

Rb-Xe spin relaxation in dilute Xe mixtures

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We present measurements of spin-relaxation of Rb atoms in He(98%)-N₂(1%)-Xe(1%) mixtures similar to those used in magnetic resonance imaging polarizers. The pressure dependence allows us to separate out contributions from Rb-Xe van der Waals molecules and binary collisions. For the first time, we observe the predicted increase in the molecular contribution at high pressure. Our data suggest that the deduced molecular breakup rate has a strong temperature dependence.

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The realization of magnetic resonance imaging of human subjects using hyperpolarized noble gases [1] has stimulated the intense development of Xe-Rb spin-exchange optical pumping [2] in high pressure buffer gases [3–5]. The need to minimize the mismatch between the Rb absorption linewidth and the linewidth of inexpensive, high power but broadband diode laser sources requires pressure broadening the Rb resonance lines with many atmospheres of He gas, chosen for its weak spin-relaxation properties [6]. Despite the widespread use of high pressure He for Xe-Rb spin exchange, there exist no systematic studies of spin relaxation and spin exchange rates under such conditions, as most of the pioneering work in Xe spin-relaxation and spin-exchange either had no buffer gas [7] or used N₂ buffer gas [8]. Two recent experiments report relaxation rates measured at a single pressure and temperature [4,5]. In this paper we report measurements of spin-relaxation rates at 80 and 150 °C, in He(98%)-N₂(1%)-Xe(1%) mixtures similar to those used in commercial polarizers.

There are a number of collisional phenomena that govern the spin-relaxation properties of Xe-Rb spin-exchange mixtures, and a comprehensive theory of their effects has recently been published by Appelt and colleagues in this journal [9]. Spin relaxation occurs either in binary collisions between Rb and Xe atoms, or in bound Rb-Xe van der Waals molecules with a binding energy of roughly 20 meV [10]. Such weakly bound molecules are easily broken up by collisions with free atoms. At multi-amagat pressures common in practical spin-exchange experiments, binary collisions are responsible for the majority of the spin relaxation but the molecular contributions are by no means insignificant.

As described in Refs. [9] and [11], the behavior of Rb-Xe molecular relaxation depends critically on the gas density. At low densities, the molecular lifetime is sufficiently long that the Rb electron spin couples strongly both to its nucleus **I** via the hyperfine interaction and to the rotational angular momentum **N** of the molecule via the spin-rotation interaction $\gamma\mathbf{S}\cdot\mathbf{N}$ [12]. This long molecular lifetime regime is characterized by a rapid increase in the spin-relaxation rate with increasing gas density due to increasing rates of molecular formation. At higher densities, the molecular contribution to spin relaxation saturates as increasing formation rates are offset by short molecular lifetimes that interrupt the precession of **S** about **N**. The molecular lifetimes are however still sufficiently long that the hyperfine interaction couples **S**

strongly to **I** and reduces the precession rate of **S** about **N** by a factor of $2I+1$. At still higher densities, several amagats, the molecular lifetimes enter the so-called “very short” regime where the hyperfine interaction is too weak to couple **S** to **I** in a molecular lifetime. The transition between the “short” and “very short” has to our knowledge never been studied before experimentally. The expected pressure dependence of relaxation due to van der Waals molecules is shown in Fig. 1.

In this paper we present a study of the pressure dependence of Rb spin relaxation in He(98%)-N₂(1%)-Xe(1%) mixtures similar to those used in magnetic resonance imaging polarizers. We observe not only the binary relaxation, but the molecular contributions to the spin relaxation in all three density regimes.

In Sec. I, we present measurements of Rb spin relaxation at 150 °C where Rb-Rb spin-exchange collisions occur at a

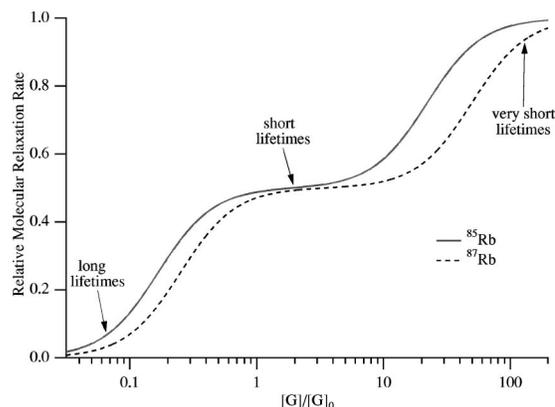


FIG. 1. Expected pressure dependence of relaxation of the two stable isotopes of Rb due to Rb-Xe van der Waals molecules, for fixed Xe gas fraction. At low pressures, the molecular lifetime is sufficiently long that the spin polarization is completely lost during a molecular lifetime. The relaxation rate is hence proportional to the three-body molecular formation rate which increases as the square of the gas density. At higher densities characterized by $[G]_0$, the relaxation becomes density independent as the increasing formation rate is compensated by a small relaxation probability in a single, short molecular lifetime. At still higher densities or very short lifetimes, the hyperfine interaction is too weak to slow down the precession of the electron spin about the field of the spin-rotation interaction.

high rate. The resulting spin-temperature equilibrium of the Rb atoms makes the interpretation of spin-relaxation transients straightforward. From the gas density dependence of the spin-relaxation rate, we isolate the contributions from Rb-Xe binary collisions and formation of Rb-Xe van der Waals molecules, including the first observation of the transition between short and very short molecular lifetimes that occurs in the 1–4 amagat density range. Direct comparison to recent experiments under similar conditions [4,5] gives good agreement.

In Sec. II, we present similar measurements at 80 °C where Rb-Rb spin-exchange collisions are infrequent and the two Rb isotopes relax independently, with different time constants. We observe the transitions between the long, short, and very short molecular lifetime regimes. In Sec. III we discuss some consequences of the molecular measurements, including evidence for a temperature dependence to the molecular breakup rates.

I. Rb RELAXATION–HIGH TEMPERATURE

Our experiment follows closely the design of other recent spin-relaxation experiments in our laboratory [13,14]. A glass cell, 8 cm long and 4 cm diameter, contains Rb metal and the gas mixture. A gas-handling system connected to the cell allows the gas density to be varied from 0.1 to 4 amagat. The gas was premixed commercially. The gas system includes a heat-activated filter to reduce gas impurities. An air-heated oven holds the cell at a temperature of 150 °C, corresponding to a Rb density of approximately $6 \times 10^{13} \text{ cm}^{-3}$. A pair of Helmholtz coils puts a uniform 8 G magnetic field on the atoms. The Rb atoms are spin polarized using circularly polarized light from a broadband diode array, intentionally tuned 1.2 nm off the atomic $5S_{1/2} \rightarrow 5P_{1/2}$ resonance to produce a spatially homogeneous, low (<5%) Rb spin polarization. Spatially homogeneous pumping limits the importance of high order diffusion modes, while low spin polarization avoids unnecessary complications from the nonlinear effects of Rb-Rb spin exchange [9]. The Rb spin polarization is monitored by Faraday rotation of a 0.5 mW, 3 mm diameter diode laser beam tuned 2 nm off the $5S_{1/2} \rightarrow 5P_{3/2}$ resonance. The large probe detuning ensures a light-induced relaxation rate of $<1/s$ at the highest gas pressures. A mechanical chopper periodically blocks the pump light and relaxation transients “in the dark” are digitized and averaged by a digital oscilloscope. The relaxation transients were fit to single exponentials $\exp[-\Gamma t]$ with a typical statistical uncertainty in the fitted decay rates of 1/s.

Figure 2 shows the decay rates as a function of gas density. The transient decay rates were highly reproducible, except when fresh gas was put into the cell the relaxation rates sometimes temporarily decreased by 5–10 s^{-1} due to reduced Rb vapor pressure. The reduced vapor pressure affects the spin-exchange corrections to the observed relaxation rates, and is likely due not to Rb-Rb relaxation [13–15].

We analyze the data of Fig. 2 using the theory of Appelt *et al.* [9]. Under the conditions of this experiment, the dominant collisional processes are Rb-Rb spin-exchange colli-

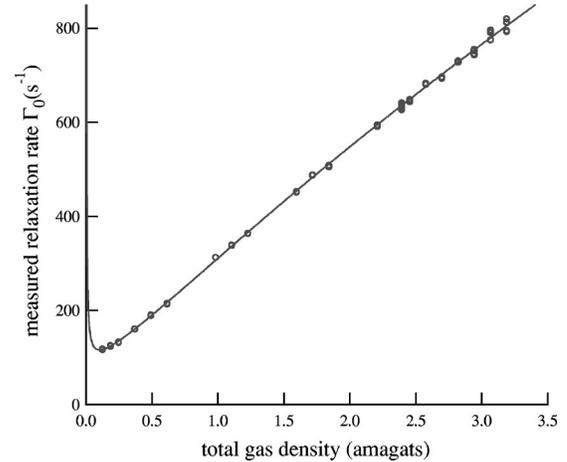


FIG. 2. Measured transient decay rates as a function of total gas density, for a mixture of 98% He, 1% N₂, and 1% Xe.

sions, Rb-Xe binary collisions, and formation and breakup of Rb-Xe van der Waals molecules. The Rb-Rb spin-exchange collisions to a good approximation [13–15] conserve the spin-angular momentum, but redistribute it between nuclear and electron spins. The Rb-Xe relaxation processes lose small amounts of spin-angular momentum to either rotational angular momentum or the nuclear spin of the Xe. In the low spin-polarization limit satisfied by our experiment, the density matrix of the Rb atoms can be accurately parametrized in terms of the angular momenta $\langle a_z \rangle$ and $\langle b_z \rangle$ stored in the two Rb hyperfine levels $a = I + 1/2$ and $b = I - 1/2$, I being the Rb nuclear spin. It is convenient to classify the Rb spin relaxation in terms of two contributions: the F-damping and S-damping rates Γ_F and Γ_S . F-damping collisions obey the selection rule $\Delta F = 0$ while S-damping collisions obey $\Delta F = 0, 1$. Rb-Rb spin-exchange collisions occur at the rate Γ_{SE} .

As shown by Appelt *et al.* [9], the effects of Rb-Xe van der Waals molecules must be included in both Γ_F and Γ_S , while binary collisions contribute only to Γ_S . It is useful to parametrize the effects of Rb-Xe van der Waals molecules in terms of

$$\Gamma_{\text{vdW}} = \left(\frac{2\phi^2/3 + \eta\phi^2/2}{T_A} \right) \quad (1)$$

which is the molecular relaxation rate in the short lifetime limit for a fictitious alkali isotope with nuclear spin $I = 0$. It is also the relaxation rate in the very short lifetime limit for arbitrary I . The ϕ factors are the rms precession angles for the spin-rotation interaction and the alkali-noble-gas spin-exchange interaction. These vary, for fixed gas composition, inversely with the square of the total pressure. The factor $1/T_A$ is the molecular formation rate per Rb atom. The molecular formation occurs via three-body collisions, and hence is proportional to the square of the pressure. Thus the combination of Eq. (1) is pressure independent for fixed gas composition and is therefore a convenient parameter with which to characterize the molecular contributions to spin relaxation. The isotopic fraction of ^{129}Xe in natural abundance Xe is $\eta = 0.264$.

The F -damping rate for isotope i ($i=85,87$) is

$$\Gamma_{iF} = (1 - J_i)\Gamma_{\text{vdW}} \quad (2)$$

while the S -damping rate is

$$\Gamma_{iS} = \langle \sigma v \rangle [\text{Xe}] + J_i \Gamma_{\text{vdW}}. \quad (3)$$

The first term represents binary collisions that occur at the rate $\langle \sigma v \rangle [\text{Xe}]$ while the second term is the S -damping contribution of van der Waals molecules. The factor $J_i = 1/(1 + \omega_i^2 \tau^2)$ depends on the hyperfine splitting $\hbar \omega_i$ between levels a_i and b_i and the molecular lifetime τ . It can be thought of as the fraction of molecules whose lifetimes are shorter than $1/\omega_i$. At low densities (long or short molecular lifetimes, $\omega_i \tau \gg 1$, $J_i \ll 1$), the nuclear spin strongly couples to the electron spin and $a \leftrightarrow b$ collisions are suppressed. At high densities (very short lifetime, $\omega_i \tau \ll 1$, $J_i \approx 1$) the hyperfine interaction is too weak to couple the nuclear and electron spins during a molecular lifetime and so $a \leftrightarrow b$ transitions are allowed. It is convenient to introduce a characteristic density G_1 defined by

$$\omega_{85} \tau = [G]_1 / [G], \quad (4)$$

where $[G] = [\text{He}] + [\text{N}_2] + [\text{Xe}]$ is the total gas density. $[G]_1$ then represents the characteristic density representative of the transition between short and very short molecular lifetimes.

As shown by Appelt *et al.* [9], relaxation and spin exchange cause the rate equations for $\langle a_z \rangle$ and $\langle b_z \rangle$ to be coupled to each other for a given Rb isotope, and spin exchange also couples the two isotopes together. For relaxation in the dark, the observed relaxation rate is usually a combination of the basic rates Γ_F and Γ_S . In general, the relaxation of the Rb spins is described by four time constants in the low polarization limit. Fortunately, one of these is much longer than the others, leading to simple single-exponential decay. In the spin-temperature limit ($\Gamma_{\text{SE}} \gg \Gamma_F, \Gamma_S$) [16] the slowest decay mode of the system decays at the rate

$$\Gamma_0 = 0.0926\Gamma, \quad (5)$$

$$\Gamma = \langle \sigma v \rangle [\text{Xe}] + (0.358 + 0.467J_{85} + 0.175J_{87})\Gamma_{\text{vdW}}. \quad (6)$$

For the analysis of our data, we have included the first order ($\Gamma_{\text{vdW}}/\Gamma_{\text{SE}}$, $\langle \sigma v \rangle [\text{Xe}]/\Gamma_{\text{SE}}$) corrections to this, which represent about a 5% correction at the highest gas densities [17]. Fluctuations in the observed relaxation rates due to vapor pressure fluctuations dominate the experimental errors. As expected, no evidence was found for multiple relaxation times in the analysis of the decay transients.

At the lowest pressures of Fig. 2, additional relaxation mechanisms come into play, in particular from diffusion to the walls and quadrupole relaxation in Rb_2 singlet molecules [18]. Both of these effects are inversely proportional to $[G]$ and we parametrize them by adding a term $a/[G]$ to Eq. (5). At low pressures, Γ_{vdW} in Eq. (6) for each isotope must be multiplied by a factor $K_i = \{1 + [\phi_\gamma / (2I_i + 1)]^2\}^{-1}$ to account for long lifetime molecules [11]. It is convenient to

define a density characteristic of the spin-rotation interaction via $[G]_0/[G] = \phi_\gamma$. This modification of the van der Waals relaxation at low pressure is much less important than diffusion and singlet molecules at this temperature, making our data insensitive to the value of $[G]_0$. We therefore assume the relationship $[G]_1/[G]_0 = \hbar \omega_{85} / \gamma N = 22.5$ holds, as deduced from the ^{85}Rb hyperfine splitting and the previously measured $\gamma N / h = 135$ MHz [12].

Taking these factors into account gives the following fitting function for the data:

$$\Gamma_0 = \frac{a}{[G]} + 0.0926 \langle \sigma v \rangle [\text{Xe}] + (0.0234K_{85} + 0.00972K_{87} + 0.0432J_{85} + 0.0162J_{87})\Gamma_{\text{vdW}} + \Gamma_{\text{corr}}, \quad (7)$$

Γ_{corr} is the small Rb-Rb spin-exchange correction given in detail in Ref. [17]. We fit Eq. (7) to the data of Fig. 2, using as free parameters a , $\langle \sigma v \rangle$, Γ_{vdW} , and $[G]_1$. The fit to the data is excellent, and gives

$$a = 2.66 \pm 0.64_{+0.37}^{-0.1} \text{ amagat/s}, \quad (8)$$

$$\langle \sigma v \rangle = 2.44 \pm 0.02_{+0.16}^{-0.07} \times 10^5 \text{ amagat}^{-1} \text{ s}^{-1}, \quad (9)$$

$$\Gamma_{\text{vdW}} = 2049 \pm 110_{-120}^{+40} \text{ s}^{-1}, \quad (10)$$

$$[G]_1 = 1.95 \pm 0.2_{+0.66}^{-0.21} \text{ amagat}. \quad (11)$$

The last two numbers are specific to a He(98%)- N_2 (1%)-Xe(1%) mixture. For each number, the first error is statistical, while the second σ^+ (σ^-) pair of numbers gives the change in the fit parameters when the assumed Rb density is increased (decreased) by 30%, changing the spin-exchange corrections to the decay transients.

A direct comparison of these results can be made with recent work on polarization imaging of dense (>7 amagat) optically pumped cells with similar gas compositions to ours [4,5]. For these experiments the width of magnetic resonance lines depends on the spin-relaxation rate. The quoted relaxation rates are total spin relaxation rates γ where $d\langle F_z \rangle / dt = -\gamma \langle S_z \rangle$. At these high pressures, $J_{85} = 0.94$ so we can assume the high pressure limit and find $\gamma \approx \langle \sigma v \rangle [\text{Xe}] + \Gamma_{\text{vdW}}$. For the 7.8 atm, 1.34% Xe cell of Ref. [4] we predict $2.5 \times 10^4 \text{ s}^{-1}$, somewhat smaller than the observed $3 \times 10^4 \text{ s}^{-1}$. For the 7.0 atm, 1% Xe cell of Ref. [5], our results predict $1.72 \times 10^4 \text{ s}^{-1}$ which is in close agreement with the observed $1.84 \times 10^4 \text{ s}^{-1}$.

Our binary rate coefficient result at 150 °C is in agreement with recent results from Princeton University at the same temperature [19], and 66% larger than the $1.41 \pm 0.07 \times 10^5 \text{ s}^{-1} \text{ amagat}^{-1}$ obtained at 27 °C by Bouchiat, Brossel, and Pottier [7]. Much of the difference between the low and high temperature results can probably be accounted for as a temperature dependence of σv . We discuss this further in Sec. II.

To isolate the contribution of Rb-Xe van der Waals molecules to Rb spin loss, we have applied the first order corrections ($\Gamma_{\text{vdW}}/\Gamma_{\text{SE}}$, $\langle \sigma v \rangle [\text{Xe}]/\Gamma_{\text{SE}}$) to the data points

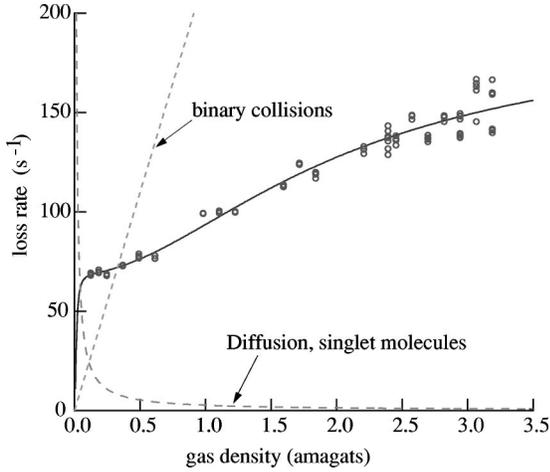


FIG. 3. Data of Fig. 2, corrected for Γ_{SE} , and with $\langle\sigma v\rangle[Xe]$ and $\gamma_{inv}P$ subtracted off. The solid line shows the contribution to the relaxation rate due to formation of van der Waals molecules. The data are only sensitive to short and very short lifetime van der Waals molecules.

themselves (increasing the highest pressure measured values by $\approx 5\%$). We then subtracted the binary spin loss contribution, $[Xe]\langle\sigma v\rangle$, and the diffusion/singlet molecule loss contribution, $a/[G]$, from the data. This adjusted data appears in Fig. 3 along with the fit from Fig. 2, altered in the same manner. It is clearly of the shape expected for the pressure dependence of the van der Waals molecule relaxation in the transition from short to very short molecular lifetimes. To our knowledge, this is the first direct observation of the transition from the short molecular lifetime ($J \ll 1$) limit to the very short ($J \approx 1$) limit.

The contribution to the relaxation from diffusion to the walls and quadrupole relaxation in Rb_2 singlet molecules is consistent with previous experiments. Aymar *et al.* [20] found a diffusion coefficient $D_0 = 0.42 \pm 0.06$ cm²/s at 27 °C. Using this, and assuming a $T^{1/2}$ temperature dependence, we expect a diffusion loss rate for the fundamental diffusion mode of our cell to be 0.81 amagat/s. Assuming the remainder, 1.85 amagat/s, to arise from Rb_2 singlet molecules requires a dimer reorientation cross section for Rb_2 in our gas mixture of 3.6 \AA^2 , approximately half that recently measured for Rb_2 in N_2 [18], a result that seems reasonable given the smaller size and polarizability of He (which constitutes 98% of our gas mixture by volume).

The breakup cross section σ_B can be obtained from Eq. (4), and we obtain $\sigma_B = 26 \text{ \AA}^2$. Again, since our gas is dominated by He, this should be loosely interpreted as the cross section for breakup of Rb-Xe molecules by He atoms.

II. Rb RELAXATION—LOW TEMPERATURE

In natural isotopic mixtures of Rb vapor, interpretation of spin-relaxation transients is considerably complicated by the two isotopes having different nuclear spin. At high temperature, Rb-Rb spin-exchange collisions occur at a high rate and simplify the interpretation of the experiments as described above. At lower temperature, when the Rb-Rb spin-exchange

rate is comparable to the relaxation rates, however, it is necessary to make a precise measurement of the Rb density and to account for multiple time constants in the decay transients. To avoid having to precisely measure the Rb density, we have chosen to repeat the measurements of the previous section at a low enough temperature (80 °C) that the Rb-Rb spin-exchange rates are much less than the spin-relaxation rates.

When spin-exchange collisions can be ignored, the ^{85}Rb and ^{87}Rb populations relax independently. Application of the Appelt *et al.* [9] theory gives two relaxation rates

$$\Gamma_{85} = \frac{1}{18} \left(\langle\sigma v\rangle[Xe] + K_{85} \frac{J_{85} + 1}{2} \Gamma_{vdW} \right) + a/[G], \quad (12)$$

$$\Gamma_{87} = \frac{1}{8} \left(\langle\sigma v\rangle[Xe] + K_{87} \frac{J_{87} + 1}{2} \Gamma_{vdW} \right) + a/[G], \quad (13)$$

where, as before,

$$K_i = \frac{[G]^2}{[G]^2 + \left(\frac{[G]_0}{2(I_i + 1)} \right)^2}$$

describes the reduction of the molecular contribution to the relaxation when the molecular lifetime is sufficiently long that $\gamma N/\hbar > 1$. Our experimental transients indeed fit quite well to a sum of decaying exponentials with these two decay rates, with amplitudes for the two decays that closely agree with theory as well. The ratio of these two rates (at high density) would be simply 2.25 were it not for the J factors, but the J 's are of course to be determined from the data. The $a/[G]$ term accounts for diffusion losses, singlet molecule formation being negligible at this temperature.

We have therefore chosen to analyze our data in the following way. We first fit the transients to a sum of exponentials $\exp(-\Gamma_{85}t) + r \exp(-2.25\Gamma_{85}t)$, with the fit value of r checked to be sure it has approximately the expected amplitude. We take a series of such relaxation transients to determine Γ_{85} at various pressures, and fit the pressure dependence to Eq. (12) with $\langle\sigma v\rangle$, $[G]_1$, and Γ_{vdW} as free parameters. We then use the fit values so determined to calculate the ratio $g = \Gamma_{87}/\Gamma_{85}$ as function of pressure and refit our transients to $\exp(-\Gamma_{85}t) + r \exp(-g\Gamma_{85}t)$. On the first iteration of this procedure, the relaxation rates changed by less than 5% at all pressures, and after the second iteration the rates changed by only 1%. Our measured Rb density was 5×10^{10} cm⁻³, implying Rb-Rb spin-exchange corrections of less than 1%.

The spin-relaxation rate Γ_{85} is shown in Fig. 4 as a function of gas density. The data qualitatively resemble the high temperature data, but at the lower temperature the Rb_2 singlet molecule contribution to the relaxation is smaller and we are able to see the decrease in the van der Waals molecule contribution to the relaxation rate at low pressures. The molecular contributions to the relaxation, obtained as before, are highlighted in Fig. 5.

We find at a temperature of 80 °C

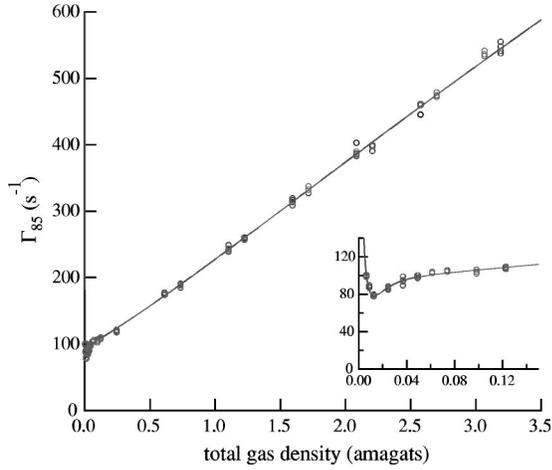


FIG. 4. Spin-relaxation rate Γ_{85} as a function of pressure, with fit. The inset shows the low pressure portion of the data.

$$a = 0.56 \pm 0.01 \text{ amagat/s}, \quad (14)$$

$$\langle \sigma v \rangle = 2.28 \pm 0.07 \times 10^5 \text{ s}^{-1} \text{ amagat}^{-1}, \quad (15)$$

$$\Gamma_{\text{vdW}} = 3240 \pm 100 \text{ s}^{-1}, \quad (16)$$

$$[G]_1 = 2.80 \pm 0.6 \text{ amagat}, \quad (17)$$

$$[G]_0 = 0.100 \pm 0.010 \text{ amagat}. \quad (18)$$

From a , we obtain a diffusion coefficient of $D_0 = 0.35 \pm 0.03 \text{ cm}^2/\text{s}$ at 80°C , in reasonable agreement with Aymar *et al.* [20].

Our binary spin-destruction rate coefficient at 80°C is only slightly smaller than our 150°C result, and considerably larger than the result of Ref. [7]. Figure 6 shows the three experimental results, along with fits assuming a $T^{0.5}$ and $T^{1.2}$ power law. The $T^{0.5}$ dependence would result from a hard sphere interaction potential. We have calculated the expected temperature dependence using the Pascale and Vande-

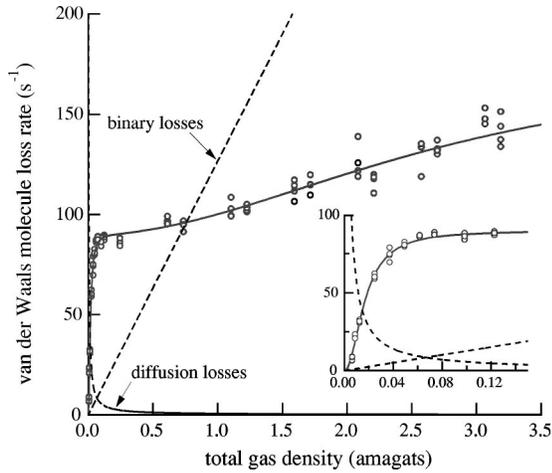


FIG. 5. Same as Fig. 3 except at 80°C . At this lower temperature, all three molecular lifetime regimes are evident. The inset shows in detail the transition from long to short molecular lifetimes.

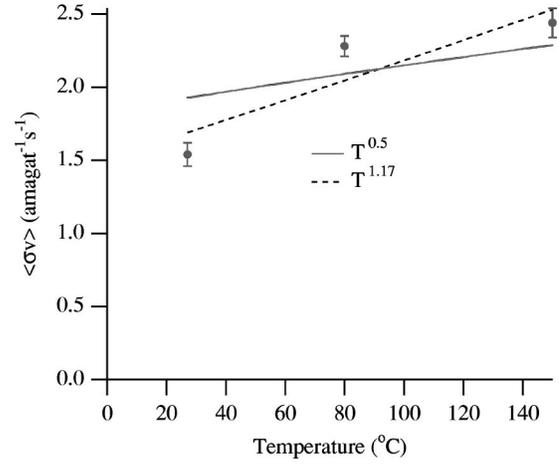


FIG. 6. Comparison of measured binary spin-destruction rate coefficients at three temperatures. The 25°C point is from Ref. [7].

planque potentials [10] and the expected R dependence of the spin-rotation interaction [12]. Because the inner wall of the Rb-Xe potential is not completely rigid, we find that the rate coefficient is predicted to follow a $T^{1.2}$ dependence. The three measured cross sections indeed favor this modest temperature dependence. We note that the substantially softer Rb-He potential gives rise to a much stronger temperature dependence for Rb-He spin relaxation [4,21].

III. ANALYSIS OF MOLECULAR CONTRIBUTIONS TO Rb SPIN RELAXATION

The measured parameters relevant to relaxation in Rb-Xe van der Waals molecules are summarized in Table I.

The ratio of the characteristic pressures is $[G]_1/[G]_0 = 28 \pm 7$ at 80°C , in reasonable accord with the expected 22.5 from the ^{85}Rb hyperfine splitting and the previously measured $\gamma N/h = 135 \text{ MHz}$ [18]. Alternatively, we deduce from $[G]_1$ and $[G]_0$ a value of $\gamma N/h = 109 \pm 26 \text{ MHz}$. Thus the scaling relationship between these two characteristic densities is as expected.

From $[G]_1$, we also find the molecular lifetime to be

$$\tau[G] = \frac{[G]_1}{\omega_{85}} = \begin{cases} 146 \pm 34 \text{ ps amagat} & (80^\circ\text{C}), \\ 99 \pm 36 \text{ ps amagat} & (150^\circ\text{C}). \end{cases} \quad (19)$$

Defining a breakup cross section via $\langle \sigma_B \rangle \langle v \rangle = 1/\tau[G]$ gives 19 and 25 \AA^2 at the two temperatures. The accuracy of these results on $[G]_1$ is not sufficient to say anything about a possible temperature dependence of τ .

TABLE I. Molecular spin loss parameters obtained from Rb spin-relaxation rates.

	80 °C	150 °C
$\Gamma_{\text{vdW}} \text{ (s}^{-1}\text{)}$	3240 ± 100	2049 ± 120
$[G]_1 \text{ (amagat)}$	2.8 ± 0.7	1.95 ± 0.7
$[G]_0 \text{ (amagat)}$	0.100 ± 0.010	

An argument for a substantial temperature dependence of the lifetime comes from the different values of Γ_{vdW} found at the two different temperatures. To this end, we rewrite Eq. (1) in terms of characteristic pressures and coupling constants. Using detailed balance, and introducing the chemical equilibrium coefficient \mathcal{K} , we can write

$$\Gamma_{\text{vdW}} = \frac{2\mathcal{K}[\text{Xe}]}{3\tau} \left(\frac{\gamma N \tau}{\hbar} \right)^2 \quad (20)$$

$$= \frac{2\mathcal{K}[\text{G}]_1[\text{Xe}]}{3[\text{G}]} \left(\frac{\gamma^2 N^2}{\hbar^2 \omega_{85}} \right). \quad (21)$$

Corrections for Rb-Xe spin exchange are at the few percent level for natural Xe mixtures. Direct calculations of \mathcal{K} from the potential curves of Pascale and Vandephanque [10] predict a $T^{-1.57}$ dependence for \mathcal{K} , in close agreement with the naive $T^{-3/2}$ exception obtained by assuming that the Boltzmann factors in the molecular partition function are all nearly one due to the weak van der Waals binding. For the same reason, we expect γN to be largely temperature independent. Based on this argument, we would expect that the ratio of the measured values of Γ_{vdW} at the two different temperatures (353 K, 423 K) should be approximately $(353/423)^{1.5} = 0.76$. The observed ratio is somewhat smaller: 0.63 ± 0.04 implying that $[\text{G}]_1$ probably varies something like T^{-1} , which in turn suggests a substantial temperature dependence for the breakup cross section of Rb-Xe molecules. Indeed, preliminary Rb-Xe spin-exchange data obtained in our lab is consistent with such a sizeable temperature dependence [17].

We can also rewrite Eq. (20) in the form

$$\mathcal{K} = \frac{3[\text{G}]\Gamma_{\text{vdW}}}{2[\text{Xe}][\text{G}]_0(\gamma N/\hbar)} \quad (22)$$

and, using the value $\gamma N/\hbar = 135$ MHz [12] obtained from magnetic decoupling studies at low pressure, we find $\mathcal{K} = 213 \pm 30 \text{ \AA}^3$ at 80°C . Using Eq. (21) at 150°C gives $\mathcal{K} = 155 \pm 56 \text{ \AA}^3$. Both numbers are about 40% lower than expected from the theoretical potential curves [10].

To our knowledge, these are the first studies of Rb-Xe spin relaxation in a predominantly He buffer gas. The pioneering studies of Bouchiat *et al.* [7] and Zeng *et al.* [8] used respectively Xe and N_2 as the third body. A study of Rb-Xe spin exchange in He buffer gas was done by Ramsey *et al.* [22], whose deduced value of $[\text{G}]_0$, 0.21 amagat at 85°C , is about a factor of 2 larger than our result.

IV. CONCLUSIONS

In summary, we have made the first systematic measurements of Rb spin-relaxation rates for Rb-Xe spin-exchange optical pumping in He-dominated buffer gas mixtures of Xe, He, and N_2 . We have observed for the first time the transition from the short to very-short molecular lifetime regime for Rb-Xe van der Waals molecules. In addition, we find evidence that the molecular lifetime is strongly temperature dependent. In the future, studies of the magnetic field dependence of the relaxation rates will provide further information on the molecular contributions to the relaxation. Indeed, preliminary magnetic decoupling studies at Princeton University of Rb-Xe in N_2 buffer gas seem to indicate unusual behavior at high pressures [19].

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