Pressure-dependent Chemical Shifts of Fluorine NMR in Some Freon Gases.

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I. Introduction

The nuclear magnetic resonance signal of a molecule in gaseous or liquid media is displaced from the position where it would appear if no medium were present. This displacement of the resonance signal occurs because the screening constants of nuclei are altered by the environment of a molecule.

It is generally recognized there are four distinct medium effects which may contribute to the change of the screening constants:

(a) The contribution due to the bulk magnetic susceptibility of medium, denoted as σ_b hereafter, which was examined by Dickinson[1].

(b) The contribution which arises from anisotropic magnetic susceptibility of neighbor molecules, denoted as σ_a. The expression of this was presented by Schneider *et al.*[2]

(c) The contribution due to polar effect which arises from a distortion of electron cloud surrounding nuclei by an electric field originating from electric polarization on neighbor molecule, which is denoted as σ_E. The expression of this has been presented by Buckingham[3].

(d) The contribution due to van der Waals interaction between molecules, denoted as σ_W hereafter, which was examined by Bothner-By[4], Schneider *et al.*[2] and others.

In the liquid phase and even in the gaseous phase, these medium effects affect the appearence of NMR spectra in complicated ways. Most of previous studies of medium effects were performed in pure liquids or in liquid solutions, and important aspects of them as mentioned above have been revealed. On the other hand, it has

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been shown by Gordon and Dailey[5], and Bernstein *et al.*[6] that the gaseous phase is more amenable to quantitative study of medium effects than the liquid phase.

In this paper we report some experimental results of pressure- or density-dependent chemical shifts of fluorine resonance in gaseous $CHClF_2$, which are interpreted by an analogous method to Bernstein *et al*'s[6]. Furthermore we report some additional phenomena on pressure dependence of chemical shifts, which were observed as temperature was varied.

II. Theoretical

List of symbols

N ; Avogadro's number. k ; Boltzmann constant. T ; temperature.

V_m ; molar volume. χ_m ; molar magnetic susceptibility.

x_1 ; mole fraction of material 1 of which fluorine resonance is observed,

μ_1 and μ_2 ; electric dipole moments of molecules 1 and 2.

ε/k and r_0 ; Lennard-Jones potential constants. u ; inter-molecular potential

α_2 ; electric polarizability of molecule 2.

I_2 ; ionization potential of molecule 2.

Q_2 ; permanent quadrupole moment of molecule 2.

In the work of Raynes, Buckingham and Bernstein[6], it has been shown that the fluorine magnetic screening constant can be expanded into an inverse power series of the molar volume :

$$\sigma = \sigma_0 + \sigma_1/V_m + \sigma_2/V_m{}^2 + \sigma_3/V_m{}^3 + \cdots\cdots . \qquad (1)$$

where σ_0 is the screening constant of an isolated molecule and σ_1 is additional screening caused by binary collisions between molecules 1 and 2, and σ_2, σ_3, ..., etc. are screenings corresponding to higher order collisions.

In this notation of molecules 1 and 2, fluorine magnetic resonance of molecules 1 are now observed.

In the gaseous phase of moderate pressure, the higher order collisions can be neglected. Then σ_1 is expressed as,

$$\sigma_1 = \frac{1}{2} N \int \sigma_{(1,2)} \exp (-u/kT) \, d\tau_2, \qquad (2)$$

where $\sigma_{(1,2)}$ is the screening constant of molecule 1 caused by molecule 2, $\int d\tau_2$ is an integral over all configurations of molecules 2 in a specimen tube and configuration $d\tau_2$ is (see Fig. 1.),

$$d\tau_2 = r^2 dr \, \sin \theta_1 d\theta_1 \, \sin \theta_2 d\theta_2 d\phi.$$

Now, σ_1 or $(\sigma - \sigma_0) \, V_m$ can be divided into four contributions[2],[4].

$$\sigma_1 = (\sigma_1)_b + (\sigma_1)_a + (\sigma_1)_E + (\sigma_1)_W. \qquad (3)$$

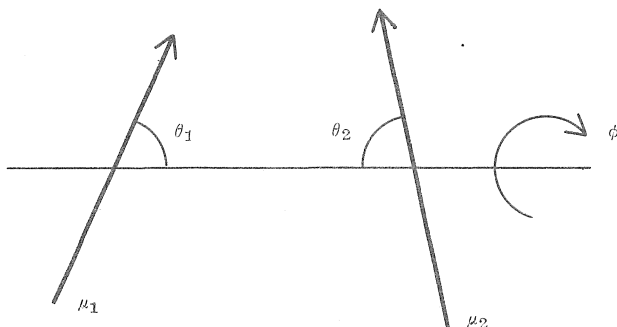Each term of Eq. (3) has been discussed by Bernstein *et al.*[4]

Fig. 1

(a) Bulk magnetic susceptibility term, $(\sigma_1)_b$;

for a cylindrical sample[1],

$$(\sigma_1)_b = 2\pi/3 \, (x_1 \chi_m{}^{(1)} + (1 - x_1)\chi_m{}^{(2)}). \tag{4}$$

(b) Magnetic anisotropy term, $(\sigma_1)_a$;

by preliminary calculation of this, it has been shown that $(\sigma_1)_a$ is negligible compared to $(\sigma_1)_W$ or $(\sigma_1)_E$, when a substance which has an appreciable anisotropic susceptibility, such as benzene, is not considered.

(c) Polar term, $(\sigma_1)_E$;

an electric field E can be expected to modify the fluorine screening constant in X—F bond in molecule 1 in the same way as that has been shown by Buckingham[3],

$$(\sigma_{1, 2})_E = -AE_z - BE^2, \tag{5}$$

where E_z is an electric field along X-F bond of molecule 1, E^2 is square of the electric field, and A and B are unknown parameters representing the nature of X. Both E_z and E^2 come of a permanent, an induced electric dipole moment and any permanent electric quadrupole moment if these exist in molecule 2.

Then, for an inter-molecular potential function u, the next expression may be employed[7],

$$u = 4\varepsilon\{ (r_0/r)^{12} - (r_0/r)^{6}\}$$
$$+ \mu_1\mu_2 r^{-3} (2 \cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos \phi)$$
$$+ 3/2\mu_1 Q_2 r^{-4} \{\cos \theta_1 (3 \cos^2 \theta_2 - 1) + 2 \sin \theta_1 \sin \theta_2 \cos \theta_2 \cos \phi\}. \tag{6}$$

Substituting Eqs. (5) and (6) into Eq. (2),

$$(\sigma_1)_E = -\pi NA/6y^2 \, [\mu_2\{ (\tau/3) H_6 (y) + (y^4\tau^3/200) H_{12} (v) \}$$
$$+ 4\alpha_2\mu_1/r_0^3 y^2 \{H_6 (y) + (\tau^2 y^4/40) H_{12}(y)\} + 2\mu_1 Q_2^2/y^2 kT r_0^5 H_8 (y)]$$
$$- \pi NB/3y^4 \, [(2\mu_2^2/r_0^3) \{H_6 (y) + (\tau^2 y^4/40) H_{12} (y)\}$$
$$+ \alpha_2\mu_1\mu_2/r_0^5 \{y^2\tau H_{12} (y) + (y^6\tau^3/60)H_{18} (y)\} + 3Q_2^2/r_0^5 H_8 (y)], \tag{7}$$

where

$$\tau = \mu_1 \mu_2 / r_0^3, \ y = 2 (\varepsilon/kT)^{\frac{1}{2}} \text{ and } H_n (y) = y^{\frac{27-n}{6}} \sum_{p=0}^{\infty} \Gamma \left(\frac{6p+n-3}{12} \right) y^p/p!.$$

(d) van der Waals term, $(\sigma_1)_W$;

it has been suggested that two effects may contribute to $(\sigma_2)_W$[2] ;

ⅰ) in the equilibrium configuration, van der Waals interaction results in an expansion of electron cloud. Then, the diamagnetic screening is diminished, it must result in a lower-field shift. This effect does not depend upon temperature at a constant density.

ⅱ) any departure from equilibrium molecular configuration causes time-dependent distortion of electron clouds. Such a distortion also has to destroy the axial symmetry of electron cloud of X-F bond and results in an increase of paramagnetic shielding, in other words, an increased lower field shift as temperature rises, since departures from the equilibrium configuration become more important as temperature increases.

The effect ⅱ) is more important in such molecule that X-F bond is more exposed to sideways attacks (e. g. CH_3F, $CHClF_2$).

Under moderate pressures, departures from the equilibrium configuration in gaseous phase depend only upon temperature, hence it may be expected that the effect ⅱ) brings about temperature-dependent σ_0 and $(\sigma_1)_W$.

Assuming the inter-molecular distance to be large enough to avoid overlapping between electron clouds of molecules 1 and 2,

$$(\sigma_{1,2})_W = - 3B\alpha_2 I_2/r^6. \tag{8}$$

Substituting Eq. (8) into Eq. (2),

$$(\sigma_1)_W = - \pi NB/y^4 r_0^3 \alpha_2 I_2 \{H_6 (y) + \tau^2/48) y^4 H_{12} (y) \}. \tag{9}$$

III. Experimental

Fluorine nuclear magnetic resonance was measured with a JEOL 3H-60 high-resolution NMR spectrometer operating at a frequency of 50 Mc.

Gaseous samples were prepared by condensing gases of known volume and pressure into glass tubes cooled to liquid air temperature. Considerable care had to be taken so as to minimize the chance of mixing up with oxygen in air.

The tubes, which have outside-diameter of 5mm and internal-diameter of 3 mm, easily withstood pressures up to about 70 atm, only depending on how good seals were made. An inaccuracy of estimation of gaseous pressures is estimated to be within 5 %.

Chemical shifts were measured relative to liquid ethyl-trifluoroacetate by the well-known side-band technique. Most measurements are accurate better than 1cps.

All measurements were made at temperatures of 90°C, 100°C and 110°C using the JEOL VT-2 equipment, because condensation of gas had to be avoided.

IV. Results and Discussion

Fig. 2 shows the pressure-dependence of fluorine chemical shifts of gaseous $CHClF_2$ at temperatures of 90°C, 100°C and 110°C. The highest density appeared in this figure corresponds to pressure of about 70 atm.

Since the plots of chemical shifts against pressure or density are on straight lines over the pressure ranges studied, neglect of higher terms in Eq. (1) may be justified within the experimental errors.

Observed values for σ_0, $(\sigma_0)_{obs}$, obtained by the extrapolation of σ-ρ plots to null density in Fig. 2. $(\sigma_0)_{obs}$ corrected for bulk magnetic susceptibility of the external reference are found to be temperature-dependent — lower field shift as temperature rises. This situation is shown in Table I.

Then, σ_1 may be found from the relation

$$\sigma_1 = M_1 \, (d\sigma/d\rho),$$

where M_1 is the molecular weight of material **1** ($CHClF_2$) and $(d\sigma/d\rho)$ is the slope of the plot of chemical shifts against density ρ in g/cm³.
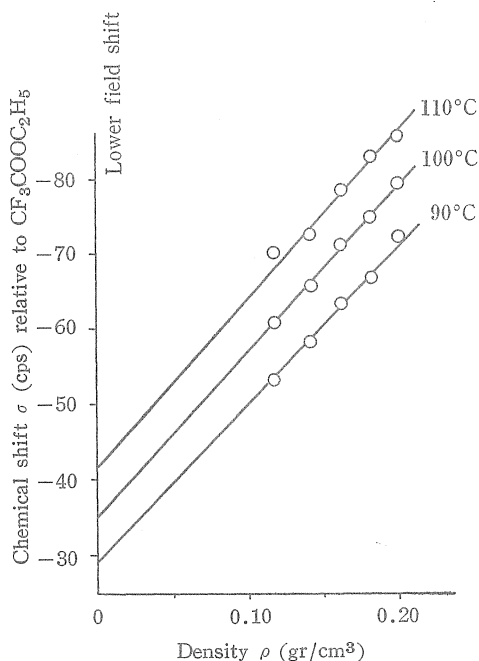

Fig. 2 Pressure-dependence of the chemical shifts of gaseous $CHClF_2$ at temperatures of 90°C, 100°C and 110°C.

Table I. Fluorine chemical shifts of $CHClF_2$ as extrapolated to null density, $(\sigma_0)_{obs}$, relative to ethyl-trifluoroacetate in ppm.

Temperature °C	$(\sigma_0)_{obs}$ ppm	$d(\sigma_0)_{obs}/dT$ ppm/°C
90	−1,81*	
100	−1,93	0.012
110	−2.05	

* ; minus means that the resonance appears at lower field side than the reference signal.

Samples investigated consist of $CHClF_2$ as material **1** dissolved in $CHClF_2$, CCl_2F_2 and CO_2 as material **2**. For binary mixtures of gases with mole fraction x_1 of material **1** and mole fractions $1-x_1$ of material **2**, σ_1 may be found from the relation

$$\sigma_1 = (x_1 M_1 + (1-x_1) M_2)(\sigma - \sigma_0)/\rho,$$

where M_2 represents molecular weight of a material **2** and ρ represents a total density. Several samples of each binary mixture were prepared, with a different concentration of the material **1**, and a value for σ_1 of each sample was determined. Extrapolation to null concentration of x_1 gives a value of $(\sigma_1)_{obs}$ for the

binary interaction between molecule 1 and molecule 2 when the material 1 is infinite dilution. This situation is indicated in Fig. 3 and $(\sigma_1)_{obs}$ are listed in Table II.
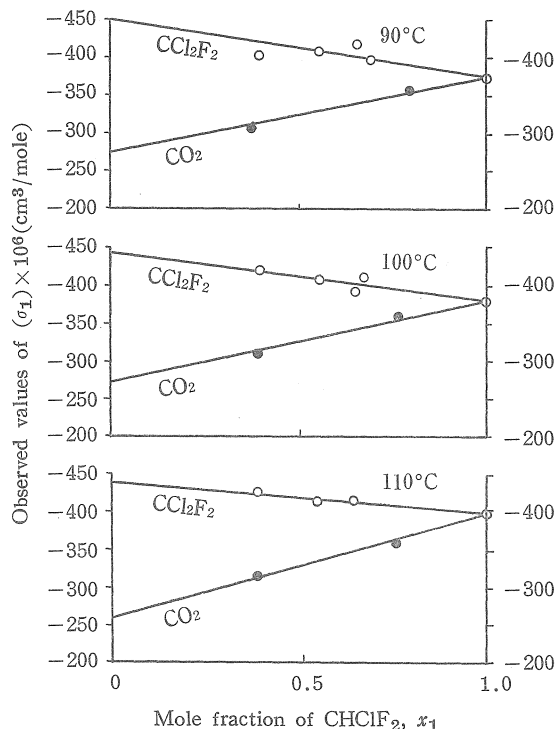

Fig. 3 σ_1 for CHClF$_2$ at various concentrations in different gaseous solvents (material 2).

The appropriate values of $(\sigma_1)_b$ as calculated by Eq. (4) and $(\sigma_1)_{obs} - (\sigma_1)_b$ are also presented in Table II

Then, $(\sigma_1)_{obs} - (\sigma_1)_b$ must be compared with $(\sigma_1)_E + (\sigma_1)_W$ in Eq. (3).

$$(\sigma_1)_{obs} - (\sigma_1)_b = (\sigma_1)_E + (\sigma_1)_W. \quad (10)$$

Consequently, values of unknown parameters A and B of C-F bond in CHClF$_2$ may be determined by finding the best fit of Eq. (10) to the values of $(\sigma_1)_{obs} - (\sigma_1)_b$ when CHClF$_2$, CCl$_2$F$_2$ and CO$_2$ are employed as material 2. The resulting values are summarized in Table III. Also included are four values of other bonding situations reported previously by several authors, to whom the method to determine the unknown parameters A and B is owed.

In order to reveal a magnitude of $(\sigma_1)_E$ and $(\sigma_1)_W$ respectively, both A and B which were determined in above are substituted into Eqs. (7) and (9). Resultant values of $(\sigma_1)_E$ and $(\sigma_1)_W$ are shown in Table IV. Also $(\sigma_1)_E + (\sigma_1)_W$ and $(\sigma_1)_E + (\sigma_1)_W - \{(\sigma_1)_{obs} - (\sigma_1)_b\}$ are shown in Table IV.

Table II. Values of $(\sigma_1)_{obs}$, $(\sigma_1)_b$ and $(\sigma_1)_{obs} - (\sigma_1)_b$.

Material 1	Material 2	Temperature °C	$(\sigma_1)_{obs}$ $\times10^6$cm^3/mole	$(\sigma_1)_b$ $\times10^6$cm^3/mole	$(\sigma_1)_{obs} - (\sigma_1)_b$ $\times10^6$cm^3/mole
CHClF$_2$	CCl$_2$F$_2$	90	-428*	-123	-305
		100	-419	-123	-296
		110	-418	-123	-295
CHClF$_2$	CHClF$_2$	90	-372	-87	-285
		100	-380	-87	-293
		110	-397	-87	-310
CHClF$_2$	CO$_2$	90	-275	-44	-231
		100	-272	-44	-228
		110	-260	-44	-216

* ; minus means that the resonance shifts toward lower field as pressure rises.

Table III. Values of parameters A and B for C–F bond of CHClF$_2$
and for other bonding situations.

Bond	Temperature °C	$A \times 10^{12}$ esu	$B \times 10^{18}$ esu	References
C–F in CHClF$_2$	90	33.7	39.7	
	100	43.0	39.0	
	110	45.7	36.3	
C–F in CHF$_3$	30	$-$ 9.9	15.1	(6)
C–F in CF$_4$	30	—	16.1	(6)
C–H in CHF$_3$	30	2.29	0.84	(6)
C–H in non-polar hydro-carbons	30	—	1.0±0.3	(6)

Table IV. Values of $(\sigma_1)_E$, $(\sigma_1)_W$ and $(\sigma_1)_E + (\sigma_1)_W - \{(\sigma_1)_{obs} - (\sigma_1)_b\}$
for various systems.

Nucleus	Material 1	Material 2	Temperature °C	$(\sigma_1)_E \times 10^6$ cm^3/mole	$(\sigma_1)_W \times 10^6$ cm^3/mole	$(\sigma_1)_E + (\sigma_1)_W - \{(\sigma_1)_{obs} - (\sigma_1)_b\} \times 10^6$ cm/mole	References
F^{19}	CHClF$_2$	CCl$_2$F$_2$	90	-26	-297	-18	
			100	-32	-291	-27	
			110	-34	-267	$-$ 6	
F^{19}	CHClF$_2$	CHClF$_2$	90	-74	-262	-51	
			100	-89	-254	-50	
			110	-92	-234	-16	
F^{19}	CHClF$_2$	CO$_2$	90	-22	-177	$+32$	
			100	-27	-172	$+29$	
			110	-31	-174	$+11$	
F^{19}	CF$_4$	CF$_4$	30	0	-146	-55	(6)
F^{19}	CHF$_3$	CO$_2$	30	$+12$	-125	-21	(6)
H^1	CH$_4$	CH$_4$	30	0	$-$ 11	$-$ 5	(6)
H^1	HCl	CO$_2$	40	-46	$-$ 4	$+$ 4	(6)

From Table IV, it is understood that for the case of CHClF$_2$ the most significant contribution to (σ_1) comes of van der Waals interaction and that since discrepancies between $(\sigma_1)_E + (\sigma_1)_W$ and $\{(\sigma_1)_{obs} - (\sigma_1)_b\}$ do not exceed 15 % of $\{(\sigma_1)_{obs} - (\sigma_1)_b\}$, the model used in these calculations is considerably good.

Examination of Table IV reveals the interesting feature that polar contributions to the fluorine screening of CHClF$_2$ are in the opposite direction to that for C—F bond in CHF$_3$. This fact may suggest that bond polarizabilities of C—F bonds in CHF$_3$ and in CHClF$_2$ are opposite direction in each other. This situation is apparent from Table III where A values for C—F bonds in them have opposite signs each other.

Temperature-dependences of A and $(\sigma_0)_{obs}$ may be interpreted in the effect ii) in Chapter II-(d), for the diverged 2p electron cloud of fluorine atom can be rather easily distorted by collisions. Furthermore, the exchange interation between two electron clouds of colliding molecules may have to be considered[8]. Unfortunately

there are no data as yet to test these interpretations.

It may be pointed out that it would be considerable interest to observe temperature-dependences of A, B and $(\sigma_0)_{obs}$ for symmetric molecules, for example, CH_3F, CHF_3 and $CHCl_3$, which will possess more significant temperature-dependencies than these of $CHClF_2$ if above interpretations come true.

V. References

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