^{1}H and ^{19}F Nuclear Magnetic Relaxation Studies of Molecular Motion in Solid Fluoroform

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Spin-lattice relaxation times of proton and fluorine nuclei in solid CHF_3 were measured by the pulsed magnetic resonance technique between 7 and 116 K. In ^{1}H resonance, non-exponential recovery of magnetization was clearly observed. T_1 data as well as magnetization recoveries were interpreted in terms of intramolecular magnetic dipole interactions between like spins and also between unlike spins, which are modulated by the isotropic reorientation of a whole molecule. A calculation of the temperature dependence of T_1 was made by using an activation energy of 17 kJ mol^{-1} and a pre-exponential factor of 1.0×10^{-16} s for the motion, yielding results in agreement with the present experimental results.

Fluoroform (CHF_3) has no phase transition below the melting point, $T_m=118$ K, and has a wide range of liquid phase up to the boiling point, $T_b=191$ K.[1] Nuclear magnetic relaxation studies of fluoroform have been concentrated on its liquid state. Spin-rotational interactions have been found to be the main relaxation mechanism in the ^{19}F resonance in the liquid state[2] as well as in the gas state.[3] The cross relaxation between ^{1}H and ^{19}F connected with the Overhauser effect has also been studied in the liquid state where effects of intermolecular magnetic interactions are predominant over those of intramolecular interactions.[4]

In this paper, we will discuss experimental results of temperature dependence of ^{1}H and ^{19}F spin-lattice relaxation times in order to elucidate the molecular motion in the solid state and to examine the cross relaxation effect between the two kinds of nuclei.

Experimental

A sample of fluoroform was purchased in a cylinder from Seitetsu Kagaku (a product of Dupont), the nominal purity being higher than 99%. The method of purification of the sample and the cryostat used in the measurement of T_1 were the same as in the case of silane reported previously.[5]

The relaxation time measurements were carried out between 7 K and just below the melting point at both 10.00 and 25.54 MHz using pulsed NMR techniques. In the ^{19}F resonance, we measured T_1 by the null-method above 80 K since the magnetization recovery showed exponential behavior over more than one decade within the experimental error.

On the other hand, the magnetization recovery for the ^{1}H resonance showed clear non-exponential behavior as shown in Fig. 1. We therefore used the $\pi/2$(comb)-τ-$\pi/2$ pulse sequences as well as the π-τ-$\pi/2$ pulse method; the two methods gave identical results within the experimental error.

Results and Discussion

The ^{19}F spin-lattice relaxation time T_1 above 80 K is shown in Fig. 2 and that below 80 K is shown in Fig. 3. A minimum in T_1 occurs at 105 K with a value of 10.7 ms at 10.0 MHz. Anomalous T_1 behavior is observed below 50 K where T_1 becomes

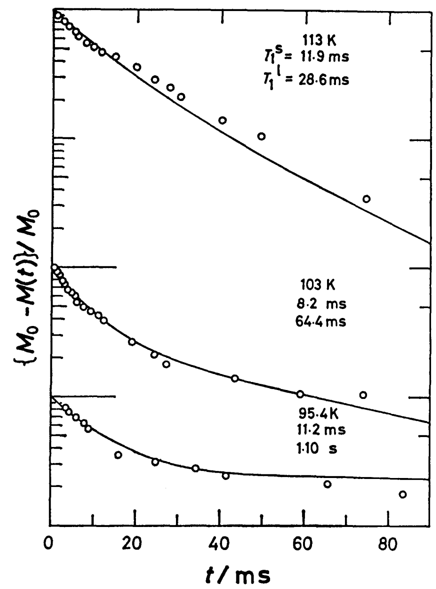

Fig. 1. Reduced magnetization recoveries in ^{1}H resonance.
Solid curves are the results of theoretical fitting.

almost independent of temperature, and on further cooling, the magnetization recovery tends to be more complex with two time constants. The relaxation mechanism in this temperature region is not obvious. The trace of paramagnetic oxygen, which has been detected by a gas chromatographic analysis (less than 0.02%), might be a candidate.[6]

A unique value of ^{1}H spin-lattice relaxation time was not to be determined because of the non-exponential recoveries as shown in Fig. 1. This behavior is due to the cross relaxation effect caused by the dipole coupling between ^{1}H and ^{19}F. In other words, for a quantitative treatment of the ^{1}H resonance data, it is necessary to consider the spin system as one of two unlike spins, ^{1}H (spin S) and ^{19}F (spin I).

In this case, we may describe the equation of motion for the magnetization as follows:[7]

$$\begin{pmatrix} \dfrac{d\langle I_z\rangle}{dt} \\ \dfrac{d\langle S_z\rangle}{dt} \end{pmatrix} = -\Gamma \begin{pmatrix} \langle I_z\rangle - I_0 \\ \langle S_z\rangle - S_0 \end{pmatrix}, \tag{1}$$

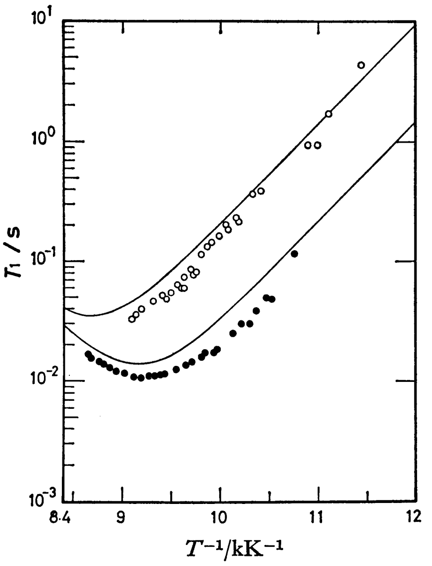

Fig. 2. The temperature dependence of ^{19}F spin-lattice relaxation time above 80 K.
●: At 10.0 MHz, ○: at 25.54 MHz, ——: calculated curves.

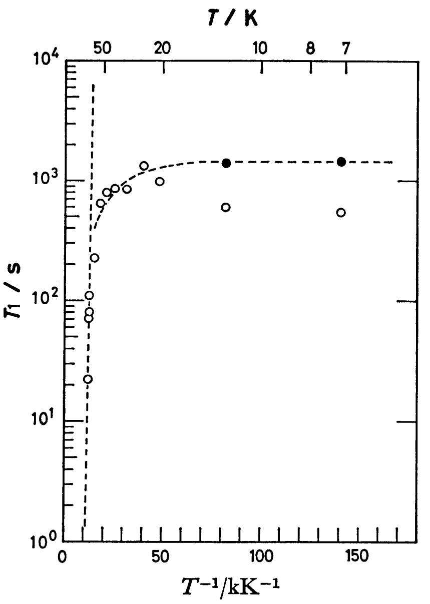

Fig. 3. The temperature dependence of ^{19}F spin-lattice relaxation time below 80 K at 25.54 MHz.

where I_0 and S_0 denote the magnetization at thermal equilibrium, and the relaxation matrix Γ is defined by

$$\Gamma \equiv \begin{pmatrix} \Gamma_{II} & \Gamma_{IS} \\ \Gamma_{SI} & \Gamma_{SS} \end{pmatrix}. \tag{2}$$

For simplicity, with only the intramolecular dipole coupling taken into account, each component of the relaxation matrix may be written as

$$\left.\begin{aligned} \Gamma_{II} &= 2\gamma_{II}^{L} + \gamma_{II}^{U}, \\ \Gamma_{IS} &= \gamma_{IS}^{U}, \\ \Gamma_{SI} &= 3\gamma_{SI}^{U}, \\ \text{and} \quad \Gamma_{SS} &= 3\gamma_{SS}^{U}, \end{aligned}\right\} \tag{3}$$

where the superscripts L and U mean the contribution of a like spin pair and that of an unlike spin pair, respectively. In the case of dipole coupling, theses are given by Abragam as follows:[7]

$$\left.\begin{aligned} \gamma_{II}^{L} &= \frac{9}{8}\gamma_I^4\hbar[J^{(1)}(\omega_I)+J^{(2)}(2\omega_I)] \\ \gamma_{II}^{U} &= \frac{3}{4}\gamma_I^2\gamma_S^2\hbar^2\left[\frac{1}{12}J^{(0)}(\omega_I-\omega_S)+\frac{3}{2}J^{(1)}(\omega_I)+\right. \\ &\qquad \left.\frac{3}{4}J^{(2)}(\omega_I+\omega_S)\right], \\ \gamma_{IS}^{U} &= \frac{3}{4}\gamma_I^2\gamma_S^2\hbar^2\left[-\frac{1}{12}J^{(0)}(\omega_I-\omega_S)+\frac{3}{4}J^{(2)}(\omega_I+\omega_S)\right], \end{aligned}\right\} \tag{4}$$

and similar equations for γ_{SS}^{U} and γ_{SI}^{U} are obtainable by interchanging the indices I and S, where $J^{(n)}(\omega)$'s are spectral densities.

The observable relaxation rates $\lambda_+=(T_1^{l})^{-1}$ and $\lambda_-=(T_1^{s})^{-1}$ are the eigenvalues of the relaxation matrix Γ.

When we use the $\pi/2$(comb)-τ-$\pi/2$ pulse sequences, these eigenvalues determine the magnetization recoveries according to the equations

$$\left.\begin{aligned} \frac{I_0-\langle I_z\rangle}{I_0} &= a_S\exp(-t/T_1^{l})+b_S\exp(-t/T_1^{s}), \\ \text{and} & \\ \frac{S_0-\langle S_z\rangle}{S_0} &= a_I\exp(-t/T_1^{l})+b_I\exp(-t/T_1^{s}), \end{aligned}\right\} \tag{5}$$

where the coefficients a and b are given by

$$\left.\begin{aligned} a_S &= (\Gamma_{SS}-\lambda_-)/(\lambda_+-\lambda_-) = b_I, \\ \text{and} & \\ b_S &= (\Gamma_{SS}-\lambda_+)/(\lambda_+-\lambda_-) = a_I. \end{aligned}\right\} \tag{6}$$

It is worth noting that not only T_1^{l} and T_1^{s} but also a and b are temperature-dependent through temperature dependence of correlation time associated with the particular type or types of molecular motion that are responsible for the relaxation. Expressions such as Eqs. 4 and 5 have been used to interprete experimental results on more complicated systems.[8–12] However, the values of a and b were taken as independent of temperature.

In calculating the matrix elements (Eq. 3) for CHF_3, isotropic reorientation of a whole molecule will be assumed to be the dominant relaxation mechanism. The spectral densities are then given by

$$\left.\begin{aligned} J^{(1)}(\omega) &= \frac{4}{15}r_{ij}^{-6}[\tau_c/(1+\omega^2\tau_c^2)], \\ \text{where} & \\ J^{(0)}:J^{(1)}:J^{(2)} &= 6:1:4, \end{aligned}\right\} \tag{7}$$

with

$$\tau_c = \tau_0\exp(V/RT), \tag{8}$$

where r_{ij} is the distance between two spins, V is the relevant activation energy, and τ_0 is the pre-exponential factor.

Taking r_{FF}=0.216 and r_{FH}=0.198 nm,[13] we obtain the explicit values of the long and short components, T_1^{l} and T_1^{s}, and the coefficients a_S and b_S, which are shown in Fig. 4 as functions of $\omega\tau_c$ in the case of ^{19}F resonance. It is clear that T_1^{l} has a minimum

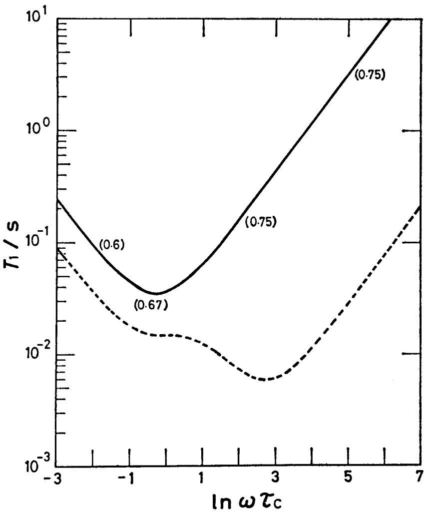

Fig. 4. Theoretical ^{19}F T_1 curves ($T_1{}^l$ and $T_1{}^s$ components) *vs.* ln $\omega\tau_c$.
The numbers in the parentheses indicate the coefficient a_S in Eq. 5.

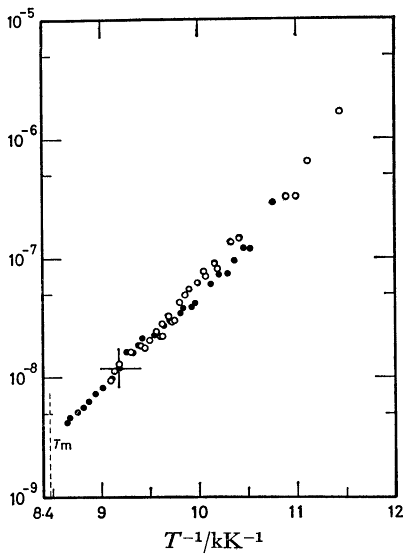

Fig. 5. The temperature dependence of the correlation time associated with isotropic reorientation.
●: From the T_1 data at 10.0 MHz, ○: from the T_1 data at 25.54 MHz.

at $\omega\tau_c=0.75$ ($\ln\omega\tau_c=-0.28$) and a_S assumes a nearly constant value of 0.75 where $\omega\tau_c\gg0.75$. Judging from the fact that the observed magnetization recovery in ^{19}F resonance can be described by a single exponential function over the time span of experiment, it is reasonable to consider that the observed T_1 is equal to $T_1{}^l$. By using the $T_1{}^l$ curve in Fig. 4 and the observed T_1 values, we can estimate the correlation time τ_c due to isotropic molecular reorientation, the temperature dependence of which is shown in Fig. 5. The straight line in this figure gives us an activation energy $V=17$ kJ mol^{-1} and $\tau_0=1.0\times10^{-16}$ s,[14] as well as the solid curve in Fig. 2.

On the other hand, the magnetization recoveries in ^{1}H resonance were analyzed by means of Eq. 5 using only one parameter τ_c. A few examples of curve-fitting are drawn in Fig. 1. The two time constants $T_1{}^l$ and $T_1{}^s$ obtained in this manner are plotted against the reciprocal of temperature in Fig. 6, where the $T_1{}^l$ and $T_1{}^s$ curves were calculated from the same parameter values as above and are shown by the solid and broken lines, respectively. Here the calculated $T_1{}^s$ curve has a shoulder around $\omega\tau_c=0.75$ besides a clear minimum at $\omega\tau_c=15$, which arises from the ($\omega_I-\omega_S$) terms in Eq. 4.

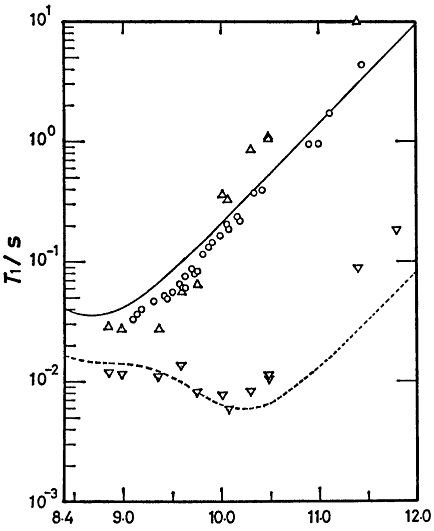

Fig. 6. The temperature dependence of T_1 at 25.54 MHz.
○: ^{19}F resonance, △: $T_1{}^l$ in ^{1}H resonance, ▽: $T_1{}^s$ in ^{1}H resonance, ——: calculated $T_1{}^l$, – – –: calculated $T_1{}^s$.

The calculated minimum value of $T_1{}^l$ is 13.9 ms at 10.0 MHz and that of $T_1{}^s$ is 5.8 ms at 25.54 MHz. There are some discrepancies between the calculated and observed T_1 values, which may be caused by the approximation that intermolecular contribution is to be ignored. However, the trend of the temperature dependence of T_1 is described satisfactorily by our simple but more or less rigorous treatment using a single correlation time τ_c.

As is apparent from the foregoing analysis of the experimental results, the data of ^{19}F relaxation can be used to deduce the relaxation behavior of protons in the present case. In other words, when there is a cross-relaxation effect between two nuclear species, one needs to know the relaxation behavior on only one of them which would then permit deductions on the other.

In the absence of structural information on CHF_3 it is difficult to rationalize the magnitude of the activation energy for molecular tumbling (17 kJ mol^{-1}). In the case of the low-temperature phase of CF_4, the activation energy was reported to be 18 kJ mol^{-1}.[15] Because the closest intermolecular approach is probably through F···F contacts, the similarity in the activation energy in these two substances would reflect the similarity in the intermolecular interaction.

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