

# Competition of Intra- and Intermolecular Spin Relaxation Mechanisms for SF<sub>6</sub> in Oxygen Gas

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We have measured <sup>19</sup>F relaxation times in SF<sub>6</sub> in oxygen gas in which there are two dominant mechanisms for spin relaxation: spin-rotation (intramolecular) and nuclear spin electron spin dipole-dipole interaction (intermolecular). By studying the dependence of the overall relaxation rate on density, temperature, and magnetic field, we are able to separate the rates quantitatively and characterize both mechanisms. The field dependence of the dipolar relaxation rates in the gas phase is consistent with a factor (1 - f(T)ω<sub>1</sub><sup>1/2</sup>). The collision efficiencies for the intermolecular mechanism are about 3 times that for hard spheres, and we have obtained the dependence on temperature.

## Introduction

We have characterized the spin-rotation (SR) relaxation mechanism for nuclear spins in several simple molecules by studying systems in which the SR mechanism is so dominant that the other mechanisms have rates which are orders of magnitude smaller.<sup>2</sup> For <sup>19</sup>F in SF<sub>6</sub> in the presence of O<sub>2</sub> there are two mechanisms which are truly competitive, ranging from rate contributions which are 20%/80% up to 70%/30% in the range of densities and temperatures which we have studied. In this paper we report the results of measurements which show that it is possible to make a quantitative separation of the two contributions and to fully characterize the intermolecular dipolar mechanism in the gas phase for the first time. Although we have also completed spin relaxation studies for <sup>129</sup>Xe in mixtures of Xe and O<sub>2</sub> gas in which the intermolecular dipolar mechanism is overwhelmingly dominant,<sup>3</sup> it is only in this present work on SF<sub>6</sub> in O<sub>2</sub> that we have sufficient sensitivity to examine the form of the dependence on the magnetic field.

For <sup>19</sup>F in SF<sub>6</sub> in the presence of oxygen gas, two important mechanisms contribute to the relaxation rate constant 1/T<sub>1</sub>:

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)^{\text{SR}} + \left(\frac{1}{T_1}\right)^{\text{DD}} \quad (1)$$

The spin-rotation mechanism (SR) arises from the coupling between the <sup>19</sup>F nuclear spin and the SF<sub>6</sub> molecular rotation. Collisions which affect the rotation of the SF<sub>6</sub> molecule, i.e., collisions which reorient the molecule or transfer rotational energy, can contribute to the <sup>19</sup>F relaxation rate via this mechanism. The intermolecular interactions which cause these changes in the rotational angular momentum are the anisotropic forces which depend on the relative orientation of the SF<sub>6</sub>-O<sub>2</sub> or the SF<sub>6</sub>-SF<sub>6</sub> colliding pair. This is an intramolecular mechanism since the spin-rotation coupling is entirely within the SF<sub>6</sub> molecule and this is the only mechanism which is important for <sup>19</sup>F relaxation in SF<sub>6</sub> in various buffer gases at densities of the order of 1-50 amagat. We have studied the SR relaxation mechanism for <sup>19</sup>F in SF<sub>6</sub> in collision with SF<sub>6</sub>, CH<sub>4</sub>, CO, N<sub>2</sub>, the rare gases, CO<sub>2</sub>, and HCl.<sup>2</sup> On the basis of these studies we know the density and temperature dependence of T<sub>1</sub><sup>SR</sup> and can make a reasonably good estimate of the magnitude of the SR relaxation rate for SF<sub>6</sub> in mixtures with O<sub>2</sub>.

The direct interaction between the nuclear spin magnetic dipole and electron spin magnetic dipole on the O<sub>2</sub> molecule, an intermolecular dipole-dipole (DD) mechanism, also contributes to <sup>19</sup>F relaxation. Ordinarily intermolecular DD is insignificant in the gas phase. For this reason the <sup>3</sup>He relaxation time in pure helium gas is extremely long.<sup>4</sup> However, in this case the <sup>19</sup>F nuclear magnetic dipole is interacting with an electron spin dipole which is about 700 times as large as the nuclear dipole. In liquids, the presence of even a trace of oxygen provides a relaxation rate which is competitive with any intramolecular mechanisms.<sup>5</sup> In the gas phase the spin-rotation mechanism can be so efficient, such as for <sup>13</sup>C in CO gas or <sup>15</sup>N in N<sub>2</sub>, that O<sub>2</sub> behaves as a buffer gas no different from CO or N<sub>2</sub>.<sup>2</sup> The <sup>19</sup>F nucleus in SF<sub>6</sub> provides a good test because it is possible to study relaxation rates in samples in which, within a reasonable range of densities and temperatures, the relaxation rates by the two mechanisms range from 20% DD/80% SR to 70% DD/30% SR. We can characterize both mechanisms in the SF<sub>6</sub>-O<sub>2</sub> pair because the two rates have different behaviors with density, temperature, and magnetic field. Spin-rotation relaxation times are known to be additive, and each term is proportional to density:<sup>2</sup>

$$T_1^{\text{SR}} = \left(\frac{T_1}{\rho}\right)_{\text{SF}_6\text{-SF}_6}^{\text{SR}} \rho_{\text{SF}_6} + \left(\frac{T_1}{\rho}\right)_{\text{SF}_6\text{-O}_2}^{\text{SR}} \rho_{\text{O}_2} \quad (2)$$

We have already studied the first term in pure SF<sub>6</sub> gas, and the second term should not be greatly different from that in SF<sub>6</sub>-CO or SF<sub>6</sub>-N<sub>2</sub>, which we also have studied.<sup>2</sup> In contrast (1/T<sub>1</sub><sup>DD</sup>) is proportional to density of O<sub>2</sub>,<sup>6</sup> as we have observed for <sup>129</sup>Xe in O<sub>2</sub> gas.<sup>3</sup> The temperature variation of (1/T<sub>1</sub><sup>SR</sup>) is usually T<sup>+3/2</sup>,<sup>7</sup> while (1/T<sub>1</sub><sup>DD</sup>) has a T<sup>-1/2</sup> to T<sup>-1</sup> dependence, as we have seen in Xe in O<sub>2</sub> gas. Finally, (1/T<sub>1</sub><sup>SR</sup>) does not depend on the magnetic field at the densities in which the extreme narrowing condition is met, that is, for densities of 0.1 amagat or greater in most cases. On the other hand, (1/T<sub>1</sub><sup>DD</sup>) can have a magnetic field dependence.<sup>8</sup> In this work we measure the <sup>19</sup>F relaxation rates as a function of O<sub>2</sub> density and temperature in three magnetic fields in order to determine whether we can separate the observed rates quantitatively into SR and DD parts and also to be able to find the temperature and field dependence of the intermolecular DD relaxation mechanism.

## Experimental Section

Samples of SF<sub>6</sub> (3 amagat) in O<sub>2</sub> (16-33 amagat) were made by freezing out the gases individually from a calibrated volume

(1) (a) University of Illinois. (b) Loyola University.  
 (2) Jameson, C. J.; Jameson, A. K.; Buchi, K. *J. Chem. Phys.* **1986**, *85*, 697-700. Jameson, C. J.; Jameson, A. K.; Smith, N. C.; Jackowski, K. *J. Chem. Phys.* **1987**, *86*, 2717-2722. Jameson, C. J.; Jameson, A. K.; Smith, N. C. *J. Chem. Phys.* **1987**, *86*, 6833-6838. Jameson, C. J.; Jameson, A. K. *J. Chem. Phys.* **1988**, *88*, 7448-7452.  
 (3) Jameson, C. J.; Jameson, A. K.; Hwang, J. K. *J. Chem. Phys.*, in press (<sup>129</sup>Xe in O<sub>2</sub>).

(4) Chapman, R.; Richards, M. G. *Phys. Rev. Lett.* **1974**, *33*, 18.  
 (5) Abragam, A. *The Principles of Nuclear Magnetism*; Oxford University Press: London, 1961.  
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 (7) Johnson, C. S.; Waugh, J. S. *J. Chem. Phys.* **1962**, *36*, 2266-2272.  
 (8) Torrey, H. C. *Phys. Rev.* **1953**, *92*, 962-969. Sholl, C. A. *J. Phys. C* **1981**, *14*, 447-464.

into a previously calibrated sample tube (0.2–0.25 mL). The dead space above the sample tube was about 0.3 mL, so the vapor pressure correction for uncondensed O<sub>2</sub> could readily be made. Measurements were taken at three fields on Bruker WP-80, WP-200SY, and AM-400 spectrometers (at magnetic fields of 1.9, 4.7, 9.4 T, respectively). The low-field (WP-80) spectrometer required a field-frequency lock, so the sample (4-mm o.d.) was contained in the inner 5-mm tube of a concentric assembly with 10-mm outside diameter. The annular region contained lock solvent (DMSO or CDCl<sub>3</sub> depending on temperature). Limitations on the temperature regulation and accuracy had been previously determined. At the two higher fields data was taken unlocked (field drift is absolutely negligible over the short times of these experiments), with the temperature being determined by using the peak separation in sealed samples of ethylene glycol or methanol standards. The temperature range of these studies (400 K ≥ T ≥ 245 K) were limited instrumentally at the high end and by SF<sub>6</sub> condensation at the low end.

T<sub>1</sub> measurements were made by the standard inversion recovery pulse sequence. In this method of measurement we drive the spin system away from thermal equilibrium with a 180° pulse and monitor the return to thermal equilibrium,

$$\frac{d\langle I_z \rangle}{dt} = -\frac{1}{T_1} [\langle I_z \rangle - I_\infty] \quad (3)$$

where I<sub>∞</sub> is the thermal equilibrium value and ⟨I<sub>z</sub>⟩ is the average component of the nuclear spin angular momentum along the field B<sub>0</sub> at any time t. The nuclear spin signal intensity A is proportional to ⟨I<sub>z</sub>⟩. The rate then should obey the form

$$\frac{A_\infty - A_t}{A_\infty - A_0} = e^{-t/T_1} \quad (4)$$

Our results do indeed give an exponential rate of recovery and the rate constant 1/T<sub>1</sub> can be determined precisely. The standard deviation in the determination of T<sub>1</sub> was less than 0.5% except at the lowest field (an electromagnet) in which it was 0.5–1.4%. Since all the measured T<sub>1</sub> values were within the range 0.010–0.017 s, highly precise data are necessary for the quantitative separation of the relaxation rates into the two mechanisms.

## Results

Figure 1 shows the results obtained at 4.7 T, at which field the resonance frequency of the <sup>19</sup>F nucleus is 188.3 MHz. Analogous plots are obtained for the same samples at 1.9 T (75.3 MHz) and 9.4 T (376.6 MHz). In Figure 2 we show a comparison for one sample in three fields.

The curves shown in these figures are the calculated result of the separate parts in (1), the functional forms of which are given in Table I. The SF<sub>6</sub>–SF<sub>6</sub> SR contribution is previously known from studies in pure SF<sub>6</sub>. The temperature dependence of (T<sub>1</sub><sup>SR</sup>/ρ) for SF<sub>6</sub>–O<sub>2</sub> is taken to be T<sup>-1.5</sup> on the basis of SF<sub>6</sub>–CO and SF<sub>6</sub>–N<sub>2</sub>, as well as extensive SR studies on other nuclei in other gas-phase systems.<sup>2</sup> The magnitude of (T<sub>1</sub><sup>SR</sup>/ρ) at 300 K is determined by iteration, with the initial guess being values close to those for SF<sub>6</sub>–CO and SF<sub>6</sub>–N<sub>2</sub>. 1/T<sub>1</sub><sup>DD</sup> = [1/T<sub>1</sub> - 1/T<sub>1</sub><sup>SR</sup>] should show a linear behavior with the oxygen density at each temperature for each magnetic field. With these rather stringent conditions, the “best” value of (T<sub>1</sub><sup>SR</sup>/ρ)<sub>SF<sub>6</sub>-O<sub>2</sub></sub> at 300 K is obtained easily to three significant figures. The results at the intermediate field (4.7 T) are shown in Figure 3. Having found the SR part, we can now characterize the DD relaxation with respect to its dependence on temperature and the magnetic field:

$$1/T_1^{\text{DD}} = B(T, \omega) \rho_{\text{O}_2} \quad (5)$$

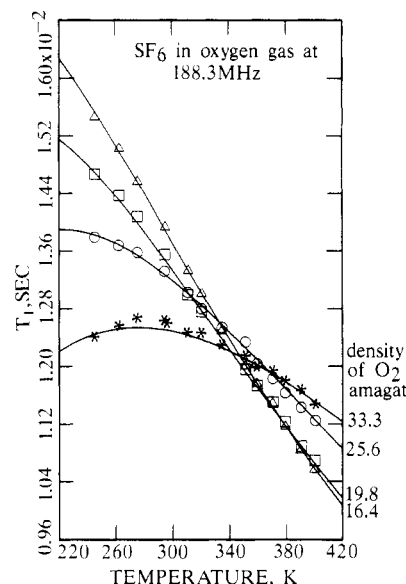
Figure 4 shows that B(T, ω) can be described by a power law, T<sup>-0.78</sup> at 4.7 T. The slopes of the plots for 1.9 and 9.4 T are different from this, which indicates to us that the field dependence has an associated temperature dependence. Table II summarizes the best fits to our numerical results at these three fields. As has been described in an earlier paper, the theoretical expression for

**TABLE I: Spin-Rotation Contribution to Relaxation Rates, Used To Fit the Data at All Three Magnetic Fields**

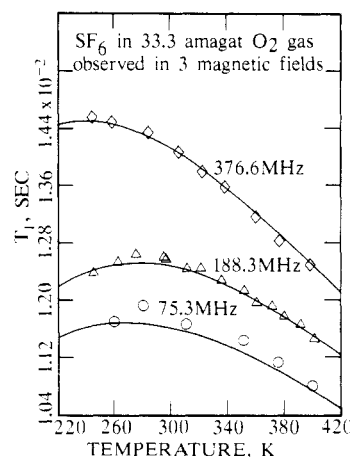
$$\left(\frac{T_1^{\text{SR}}}{\rho}\right)_{\text{SF}_6\text{-SF}_6} = (2.132 \times 10^{-3}) \left(\frac{T}{300}\right)^{-1.75} \text{ s amagat}^{-1}$$

$$\left(\frac{T_1^{\text{SR}}}{\rho}\right)_{\text{SF}_6\text{-O}_2} = (7.85 \times 10^{-4}) \left(\frac{T}{300}\right)^{-1.5} \text{ s amagat}^{-1}$$

$$T_1^{\text{SR}} = \left(\frac{T_1^{\text{SR}}}{\rho}\right)_{\text{SF}_6\text{-SF}_6} \rho_{\text{SF}_6} + \left(\frac{T_1^{\text{SR}}}{\rho}\right)_{\text{SF}_6\text{-O}_2} \rho_{\text{O}_2}$$



**Figure 1.** Measured relaxation times, T<sub>1</sub>, at 188.3 MHz for various samples containing 3 amagat SF<sub>6</sub> and various densities of O<sub>2</sub>. The curves are calculated from 1/T<sub>1</sub> = [1/T<sub>1</sub><sup>SR</sup> + 1/T<sub>1</sub><sup>DD</sup>], where T<sub>1</sub><sup>SR</sup> = (T<sub>1</sub><sup>SR</sup>/ρ)<sub>SF<sub>6</sub>-SF<sub>6</sub></sub> ρ<sub>SF<sub>6</sub></sub> + (T<sub>1</sub><sup>SR</sup>/ρ)<sub>SF<sub>6</sub>-O<sub>2</sub></sub> ρ<sub>O<sub>2</sub></sub> and 1/T<sub>1</sub><sup>DD</sup> = B(T) ρ<sub>O<sub>2</sub></sub>, where T<sub>1</sub><sup>SR</sup> is given in Table I and B(T) is given in Table II.



**Figure 2.** Comparison of measured relaxation times for a sample (containing 3 amagat SF<sub>6</sub> and 33.3 amagat O<sub>2</sub>) at three different magnetic fields. The labels are the <sup>19</sup>F resonance frequencies at these fields. The curves are T<sub>1</sub> functions calculated by the same equations as in Figure 1.

(1/T<sub>1</sub><sup>DD</sup>) for a hard sphere potential, at the high translational energy limit, in the zero-field limit (ω = 0) is known:<sup>9-11</sup>

$$\left(\frac{1}{T_1^{\text{DD}}}\right)_{\text{theor limit}} = \frac{16}{3} S(S+1) \gamma_1^2 \gamma_2^2 \frac{\hbar^2}{d^2} \left(\frac{\pi \mu}{8kT}\right)^{1/2} N_S \quad (6)$$

(9) Chen, F. M.; Snider, R. F. *J. Chem. Phys.* **1967**, *46*, 3937–3940.

(10) Oppenheim, I.; Bloom, M. *Can. J. Phys.* **1961**, *39*, 845–869.

(11) Shizgal, B. *Can. J. Phys.* **1976**, *54*, 164–175.

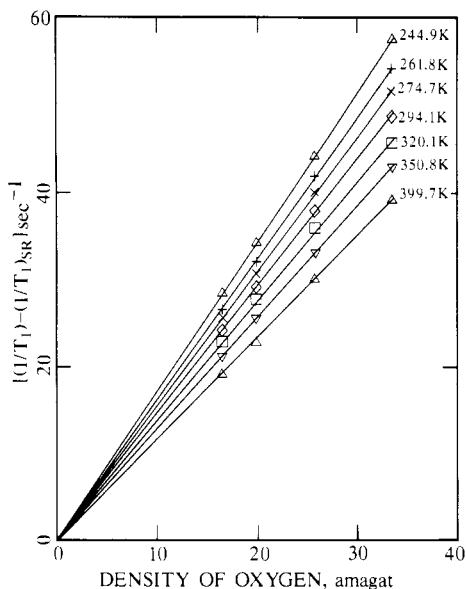


Figure 3. "Best"  $(T_1^{SR}/\rho)_{SF_6-O_2}$  obtained when  $(1/T_1 - 1/T_1^{SR})$  vs  $\rho_{O_2}$  gives straight lines at each temperature for all three fields, as shown here for  $\omega = 188.3$  MHz (field = 4.7 T).

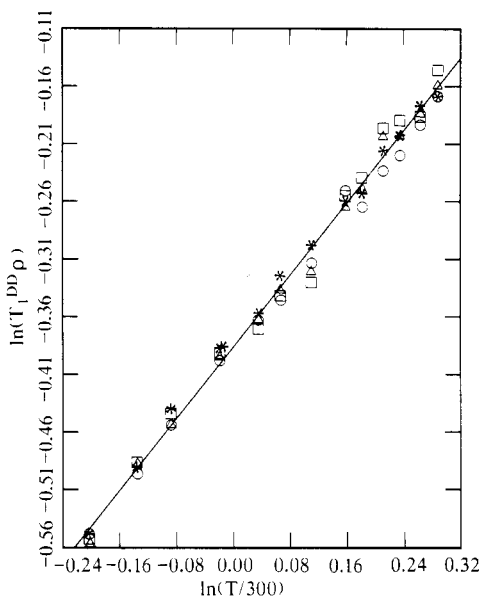


Figure 4. Plot of  $-\ln B(T)$  at 188.3 MHz. The temperature dependence of  $B(T)$  and of the dipolar relaxation is consistent with a power law  $T^{-0.78}$  at 188.3 MHz.

where  $N_S$  is the number density of S-bearing molecules,  $S(S+1) = 2$  for  $O_2$ ,  $\gamma_I$  and  $\gamma_S$  are respectively the  $^{19}F$  and electron spin magnetogyric ratios, and  $d$  is the hard sphere diameter. For finite temperatures, the relaxation rate can be written with a factor, which we denote by  $F(V/kT)$  to indicate its expected dependence on the intermolecular potential in the dilute gas.  $F(V/kT)$  goes to 1 at the high translational energy limit for a hard sphere potential. Furthermore, we have given in our previous work the theoretical arguments which lead to the field dependence being described by a factor  $[1 - f(T)\omega^{1/2}]$ , and which predict that in the gas phase  $f(T)$  can be written approximately as<sup>3</sup>

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

Thus, we consider our experimental dipolar relaxation rates in terms of

$$\frac{1}{T_1^{DD}} = \left( \frac{1}{T_1^{DD}} \right)_{\text{theor limit}} F(V/kT) \{1 - f(T)\omega^{1/2}\} \quad (8)$$

TABLE II: Intermolecular Dipole-Dipole Contribution to the Relaxation Rate

$$\frac{1}{T_1^{DD}} = B(T, \omega) \rho_{O_2}$$

$\omega_F/2\pi$ , MHz	$B(T, \omega)$ , $s^{-1} \text{ amagat}^{-1a}$
75.3	$(1.662 \pm 0.066)(T/300)^{-(0.659 \pm 0.058)}$
188.3	$(1.470 \pm 0.016)(T/300)^{-(0.783 \pm 0.010)}$
376.6	$(1.196 \pm 0.032)(T/300)^{-(0.718 \pm 0.028)}$

$$\frac{1}{T_1^{DD}} = B(T, \omega=0) \left[ 1 - f(t) \left( \frac{\omega_F/2\pi}{\text{MHz}} \right)^{1/2} \right] \rho_{O_2}$$

$$B(T, \omega=0) = \frac{16}{3} S(S+1) \frac{\gamma_F^2 \gamma_S^2 \hbar^2}{\bar{v} d^2} F(V/kT)^b$$

$$B(T, \omega=0) = (2.07 \pm 0.05)(T/300)^{-0.838 \pm 0.016}$$

$$\frac{f(T)}{\text{MHz}^{-1/2}} = (0.0214 \pm 0.0010) - (1.9 \times 10^{-5})(T - 300) + (1.2 \times 10^{-7})(T - 300)^2$$

$$\frac{f(T)}{\text{MHz}^{-1/2}} = (0.0216 \pm 0.0010)(T/300)^{-0.20 \pm 0.07}$$

<sup>a</sup> Obtained from a plot of  $\ln T_1^{DD} \rho_{O_2}$  vs  $\ln(T/300)$ . <sup>b</sup>  $F(V/kT)$  is shown in Table III.

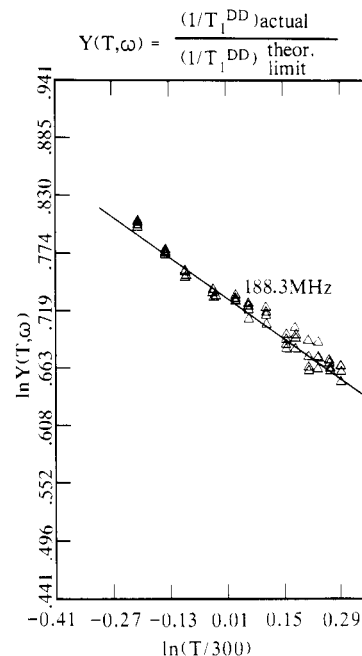


Figure 5. Dependence of the intermolecular dipolar relaxation rate on the intermolecular potential and the magnetic field,  $Y(T, \omega)$ , expressed as  $Y(T, \omega) = F(V/kT)(1 - f(T)\omega^\alpha)$ . Shown here are data for all the samples and temperatures at 4.7 T.  $T_1^{-1}$  (theoretical limit) is given in (6).

We show here that the field dependence is indeed consistent with the form shown above.

In Figure 5 we show the ratio  $[(T_1^{DD})_{\text{obsd}}^{-1}/(T_1^{DD})_{\text{theor limit}}^{-1}]$  for all samples at the intermediate field (4.7 T) and one sample for three magnetic fields in Figure 6. The relative vertical coordinates of the points in Figure 6 are given by  $\ln(1 - f(T)\omega^\alpha)$  since  $F(V/kT)$  is field independent. We see in Figure 6 that the exponent  $\alpha$  is a positive number. If we assume that  $\alpha = 1/2$ , then we can find a best fit to the function  $f(T)$  by

$$f(T) = \frac{\frac{T_1^{DD}(\omega_2)}{T_1^{DD}(\omega_1)} - 1}{\frac{T_1^{DD}(\omega_2)}{T_1^{DD}(\omega_1)} \omega_2^{1/2} - \omega_1^{1/2}} \quad (9)$$

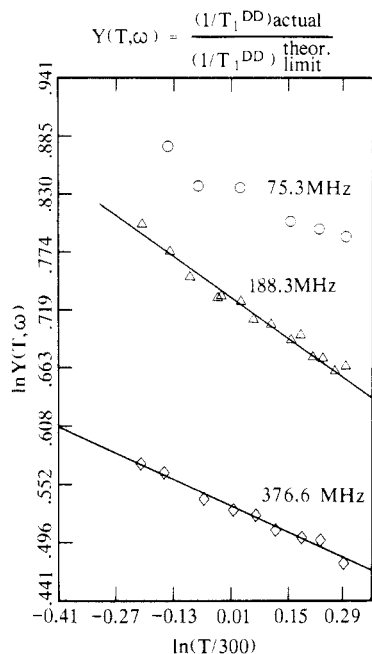


Figure 6. Same plot as Figure 5 for one sample in three magnetic fields. In this plot the relative vertical coordinates are  $\ln(1 - f(T)\omega^\alpha)$ .

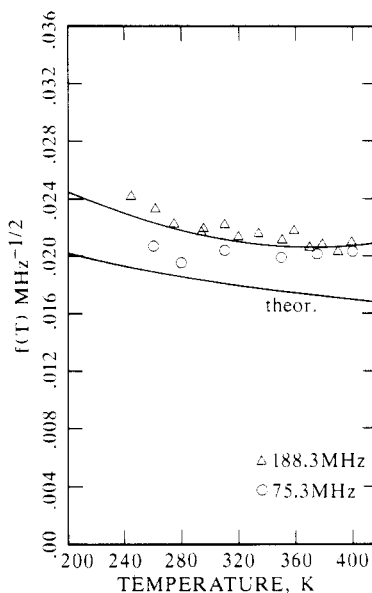


Figure 7. Best fit  $f(T)$ , compared with our theoretical estimate, if the field-dependent relaxation time is of the form  $1/T_1^{DD}(\omega) = [1/T_1^{DD}(\omega=0)]\{1 - f(T)\omega^{1/2}\}$ .

We find that  $\alpha = 1$  gives a considerably poorer fit. The function obtained by (9) based on  $\omega_1/2\pi = 376.6$  MHz is shown in Figure 7. The quadratic "best fit" curve is

$$f(T) = 0.0214 - (1.9 \times 10^{-5})(T - 300) + (1.2 \times 10^{-7})(T - 300)^2 \text{ MHz}^{-1/2} \quad (10)$$

or

$$f(T) = 0.0216(T/300)^{-(0.20 \pm 0.07)} \text{ MHz}^{-1/2} \quad (11)$$

This may be compared to the theoretical estimate from (7):

$$f(T) = 0.0183(T/300)^{-1/4} \text{ MHz}^{-1/2} \quad (12)$$

We see that our theoretical estimate is rather good for this system. The theoretical function in (12) is also shown in Figure 7 for comparison with the empirical data.

Finally, using this "best"  $f(T)$  function in (8) and using (6) for the zero-field, hard sphere, high-energy limit, we should be able to calculate  $F(V/kT)$  from every  $T_1$  measurement and find a

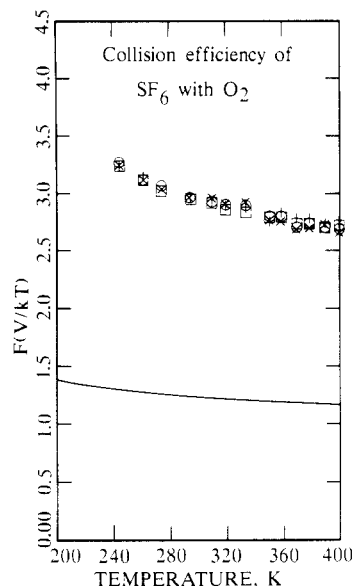


Figure 8. A single empirical function, the collision efficiency relative to hard spheres at the high energy limit,  $F(V/kT)$ , describing the dependence of the  $^{19}\text{F}$  relaxation rate on the intermolecular potential, obtained from data taken in all samples at 4.7 T. Also shown is the theoretical function  $[e^{V_0/kT} + 0.31(e^{V_0/2kT} - 1)^2 - 0.72e^{V_0/2kT}(e^{V_0/2kT} - 1)]$ , where  $V_0/k = 95$  K, based on the Bloom–Oppenheim CAA approximation.

TABLE III: Effective Cross Section for  $\text{SF}_6\text{-O}_2$  Intermolecular Dipole–Dipole Interaction

	$\sigma_{\text{eff}} = F(V/kT)\pi d^2$
hard sphere cross section	$\pi d^2 = 56.88 \text{ \AA}^2$ <sup>a</sup>
collision efficiency	$F(V/kT) = (2.95 \pm 0.07) - (3.43 \times 10^{-3})(T - 300) + (7.7 \times 10^{-6})(T - 300)^2$ <sup>b</sup>
	$F(V/kT) = (2.95 \pm 0.07)(T/300)^{-(0.338 \pm 0.016)}$ <sup>c</sup>

<sup>a</sup>Using  $d = r_0 = 4.255 \text{ \AA}$  from Maitland et al. Table A3.2. <sup>b</sup>Using a least-squares fit to a quadratic function, using data from all samples at all three magnetic fields. <sup>c</sup>Using a least-squares fit to a straight line of  $\ln F(V/kT)$  vs  $\ln T$  using data for all the samples at all fields.

unique  $F(V/kT)$  empirical function from our data at all three magnetic fields. Shown in Figure 8 is  $F(V/kT)$  obtained from the intermediate field for all samples. The values obtained in all three fields are superimposable with these. As we can see, this empirical function is relatively well-defined, which allows us to believe that we have used the correct form of the field dependence. The least-squares fit to all data points is shown in Table III.

We can consider this empirical  $F(V/kT)$  as a measure of the efficiency of the  $\text{SF}_6\text{-O}_2$  collisions (relative to collisions between hard spheres) in causing transitions between the nuclear spin states of the  $^{19}\text{F}$  nucleus via direct interaction with the electron spin dipole. There is also a scalar indirect interaction via the electrons which we shall dismiss (see below) as being insignificant. The magnitude of  $F(V/kT)$  is rather larger than expected. If we use Bloom and Oppenheim's model,  $F(V/kT)$  can be calculated from<sup>10</sup>

$$F(V/kT) = 2\pi \int_0^\infty dy \left[ \int_0^\infty [g(x)]^{1/2} j_{5/2}(xy) x^{-3/2} dx \right]^2 \quad (13)$$

where  $x$  is the reduced intermolecular distance,  $r/d$ , and  $g(x)$  is the radial distribution function  $g(x) = e^{-V(x)/kT}$  of the  $\text{SF}_6$  and  $\text{O}_2$  molecules in the dilute gas. When  $V$  is approximated by a square well potential,  $F(V/kT)$  can be calculated from (13) in the simple form:<sup>12</sup>

$$F(V/kT) = e^{-V_0/kT} + 0.31(e^{-V_0/2kT} - 1)^2 - 0.72(e^{-V_0/2kT} - 1)e^{-V_0/2kT}$$

$$\text{for } V = \infty, x < 1; V = V_0, 1 < x < 1.8; V = 0, x > 1.8 \quad (14)$$

(12) Bloom, M.; Lipsicas, M.; Muller, B. H. *Can. J. Phys.* **1961**, *39*, 1093–1109.

This reduces to  $F(V/kT) = 1.0$  for a hard sphere potential, ( $V = \infty$ ,  $x < 1$  and  $V = 0$ ,  $x \geq 1$ ). We find that, using the usual recipe of a square well depth,  $V_0 = 0.56\epsilon$  which is  $V_0/k \approx 95.5$  K for SF<sub>6</sub>-O<sub>2</sub>, gives values of  $F(V/kT)$  equal to 1.17 and 1.3 at 400 and 245 K, respectively, much smaller than the actual values of 2.69 and 3.2 at the same temperatures. Reproducing the latter values by using (14) would require multiplying the expression by 2.1 and a square well with depth about 150 K to mimic the shape of the empirical curve. It appears that a large part of the discrepancy between the calculated  $F(V_0/kT)$  and the  $F(V/kT)$  from experiment cannot be attributed to the inadequacy of the square well potential compared to a realistic potential, but is more likely due to the inadequacy of the approximations which resulted in (13).

Although we refer to (6) as the "theoretical limit", that is, the limiting case reached under the Born or the equivalent CAA approximation, exact calculations by Shizgal have shown that with a hard sphere spherical potential this limiting value is approached more slowly than by the CAA approximation and is exceeded at high translational energies. With the exact calculations using the hard sphere potential,  $F(V/kT)$  approaches 7/6 rather than 1 at very high translational energies. This does not affect the use of (6) and (8) together as a means of describing our data.

Why is there a field dependence in the gas phase and why does it take the form associated with the low-frequency limit ( $1 - f(T)\omega_1^{1/2}$ ) as opposed to the high-frequency limiting form,  $g(T)\omega_1^{-2}$ , or some other form? First, are we in the low-frequency limit, that is, does the nuclear spin bearing molecule suffer several collisions during one Larmor precession of the nucleus? The answer is yes. For example, at 4.7 T at 300 K in a sample of SF<sub>6</sub> in 30 amagat O<sub>2</sub>, SF<sub>6</sub> suffers 1200 hard sphere collisions per Larmor period of the nucleus, or, since we found the collision efficiency  $F(V/kT)$  is around 3.0, 3600 effective collisions during one Larmor period. Also, there are five effective SF<sub>6</sub>-O<sub>2</sub> collisions during one Larmor period of the electron spin.

Why should there be a magnetic field dependence? The duration of a collision, during which time SF<sub>6</sub> and O<sub>2</sub> are close enough for the dipole-dipole interaction to cause spin transitions (i.e., while they are within a distance that is the characteristic length of the interaction,  $d$ ), lasts for only 1/6200 of the Larmor period of the <sup>19</sup>F nucleus, but lasts for a sizable fraction (1/9) of the Larmor period of the electron spin at 4.7 T. Therefore, our SF<sub>6</sub>-O<sub>2</sub> system is not in the  $\omega = 0$  limit, so that a magnetic field dependence of the dipolar relaxation rate can be observed.

We have considered only the *direct* dipole-dipole interaction contribution from the electron spin. Although there is also an indirect (through the electrons) scalar  $AI \cdot S$  interaction (a primary mechanism for the large <sup>129</sup>Xe chemical shifts in the presence of O<sub>2</sub>),<sup>13</sup> the scalar coupling mechanism is far too small to be considered in <sup>129</sup>Xe in O<sub>2</sub> or for <sup>19</sup>F in SF<sub>6</sub> in O<sub>2</sub>. This contribution can be written in the form<sup>5</sup>

$$\frac{1}{T_1^{sc}} = \frac{2}{3} S(S+1) \left( \frac{A}{\omega_S \hbar} \right)^2 \frac{1}{\tau_S}$$

The magnitude of  $(A/\omega_S \hbar)^2 (1/\tau_S)$  in the scalar coupling relaxation rate should therefore be compared with its counterpart in the dipolar relaxation rate,  $[8\gamma_I^2 \gamma_S^2 \hbar^2 / (\pi \bar{v}^2 d^4)] (1/\tau_{DD})$ . At the intermediate magnetic field of 4.7 T, in 30 amagat sample at 300 K,  $A$  has to be of the order of 1 MHz in order for the scalar coupling term to be equal to the dipolar term in SF<sub>6</sub> in O<sub>2</sub>, if  $\tau_S$  and  $\tau_{DD}$  are about the same. Since an intermolecular coupling is being considered here,  $A$  is more likely to be of the order of a kilohertz. The scalar coupling can become important when rapid electron spin exchange provides an extremely short  $\tau_S$ . This is not the case for O<sub>2</sub> in the gas phase. While  $\tau_{DD} = [\rho_{O_2} \bar{v} \pi d^2 F(V/kT)]^{-1} = 1.5 \times 10^{-12}$  s for SF<sub>6</sub> in 30 amagat O<sub>2</sub> gas at 300 K, at this density  $\tau_{exch}$  is not as short, of the order of  $1 \times 10^{-11}$  s (an estimate based on the electron spin exchange frequency  $1.5 \times 10^{13}$  s<sup>-1</sup> measured in solid O<sub>2</sub> at 4 K,<sup>14</sup> and the fact that the exchange rate is proportional to  $\rho_{O_2}^2$ ).

### Conclusions

We have found that we are able to separate and characterize the two mechanisms involved in the relaxation of the <sup>19</sup>F nuclear spin in SF<sub>6</sub> in oxygen gas. The SR part is unremarkable. It corresponds to a cross section for reorientation of the rotational angular momentum vector of SF<sub>6</sub> by O<sub>2</sub>,  $\sigma_J = 14.2 \text{ \AA}^2 (T/300)^{-1}$  which is 0.25 times the hard sphere cross section. It is very slightly higher than expected but fits quite well with other pairs such as SF<sub>6</sub>-CO and SF<sub>6</sub>-N<sub>2</sub>. The DD part is found to be consistent with the theoretical limit for high translational energy hard spheres in zero field, multiplied by a factor  $F(V/kT)$ , which is temperature-dependent and expected to depend on the SF<sub>6</sub>-O<sub>2</sub> intermolecular potential, and a factor which is the same form as derived in the low-frequency limit for dipolar relaxation in liquids,  $\{1 - f(T)\omega_1^{1/2}\}$ . Our theoretical estimate of  $f(T)$  in the gas phase involves  $d/\bar{v}$  rather than the  $d^2/D$  term in liquids. We find that our experimental data are consistent with the theoretical ideas with which we have arrived at these functional forms. Indeed our experimental values for function  $f(T)$  are quite close to the theoretical values, with the empirical temperature dependence being about the same as  $\bar{v}^{-1/2}$ .

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