^{19}F nuclear spin relaxation by intermolecular magnetic dipole coupling. CF_4 and SiF_4 in oxygen gas

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(Received 10 August 1990; accepted 24 September 1990)

The ^{19}F spin relaxation in CF_4 in oxygen gas and in SiF_4 in oxygen gas has been measured as a function of density, temperature, and magnetic field. The spin–rotation (intramolecular) and the nuclear spin dipole–electron spin dipole interactions (intermolecular) are the dominant mechanisms. The field dependence of the dipolar relaxation rates is characterized for CF_4–O_2 and SiF_4–O_2, and compared with those for other spherical top-O_2 systems. Agreement of theoretical estimates with the observed field dependence is satisfactory. The temperature dependences of the collision efficiencies for the CF_4–O_2 and SiF_4–O_2 intermolecular relaxation have been determined. The magnitudes are found to be roughly three times that for hard spheres.

INTRODUCTION

Nuclear spin relaxation times provide information about molecular dynamics. In the gas phase this information comes in the form of collision cross sections for molecular reorientation and transfer of rotational energy when the spin-rotation relaxation mechanism dominates. Other types of collision cross sections closely related to those from depolarized Raman scattering or nonresonant microwave absorption are obtained when the quadrupolar interaction is solely responsible for relaxation. These are *intra*molecular mechanisms, i.e., the interactions involved in the spin relaxation are always present within the molecule of interest; collisions interrupt molecular rotation and thereby introduce the fluctuations of local magnetic fields or electric field gradients that lead to nuclear spin relaxation. On the other hand, in an *inter*molecular mechanism the interaction which produces spin relaxation is "on" only during a collision. These therefore contain information about the system dynamics in the duration of a collision. By their nature, the dependence of *inter*molecular relaxation mechanisms on density, temperature, and magnetic field are very different from those of *intra*molecular mechanisms. It is possible to take advantage of such differences to separate out the intermolecular mechanisms precisely from the ever-present intramolecular ones in the gas phase. One specific situation in which the intermolecular mechanism can become competitive is in relaxation where electron spin dipole–nuclear spin dipole interactions are present. In particular, the electron-spin-bearing collision partner is molecular oxygen. In this paper, we show that this separation can be carried out quantitatively and we examine the nature of the information which can be obtained about the collision pair.

Why should there be a magnetic field dependence? The duration of a collision, during which time CF_4 and O_2 or SiF_4 and O_2 molecules are close enough for the electron spin dipole–nuclear spin dipole interaction to cause nuclear spin transition, lasts for only a tiny fraction (1 part in 10^4) of the Larmor period of the ^{19}F nucleus, but lasts for a sizable fraction (0.04–0.2) of the Larmor period of the electron spin at the magnetic fields of this study, 1.9–9.4 T.

For ^{19}F nuclei in molecules in the gas phase, the spin rotation (SR) mechanism is known to dominate the spin relaxation.[1] O_2 gas is just another buffer gas providing collisions which lead to reorientation of the ^{19}F-bearing molecules, thereby causing ^{19}F spin relaxation via the *intra*molecular spin rotation interaction. In addition, the O_2 molecule provides an *inter*molecular dipole–dipole (DD) mechanism. In this paper we separate out these two mechanisms, of which the SR part is well understood and characterized by previous studies.[1-3] We show how effectively such a separation can be achieved empirically by studying the density and temperature dependence of the observed T_1 and making use of the known SR relaxation characteristics. The remaining contribution $1/T_1^{DD}$ is then characterized in terms of an effective cross section which is temperature dependent.

For a mixture of CF_4 and O_2 the $T_1(^{19}F)$ is given by

$$\frac{1}{T_1} = \frac{1}{T_1^{SR}} + \frac{1}{T_1^{DD}}, \tag{1}$$

where T_1^{SR} is known by theory[4] and experiment[2,5,6] to be additive in the sense that

$$T_1^{SR} = (T_1/\rho)_{CF_4-CF_4}\rho_{CF_4} + (T_1/\rho)_{CF_4-O_2}\rho_{O_2} \tag{2}$$

$(T_1/\rho)^{SR}_{CF_4-CF_4}$ is fully characterized by our T_1 measurements in pure CF_4 gas.[2] An initial guess for $(T_1/\rho)^{SR}_{CF_4-O_2}$ can be estimated from T_1 measurements in CF_4 in various buffer gases.[2] A behavior not unlike that of CF_4–N_2 may be expected, so we may assume

$$(T_1/\rho)^{SR}_{CF_4-O_2} = (T_1/\rho)^{SR}_{CF_4-O_2}(300\ \mathrm{K})\cdot(T/300)^{-1.5}. \tag{3}$$

When the estimate for $(T_1/\rho)^{SR}_{CF_4-O_2}$ at 300 K is good, the remainder, $(1/T_1 - 1/T_1^{SR})$ should show a direct proportionality to the O_2 density at all temperatures and all fields. Thus, $1/T_1^{DD}$ can be isolated and its dependence on temperature and magnetic field can be characterized. We report these studies for CF_4 in O_2 and for SiF_4 in O_2.

0021-9606/91/010172-07$03.00

EXPERIMENT

Samples of CF_4 in O_2 and of SiF_4 in O_2 were made by freezing out the gases individually from a calibrated volume into a previously calibrated sample tube. Nuclear magnetic resonance (NMR) measurements were made at magnetic fields of 1.9, 4.7, and 9.4 T on Bruker WP80, WP-200SY, and AM-400 spectrometers, respectively. T_1 measurements used a standard inversion recovery pulse sequence. Further details can be found in Ref.7. The standard deviation in the determination of T_1 was less than 0.5% except at the lowest field in which it was 0.5–1.5%.

From Eq. (1) it is clearly advantageous to use relatively high densities of CF_4 gas because $(T_1/\rho)_{CF_4\text{–}CF_4}$ is well known and furthermore, high densities in Eq. (2) lead to large values of T_1^{SR} so that the measured $1/T_1$ is largely $1/T_1^{DD}$. On the other hand, the iterative determination of $(T_1/\rho)^{SR}_{CF_4\text{–}O_2}$ at 300 K converges faster when most of T_1^{SR} is due to CF_4–O_2 collisions, i.e., if CF_4 is kept at constant small densities and ρ_{O_2} is varied over a wide range. The samples with small constant ρ_{CF_4} (variable ρ_{O_2}) lead to best initial estimates of the value of $(T_1/\rho)^{SR}_{CF_4\text{–}O_2}$ at 300 K. Then systematic adjustment of the unknown $(T_1/\rho)^{SR}_{CF_4\text{–}O_2}$ contribution is possible. The experimental procedure used for CF_4 is a combination of both strategies. The samples studied contained a range of densities of O_2 (4 to 33 amagat), to observe the competition between DD and SR, covering the range of relaxation rates such that the rates are 11–78% due to the DD mechanism and 89–22% due to the SR mechanism.

The strategy used for SiF_4 was somewhat different due to the smaller effective spin rotation constant for ^{19}F in SiF_4. The characterization of the SR mechanism for SiF_4 in various buffer gases had not been carried out previously. With the smaller spin rotation interaction it would have been possible to achieve the same range of DD/SR ratios as in CF_4 only by using a lower range of total densities and with lower densities of oxygen. We chose to leave the SR contribution less well defined, determining $(T_1/\rho)^{SR}_{SiF_4\text{–}O_2}$ at 300 K to fewer significant digits than the CF_4–O_2 system. Total densities of SiF_4–O_2 mixtures were 30–34 amagat in all samples with 6–32 amagat of O_2, insuring the dominance of the DD contribution. The results bear out these estimates.

RESULTS AND DISCUSSION

In Fig. 1, the curves are not individually fitted to the experimental data. All curves are given by Eq. (1), where

$$T_1^{SR} = \sum_{i = CF_4, O_2} (T_1/\rho)_{i,300\,K} (T/300)^{n_i} \rho_i \qquad (4)$$

and

$$1/T_1^{DD} = B(T/300)^m \rho_{O_2}. \qquad (5)$$

n_i are the values -1.41 for CF_4–CF_4 (taken from a study in pure CF_4 gas),[2] and -1.50 for CF_4–O_2 (assumed). $(T_1/\rho)^{SR}_{300\,K}$ for CF_4–CF_4 is taken from the pure gas experiments,[2] and the best value of $(T_1/\rho)^{SR}_{300\,K}$ found for CF_4–O_2 is 0.0012 s amagat^{-1}. At each magnetic field, B and m are numbers which result from a best fit to Eq. (5) of the data points of the 3 samples labeled H, I, and J in Fig. 1. Note that this gives a good description of the eight other samples as well, which is an indication that we have a reasonably good accounting of the spin–rotation contribution from CF_4–O_2 collisions in using $(T_1/\rho)^{SR}_{CF_4\text{–}O_2} = 0.0012\,(T/300)^{-1.5}$. As in Fig. 1, all the curves in Fig. 2 for a given magnetic field are described by the Eqs. (1), (4), and (5). Here n_i are -1.5 for SiF_4–SiF_4 (taken from a study in pure SiF_4 gas),[3] and -1.50 for SiF_4–O_2 (assumed). $(T_1/\rho)^{SR}_{300\,K} = 0.0812$ s amagat^{-1} for SiF_4–SiF_4 is taken from the pure gas experiments,[1,3] and the best value of $(T_1/\rho)^{SR}_{300\,K}$ for SiF_4–O_2 is found to be 0.006 s amagat^{-1}. At each magnetic field, B and m are numbers which result from a best fit to Eq. (5) of data points of the 3 samples with the highest density of O_2. That this gives a good description of the two samples with the lower densities of O_2 as well, is an indication of the reasonably good estimate for the spin rotation contribution from SiF_4–O_2 collisions with $(T_1/\rho)^{SR}_{SiF_4\text{–}O_2} = 0.006\,(T/300)^{-1.5}$.

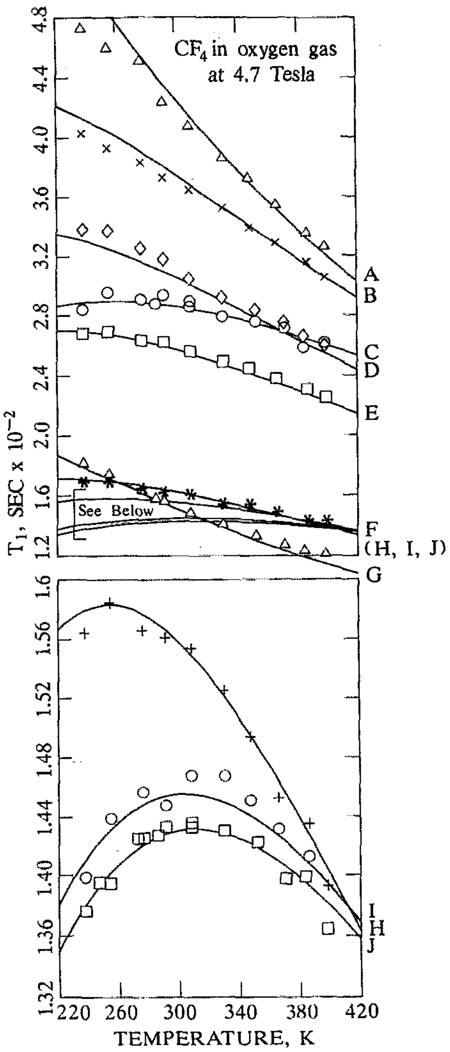

FIG. 1. The curves are not individually fitted to the experimental data. All curves are given by the same equation (see text). The densities of CF_4 and O_2, respectively, in the samples are $A = 26.641$, 4.166 amagat; $B = 27.392$, 7.444; $C = 26.385$, 14.183; $D = 21.679$, 9.992, $E = 18.193$, 13.684; $F = 3.452$, 21.554; $G = 2.757$, 13.007; $H = 3.053$, 26.020; $I = 3.015$, 32.375; $J = 2.735$, 33.447.

It is clear in Fig. 2 that the characteristics of the intermolecular DD mechanism (which varies with temperature

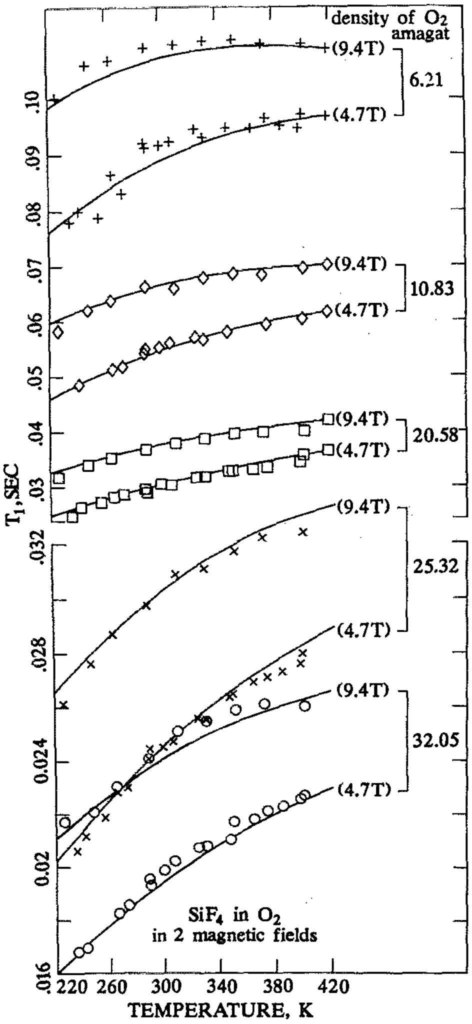

FIG. 2. As in Fig. 1, the curves for a given magnetic field are all described by a single equation (see text). Densities of SiF_4 in O_2 are (in amagat) 27.00 SiF_4 in 6.21 O_2, 18.75 SiF_4 in 10.83 O_2, 14.15 SiF_4 in 20.58 O_2, 6.15 SiF_4 in 25.32 O_2, and 1.40 SiF_4 in 32.05 O_2.

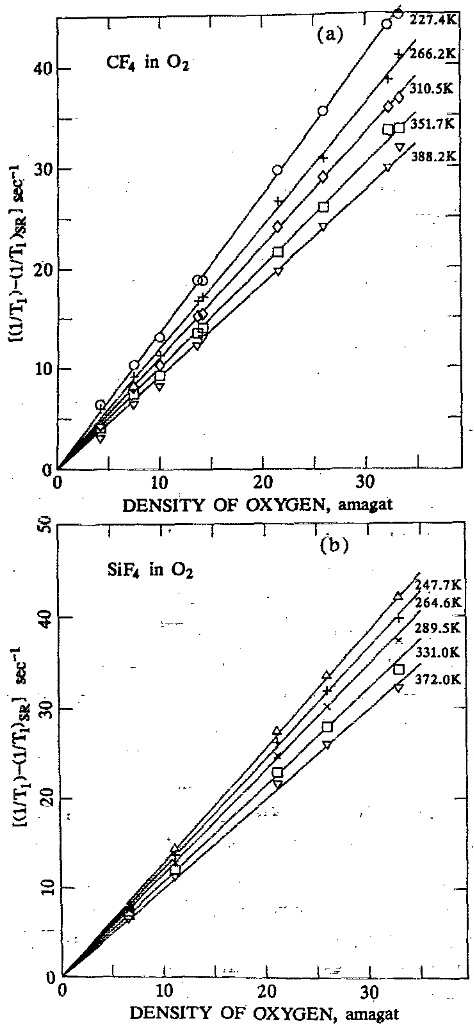

FIG. 3. (a) and (b) data taken at a magnetic field of 9.4 T are shown, giving a clear linear dependence of the remainder relaxation rate after the spin rotation contributions by XF_4–XF_4 and XF_4–O_2 collisions are subtracted out. Data at other fields give the same linear dependence on the density of O_2.

in the opposite sense to that of SR mechanism) are more pronounced in SiF_4–O_2 samples of comparable composition, that is, the SR contribution in SiF_4–O_2 samples is smaller than in CF_4–O_2 samples of comparable composition. For example, compare the temperature variation of T_1 of CF_4 in O_2 in the sample labeled B in Fig. 1 with the SiF_4–O_2 sample containing 6.21 amagat O_2 in Fig. 2, D or E (Fig. 1) with the 10.83 amagat (Fig. 2), H (Fig. 1) with the 25.32 amagat (Fig. 2), and I or J (Fig. 1) with the 32.05 amagat sample (Fig. 2). These SiF_4–O_2 samples had relaxation rates that varied with temperature such that the rates are 68–90% DD for the sample with 6.21 amagat O_2, 74–91% DD for the sample with 10.83 amagat O_2 and 81–95% DD for the 3 samples with highest densities in O_2.

Figure 3 shows that with the properly chosen single value of $(T_1/\rho)^{SR}_{300\,K}$ for the CF_4–O_2 collisions, the remainder, $(1/T_1 - 1/T_1^{SR})$, presumably entirely due to the intermolecular dipole–dipole interaction mechanism, should show a direct proportionality to the density of oxygen at all temperatures and all fields. This is indeed found and Fig. 3 shows the typical results at one field. The same direct proportionality to the density of oxygen is found at all fields, confirming the adequate characterization of the $1/T_1^{SR}$ contribution. The temperature dependence of this remainder which we now identify as $1/T_1^{DD}$ appears to follow a power law. Figure 4 shows this for all the samples of SiF_4 in O_2 at 4.7 T. The results for CF_4 in O_2 give the same typical plot as Fig. 4 at each of 3 fields, with a different slope for each field. A part of this temperature dependence has to do with the explicit $(\pi\mu/8kT)^{1/2}$ which appears in the theoretical limit for a hard sphere potential at the high translational energy limit, in the zero magnetic field limit ($\omega = 0$), which is given by

$$\left(\frac{1}{T_1^{DD}}\right)_{\text{theor.lim.}} = \frac{16}{3} S(S+1)\gamma_I^2\gamma_S^2 \frac{\hbar}{d^2}\left(\frac{\pi\mu}{8kT}\right)^{1/2} N_S. \quad (6)$$

The number density N_S of molecules carrying spin S is known from ρ_{O_2}. Different theoretical approaches by Chen and Snider,[8] Bloom and Oppenheim,[9] and by Shizgal[10] all lead to this same limiting form.

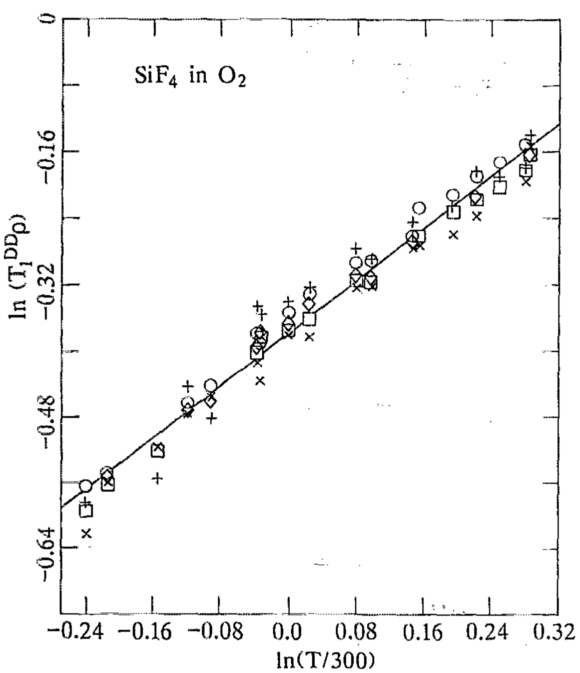

FIG. 4. The non-SR contribution to T_1 exhibits a power law dependence on temperature. This figure includes all samples of SiF$_4$ in O$_2$ observed at a magnetic field of 4.7 T. The slope is 0.78. A similar plot is obtained for SiF$_4$ in O$_2$ at 9.4 T and for CF$_4$ in O$_2$ for each of 1.9, 4.7, and 9.4 T.

We take the ratio of the measured $1/T_1^{DD}$ to the theoretical limit given by Eq. (6). These ratios,

$$j(T,\omega) = (1/T_1^{DD})_{\text{obs}}/(1/T_1^{DD})_{\text{theor.lim.}},$$

are shown in Figs. 5(a) and 5(b). These ratios contain the information about the field dependence and the collision efficiency, both of which are temperature dependent.

In the low frequency limit the field dependence of the intermolecular dipole relaxation in the gas phase can be written in the form,[7,11]

$$\frac{1}{T_1^{DD}} = \frac{1}{T_1^{(0)}}\{1 - f(T)\sqrt{\omega_I}\}. \tag{7}$$

Comparison of the T_1^{DD} at two magnetic fields directly provides the empirical function $f(T)$ in the above equation, without making any assumptions as to the temperature dependence or functional form of $T_1^{(0)}$ or of $f(T)$, only that $T_1^{(0)}$ is field-independent. From the form of Eq. (7), empirical values of $f(T)$ can be obtained from the data at any two magnetic fields with ^{19}F resonance frequencies ω_1 and ω_2 as follows:

$$f(T) = \left(\frac{T_1^{DD}(\omega_2)}{T_1^{DD}(\omega_1)} - 1\right)\left(\frac{T_1^{DD}(\omega_2)}{T_1^{DD}(\omega_1)}\,\omega_2^{1/2} - \omega_1^{1/2}\right)^{-1}. \tag{8}$$

The results are shown in Figs. 6(a) and 6(b), fitted to a quadratic function of temperature. Using this $f(T)$ function, T_1 values at all magnetic fields can be converted to the zero-field limit $T_1^{(0)}$.

Finally, the ratios $(1/T_1^{(0)})/(1/T_1^{DD})_{\text{theor.lim.}}$ provide the collision efficiencies which depend on the CF$_4$–O$_2$ or SiF$_4$–O$_2$ intermolecular potential. We denoted these collision efficiencies by $F(V/kT)$ which are shown in Fig. 7(a) and 7(b). These results include all the data for SiF$_4$ in O$_2$ (5 samples, 2 fields, all temperatures in this study). Only the data for the three samples with the highest density of oxygen are shown for CF$_4$ in O$_2$ at 2 fields, all temperatures. In both systems the temperature dependence of $F(V/kT)$ is sufficiently well defined by the data shown in Fig. 7. With the measured collision efficiencies, one can define the effective cross sections

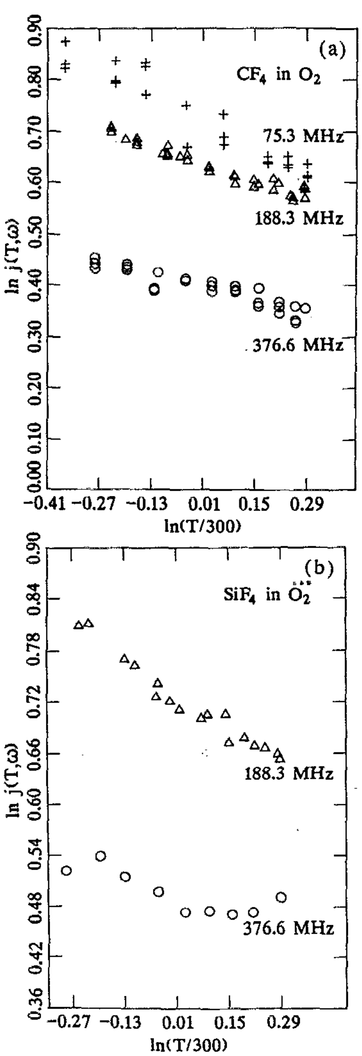

FIG. 5. The $j(T,\omega)$ plotted here is the ratio $(1/T_1^{DD})_{\text{actual}}/(1/T_1^{DD})_{\text{theor.lim.}}$. The points shown in (a) are for 3 samples of CF$_4$ with the highest O$_2$ densities at 1.9, 4.7, and 9.4 T. In (b) are data for one sample of SiF$_4$ in O$_2$ at magnetic fields at 4.7 and 9.4 T in which the resonance frequencies are as shown above.

$$\sigma_{\text{eff}} = F(V/kT)\cdot\pi d^2, \tag{9}$$

where the parameter d is the same one used in the theoretical limit, Eq. (6). The empirical results $F(V/kT)$ in Fig. 7 can be compared with theoretical estimates based on the relaxation theory of Bloom and Oppenheim,[12]

$$F(V/kT) = 2\pi\int_0^\infty dy\left\{\int_0^\infty [g(x)]^{1/2} j_{5/2}(xy)\,x^{-3/2}\,dx\right\}^2, \tag{10}$$

where x is the reduced intermolecular distance r/d, and $g(x)$

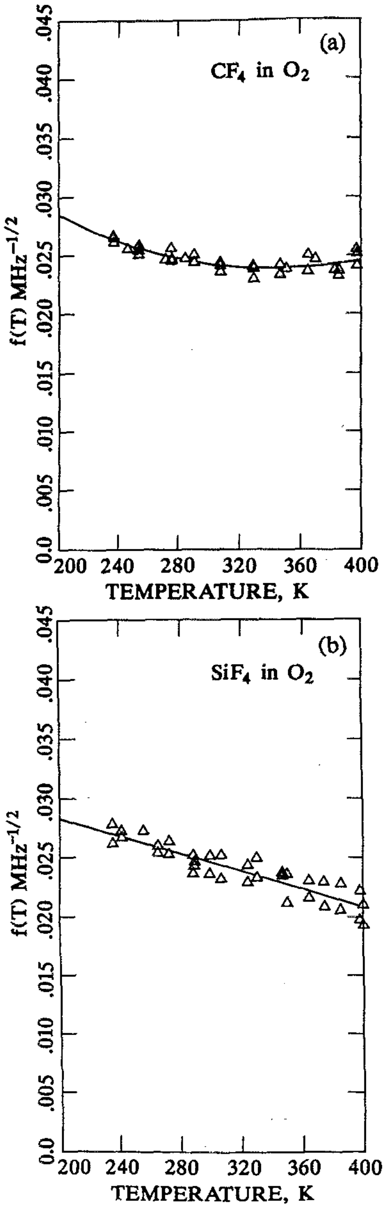

FIG. 6. The field dependence of the intermolecular dipole–dipole relaxation times is expressed in the form $1/T_1 = (1/T_1^{(0)})(1 - f(T)\sqrt{\omega_I})$. The experimental values of $f(T)$ are shown for (a) CF$_4$ in O$_2$ (the 3 samples with the highest O$_2$ densities) and (b) SiF$_4$ in O$_2$ (the data points only for the 2 samples with the highest O$_2$ densities are drawn in).

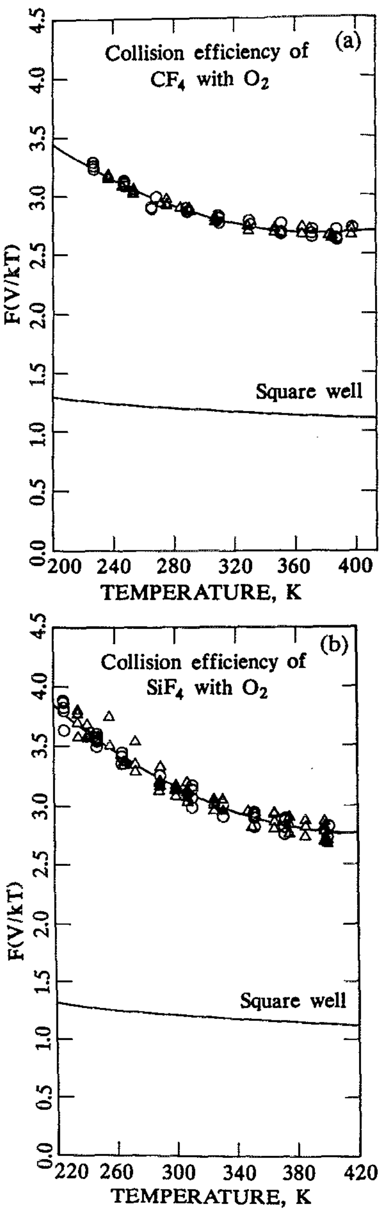

FIG. 7. This function is obtained from $(1/T_1^{(0)})/(1/T_1)_{\text{theor.lim.}}$ where the theoretical limit is given in Eq. (6). At 188.3 (△) and 376.6 MHz (○), part (a) shows the data for the three samples of CF$_4$ with the highest oxygen densities; part (b) shows the data for all samples of SiF$_4$ in O$_2$. Each is compared with the function based on the Bloom–Oppenheim model (CAA approximation, Ref. 12) for a square well potential (Ref. 13) with depth $V_0/k = 76$ and 80 K, respectively, for the CF$_4$–O$_2$ and the SiF$_4$–O$_2$ collision pair.

is the radial distribution function $g(x) = e^{-V(x)/kT}$ of the CF$_4$–O$_2$ molecular pair in the dilute gas. For a square well potential with depth V_0, the $F(V/kT)$ can be written in closed form[13]

$$F(V_0/kT) = e^{-V_0/kT} + 0.31(e^{-V_0/2kT} - 1)^2 - 0.72(e^{-V_0/2kT} - 1)e^{-V_0/2kT}. \tag{11}$$

The above functions are plotted in Fig. 7 for square wells of depth 0.56ϵ which are $V_0/k = 76$ K and an estimated 80 K, respectively, for CF$_4$–O$_2$ and for SiF$_4$–O$_2$. The much smaller theoretical estimates compared to experiment are likely due to the inadequacy of the approximations which result in the form of $F(V/kT)$ in Eq. (10) rather than the assumed potential shape which gives $F(V_0/kT)$. The results are summarized in Tables I[14] and II.

The ratios $j(T,\omega)$ shown in Fig. 5 are the values we have represented by $F(V/kT)\{1 - f(T)\sqrt{\omega_I}\}$. In analogy with liquid phase models (see discussion in Ref. 11), $j(T,\omega)$ can also be interpreted as the reduced spectral density functions for an interacting CF$_4$–O$_2$ molecular pair, as defined by

TABLE I. Empirical characterization of the ^{19}F dipolar interaction with electron spins in CF_4 in O_2 gas and theoretical estimates.

$r_0/\text{Å}$	3.992 [a]
$\left(\frac{\omega_I}{2\pi}\right)/\text{MHz}$	75.3, 188.3, 376.5
$B(T,\omega=0)/\text{s}^{-1}\ \text{amagat}^{-1}$	$(2.173\pm0.041)(T/300)^{-0.831\pm0.014}$
$f(T)_{\text{obs.}}$ [b] $/\text{MHz}^{-1/2}$	$(0.0243\pm0.0005)-(1.93\pm0.18)\times10^{-5}(T\text{-}300)$ $+2.23\times10^{-7}\ (T\text{-}300)^2$
$f(T)_{\text{theor.est.}}/\text{MHz}^{-1/2}$	$0.0223\ (T/300)^{-0.33}$
$F(V/kT)$ [b]	$(2.829\pm0.031)-(0.376\pm0.008)\times10^{-2}\ (T\text{-}300)$ $+2.45\times10^{-5}\ (T\text{-}300)^2$
$F(V_0/kT)_{\text{square well}}$ [c]	1.184 at 300 K

[a] From Maitland *et al.* Table A3.2 (Ref. 14).

[b] Experimental results were fitted to a quadratic function in temperature, $T = 240$–400 K.

[c] Square well $V_0/k = 76$ K was used, from $V_0 = 0.56\,\epsilon$ using ϵ from Maitland *et al.* Table A3.1 (Ref. 14).

Abragam:[15]

$$j(T,\omega) = \tfrac{1}{10}\{\bar{j}_2(\omega_I-\omega_S)+3\bar{j}_2(\omega_I)+6\bar{j}_2(\omega_I+\omega_S)\}. \tag{12}$$

The $j(T,\omega)$ functions shown in Fig. 5 are for $\omega/2\pi = 75.3$, 188.3, and 376.6 MHz. If the interpretation of $j(T,\omega)$ is taken to be that of reduced spectral density functions, then the magnitude of the field dependence can be estimated theoretically. The expected behavior of the limiting form of $\bar{j}(\omega)$ is

$$\bar{j}_2(\omega) = \bar{j}_2(0) - \frac{1}{8}\left(\frac{\omega d}{\bar{v}}\right)^{1/2} + \cdots \tag{13}$$

in replacing the translational correlation time in liquid models $\tau_{\text{tr}} = d^2/D$ by the analogous characteristic time in the gas phase, $d/\bar{v}$. Using this, a theoretical estimate for $f(T)$ has been derived[7,11] in the low Larmor frequency limit:

$$f(T) = \frac{1}{24}\left(\frac{d}{\bar{v}}\right)^{1/2}[3+7(\gamma_S/\gamma_I)^{1/2}]. \tag{14}$$

This equation is based on Abragam's $\bar{j}_2(0) = 2/15$,[15] rather than the alternate Hwang and Freed value $\bar{j}_2(0) = 4/27$.[16] Using Eq. (14), this theoretical estimate is $f(T) = 0.017\,21\ (T/300)^{-0.25}\ \text{MHz}^{1/2}$ for CF_4 in O_2 and $f(T) = 0.017\,86\ (T/300)^{-0.25}\ \text{MHz}^{1/2}$ for SiF_4 in O_2.

The actual magnetic field (or frequency) dependence observed in Fig. 5 can then be compared with this. As we have also found for SF_6 in O_2 (Ref. 7) for CH_4 in O_2,[17] and for SeF_6 in O_2 and TeF_6 in O_2 as well,[18] the experimental function $f(T)$ obtained from studies at 2 or 3 fields is greater than the theoretical estimate from Eq. (14) by a factor of 1.2 to 1.4 in all cases of ^{1}H and ^{19}F observed in the presence of oxygen. This expression [Eq. (14)] for the theoretical estimate was derived by replacing a translational correlation time for liquids by an analogous characteristic time in the gas, the average duration of a collision, taken to be $d/\bar{v}$. The characteristic length d was arbitrarily set to the parameter r_0 in the conformal isotropic intermolecular potential function for CF_4–O_2 (or SiF_4–O_2). If instead we use the more appropriate distance, d_{eff} obtained from the effective cross section in Eq. (9), the original $(d/\bar{v})^{1/2}$ factor in $f(T)$ in Eq. (14) will be multiplied by a factor $[F(V/kT)]^{1/4}$. In Table III, a comparison is made between this improved theoretical estimate of $f(T)$ and the observed $f(T)$. The agreement between experimental and theoretical values is uniformly good, leading to the conclusion that the magnetic field dependence in these systems is now well understood. Furthermore, the modest temperature dependence of $[F(V/kT)]^{1/4}$ would modify the theoretical estimate for the temperature dependence of $f(T)$ from one which is exactly that of $\bar{v}^{-1/2}$, i.e., $T^{-1/4}$ to one which is closer to $T^{-0.34}$.

From the final results it is possible to verify whether the

TABLE II. Empirical characterization of the ^{19}F dipolar interaction with electron spins in SiF_4 in O_2 gas and theoretical estimates.

$r_0/\text{Å}$	4.209 [a]
$\left(\frac{\omega_I}{2\pi}\right)\Big/\text{MHz}$	188.3 and 376.5
$B(T,\omega=0)/\text{s}^{-1}\ \text{amagat}^{-1}$	$(2.215\pm0.047)\ (T/300)^{-1.043\pm0.011}$
$f(T)_{\text{obs.}}$ [b] $/\text{MHz}^{-1/2}$ [b]	$(0.0243\pm0.001)-(4.12\pm0.27)\times10^{-5}(T\text{-}300)$ $+6.11\times10^{-8}\ (T\text{-}300)^2$
$f(T)_{\text{theor.est.}}/\text{MHz}^{-1/2}$	$0.0239\ (T/300)^{-0.39}$
$F(V/kT)$ [b]	$(3.160\pm0.0617)-(0.640\pm0.010)\times10^{-2}\ (T\text{-}300)$ $+2.68\times10^{-5}\ (T\text{-}300)^2$
$F(V_0/kT)_{\text{square well}}$ [c]	1.195 at 300 K

[a] Estimated from $r_0(CF_4\text{–}O_2) + r(\text{Si–F}) - r(\text{C–F})$.

[b] Experimental results were fitted to a quadratic function in temperature, $T = 240$–400 K.

[c] Using estimated $V_0/k = 80$ K.

TABLE III. Improved theoretical estimate for $f(T)$. All values shown are for 300 K.

$\frac{1}{24}\left(\frac{d}{\bar{v}}\right)^{1/2}$	$[3 + 7\gamma_S/\gamma_I]$	$[F(V/kT)]^{1/4}$	$f(T)_{\rm calc}$	$f(T)_{\rm obs}$
CH_4 [a]	0.01295	1.195	0.0155	0.0157
CF_4	0.01721	1.296	0.0223	0.0243
SiF_4	0.0179	1.333	0.0239	0.0243
SF_6 [b]	0.0183	1.310	0.0240	0.0214
SeF_6 [c]	0.01875	1.383	0.0259	0.0246
TeF_6 [c]	0.01916	1.3916	0.0267	0.0247

[a] Reference 17.
[b] Reference 7.
[c] Reference 18.

observations in this study were indeed in the range of conditions referred to as the "low frequency" limit. The low (Larmor) frequency limit refers to the physical situation in which the nuclear-spin-bearing molecule suffers several collisions during one Larmor precession. The CF_4 molecule in a 30 amagat sample of O_2 at 300 K suffers 3200 effective collisions with O_2 during one Larmor cycle of the ^{19}F nucleus in a field of 4.7 T, or 1600 effective collisions per Larmor cycle in a field of 9.4 T. For SiF_4 in a similar situation the numbers are, respectively, 3870 and 1930. At this field there are 4.6 (for CF_4) and 5.5 (for SiF_4) effective collisions per Larmor cycle of the electron spin. Thus, the observations reported in this work are in the low frequency limit. Further, they satisfy the condition that the duration of a collision is a fraction (less than one) of a Larmor cycle, i.e.,

$$0 < \omega_S \frac{d}{\bar{v}} < 1.$$

This fraction for CF_4 in O_2 at 300 K is 0.045, 0.101, and 0.202 at the magnetic fields of this study, 1.9, 4.7, and 9.4 T, respectively. For SiF_4 in O_2 at 300 K the duration of a collision is a fraction 0.043, 0.109, and 0.218 of the Larmor cycle of the electron spin at these magnetic fields.

The field dependence in both CF_4 in O_2 and SiF_4 in O_2 is such that the factor $\{1 - f(T)\sqrt{\omega_I}\} = 0.67$ and 0.53 at 300 K for fields of 4.7 and 9.4 T, respectively, where $\omega_I = 188.3$ and 376.5 MHz. These values are still in the range where the "low frequency" limiting expressions for spectral density functions are known to hold. At yet higher magnetic fields we do not expect the $\{1 - f(T)\sqrt{\omega_I}\}$ dependence to hold, for the terms in ω^2 eventually become important as is well known in studies in liquids.[19,20]

CONCLUSION

We were able to separate completely and precisely an *intra* (SR) and an *inter*molecular relaxation in the gas phase for ^{19}F in CF_4 and in SiF_4 in oxygen gas. For ^{19}F in CF_4 in O_2, in mixtures such that the relaxation rates are 10% intermolecular DD/90% SR up to 80% DD/20% SR, we successfully determined the density, temperature, and magnetic field dependence of the intermolecular DD relaxation rate, since the dependence of the rate of the two mechanisms on these 3 factors are opposite [i.e., ρ vs $1/\rho$, ca. T^{-1} vs $T^{+3/2}$, 1 vs $(1 - f(T)\omega_F^{1/2})$]. SiF_4 has a smaller effective spin rotation constant for ^{19}F than does CF_4. Nevertheless, an equally precise separation was possible for ^{19}F in SiF_4 in oxygen mixtures in which the relaxation rates are 70% DD/30% SR to 95% DD/5% SR. The DD part is found to be consistent with the theoretical limit for high translational energy hard sphere collisions in zero magnetic field, multiplied by a function $F(V/kT)$ which is temperature dependent and should contain information about the CF_4–O_2 (or SiF_4–O_2) intermolecular potential, and a third function which expresses the magnetic field dependence, a factor which is of the form $(1 - f(T)\omega_I^{1/2})$. Our theoretical estimate of $f(T)$ in the gas phase involves $d/\bar{v}$ rather than the d^2/D term in liquids. The theoretical values of the function $f(T)$ come very close to the empirical values when d is replaced by that which is the temperature dependent *effective diameter* for intermolecular dipole–dipole interactions.

ACKNOWLEDGMENT

This work has been supported in part by the National Science Foundation (Grants No. CHE85-05725 and No. CHE89-01426.

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