

Nuclear spin relaxation by intermolecular magnetic dipole coupling in the gas phase. ^{129}Xe in oxygen

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The nuclear spin relaxation times (T_1) of ^{129}Xe in xenon- O_2 gas mixtures have been measured as a function of temperature and density at different magnetic fields. This system is used to characterize the intermolecular dipolar relaxation of nuclear spins in the gas phase. An empirical Boltzmann-averaged collision cross section associated with the collision-induced transitions between ^{129}Xe nuclear spin states is obtained as a function of temperature.

INTRODUCTION

Nuclear spin relaxation by intermolecular magnetic dipole coupling is usually not an important mechanism unless the other magnetic dipole is that of an electron spin. For rare gas nuclei, spin relaxation is entirely by an intermolecular mechanism. The dipolar interaction between the ^3He nuclei causes the relaxation in helium gas,¹ while for the other monoatomic gases other mechanisms dominate, such as the transient spin-rotation interaction during collision for ^{129}Xe in xenon gas,² and the quadrupolar mechanism for ^{21}Ne , ^{83}Kr , and ^{131}Xe .^{3,4} Nuclear spin relaxation due to the intermolecular dipolar interaction with electron spins of paramagnetic centers has been extensively studied in the liquid phase, for instance, spin relaxation in the presence of free radicals, dissolved oxygen, or paramagnetic metal complexes.⁵ However, there have been very few studies in the gas phase. ^1H spin relaxation in CH_4 in the presence of O_2 was observed by Johnson and Waugh⁶ and by Lipsicas, Bloom, *et al.*^{7,8} The latter authors used both NO and O_2 with hydrocarbons (CH_4 , C_2H_6 , $\text{CH}_2=\text{CH}_2$, and $\text{CH}_2=\text{CF}_2$).^{9,10}

Nuclear spin relaxation by intermolecular magnetic dipole coupling in the gas phase is not well characterized. In this paper we consider the spin-lattice relaxation time T_1 . Some important aspects which need to be explored are the following:

(1) The temperature dependence of intermolecular dipolar T_1 in the gas phase is not known. There have been no reliable experimental data. For ^3He in helium gas of density ρ theoretical calculations by Shizgal show that $T_1\rho$ has a complex dependence on temperature, exhibiting a minimum at 1 K, $T_1\rho \sim T^{+0.534}$ for $T > 2$ K, at much higher temperatures, $T_1\rho \sim T^{1/2}$ and is independent of the depth of the potential well.¹ Theories predict that $T_1\rho \propto T^{1/2}$ for hard spheres in the high-temperature limit.^{6,11-13} In this work we determine the temperature dependence of T_1 for this intermolecular dipolar mechanism in a system which is not in the high temperature limit.

(2) Is T_1 for this mechanism linearly dependent on the density of the gas in the same density regime for which the ρ^2 terms can be neglected in the spin-rotation mechanism (e.g., $0.5 < \rho < 40$ amagat)? The dependence on the concentration of electron spins is well documented in the liquid phase. It has been shown theoretically as well as experimentally that

$T_1^{-1} \propto N_S$.^{14,15} In the gas phase the early experimental data for ^1H in CH_4 in O_2 were fitted to $T_1^{-1} = A(T)\rho^{-1} + B(T)x_{\text{O}}\rho + C(T)x_{\text{O}}\rho^2$, i.e., a linear behavior of T_1 inter with oxygen concentration. The $C(T)x_{\text{O}}\rho^2$ term was attributed to the translational diffusion mechanism which needs to be considered at high gas densities, as in liquids.^{14,16} Its relative importance compared to the linear term in density is reported as $C(T)/B(T) = 0.009$ amagat⁻¹ at 194 K in high density samples (up to 80 amagat)⁶ or $C(T)/B(T) = 1.5 \times 10^{-3}$ at 195 K in samples up to 350 amagat.¹⁰ For CH_4 in infinite dilution in low density oxygen gas, the above equation simplifies to $T_1^{-1} = A(T)\rho_{\text{O}_2}^{-1} + B(T)\rho_{\text{O}_2}$. In this paper we study a system in which there is no intramolecular mechanism which can give rise to a term in $A(T)\rho_{\text{O}_2}^{-1}$ and we restrict our measurements to the density regime such that the ρ^2 term does not contribute significantly.

(3) Is T_1 field dependent in the gas phase? In the liquid phase it is found that the magnetic field dependence can be expressed in the form¹⁷

$$\frac{1}{T_1} = \frac{1}{T_1^{(0)}} - B\omega^{1/2} \quad (1)$$

in the limit that $\omega\tau \ll 1$, where ω is a Larmor frequency and τ is the translational correlation time which is inversely related to the translational diffusion coefficient.¹⁴ The field dependence of T_1 in a solution containing free radicals has been observed over a wide range of fields,^{15,18} corresponding to $\omega_S\tau = 0.5$ to 50, and Eq. (1) is found to also hold within 1% in the range $0 < \omega_S\tau < 1$.¹⁵ ω_S is the Larmor frequency of the electron spin. In the gas phase there had been no experimental data to indicate whether there is a field dependence. No consistent difference was found by Siegel and Lipsicas between T_1 values measured at 12 and 30 MHz for ^1H T_1 of CH_4 in O_2 .⁷

(4) How is a cross section defined in an intermolecular dipolar relaxation mechanism? In the intermolecular relaxation mechanisms by spin-rotation interaction or by the quadrupolar mechanism, $T_1 \propto \sigma_r$ or σ_θ where the cross sections σ_r and σ_θ are mathematically well defined in terms of classical collision integrals or the quantum-mechanical scattering matrix and thus on the intermolecular potential surface.^{19,20} In this paper we shall define an effective intermolecular cross section which is analogous to σ_r and σ_θ in that the mean

relative velocities, the magnetic dipole parameters, and other constants have been separated out.

(5) Is it possible to observe the eccentricity of the spin-bearing nuclei, i.e., the effect of the spins not being located at the centers of the interacting molecules? This has been examined in the liquid phase,^{15,21} where it was found that the relaxation rate of an off-center nuclear spin is about 15% greater than that of a centered nuclear spin in the same molecule.²¹ We do not answer this question in this paper. Our measurements on ¹⁵N¹⁵NO in oxygen gas address this question and will be reported separately.²²

For the study of intermolecular dipolar relaxation in the gas phase, the best system is ¹²⁹Xe in oxygen gas. In the absence of O₂, the dominant relaxation mechanism in xenon gas is the spin-rotation interaction for the collision pair Xe₂.² For the Xe-O₂ pair such a mechanism also exists although the Xe-O₂ well depth is much smaller than that of Xe₂. However, in the presence of even a very small concentration of O₂, the nuclear spin-electron spin dipole mechanism for ¹²⁹Xe relaxation becomes dominant.²³ The xenon probe molecule is ideal for this study. It has *no intramolecular* spin relaxation mechanisms and the intermolecular mechanisms other than the one we are interested in are very inefficient in comparison. These conditions allow us to characterize the intermolecular *I-S* dipolar relaxation in the gas phase with a minimum of ambiguity. Other rare gas nuclei such as ³He have these advantages too, but suffer from low NMR sensitivity.

EXPERIMENTAL

Samples of approximately 5 amagat of Xe in O₂ (9–33 amagat) were made by freezing out the gases from a calibrated volume. Densities of oxygen were corrected for the residual gas remaining in the approximately 0.3 ml of dead space above the seal. ¹²⁹Xe spin relaxation (*T*₁) measurements were made by the inversion recovery method (π - τ - $\pi/2$ -pulse sequence) at two magnetic fields (4.7 and 9.4 T) using Bruker spectrometers (WP-200SY and AM-400). The sample tubes (5 cm long, <4 mm o.d.) fit in a standard 5 mm NMR tube with methanol (below 330 K) and ethylene glycol (at higher temperatures). The proton FIDs of these temperature standards were used to shim the field as samples were changed. This was necessary since the varying densities of oxygen changed the volume susceptibility of the sample in a pronounced manner from one sample to the next and the ¹²⁹Xe signal was not strong enough to see readily with a single scan. There is a marked ¹²⁹Xe chemical shift change with temperature and density for Xe in oxygen.²³ In the course of these experiments the ¹²⁹Xe resonance frequency changed with sample and temperature by over 5 kHz at 9.4 T. Consequently, we searched for the signal quickly using a wide sweep width before narrowing it to 1000 Hz for data collection. Temperatures were measured using sealed samples of temperature standards (methanol below 300 K and ethylene glycol). The measured temperature at the sample was often more than 10 deg different from that set by the thermocouple located immediately below. Even so, temperature regulation was consistent, with drifts of less than 1 deg over 20 h time periods. Instrumental limitations restrict the

high temperature to 400 K while Xe condensation limited the lowest temperature to 230 K. ¹²⁹Xe spin relaxation times in these experiments ranged from 0.07 to 0.3 s, which are short compared to pure xenon gas in which they are 2600 s for a 66 amagat sample and 1×10^4 s for a 30 amagat sample.²⁴

RESULTS AND DISCUSSIONS

The results of measurements in two fields are shown in Figs. 1–3 for various sample densities, and various temperatures. $1/T_1$ is found to be slightly field dependent, has an overall temperature dependence of $T_1^{-1} \propto T^{-0.3}$ at 4.7 T and is essentially temperature independent at 9.4 T.

Temperature dependence

Nuclear spin relaxation by intermolecular dipolar interaction has been considered in a formal kinetic theory and also in a correlation function approach. Chen and Snider used a quantum mechanical formulation of molecular kinetic theory (Waldman-Snider), and they related the observed *T*₁ to scattering matrices which describe the rotationally inelastic and the elastic molecular collisions.¹³ In the extreme narrowing limit, both approaches lead to expressions for the intermolecular dipolar relaxation of spin *I* by spin *S* (¹²⁹Xe and O₂, respectively) which can be written in the form

$$\frac{1}{T_1^{(0)}} = \frac{16}{3} S(S+1) \gamma_I^2 \gamma_S^2 \frac{\hbar^2}{d^2} \left(\frac{\pi \mu}{8kT} \right)^{1/2} N_S F(V/kT), \quad (2)$$

where *N*_{*S*} is the number density of *S*-bearing molecules. γ_I and γ_S are the magnetogyric parameters of the spins *I* and *S*, and *d* is the characteristic length of the intermolecular interaction, loosely referred to as the molecular diameter. The $(\pi \mu / 8kT)^{1/2}$ term is the reciprocal mean relative velocity

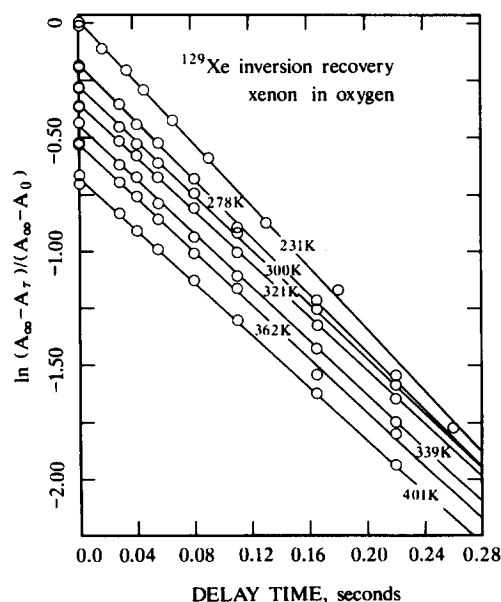


FIG. 1. Typical inversion recovery data for ¹²⁹Xe in a gas sample containing 5.5 amagat Xe and 15.5 amagat O₂, obtained on a Bruker WP200-SY at 55.35 MHz.

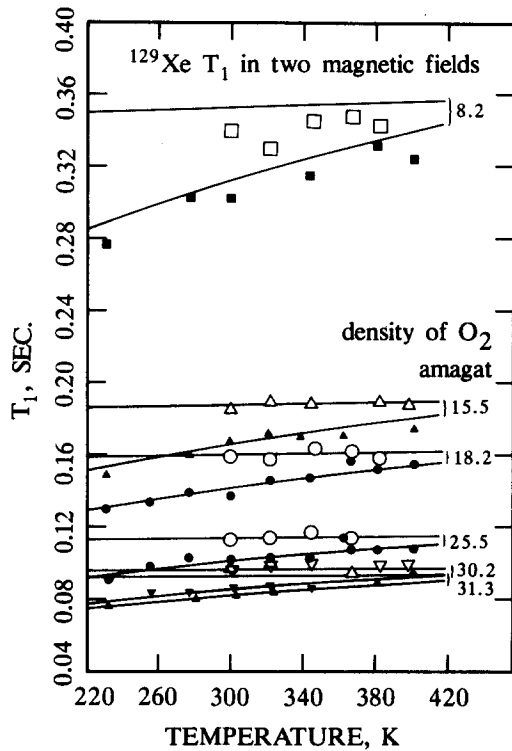


FIG. 2. Relaxation times for ^{129}Xe in mixtures of O_2 and xenon gas at 55.35 (filled symbols) and 110.7 MHz (open symbols).

\bar{v}^{-1} . For a spherical intermolecular potential, we can write $F(V/kT)$ as

$$F(V/kT) = \int_0^\infty \frac{dE}{kT} e^{-E/kT} 4p(E), \quad (3)$$

where E is the relative translational energy. The kinetic theory expression for $p(E)$ is¹

$$p(E) = \frac{2d^2}{K^2} \sum_{ll'} (2l+1)(2l'+1) \begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 r_{ll'}^2, \quad (4a)$$

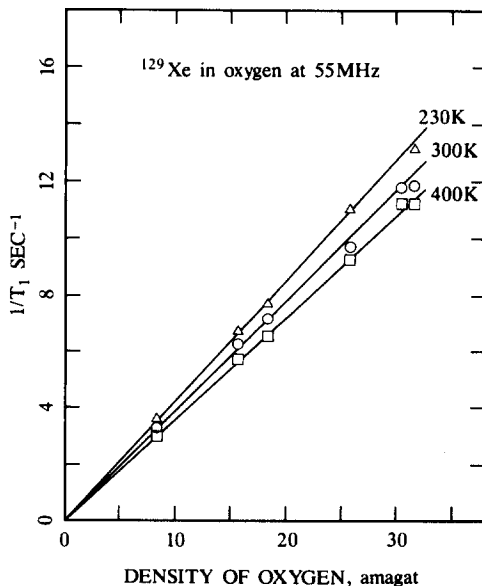


FIG. 3. The density dependence of ^{129}Xe spin relaxation rates at 55.35 MHz.

where $K^2 = 2\mu E/\hbar^2$, μ is the reduced mass of the collision pair, $\begin{pmatrix} l & l' & 2 \\ 0 & 0 & 0 \end{pmatrix}$ is the usual 3- j symbol, and the integrals $r_{ll'}$ for spherical intermolecular potentials $V(r)$ are given by

$$r_{ll'} = \int_0^\infty u_l(K,r) u_{l'}(K,r) r^{-3} dr$$

in which $u_l(K,r)$ are the solutions of the radial Schrödinger equation with potential $V(r)$. Shizgal has calculated $p(E)$ for realistic potentials for He-He interaction, and finds that this is very sensitive to the depth ϵ of the He₂ well for temperatures such that $(\epsilon/kT) > 1$. $F(V/kT)$ is only mildly temperature dependent at temperatures such that $(\epsilon/kT) < 1$, behaving as $\sim T^{-0.034}$ between 10 and 20 K. When the modified Born approximation is used, $p(E)$ simplifies to^{1,13}

$$p(E)^{\text{MBA}} = \int_0^{2Kd} [j_1(x)]^2 \frac{dx}{x} \quad (4b)$$

for rigid-core molecules of diameter d . $j_1(x)$ is the first spherical Bessel function. Shizgal has calculated the exact expression [Eq. (4a)] for a hard sphere potential for two interacting atoms. $[(1/2)p(E)]$ is plotted in Fig. 5 of Ref. 11.] The high energy limit of $p(E)$ is 0.29 whereas the approximate [Eq. (4b)] leads to $\frac{1}{4}$.

On the other hand, the correlation function approach, using an approximation which is in the same spirit as the Born approximation (called the constant acceleration approximation, CAA) leads to¹²

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

where $x = r/d$ and $g(x) = e^{-V(x)/kT}$ is the radial distribution function in the dilute gas. For a hard sphere potential, $F(V/kT)$ becomes equal to 1 in Eq. (5). When $V(x)$ is approximated by a square-well potential of depth V_0 , Eq. (5) becomes⁸

$$F(V_0/kT) = F(z) = e^z + 0.31(e^{-z/2} - 1)^2 - 0.72 e^{z/2}(e^{z/2} - 1) \quad (6)$$

which is greater than 1.0 and behaves roughly as $\sim T^{-0.2}$.

For a hard sphere spherical potential, and at the high temperature limit, exact kinetic theory leads to $F(V/kT) = 1.16$, whereas the Born approximation (or its counterpart, CAA) leads to $F(V/kT) = 1.0$. The equivalence of these two approximations for a general anisotropic intermolecular potential has also been shown.²⁵

In this work, the function $F(V/kT)$ can be obtained experimentally without prejudice as to its functional dependence on T . If we assume that $\langle S(S+1) \rangle = 2$ is a constant of the motion for O_2 in Eq. (2), then from the measured T_1 at various temperatures we obtain an empirical function:

$$F(V/kT) = [T_1 \rho_{\text{O}_2} C]^{-1} (T/300)^{1/2}, \quad (7)$$

where C contains the constant factors

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

From Eq. (7) we see that the form of the temperature dependence of the relaxation time can be obtained from a

plot of $\ln(T_1 \cdot \rho_{O_2})$ vs $\ln T$. If this gives a straight line with slope n , the temperature dependence of $F(V/kT)$ is $T^{1/2-n}$. The function $F(V/kT)$ can be derived from this work only after the field dependence (which also has a temperature dependence) is resolved.

An effective cross section

In the *intermolecular* dipolar mechanism, the expression for $1/T_1$ can be written in the usual form in the collision theory of rate processes,¹ $T_1^{-1} \propto$ (kinetic cross section). In *intramolecular* relaxation mechanisms, Gordon has defined kinetic cross sections $\bar{\nu}\sigma_J$ and $\bar{\nu}\sigma_\theta$, and these are related to the observed relaxation times as $T_1 \propto$ (kinetic cross section).¹⁹ The difference comes from the different dependences on collision frequency $Z = \rho\bar{\nu}\sigma$. In the *intramolecular* mechanisms, the magnetic interactions exist even in the absence of collisions, and the collisions make spin relaxation possible by making these interactions time dependent:

$$\frac{1}{T_{1 \text{ intra}}} \propto \frac{1}{Z}$$

In the *intermolecular* mechanisms, the interaction only exist during a collision so the relaxation rate should be proportional to the collision frequency,

$$\frac{1}{T_{1 \text{ inter}}} \propto Z$$

Thus, $T_{1 \text{ intra}} \propto \sigma_J$ or σ_θ whereas $[T_{1 \text{ inter}}]^{-1} \propto \sigma_{\text{eff}}$. That is,

$$\frac{1}{T_{1 \text{ inter}}} \sim |H^{(1)}|^2 t^2 Z_{\text{eff}}$$

The probability per collision for a transition between nuclear spin states is proportional to $|H^{(1)}|^2 t^2$ where $|H^{(1)}|^2$ (magnitude of dipole-dipole interaction)² $\sim \langle S(S+1) \rangle (\gamma_I^2 \gamma_S^2 \hbar^2 / d^6)$, t = duration of a collision = d/v , Z_{eff} = effective collision frequency = $N_S \bar{\nu} \sigma_{\text{eff}}$, and $1/T_1 \sim \langle S(S+1) \rangle (\gamma_I^2 \gamma_S^2 \hbar^2 / \bar{\nu} d^4) N_S \sigma_{\text{eff}}$. Comparing this with Eq. (2), we see that $\sigma_{\text{eff}} \sim d^2 F(V/kT)$. For hard spheres at the high temperature limit, at which limit the cross section may be considered as $\sigma_{\text{geom}} = \pi d^2$, the function $F(V/kT)$ approaches 1. Thus we can consider $F(V/kT)$ as a collision efficiency and define an effective cross section as follows:

$$\frac{\sigma_{\text{eff}}}{\sigma_{\text{geom}}} \equiv F(V/kT). \quad (8)$$

The field dependence of $1/T_1$ in the gas

The static magnetic field B_0 in which the T_1 experiments are carried out determines the Larmor frequencies of the spins I and S , $\omega_I = \gamma_I B_0$ and $\omega_S = \gamma_S B_0$. In the language of the time-correlation function approach to spin relaxation, the field dependence is expressed in terms of the ω dependence of various spectral density functions $j(\omega)$ which are Fourier transforms of autocorrelation functions.¹⁴ In the liquid phase the experimental field dependence of T_1 yields the shape of the dimensionless spectral density functions $\bar{j}_2(\omega)$ which are characteristic of the relative dynamics of the I - and S -bearing molecules.^{15,26} Sholl has reviewed the ω dependence of spin relaxation for like spins. For unlike spins I

and S in a liquid in which the relative translational diffusion coefficient is D , the relaxation rate of nucleus I in a molecule of diameter d in the presence of spin S is given by^{14,15}

$$\frac{1}{T_1} = \frac{4\pi}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{N_S}{dD} \left\{ \begin{array}{l} \bar{j}_2(\omega_I - \omega_S) \\ + 3\bar{j}_2(\omega_I) \\ + 6\bar{j}_2(\omega_I + \omega_S) \end{array} \right\}. \quad (9)$$

In the low-frequency limit, which is strictly defined as that for which

$$\omega^2 \tau^2 \ll 1,$$

where τ is the translational correlation time in the liquid, the dimensionless spectral density function has the limiting form^{5,27}

$$\bar{j}_2(\omega) = \bar{j}_2(0) - \frac{1}{18} \left(\frac{\omega d^2}{D} \right)^{1/2} + \mathcal{O} \left(\frac{\omega d^2}{D} \right) \quad (10)$$

and $\bar{j}_2(0)$ is model dependent, equal to $\frac{2}{3}$,¹⁴ or $\frac{4}{27}$.²⁸ In the low-frequency limit, Eq. (10) may be substituted into Eq. (9), leading to

$$\frac{1}{T_1} = \frac{1}{T_1^{(0)}} \{1 - f(T) \sqrt{\omega_I}\}, \quad (11)$$

where

$$\frac{1}{T_1^{(0)} \text{ LIQ}} = \frac{4\pi}{15} \gamma_I^2 \gamma_S^2 \hbar^2 S(S+1) \frac{N_S}{dD} \cdot 10\bar{j}_2(0)$$

and

$$f(T)_{\text{LIQ}} = \frac{1}{18} \left(\frac{d^2}{D} \right)^{1/2} \frac{\left[3 + 7 \left(\frac{\gamma_S}{\gamma_I} \right)^{1/2} \right]}{10\bar{j}_2(0)}. \quad (12)$$

It has been shown experimentally¹⁵ that a field-dependent term of the form $-\omega^{1/2}$ [as given in Eq. (11)] holds for the liquid phase even under less stringent conditions: i.e., it is sufficient that

$$0 < \omega_S \tau < 1, \quad (13)$$

where $\tau = d^2/D$; it is not required that $\omega_S^2 \tau^2 \ll 1$. In studies in which $\omega_S \tau$ was varied from 0.5 to 50, the $-\omega^{1/2}$ law agrees with experiment to within 1% if the condition expressed in Eq. (13) is satisfied; i.e., deviation from $-\omega^{1/2}$ behavior becomes observable for $\omega_S \tau > 2.1$, or in terms of Eq. (11), when $f(T) \sqrt{\omega_I} > 0.35$.¹⁵

In the formal kinetic theory of gas phase relaxation, there have been no theoretical studies of the field dependence of intermolecular dipole-dipole relaxation, which would require a field-dependent transition operator. Let us use the correlation function approach which, as stated in Eq. (2), leads to the same field-independent limiting form as kinetic theory. First, it is necessary to determine the gas phase conditions under which the low-frequency limiting form of the field dependence can be observed. In the translational diffusion model for relaxation in the liquid, the characteristic time for encounters between I -bearing and S -bearing molecules is the translational correlation time $\tau_{tr} = d^2/D$. In the gas, the analogous characteristic time is d/\bar{v} . Thus, the condition analogous to Eq. (13) in the gas phase is

$$0 < \omega_s \frac{d}{\bar{v}} < 1, \quad (14)$$

where d is the characteristic length of the intermolecular interactions which we will take to be r_0 , that intermolecular separation for which $V = 0$ in the isotropic part of the intermolecular potential. For Xe in O₂ we use 3.65 Å, the arithmetic mean of the characteristic lengths for Xe–Xe and O₂–O₂ interactions.²⁹ For Xe in O₂, d/\bar{v} is 7.33×10^{-13} s at 300 K, so that $\omega_s d/\bar{v}$ is 0.61 and 1.21 for magnetic fields in which the ¹²⁹Xe resonance frequencies are 55.4 and 110.7 MHz, respectively (4.7 and 9.4 T). Under these conditions we expect the $-\omega^{1/2}$ law to be just still valid so that the analogous equation to Eq. (11) is

$$\frac{1}{T_{1\text{GAS}}} = \frac{1}{T_1^{(0)}} \{1 - f(T)\sqrt{\omega_I}\}, \quad (15)$$

where $1/T_1^{(0)}$ is given by Eq. (2). Following Sholl,⁵ the form of the function $f(T)$ for the gas should be very similar to that given in Eq. (12) for the liquid, except that we replaced d^2/D by d/\bar{v} for the gas:

$$f(T)_{\text{GAS}} \approx \frac{1}{24} \left(\frac{d}{\bar{v}}\right)^{1/2} [3 + 7(\gamma_S/\gamma_I)^{1/2}]. \quad (16)$$

Note that there is a $T^{-1/4}$ dependence in $\bar{v}^{-1/2}$ in Eq. (16). In this work, we determine $f(T)$ experimentally, verify whether we are in the range $f(T)\sqrt{\omega_{\text{Xe}}} < 0.35$ in which the $-\omega^{1/2}$ law is expected to hold, and compare the experimental $f(T)$ with the values which can be calculated from Eq. (16).

Our measurements at three fields for ¹⁹F in SF₆ in O₂³⁰ and also ¹²⁹Xe in O₂ in this work reveal that the field dependence is not negligible at the frequencies used here, i.e., $f(T)\sqrt{\omega_I} \approx 0.2$ – 0.3 , which are still within the limits for which $-\omega^{1/2}$ behavior is expected.

From Eqs. (15) at two magnetic fields corresponding to ¹²⁹Xe resonance frequencies ω_1 and ω_2 , we obtain the ratio

$$\frac{T_1(\omega_2)}{T_1(\omega_1)} = \frac{1 - f(T)\sqrt{\omega_1}}{1 - f(T)\sqrt{\omega_2}},$$

so that

$$f(T) = \frac{[T_1(\omega_2)/T_1(\omega_1) - 1]}{\{[T_1(\omega_2)/T_1(\omega_1)]\sqrt{\omega_2} - \sqrt{\omega_1}\}}. \quad (17)$$

This allows us to obtain $f(T)$ in Eq. (15) directly from the observed T_1 values shown in Fig. 2 at two fields, without making any assumptions about the temperature dependence or functional form of $F(V/kT)$ or of $f(T)$.

The results of analyzing our T_1 data by Eq. (17) are the $f(T)$ values shown in Fig. 4. The temperature dependence of $f(T)$ is not very precisely determined by experiment, a fit to a quadratic function in temperature shows that an adequate description of the points in Fig. 4 is given by the function

$$f(T) = 1.19 \times 10^{-5} - 5.6 \times 10^{-7} (T/300) - 2.4 \times 10^{-10} (T - 300)^2 \text{ s}^{1/2}.$$

On the other hand, from Eq. (16) we calculate

$$f(T) = 1.225 \times 10^{-5} (T/300)^{-1/4} \text{ s}^{1/2}.$$

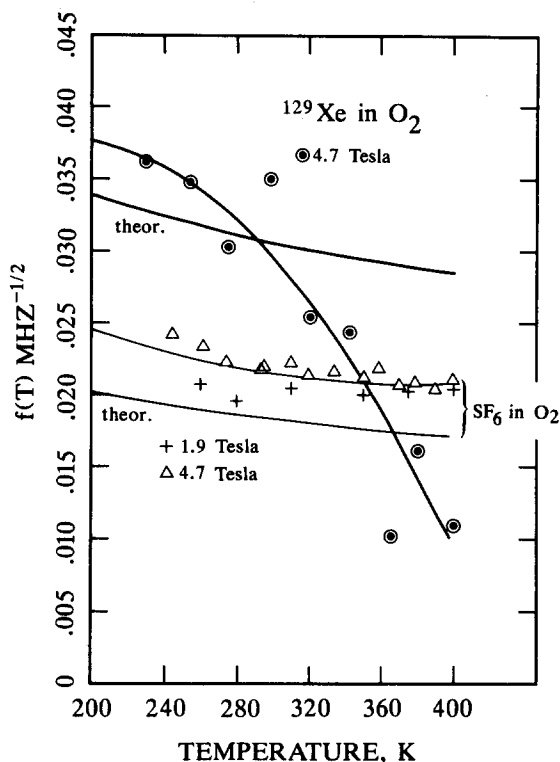


FIG. 4. The field dependence of ¹²⁹Xe spin relaxation rates in the presence of oxygen is expressed in the form $1/T_1 = 1/T_1^{(0)}\{1 - f(T)\sqrt{\omega_I}\}$. The experimental values of $f(T)$ shown above are obtained using Eq. (17). The theoretical estimate from Eq. (16) is also shown. Comparison is made with SF₆ in O₂. All experimental points used 9.4 T as the reference field in Eq. (17).

which gives $f(T)\sqrt{\omega_{\text{Xe}}} \sim 0.23$ and 0.32 at 300 K at 4.7 and 9.4 T, respectively. These magnitudes are consistent with our experimental values at 300 K, $f(T)\sqrt{\omega_{\text{Xe}}} = 0.22$ and 0.31 , respectively, although the observed temperature dependence is about T^{-2} and is not consistent with the $T^{-1/4}$ form predicted by Eq. (16). In Fig 4, SF₆ in O₂ results³⁰ are also shown for comparison. The SF₆ data follow the temperature dependence predicted by Eq. (16). We have no explanation for the qualitatively different behavior of the Xe data. Very high relative translational energies correspond to the $\omega = 0$ limit even at these magnetic fields (4.7 and 9.4 T) because the electron spin dipoles do not have time to precess in the duration of a collision. Thus, if the form of Eq. (15) is retained, then at high enough temperatures the empirical $f(T)$ should eventually go to zero. However, it is not clear why Xe in O₂ appears to be approaching this limit well before SF₆ in O₂, in the same temperature range.

Using the $f(T)$ values from the field-dependent studies, we can find empirical values of $F(V/kT)$ from Eqs. (15) and (2). These are shown in Fig. 5, and the functional form can be fitted to

$$F(V/kT) = (5.94 \pm 0.18) (T/300)^{-0.27 \pm 0.02}$$

or to a quadratic form:

$$F(V/kT) = 6.00 - 4.3 \times 10^{-3} (T - 300) - 1.9 \times 10^{-5} (T - 300)^2.$$

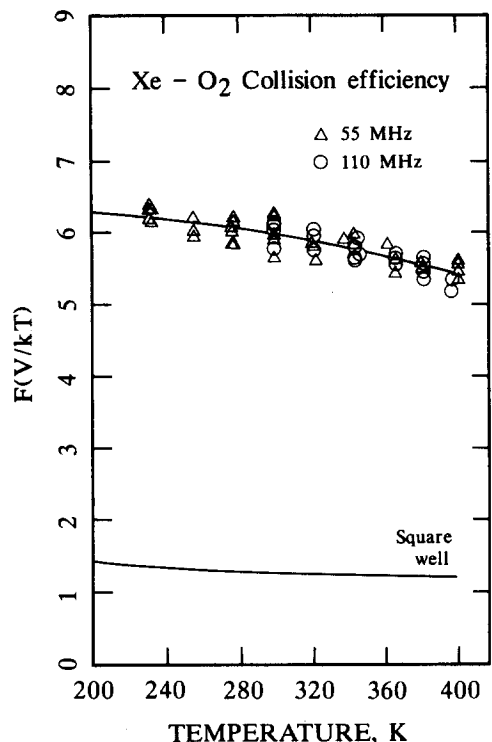


FIG. 5. The collision efficiency, $F(V/kT)$ obtained empirically from relaxation times, compared with that calculated from Bloom-Oppenheim theory using a square-well potential.

The scatter in the data points shown in Fig. 5 are largely due to errors in density. These are fairly large collision efficiencies. In this temperature range Xe in O₂ is clearly not in the high translational energy limit in a hard sphere potential. Also shown in Fig. 5 this is the function $F(V_0/kT)$ calculated in Eq. (6) using a square-well potential, of depth $V_0 = 0.56 \epsilon$, where ϵ is taken to be 182.2 K, the geometric mean of the Xe-Xe and O₂-O₂ well depths.²⁹ Not unexpectedly, we see that the observed $F(V/kT)$ is greater than that which is calculated by the Openheim and Bloom model [Eq. (6)] using a square-well potential. However, to the extent that it can be determined, the temperature dependences are

essentially the same in this range of temperatures. Although the least squares fit to a quadratic function is concave downwards as shown in Fig. 5, the data points are not inconsistent with our findings in other systems, namely concave upwards.³⁰

The quantities resulting from this study are summarized in Table I. As defined in Eq. (8), the effective cross section is given by

$$\sigma_{\text{eff}} = \sigma_{\text{geom}} \cdot F(V/kT) = 250(T/300)^{-0.27} \text{ \AA}^2. \quad (18)$$

This is an empirical Boltzmann-averaged collision cross section associated with the collision-induced transitions between ¹²⁹Xe nuclear spin states. However, the results of this work are not necessarily attached to a cross section interpretation. The data measured at various densities and different magnetic fields are all represented by the simple empirical functional form which is

$$F(V/kT)\{1 - f(T)\sqrt{\omega_I}\},$$

which can be interpreted either in terms of effective cross sections for nuclear spin relaxation by intermolecular dipolar coupling, as in Eq. (18) or alternatively, in the time correlation function approach. In the latter interpretation, the field-dependent empirical function $F(V/kT)\{1 - f(T)\sqrt{\omega_I}\}$ is our representation of

$$j(\omega) \equiv \frac{1}{10} \{ \bar{j}_2(\omega_I - \omega_S) + 3\bar{j}_2(\omega_I) + 6\bar{j}_2(\omega_I + \omega_S) \}, \quad (19)$$

the reduced spectral density functions for an interacting Xe-O₂ molecular pair, in the "low-frequency limit." The functions are shown in Fig. 6 for $\omega = 55.35$ MHz and $\omega = 110.7$ MHz and can be described by the following functional forms:

$$\begin{aligned} \frac{\omega_I}{2\pi} &= 55.35 \text{ MHz:} \\ j(\omega) &= 4.65 + 2.8 \times 10^{-3}(T - 300) \\ &\quad + 1.1 \times 10^{-5}(T - 300)^2, \\ &T = 230\text{--}400 \text{ K,} \end{aligned} \quad (20)$$

TABLE I. Summary of parameters for Xe-O₂ and the results on ¹²⁹Xe spin relaxation in oxygen gas in the temperature range 230–400 K.

	$\frac{1}{T_1} = \frac{16}{3} S(S+1) \gamma_I^2 \gamma_S^2 \frac{\hbar^2}{d^2} \left(\frac{\pi\mu}{8kT} \right)^{1/2} \rho_O \cdot F(V/kT) \cdot \{1 - f(T)\omega_{Xe}^{1/2}\}$	
μ (amu)		25.639 ^a
d (Å)		3.65 ^b
$2\pi\omega_{Xe}$ (MHz)	55.35	110.7
$B(T) = (T_1 \rho_{O_2})^{-1} \text{ s}^{-1} \text{ amagat}^{-1}$	$0.388(T/300)^{-0.03c}$	$0.343(T/300)^{-0.03d}$
$B(T, \omega = 0 \text{ limit})$		$0.491(T/300)^{-0.77 \pm 0.02}$
$F(V/kT)$		$6.00 - 4.3 \times 10^{-3}(T - 300) - 1.9 \times 10^{-5}(T - 300)^2$
$f(T) \text{ (s}^{1/2}\text{)}$		$1.19 \times 10^{-5} - 5.6 \times 10^{-7}(T - 300) - 2.4 \times 10^{-10}(T - 300)^2$
$\sigma_{\text{eff}} \text{ (Å}^2\text{)}$		$250(T/300)^{-0.27}$

^a For ¹²⁹Xe-nat O₂.

^b Arithmetic mean of the values characteristic of the Xe-Xe and O₂-O₂ interaction from the conformal intermolecular potentials scaled by an extended law of corresponding states (Ref. 29).

^c At 55 MHz.

^d At 111 MHz.

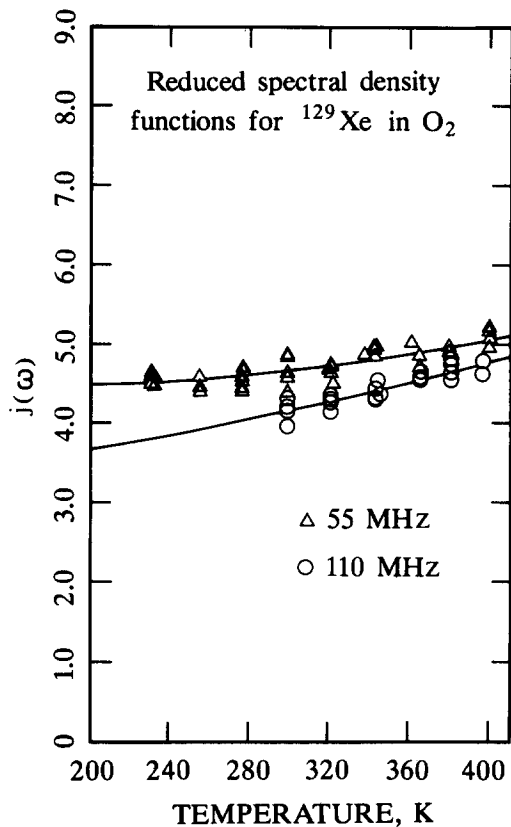


FIG. 6. The empirical values of the dimensionless reduced spectral density functions $j(\omega)$, as defined in Eq. (19), are shown here for Xe in O₂ at $\omega/2\pi = 55.35$ and 110.7 MHz. The curves are the least squares fits to quadratic functions in temperature, given in Eqs. (20) and (21).

$$\frac{\omega_I}{2\pi} = 110.7 \text{ MHz};$$

$$j(\omega) = 4.16 + 5.5 \times 10^{-3}(T - 300) + 5.7 \times 10^{-6}(T - 300)^2, \quad T = 300\text{--}400 \text{ K}. \quad (21)$$

The scalar mechanism

The primary mechanism for the large chemical shifts of ¹²⁹Xe interacting with O₂ molecules is the scalar interaction $A \cdot \mathbf{I} \cdot \mathbf{S}$, where A is the scalar part of the nuclear spin–electron spin coupling constant. \mathbf{I} and \mathbf{S} are the nuclear and electron spin angular momenta (in units of \hbar).^{23,31} This interaction also contributes to the ¹²⁹Xe spin relaxation as follows¹⁴:

$$\frac{1}{T_1^{\text{sc}}} = \frac{2}{3} S(S+1) \left(\frac{\langle A(R) \rangle}{\omega_S \hbar} \right)^2 \frac{1}{\tau_S}. \quad (22)$$

This mechanism can provide an important contribution when τ_S is very short, such as when a Heisenberg-type of spin exchange is occurring. The spin exchange in solid O₂ at 4 K has been measured, the rate is $1.5 \times 10^{13} \text{ s}^{-1}$.³² Since this is a bimolecular process the exchange frequency is proportional to $\rho_{\text{O}_2}^2$, and is estimated to be $\sim 5 \times 10^{10} \text{ s}^{-1}$ in the gas phase at 30 amagat density of O₂. This is small compared to other contributions to the electron spin relaxation rate such as the mechanism described by Gordon.³³ O₂–O₂ collisions change the molecular rotation of the O₂ molecule; the electron spin sees this as a sudden switching of its quantization

axis, leading to a superposition of electron spin states. With this interpretation the nonresonant magnetic dipole absorption in the microwave spectrum of O₂ gas provides a cross section $\sigma = 22 \text{ \AA}^2$ or $\rho \bar{v} \sigma = 0.54 \text{ kmHz/atm}$,³³ which leads to $\tau_S = 9.8 \times 10^{-12} \text{ s}$ in 30 amagat O₂ gas. An average value of $A(R)$ can be obtained from the chemical shift experiments.²³ The contact part of the observed shift dominates except at high temperatures, since

$$\sigma_{\text{contact}}(R) = - \frac{\gamma_e S(S+1)}{\gamma_N 3kT} A(R). \quad (23)$$

The $1/T$ dependence of the shift expressed in Eq. (23) was observed below 350 K. At 300 K the experimental value of the chemical shift of ¹²⁹Xe due to collisions with O₂ is²³

$$\langle \sigma(R) \rangle^{300 \text{ K/ppm}} = -1.061 (\rho_{\text{O}_2}/\text{amagat}).$$

From this we obtain an average scalar coupling constant at 300 K,

$$\langle A(R) \rangle^{300 \text{ K/MHz}} = 4.2 \times 10^{-3} (\rho_{\text{O}_2}/\text{amagat}).$$

Using $\tau_S = 9.8 \times 10^{-12} \text{ s}$ from the nonresonant microwave experiments and this average scalar coupling in Eq. (22), leads to

$$\frac{1}{T_1^{\text{sc}}} = 3 \times 10^{-2} \text{ s}^{-1}$$

for ¹²⁹Xe at 9.4 T, in 30 amagat O₂ gas at 300 K. This value is about 0.3% of the observed value of $1/T_1$ which is 10.4 s^{-1} . Thus, while the scalar mechanism is responsible for the chemical shift, the dipolar mechanism dominates the relaxation of ¹²⁹Xe in oxygen gas, as we have assumed in this work.

SUMMARY AND CONCLUSIONS

From these T_1 measurements of ¹²⁹Xe in Xe/O₂ gas mixtures we have verified the following:

(1) At these O₂ concentrations the ¹²⁹Xe relaxation is entirely dominated by the intermolecular magnetic dipole coupling mechanism. The direct proportionality of the relaxation rate ($1/T_1$) to the oxygen density is verified, i.e.,

$$\frac{1}{T_1} = B(T) \rho_{\text{O}_2}$$

describes the relaxation of ¹²⁹Xe in these samples very well. The contribution to ($1/T_1$) due to the intermolecular spin-rotation mechanism which is observed in pure xenon gas is found to be negligible when the oxygen densities in the mixture are significant (mole fraction of O₂ greater than 0.005).

(b) Analysis of the data at two fields permit the interpretation of the results in terms of

$$\frac{1}{T_1} = \frac{1}{T_1^{(0)}} [1 - f(T) \sqrt{\omega}],$$

where the values of the temperature-dependent parameter $f(T)$ are determined experimentally. We do not as yet have a description of $f(T)$ in molecular scattering terms. This would require a field-dependent transition operator. However, we propose in Eq. (16) an expression for $f(T)$ which is based on the correlation function approach.

(3) An effective cross section for intermolecular magnetic dipole coupling is defined and it obtained empirically for the Xe–O₂ collision pair. This quantity involves the Xe–O₂ intermolecular potential function in $F(V/kT)$.

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