe) and the apparatus have been described elsewhere (Florkowski *et al.* 1969).

The temperature dependence of  $T_1$  and  $T_2$  in liquid  $\text{CF}_2\text{Cl}_2$  is presented in Fig. 1. The measured values of  $T_1$  at a resonant frequency of 14 MHz are equal to those at 28 MHz in paper I and can be explained on the basis of spin-rotational interaction, which gives the dominant contribution to the spin-lattice relaxation rate at this frequency (field) region.

However, in the low magnetic field region below 10 Oe the values of relaxation time  $T_1$  become shorter than those observed at higher fields (Fig. 2). Moreover the measured values of  $T_2$  are shorter than  $T_1$  (Fig. 1). These two facts cannot be interpreted on the basis of the spin-rotation interaction itself and other interactions have to be taken into account.

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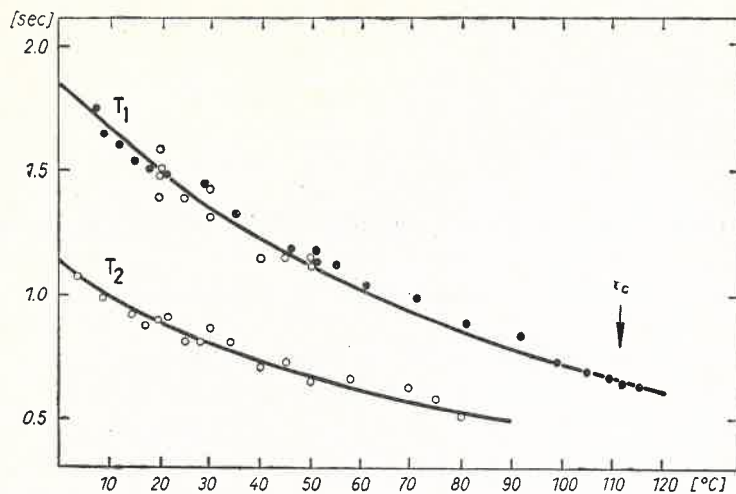


Fig. 1. Temperature dependence of fluorine relaxation times  $T_1$  and  $T_2$  in liquid  $\text{CF}_2\text{Cl}_2$  (o — the results at 14 MHz, ● — the results at 28 MHz from paper I,  $t_c$  — critical temperature)

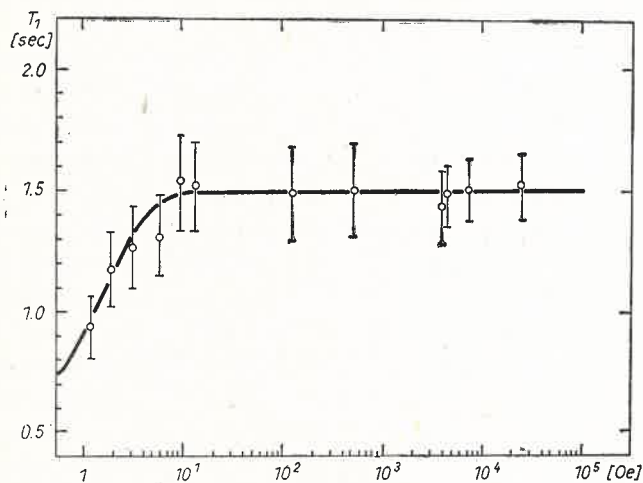


Fig. 2. Field dependence of fluorine spin-lattice relaxation time  $T_1$  for liquid  $\text{CF}_2\text{Cl}_2$  at  $20^\circ\text{C}$

It is known that the relaxation rate  $1/T_1$  and  $1/T_2$  for nuclei of spin  $I = 1/2$ , such as  $^{19}\text{F}$ , can be presented as a sum of the contributions following from the dipole-dipole interaction, the anisotropy of the chemical shift, spin-rotation interaction, and the indirect scalar interaction (Abragam 1961).

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

$$\frac{1}{T_2} = \left(\frac{1}{T_2}\right)_d + \left(\frac{1}{T_2}\right)_\sigma + \left(\frac{1}{T_2}\right)_{SR} + \left(\frac{1}{T_2}\right)_{Sc} \quad (2)$$

In the extreme narrowing case  $\omega_F \tau_c \ll 1$  ( $\omega_F$ —Larmor precession frequency for nucleus  $^{19}\text{F}$ ,  $\tau_c$ —correlation time for molecular reorientation), which is fulfilled for liquid of low viscosity such as  $\text{CF}_2\text{Cl}_2$ , we have

$$\left(\frac{1}{T_1}\right)_d = \left(\frac{1}{T_2}\right)_d, \left(\frac{1}{T_1}\right)_\sigma = \frac{6}{7} \left(\frac{1}{T_2}\right)_\sigma, \left(\frac{1}{T_1}\right)_{SR} = \left(\frac{1}{T_2}\right)_{SR} \quad (3)$$

The dipolar term  $1/T_{1d}$  is a sum of contributions following from intramolecular and intermolecular dipole-dipole interactions between nuclei. In  $\text{CF}_2\text{Cl}_2$  the considered  $^{19}\text{F}$  nuclei of spins  $I = 1/2$  can interact one with another and with the chlorine nuclei of spins  $S = 3/2$ . The resulting dipolar contribution to the fluorine relaxation time can be expressed as a special case of a general formula presented elsewhere (Blicharski *et al.* 1960)

$$\left(\frac{1}{T_1}\right)_d = \frac{3}{2} \hbar^2 \gamma_F^4 r_{FF}^{-6} \tau_c (1 + \alpha_{Cl} + \alpha_{inter}) \quad (4)$$

with

$$\tau_c = \frac{4\pi\eta a^2}{3kT} \quad (5)$$

$$\alpha_{Cl} = \frac{20}{3} \left(\frac{\gamma_{Cl}}{\gamma_F}\right)^2 \left(\frac{r_{FF}}{r_{FCl}}\right)^6 \quad (6)$$

$$\alpha_{inter} = \frac{3\pi}{2} \frac{Nr_{FF}^6}{a^3} \left[1 + \frac{10}{3} \left(\frac{\gamma_{Cl}}{\gamma_F}\right)^2\right] \quad (7)$$

where  $T$  is the absolute temperature,  $a$  is the molecular radius,  $N$  is the number of molecules per  $\text{cm}^3$ ,  $\eta$  is the viscosity of liquid,  $\gamma_F$ ,  $\gamma_{Cl}$  are giromagnetic ratios for fluorine and chlorine nuclei, and  $r_{FF}$ ,  $r_{FCl}$  are internuclear distances.

From the density data and molecular structure for  $\text{CF}_2\text{Cl}_2$  (Landolt-Börnstein 1955) it follows the value  $N$  and  $a = 2.63 \text{ \AA}$ ,  $r_{FF} = 2.20 \text{ \AA}$ ,  $r_{FCl} = 2.53 \text{ \AA}$ . Taking into account  $\gamma_{Cl}/\gamma_F = 0.104$  (for  $^{35}\text{Cl}$ ), one finds  $\alpha_{Cl} = 0.03$  and  $\alpha_{inter} = 0.09$ . This means that the contribution is produced mainly by intramolecular interaction between fluorine nuclei, whereas the interaction with chlorine nuclei and intermolecular interaction play a small role.

The anisotropy of chemical shifts gives the contribution  $1/T_{1\sigma}$  to the relaxation rate, which may be presented by following formula (McConnell and Holm 1956)

$$\left(\frac{1}{T_1}\right)_\sigma = \frac{2}{15} \omega_F^2 \Delta\sigma^2 \tau_c \quad (8)$$

where  $\Delta\sigma$  is the anisotropy of the chemical shift constant.

The spin-rotation contribution  $1/T_{1SR}$  is given by the following formula (Blicharski 1963, 1968)

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{SR} &= \frac{8\pi^2}{3} c_I^2 \left[1 + \frac{2}{9} \left(\frac{\Delta c_I}{c_I}\right)^2\right] \langle J(J+1) \rangle \bar{q} \bar{\tau}_J \\ &= \frac{8\pi^2}{9} (c_{xx}^2 + c_{yy}^2 + c_{zz}^2) \langle J(J+1) \rangle \bar{q} \bar{\tau}_J \end{aligned} \quad (9)$$

where  $c_{ii}$  ( $i = x, y, z$ ),  $c_I$  and  $\Delta c_I$  are spin-rotation tensor elements constant and anisotropy respectively,  $\langle J(J+1) \rangle$  is the average square of molecular angular momentum  $J$ ,  $\bar{\tau}_J$  is the effective correlation time for  $J$ ,  $\bar{q} = \bar{\tau}_J/\tau_c$  is the quenching factor.

The indirect scalar interaction  $\hbar J_{FCl} I \cdot S$  between the fluorine and chlorine nuclei is time dependent owing to the fast quadrupole relaxation of chlorine nuclei. If we neglect the correlation between the pairs of interacting nuclei then the resulting scalar contributions to the fluorine relaxation rate may be written as the double value of that for a single pair F—Cl (Abragam 1961).

$$\left(\frac{1}{T_1}\right)_{sc} = 5 J_{FCl}^2 \frac{T_{2Q}}{1 + (\omega_F - \omega_{Cl})^2 T_{2Q}^2} \quad (10)$$

$$\left(\frac{1}{T_2}\right)_{sc} = \frac{5}{2} J_{FCl}^2 \left[ T_{1Q} + \frac{T_{2Q}}{1 + (\omega_F - \omega_{Cl})^2 T_{2Q}^2} \right] \quad (11)$$

with

$$\frac{1}{T_{1Q}} = \frac{1}{T_{2Q}} \equiv \frac{1}{T_Q} = \frac{1}{10} \left( \frac{e^2 q Q}{\hbar} \right)^2 \tau_c' \quad (12)$$

where  $\omega_F = \gamma_F H$  and  $\omega_{Cl} = \gamma_{Cl} H$  are Larmor precession frequencies for F and Cl nuclei respectively,  $H$  is the magnetic field,  $T_{1Q}$  and  $T_{2Q}$  are nuclear quadrupole relaxation times for Cl, and  $e^2 q Q/\hbar$  is the quadrupole coupling constant.

It was pointed out in paper I that the observed  $T_1$  values for  $CF_2Cl_2$  at 28 MHz in the high temperature region can be explained on the basis of spin-rotation interaction. If one assumed  $T_1 \cong T_{1SR}$ ,  $\langle J(J+1) \rangle = 11.2 T$ ,  $\bar{\tau}_J = \text{const}$ , then the function  $T_1 T^2/\eta$  should be inde-

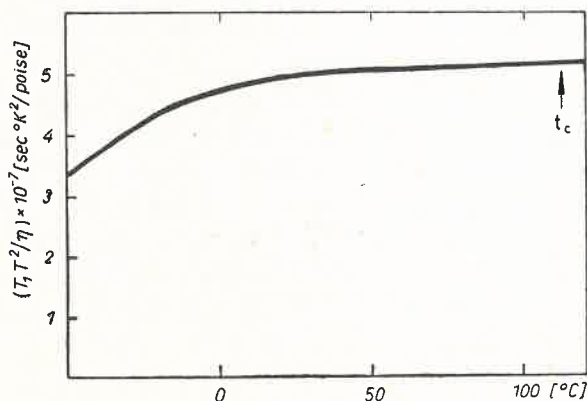


Fig. 3. Temperature dependence the function  $T_1 T^2/\eta$  for liquid  $CF_2Cl_2$

pendent of temperature. Taking the experimental results of  $T_1$  from the present paper and paper I and the viscosity data for liquid  $CF_2Cl_2$ <sup>1</sup>, it is found that the function  $T_1 T^2/\eta$  is constant in the region of temperature above 20°C (Fig. 3).

Another possible assumption on  $\bar{\tau}_J$  is  $\bar{\tau}_J = \text{const}/\sqrt{T}$ . In such case the value  $T_1 T/\eta$  should be constant at high temperatures where spin-rotation interaction is important. For

<sup>1</sup> R. E. Franz, Ltd. — private communication.

$\text{CF}_2\text{Cl}_2$  it is not supported by experimental data. Thus, rather the first assumption  $\bar{\tau}_J = \text{const}$  is valid.

At low temperatures the observed  $T_1$  is shorter than the value predicted by spin-rotation interaction and one should take into account other interactions. From the fact that  $T_1$  is field independent at high magnetic fields (Figs 1 and 2), it follows that contribution  $1/T_{1s}$  and  $1/T_{1Sc}$  play a small role in the relaxation process. One can explain the observed values of  $T_1$  at 14 MHz and 28 MHz in the whole investigated temperature region by taking into account the spin-rotation contribution  $1/T_{1SR}$ , which is proportional to  $T^2/\eta$  and the dipolar contribution  $1/T_{1d}$ , which is proportional to  $\eta/T$ . A good fit to the experimental results is given by the following equation

$$\frac{1}{T_1} = A_1 \frac{T^2}{\eta} + A_2 \frac{\eta}{T} = 1.95 \times 10^{-7} \frac{T^2}{\eta} + 0.52 \times 10^4 \frac{\eta}{T} \quad (13)$$

where

$$A_1 = \frac{2\pi c_I^2 \tau_J^2 k}{a^3} \left[ 1 + \frac{2}{9} \left( \frac{\Delta c_I}{c_I} \right)^2 \right] \frac{\langle J(J+1) \rangle}{T} \quad (14)$$

$$A_2 = 2\pi \hbar^2 \gamma_F^4 a^3 / k. \quad (15)$$

In the low magnetic field region below 10 Oe and at temperature 20°C the  $T_1$  value decreases with the decreasing field (Fig. 2). This decrease of  $T_1$  may be caused by the indirect scalar interaction between fluorine and chlorine nuclei. Good agreement with measured value of  $T_1$  at low magnetic fields may be obtained if one takes

$$\frac{1}{T_1} = \frac{1}{1.5} + 5J_{FCl}^2 \frac{T_Q}{1 + (\gamma_F - \gamma_{Cl})^2 H^2 T_Q^2} \quad (16)$$

where  $|J_{FCl}|/2\pi = (12 \pm 3)$  Hz,  $T_Q = (40 \pm 8)$   $\mu\text{sec}$ .

Taking the above value  $T_Q$  and the quadrupole coupling constant  $e^2qQ/h = 76$  MHz from the nuclear quadrupole resonance data (Livingstone 1951) we can evaluate the correlation time at 20°C  $\tau_c' = 1.1 \times 10^{-12}$  sec from Eq. (12). This value is in good agreement with that following from Eq. (5) if we introduce microviscosity coefficient (Spernal and Wirtz 1953). Using the presented values  $J_{FCl}$  and  $T_Q$ , it is easily found that the scalar contribution to spin-lattice relaxation rate  $1/T_{1Sc}$  is negligible at high frequencies because of  $(\omega_F - \omega_{Cl})T_Q \gg 1$ , whereas it is important for spin-spin relaxation and gives the contribution:

$$\left( \frac{1}{T_2} \right)_{Sc} = \frac{5}{2} J_{FCl}^2 T_Q. \quad (17)$$

This contribution is the cause of the observed difference between  $T_1$  and  $T_2$  at frequency 14 MHz (Fig. 1), according to the relation

$$\frac{1}{T_2} - \frac{1}{T_1} = \frac{5}{2} J_{FCl}^2 T_Q. \quad (18)$$

In the previous consideration we neglected the contribution  $1/T_{1\sigma}$  at frequency 14 MHz and 28 MHz. If we know the correlation time  $\tau_c$  and the anisotropy of the chemical shift  $\Delta\sigma = 200$  ppm (paper III), we can calculate the contribution  $1/T_{1\sigma}$ , which is really very small compared with the experimental value  $1/T_1$ . It is even small compared with the dipolar contribution because at 28 MHz we have

$$\left(\frac{1}{T_1}\right)_\sigma / \left(\frac{1}{T_1}\right)_d = \frac{4}{45} (\omega_F \Delta\sigma / \hbar \gamma_F^2 r_{FF}^{-3})^2 = 0.007. \quad (19)$$

The contribution  $1/T_{1\sigma}$  can be detectable in a very high frequency region and at low temperatures, where the parameter  $\varepsilon = \omega_F \Delta\sigma / \hbar \gamma_F^2 r_{FF}^{-3}$  is sufficiently high and the spin-rotation contribution is negligible. This problem will be considered elsewhere.

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