all excitation levels. This is typical of a molecule close to the local mode limit as discussed in ref 1, 12, and 13. These degeneracies are somewhat removed by deuterium substitution at $v_{tot} \leq 3$, but at larger quantum levels the energy level pattern of $^{74}GeD_4$ approaches that of a molecule close to the local mode limit.

Infrared absorption intensity calculations using a bond dipole moment model[1,13,14] show that usually transitions from the ground vibrational state to the lowest F_2 components within each overtone manifold carry by far most of the intensity. This is again typical of a molecule close to the local mode limit.[1,13] Quantitative calculations are not possible at the moment due to the lack of experimental data.

Discussion

It is pleasing that the simple local mode model based on coupled Morse oscillators is able to explain well the observed stretching vibrational band origins up to $v_{tot} = 9$. It is also remarkable that a single stretching surface describes well all observed stretching vibrational term values of GeH_4 and GeD_4 isotopic species. This is not obvious because of the complicated average of the Hamiltonian used over bending degrees of freedom. It is probably most easily understood by noticing that for example terms of the type $x_{sb}(v_s + d_s/2)(v_b + d_b/2)$ (x_{sb} is an anharmonicity parameter that is isotope dependent, v_s and v_b are stretching and bending quantum numbers, d_s and d_b are degeneracies of modes s and b) have been neglected. It seems that at least the available band origin data support the conclusion that stretching vibrations in germane are only weakly coupled to bends. It would be of interest to observe higher stretching states of GeD_4 in order to see whether this conclusion is still valid.

It is somewhat surprising that both of the potential energy models used give almost equally good fits as far as the standard deviations of the fits are concerned. Only potential model II possesses correct asymptotic limits at large stretching amplitudes. Thus, one might expect that model I could break down in the case of the highest observed overtone levels. Apparently, it is necessary to go even to higher quantum levels before model I cannot be applied. The potential energy constants of both models are similar. The only larger difference occurs in $f_{rr'}$, as expected. Model I produces the splittings of the (2000) local mode pairs better than model II. The recent infrared–infrared double-resonance type studies applied to CH_4 and SiH_4[9] might reveal which of the potential energy functions used in this work produces better the local mode splittings of higher vibrational states.

In this work only vibrational band origins have been used to determine the potential energy surface. It might be interesting to also include other type of data, for example rotational constants. In the case of germane this might be done best by treating the rotational motion perturbatively as in the standard anharmonic force field calculations.[15] It might also be feasible to try to simulate some of the high overtone band contours by using a simple local mode model for the rotational structure.[16] A very recent experimental work is particularly relevant in this context.[17]

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Proton Relaxation in Methane with Oxygen Gas

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The proton relaxation rate for methane in oxygen gas is reexamined as a function of density, temperature, and magnetic field. The relaxation due to intermolecular nuclear spin dipole–electron spin dipole interaction has an efficiency about 2 times that for the theoretical limit of hard spheres and is field-dependent.

Introduction

The early interest (1960s) in the nuclear spin relaxation rates in gases was motivated by the hope that information about the intermolecular potential surface could be obtained from such measurements. In the intervening years it has become clear that no single property can provide a potential surface. Improved ab initio calculations combined with dispersion terms using universal damping functions, tested with detailed spectra from the collision pair, with molecular beam scattering cross sections, and with classical virial and transport properties, are beginning to provide increasingly accurate potential functions. Such approaches and direct inversion techniques applied to experimental data yield isotropic potential functions that systematically improve as more data are used for fine-tuning. As ways of obtaining the isotropic

potential function improved, interest has returned to experiments that are especially sensitive to or arise entirely from the anisotropy of the intermolecular potential (e.g., nuclear spin relaxation times). For example, the best potential function for H_2–Ne required a modification in one parameter in order to fit the new precise proton spin relaxation data in the H_2–Ne gas mixture.[2] Methods of calculating surfaces and methods of doing dynamic scattering calculations on such surfaces have evolved to a point where it is now possible to do an essentially exact evaluation of collision cross sections for the N_2–He interaction;[3] two of these cross sections can be obtained directly from ^{14}N and ^{15}N spin relaxation in the gas phase, dominated by the intramolecular quadrupolar and spin

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TABLE I: Field Dependence of ^{1}H Relaxation Time in CH$_4$ in Oxygen Gas (ρ_{CH_4} = 0.5 amagat, ρ_{O_2} = 33.5 amagat)

	200 MHz			400 MHz			
	T/K	$T_1(obs)/s$	T_1^{DD}/s	T/K	$T_1(obs)/s$	T_1^{DD}/s	f^a/MHz$^{-1/2}$
control w/o O$_2$	323.4	0.284		323.1	0.288		
sample	323.4	0.0257	0.0269	323.1	0.0290	0.0304	0.016 ± 0.001
control w/o O$_2$	266.5	0.371		266.9	0.368		
sample	266.5	0.0235	0.0242	266.9	0.0272	0.0282	0.018 ± 0.001

^{a} See text and eq 10.

rotation mechanisms, respectively.

The connection between the potential and spin relaxation is a direct one in the case of *inter*molecular spin dipole–dipole relaxation, since the dipole–dipole interaction exists only during a collision. In the gas phase this mechanism is important only in the case where the magnetic dipole on the collision partner is that due to an electron spin. The connection with the intermolecular potential motivated the early gas-phase work involving paramagnetic relaxation, the classic case of ^{1}H in CH$_4$ in the presence of O$_2$.[4,5] The temperature dependence of the proton relaxation in CH$_4$ and three other hydrocarbons in the presence of O$_2$ and NO was studied by Lipsicas et al.[6] Their experimental results were not in good agreement with those of Johnson and Waugh at low temperature. In seeking an interpretation that could be consistent with their low-temperature data for CH$_4$ in O$_2$, and also to explain the relative efficiencies of NO and O$_2$ as collision partners, Lipsicas et al. became concerned with the following questions. Is $\langle S(S + 1)\rangle$ defined and is it a constant of the motion for O$_2$? Is it defined in the time duration of the collision, i.e. as μ_J resulting from coupling of S with J, and if so then is it temperature-dependent? Lipsicas et al. tried to address this question by a comparison of relaxation in the presence of O$_2$ and NO, but the temperature dependence of ^{1}H T_1 for molecules in O$_2$ and NO was not sufficiently precise to draw definite conclusions. They reported that O$_2$ is about 10 times as effective as NO.[6] However, NO is very reactive and it is not clear from their studies that this was taken into account in the sample preparation. In this paper we reexamine the CH$_4$–O$_2$ system, making measurements of T_1 of ^{1}H in CH$_4$–O$_2$ gas mixtures in the same manner as our ^{19}F spin relaxation studies in SF$_6$ in O$_2$.[7]

Experimental Section

In relaxation studies of molecules in oxygen gas by previous workers the probe molecule was the major component in the sample, with O$_2$ mole fractions being usually less than 0.10. Total densities ρ were also much larger than ours, typically 30–450 amagat, under which conditions the ρ^2 term in $1/T_1$ was required in the analysis. To characterize the intermolecular dipolar interaction, we use samples with higher oxygen concentrations than used by previous authors[4,6] but keep the total gas density below 35 amagat, in order than the ρ^2 term remains insignificant. Typically our samples contained 0.5 amagat CH$_4$ and 5–35 amagat O$_2$. Sample preparation techniques have been described earlier.[7]

We also observe the effect of the magnetic field on the proton relaxation times. Siegel and Lipsicas[6] reported measurements of T_1 of CH$_4$ contaminated with oxygen at two magnetic fields (in which the proton resonance frequencies were 12 and 30 MHz) and found no consistent difference. When T_1 measurements are compared at two fields, with the expected difference being small, it is important to run a control T_1 determination. A given pure CH$_4$ sample that relaxes entirely by spin rotation mechanism in the extreme narrowing limit should have exactly the same T_1 at the same temperature in any field. Only when this is found to be the case can we be assured that incorrect pulse widths, temperature control, and other spectrometer differences are not giving
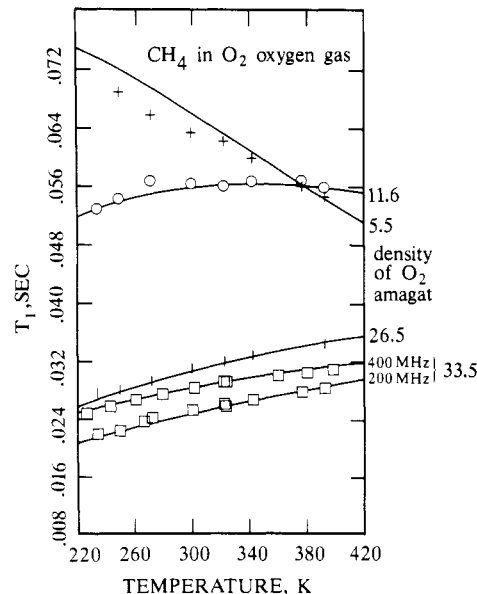

Figure 1. Temperature dependence of ^{1}H spin relaxation times in samples containing 0.5 amagat CH$_4$ in various densities of O$_2$. Data taken at 200 MHz (and also 400 MHz for the sample with 33.5 amagat O$_2$).

us spurious small differences in measured values of T_1 at different fields. Here we report T_1 measurements of the CH$_4$–O$_2$ sample with the highest O$_2$ density at 200 and 400 MHz under conditions such that the pure CH$_4$ control sample gives the same T_1 in both fields as shown in Table I.

Results and Discussion

We have already established that in pure CH$_4$ gas the ^{13}C and ^{1}H nuclear relaxation is dominated by the spin rotation mechanism.[8] For CH$_4$ in O$_2$, the total relaxation rate is a sum of the rates of each mechanism.

$$\frac{1}{T_1} = \frac{1}{T_1^{SR}} + \frac{1}{T_1^{DD}} \qquad (1)$$

We have also previously established that the SR mechanism is additive;[9] therefore

$$T_1^{SR} = \left(\frac{T_1}{\rho}\right)^{SR}_{CH_4-CH_4}\rho_{CH_4} + \left(\frac{T_1}{\rho}\right)^{SR}_{CH_4-O_2}\rho_{O_2} \qquad (2)$$

The analysis of our data by the use of eq 1 and 2 allows us to separate out $1/T_1^{DD}$ and verify that it is linearly dependent on density. By measuring T_1 at different densities and temperatures, we are able to separate out the $1/T_1^{SR}$ and $1/T_1^{DD}$ more effectively than by a fit to density at one temperature, due to the opposite temperature dependence of these two mechanisms. $1/T_1^{SR}$ increases with temperature as $T^{+3/2}$ whereas $1/T_1^{DD}$ decreases with temperature, roughly as $T^{-1/2}$ or T^{-1}.

It should be noted that previous workers fitted the $1/T_1^{SR}$ part to $A(T)/\rho$; that is, the $(T_1/\rho)^{SR}_{CH_4-O_2}$ was assumed to be equal to

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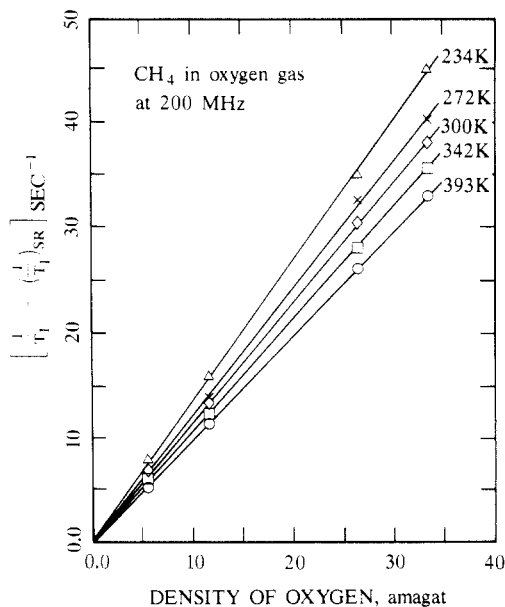
Figure 2. Density dependence of ^1H dipole–dipole relaxation rate in samples containing 0.5 amagat CH_4 in varying densities of oxygen. Data taken at 200 MHz.
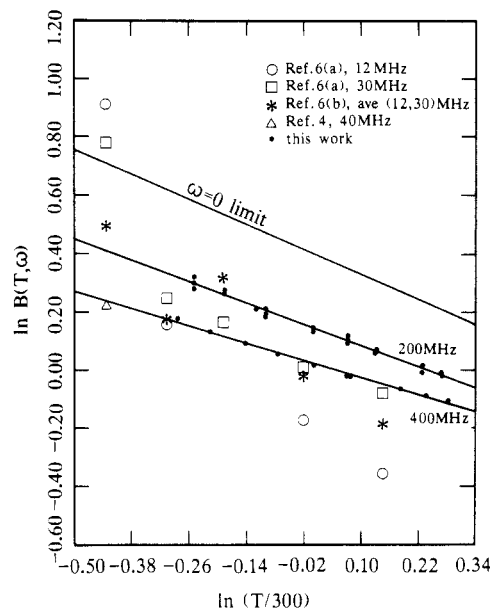

Figure 3. Temperature dependence of ^1H dipole–dipole relaxation rate in samples containing 0.5 amagat CH_4 in varying densities of oxygen: (●) this work, at 400 and 200 MHz, using $1/T_1^{DD} = B(T)\rho_{O_2}$. Values of $B(T)$ from other workers are also shown for comparison.

$(T_1/\rho)^{SR}_{CH_4-CH_4}$. We find this is a reasonably good assumption for their reported 5–10% accuracy in $1/T_1$ values. We obtain the best fit with

$$\left(\frac{T_1}{\rho}\right)^{SR}_{CH_4-O_2} = 0.019(T/300)^{-1.5} \qquad (3)$$

in this work, whereas results from measurements in pure methane give[8]

$$\left(\frac{T_1}{\rho}\right)^{SR}_{CH_4-CH_4} = 0.0205(T/300)^{-1.5} \qquad (4)$$

in good agreement with previous reports in pure CH_4.[10-13]

The $1/T_1^{DD}$ part was fitted by previous workers to a form $B(T)x_0\rho + C(T)x_0\rho^2$ for samples with $x_0 = 0.016–0.10$ and ρ up to 80 amagat total density,[4] or $x_0 = 0.005–0.03$ and $\rho = 40–450$ amagat.[6] The $C(T)x_0\rho^2$ term was included in previous analyses to take into account the onset of liquid behavior in high-density samples consisting of mostly CH_4 with small amounts of oxygen. From a comparison of the $CH_4–CH_4$ and the $CH_4–O_2$ interactions it might be expected that the $C(T)x_0\rho^2$ term might well be more important in their samples and densities than in ours. In order to verify whether the ρ^2 term is significant in our density regime, we prepared samples with small amounts of CH_4 (0.5 amagat) and varying densities of O_2 (5–35 amagat) so that $\rho_{total} \approx \rho_{O_2}$. In plotting $1/T_1^{DD}$ against ρ_{O_2}, we should be able to detect a ρ^2 dependence if the $C(T)$ term is indeed as large as reported in the previous work. Using the reported ratio $C(T)/B(T) = 9 \times 10^{-3}$ amagat^{-1},[4] at 30 amagat the ratio of contributions to $1/T_1^{DD}$, $C(T)\rho^2/B(T)\rho$ would be 0.27. In Figure 2 we see no evidence of a quadratic term in density of this magnitude. On the other hand, if we use the values reported by Lipsicas et al.,[6] $C(T)/B(T) = (1.5–3.0) \times 10^{-3}$ amagat^{-1}, $C(T)\rho^2/B(T)\rho$ in our highest density sample would be 0.05–0.09. Figure 2 shows that a linear dependence on ρ_{O_2} appears to hold at these temperatures in this density regime. Therefore our analysis is based on the form

$$\frac{1}{T_1^{DD}} = B(T)\rho_{O_2} \qquad (5)$$

There had been some disagreement in the temperature dependence of the intermolecular dipolar relaxation rate in the $CH_4–O_2$ system. In Figure 3 we show our results at 200 MHz, which can be described by

$$B(T, \omega) = \frac{1}{T_1^{DD}\rho_{O_2}} = (1.157 \pm 0.013)(T/300)^{-0.61\pm0.01} \qquad (6)$$

Since the values plotted in Figure 3 correspond to ln $(B(T))$, we also show in this figure the values of ln $(B(T))$ from the earlier reported data.[4,6] It appears that most of their values of $B(T)$ are smaller than ours. When data are fit to a quadratic function, experimental errors can sometimes lead to an exaggerated quadratic term when the relationship is very nearly linear. It is possible that the $C(T)$ coefficient in their analysis is somewhat high, in which case $B(T)$ values will be too low.

Lipsicas and Siegel attributed the unusual temperature dependence of the data points indicated in Figure 3 to a temperature-dependent effective paramagnetic moment.[6] By considering the effective paramagnetic moment of O_2 as a transient quantity, a time-correlated magnetic moment was used in the analysis and their $B(T)$ data were fitted to the form $B(T) = (K_1T^{-1/2})$ exp-$(K_2T^{-1/2-n})^2$ erfc$(K_2T^{-1/2-n})$ for $n = 1–5$. In this equation $T^{-1/2-n}$ is said to be proportional to the ratio of the mean collision time to the electron spin relaxation time, and K_1 and K_2 are adjustable parameters.[6] We see in Figure 3 that the experimental errors in their data lead to an incorrect temperature dependence at low temperatures. Our data show no unusual behavior with temperature and therefore no need to invoke an unusual functional form for $B(T)$. While NO has a temperature-dependent magnetic moment,[14] due to the existence of a ground state and a low-lying electronic state that have different magnetic dipole moments, this is not the case for O_2 molecule. Furthermore, we do not need to consider a transient effective paramagnetic moment for O_2 in the proton relaxation provided that $\tau_e > \tau_{DD}(^1H)$. The electron spin exchange mechanisms, which usually give rise to short T_{1e} for the electron spin, are not important for O_2 in the gas phase. The nonresonant part of the magnetic dipole absorption in the microwave spectrum of O_2 gas yields cross sections such that $\rho\bar{v}\sigma = 0.54 \times 10^3$ MHz/atm,[15] which corresponds to $\tau_e = 9.8 \times 10^{-12}$ s at 30 amagat, to be compared with our $\tau_{DD}(^1H, \omega = 0) = 1.35 \times 10^{-12}$ s. Finally, we also can dismiss the rotational energy transfer during $CH_4–O_2$ collisions affecting the electron spin

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angular momentum via a change in the O$_2$ molecular rotation. In a Hund's case (b) molecule, such as an O$_2$ molecule, the electron spin angular momentum is only weakly coupled to the angular momentum of molecular rotation. The collision causes a *sudden* change in the molecular rotation, and the spin cannot follow this change in the rotational motion because it is so weakly coupled.[15] The electron spin is only slightly disturbed during a collision. Therefore, the effective $S(S + 1)$ seen by the ^{1}H nucleus in the CH$_4$ molecule in oxygen gas can be considered a constant in this case. Thus, we do not attempt to separate out any temperature dependence that may be associated with μ_{eff}^2 but rather use

$$\mu_{eff}^2 = g_e^2 S(S + 1)\mu_B^2 = 8.0128\mu_B^2 \tag{7}$$

We had observed for SF$_6$ in O$_2$ gas that a field dependence of the form[7]

$$\frac{1}{T_1^{DD}} = \frac{1}{T_1^{(0)}}\{1 - f(T)\omega_F^{1/2}\} \tag{8}$$

is consistent with the experimental data at three magnetic fields (1.9, 4.7, and 9.4 T). For ^{129}Xe in O$_2$ the relaxation is completely dominated by the intermolecular dipolar mechanism, and the observed relaxation times at 4.7 and 9.4 T were analyzed in the same way.[16]

From eq 8 and the two sets of T_1 data shown in Figure 1 for one sample, we can find $f(T)$ by

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

where $T_1(\omega_2)$ and $T_1(\omega_1)$ are the dipolar relaxation times at the proton resonance frequencies ω_2 and ω_1. By taking the precaution of running a control T_1 experiment in a pure CH$_4$ sample along with the CH$_4$–O$_2$ sample, we know that our experimental conditions are such that the difference between $T_1^{obs}(\omega_2)$ and $T_1^{obs}(\omega_1)$ is real even though small. We used the sample with the highest density of oxygen so that the $1/T_1$ is nearly entirely $1/T_1^{DD}$ and the $1/T_1^{SR}$ part is small. In this sample, only 2–4% of the observed $1/T_1$ is due to spin rotation in the range 230–400 K. In Table I we show typical values of T_1 at these two fields. The $f(T)$ obtained by eq 9 from the measurements at 200 and 400 MHz can be described adequately by

$$f(T) = (1.54 \pm 0.08) \times 10^{-2}(T/300)^{-0.64\pm0.13} \text{ MHz}^{-1/2} \tag{10a}$$

or

$$f(T) = (1.57 \pm 0.08) \times 10^{-2} + 3.1 \times 10^{-5}(T - 300) - 4.1 \times 10^{-8}(T - 300)^2 \text{ MHz}^{-1/2}$$

We have derived a theoretical estimate of $f(T)$:[16]

$$f(T) = \frac{1}{24}\left(\frac{d}{\bar{v}}\right)^{1/2}[3 + 7(\gamma_S/\gamma_I)^{1/2}] \tag{10b}$$

Using $d = 3.55$ Å for CH$_4$ in O$_2$, this theoretical estimate is $1.295 \times 10^{-2}(T/300)^{-1/4}$ MHz$^{-1/2}$, which is of the right order of magnitude and temperature dependence. For CH$_4$ in O$_2$ at 300 K, $d/\bar{v} = 4.61 \times 10^{-13}$ s is an average length of time during which the interaction between the nuclear dipole and the electron spin dipole can lead to transitions between the ^{1}H magnetic levels. During this time, the electron spin precesses through $^1/_{16}$ of a Larmor cycle in a field of 4.7 T. This field dependence was not observed in the earlier work at 12, 30, and 40 MHz.[4,6]

It should be noted that the discrepancy in Figure 3 between the old data and our values of $B(T)$ is not due to the field dependence of T_1. The previous data taken at 12, 30, and 40 MHz all correspond to lower $B(T)$ values than ours taken at 200 MHz.

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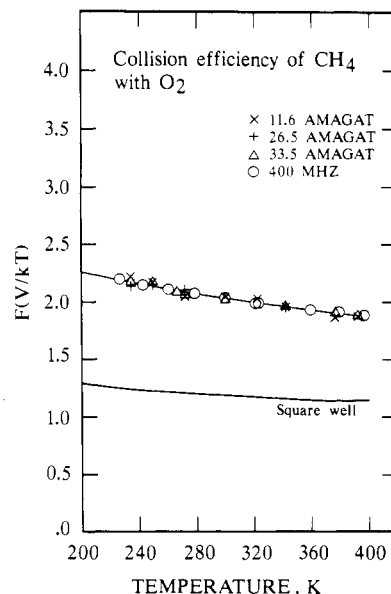

Figure 4. Empirical values of $F(V/kT)$ obtained by eq 11 and 12 and values calculated using a square-well potential and Bloom–Oppenheim theory, eq 16.

This is in the wrong direction for the discrepancy arising from the field dependence; $B(T)$ should be larger at lower magnetic fields. Using our empirical $f(T)$, we find $B(T, \omega = 0) = (1.48 \pm 0.02)(T/300)^{-0.78\pm0.01}$.

The theoretical limit of $1/T_1^{DD}$ for high translational energy, hard spheres, and $\omega = 0$ has been shown to be[5,17-19]

$$\left(\frac{1}{T_1^{DD}}\right)_{th\,lim} = \frac{16}{3}S(S + 1)\gamma_I^2\gamma_S^2\frac{\hbar^2}{d^2}\left(\frac{\pi\mu}{8kT}\right)^{1/2}\rho_{O_2} \tag{11}$$

The overall temperature dependence that we observed for $1/T_1^{DD}$ in CH$_4$ on O$_2$ gas, as expressed in eq 6 at 4.7 T, is $T^{-0.66}$. Since $f(T)$ changes with temperature as $T^{-1/4}$, $(1 - f(T)\omega^{1/2})$ has a mild, approximately $T^{+0.1}$ dependence. The theoretical hard-sphere limit, $T^{-1/2}$ in eq 11, is corrected by this field-dependent term to $T^{-0.4}$, which can be compared with the observed $T^{-0.66}$. The discrepancy between these functional forms can be expressed as a factor $F(V/kT)$, which contains some information about the deviation of the true CH$_4$–O$_2$ intermolecular function from the hard-sphere limiting case. We then write the observed dipolar relaxation rate as

$$\frac{1}{T_1^{DD}} = \left(\frac{1}{T_1^{DD}}\right)_{th\,lim}(1 - f(T)\omega_H^{1/2})F(V/kT) \tag{12}$$

The analysis of $1/T_1^{DD}$ by use of eq 12 then allows us to find empirical values (dimensionless) of the function $F(V/kT)$. Following eq 11 and 12 this empirical function is obtained by evaluating for each sample at each temperature

$$F(V/kT) = [T_1^{DD}\rho_{O_2}C(300/T)^{1/2}(1 - f(T)\omega_I^{1/2})]^{-1}$$

where the temperature-independent constants are

$$C = \frac{16}{3}S(S + 1)\gamma_I^2\gamma_S^2\frac{\hbar^2}{d^2}\left(\frac{\pi\mu}{8k300}\right)^{1/2}$$

μ is the reduced mass of the CH$_4$–O$_2$ collision pair, $d = 3.55$ Å is obtained from the arithmetic mean of $r_0 = 3.7205$ Å for CH$_4$–CH$_4$, and $r_0 = 3.382$ Å for O$_2$–O$_2$.[20] In this procedure, no

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TABLE II: Collision Efficiency and Cross Section for CH_4 in O_2

T/K	$F(V/kT)^a$	$\sigma_{eff}{}^b/Å^2$	T/K	$F(V/kT)^a$	$\sigma_{eff}{}^b/Å^2$
234	2.181	86.4	323	1.996	79.0
250	2.145	84.9	342	1.963	77.7
272	2.096	83.0	377	1.910	75.6
300	2.039	80.7	393	1.888	74.8

^{a}Can be described by empirical equations $F(V/kT) = (2.039 \pm 0.020) - 0.019(T - 300) + 3.37 \times 10^{-5}(T - 300)^2$ or $= (2.037 \pm 0.019)(T/300)^{-0.28\pm0.01}$. ^{b}Hard-sphere cross section is 39.6 Å^2, based on $d = 3.55$ Å (see text).

specific mathematical functional form is assumed for $F(V/kT)$; the values are obtained directly from experiment. These values are shown in Figure 4 and in Table II.

Under an approximation analogous to the Born approximation for the anisotropic potential, and accounting for the rigid core of molecular diameter d, Chen and Snider have derived an expression for $F(V/kT)$[17]

$$F(V/kT) = 4 \int_0^\infty \exp(-ax^2)[j_1(x)]^2 x \, dx \quad (13)$$

where $a \equiv \hbar^2/8\mu kT d^2$ and $j_1(x)$ is the first spherical Bessel function. For hard-sphere potentials $F(V/kT) < 1$ and is expected to approach 1.0 at the high-temperature limit.[17] On the other hand, the correlation function approach of Bloom and Oppenheim, under the CAA (constant acceleration) approximation, leads to a different expression for T_1 such that $F(V/kT)$ in eq 11 is given by[18]

$$F(V/kT) = 2\pi \int_0^\infty dy \left[\int_0^\infty \frac{[g(x)]^{1/2} j_{5/2}(xy) \, dx}{x^{3/2}} \right]^2 \quad (14)$$

where $j_{5/2}(x)$ is a Bessel function of order $^5/_2$ and where $g(x)$ is the radial distribution function for the gas. In an infinitely dilute gas

$$g(x) = \exp(-V(x)/kT) \quad (15)$$

where $V(x)$ is the isotropic part of the intermolecular potential. For the very dilute gas of hard spheres, $F(V/kT)$ in eq 14 reduces to 1.0. $F(V/kT)$ values that are greater than 1.0 indicate that the attractive part of the potential is playing a part in intermolecular dipolar relaxation. The effect of the attractive potential is to increase the time spent by the molecules in the vicinity of one another, thus increasing the probability for a molecular reorientation. Indeed, in Figure 4 we see that the values are greater than 1.0 for the temperatures we have studied. $F(V/kT)$ tends to increase with decreasing temperature because of the increased importance of the attractive part of the potential at lower relative velocities of the colliding molecules.

A specific functional form for $F(V/kT)$ has been suggested by Bloom, Lipsicas, and Muller[5] when a square-well potential of depth V_0 is used in eq 14.

$$F(V_0/kT) = F(z) = e^z + 0.31(e^{z/2} - 1)^2 - 0.72e^{z/2}(e^{z/2} - 1) \quad (16)$$

This function has a temperature dependence $\sim T^{-0.20}$ near room temperature and goes to 1.0 as $T \rightarrow \infty$. If we use a value $\epsilon/k = 134.6$ K for CH_4-O_2 (geometric mean of ϵ/k for CH_4-CH_4 and O_2-O_2[20]), then for the square-well potential of depth $V_0 = 0.56\epsilon$ we calculate $F(V_0/kT) = 1.247, 1.182,$ and 1.132 at 230, 300, and 400 K. Our empirical values of $F(V/kT)$ at these temperatures are 2.19, 2.04, and 1.88, respectively, the temperature dependence being $\sim T^{-0.28}$. The model gives values for $F(V/kT)$ that are about 60% of the observed magnitude, and the temper-

ature dependence of the model $F(V/kT)$ is about the same as that of the empirical $F(V/kT)$ function (see Figure 4).

This function of the CH_4-O_2 intermolecular potential may be viewed as a collision efficiency, that is

$$F(V/kT) = \langle \sigma_{eff} \rangle / \sigma_{geom} \quad (17)$$

where $\langle \sigma_{eff} \rangle$ is a thermal average effective cross section for intermolecular dipolar relaxation. The values are given in Table II.

It is important to remember the assumptions made in the data analysis that allow us to extract the empirical function $F(V/kT)$ for CH_4-O_2 binary collisions:

(1) The form $1/T_1{}^{DD} = B(T)\rho_{O_2}$ was used in the analysis. The existence of a small term of higher order in density, which we failed to observe in Figure 2, would mean that our analysis leads to $B(T)$ and $F(V/kT)$ somewhat too large.

(2) $T_1{}^{SR}/\rho$ for CH_4-O_2 was obtained in the fitting to the data in Figure 1. The value obtained is completely consistent with all other spin rotation relaxation studies that we have made in various probe molecules with various collision partners.[8,9] If this value is too large, then it would lead to a collision efficiency $F(V/kT)$, which is too large. Thus, the uncertainties in $(T_1{}^{SR}/\rho)_{CH_4\text{-}O_2}$ are buried in our $F(V/kT)$.

(3) $\langle S(S + 1) \rangle$ and thus μ_{eff} are taken to be a constant of the motion for O_2. If the effective paramagnetic moment of O_2 is different from this, then this would be hidden in $F(V/kT)$. A temperature-dependent $\langle S(S + 1) \rangle$ was assumed in the early work to explain the unusual temperature dependence of $1/T_1{}^{DD}$, which we have seen to be inaccurate.

(4) The field dependence is assumed to be of the form

$$\frac{1}{T_1{}^{DD}} = \frac{1}{T_1{}^{(0)}}\{1 - f(T)\omega_I{}^{1/2}\}$$

This form is based on theory, has been verified extensively in liquids, and is consistent with results obtained at three fields for ^{19}F in SF_6 in oxygen gas. Any uncertainties in our determination of $f(T)$ will of course affect the values of $F(V/kT)$ we obtain.

Summary and Conclusions

The relaxation times of ^1H in CH_4 in various densities of oxygen gas have been measured in two fields. The spin rotation relaxation rate is separated out, and the intermolecular dipolar relaxation rate is found to be consistent with the following field dependence

$$\frac{1}{T_1{}^{DD}} = \frac{1}{T_1{}^{(0)}}\{1 - f(T)\omega_I{}^{1/2}\}$$

where $f(T)$ was obtained by measurements at two values of ω_I and where

$$\frac{1}{T_1{}^{(0)}} = {}^{16}/_3 S(S + 1)\gamma_I{}^2\gamma_S{}^2 \frac{\hbar^2}{d^2} \left(\frac{\pi\mu}{8kT} \right)^{1/2} \rho_{O_2} F(V/kT)$$

$F(V/kT)$ is obtained empirically from the temperature dependence of the intermolecular dipolar relaxation rate. The values calculated with Oppenheim and Bloom's theory, using a square-well potential of depth $V_0/k = 75.4$ K, are about 60% of the values obtained empirically. The quadratic dependence on density was not important in our samples of densities ≤ 35 amagat, and the paramagnetic moment of O_2 need not be temperature dependent in order to interpret the observed temperature dependence of T_1 for the proton.