

^{129}Xe -Xe Molecular Spin Relaxation

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(Received 22 October 2001; published 28 February 2002)

We identify the formation of bound ^{129}Xe -Xe molecules as the primary fundamental spin-relaxation process at densities below 14 amagat. Low pressure Xe relaxation rate measurements as a function of gas composition show that Xe-Xe molecular relaxation contributes $1/T_1 = 1/4.1$ h to the total observed relaxation rate. The measured rate is consistent with theoretical estimates deduced from previously measured NMR chemical shifts. At atmospheric pressure the molecular relaxation is more than an order of magnitude stronger than binary relaxation. Confusion of molecular and wall relaxation mechanisms has historically caused wall relaxation rates to be overestimated.

DOI: 10.1103/PhysRevLett.88.113201

PACS numbers: 34.30.+h, 32.80.Bx, 33.25.+k

With the discovery [1] that hyperpolarized ^{129}Xe and ^3He gases are extremely effective for magnetic resonance imaging, and the applications of hyperpolarized gases to a wide variety of problems including polarized targets [2], neutron polarization [3], surface science [4], probing of biological systems [5], polymer science [6], precision measurements [7], and quantum computation [8], the spin-relaxation mechanisms for these spin-1/2 nuclei have assumed great importance, and much progress has been made in their study. Important recent studies of solid [9–11] and liquid [12,13] Xe in particular elucidated many of the key phenomena that govern Xe relaxation. A recent remeasurement [14] of the Xe-Xe relaxation rate at high gas pressures agreed well with older results [15,16]. The longitudinal Xe-Xe spin relaxation originates from the nuclear spin-rotation interaction [11,16,17] that is also responsible for the NMR frequency shift in solids [18] and gases [19].

In this Letter we identify a new gas-phase, room temperature spin-relaxation mechanism due to spin-rotation coupling in bound Xe-Xe van der Waals molecules. For fixed gas composition, this relaxation mechanism is independent of density and thus is difficult to isolate from wall relaxation. By measuring Xe spin-relaxation rates as a function of gas composition, we isolate Xe-Xe relaxation from wall relaxation. The measured relaxation time of 4.1 h for pure Xe is in good agreement with the spin-rotation coupling strength deduced from other gas and solid relaxation rates and sets an important bound on the storage time for undiluted room temperature hyperpolarized Xe gas. This new relaxation mode must also be accounted for in studies of surface relaxation.

The interactions of importance for a ^{129}Xe nucleus (spin $K = 1/2$, magnetic moment μ_K) in a Xe-Xe pair separated by distance R are

$$H = V(R) + \hbar\mathbf{K} \cdot \boldsymbol{\Omega} + c_K(R)\mathbf{K} \cdot \mathbf{N} + \dots, \quad (1)$$

where the first term is the spin-independent Xe-Xe interac-

tion potential [20] (well depth 24.4 meV at an interatomic separation of $R_0 = 4.36$ Å), the second term is the nuclear Zeeman coupling to the magnetic field $\mathbf{B} = K\boldsymbol{\Omega}/\mu_K$, and the last term is the coupling of the nuclear spin to the rotational angular momentum \mathbf{N} of the molecule with energy $c_K(R)$, assumed to dominate over other spin-dependent interactions such as the nuclear spin-dipolar interaction.

Since the Xe-Xe potential is quite similar to the previously studied alkali–noble-gas van der Waals molecules such as Rb-Xe [21], we use those molecules as a prototype for Xe-Xe relaxation. The relaxation rate is the rate $1/T_K$ at which free Xe atoms are formed into molecules, multiplied by the fraction $W(\tau_B)$ of spin lost during the lifetime τ_B of the molecule. By detailed balance, the formation rate is simply related to the chemical equilibrium coefficient \mathcal{K} and the molecular lifetime τ_B : $1/T_K = 2\mathcal{K}[\text{Xe}]/\tau_B$. We further assume that each collision of a Xe-Xe molecule with a third body breaks up the molecule, so that the coherence time for the nuclear spin precession in the molecule is equal to the molecular lifetime. With these assumptions, the Xe nuclear spin-relaxation rate due to van der Waals molecules is

$$\begin{aligned} \Gamma_{\text{vdW}} &= \frac{W}{T_K} = \frac{1}{T_K} \frac{2\langle c_K^2 N^2 \rangle \tau_B^2}{3\hbar^2(1 + \Omega^2 \tau_B^2)} \\ &= \frac{4\mathcal{K}[\text{Xe}]\langle c_K^2 N^2 \rangle \tau_B}{3\hbar^2(1 + \Omega^2 \tau_B^2)}. \end{aligned} \quad (2)$$

Here $\langle c_K^2 N^2 \rangle$ is the mean-square value of the spin-rotation interaction, averaged over the molecular rovibrational states. The expression for W [22] is valid for $\langle c_K N \rangle^2 \tau_B^2 / \hbar^2 \ll 1$, which is valid for this experiment. The field-dependent term in the denominator allows for decoupling of the relaxation due to precession of the nuclei about the external magnetic field [23]. At high pressures and magnetic fields of 10 T or less typical of spin-exchange optical pumping, $\Omega \tau_B \ll 1$ and so we ignore the magnetic field in most of the following.

Since the lifetime is inversely proportional to the density, Eq. (2) predicts that the relaxation rate is independent of pressure for a given gas composition. The important case of pure Xe gives the maximum molecular spin-relaxation rate.

Since the Xe-wall relaxation rate is also independent of density, the primary means of experimentally separating the molecular and wall contributions to the Xe relaxation rate is through the composition dependence. By introducing a buffer gas such as He, Ar, or N₂ at density [B], the molecular lifetime is shortened but the wall relaxation is unaffected. In terms of breakup rate coefficients for the different species,

$$\frac{1}{\tau_B} = k_B[B] + k_{Xe}[Xe], \quad (3)$$

the total relaxation rate from van der Waals molecules becomes, in terms of the pure Xe rate Γ_{vdW}^{Xe} ,

$$\Gamma_{vdW} = \frac{\Gamma_{vdW}^{Xe}}{(1 + r[B]/[Xe])}, \quad (4)$$

where $r = k_B/k_{Xe}$. Thus the relaxation rate depends on the [B]/[Xe] ratio but is independent of total gas density for a given composition.

We measured the spin-relaxation rate of ¹²⁹Xe as a function of composition as follows. A prototype commercial continuous flow ¹²⁹Xe polarizer [24] from Amersham Health produced roughly 100 cm³ quantities of 20%–30% polarized isotopically enriched Xe (82% ¹²⁹Xe) at atmospheric pressure. The Xe was mixed with He, Ar, or N₂ buffer gas and transferred to a 7.5 cm diameter quartz cell with a very reproducible wall relaxation time of 3.0 h. The Xe polarization as a function of time was detected using a series of small angle free-induction decays (FID) excited and detected by a surface coil every 10 min. Polarization loss due to the FID was negligible. The magnetic field was 20.4 G. Plotting the FID amplitude as a function of time and fitting to an exponential decay gave the spin-relaxation rates. The long spin-relaxation times restricted the data taking to about 2–3 decays per day.

Figure 1 shows the relaxation rates as a function of composition, for fixed Xe density of 0.15 amagat. Error bars indicate statistical errors on the FIDs. In the case of He, the first gas studied, wall relaxation rates were less stable than for the subsequent gases. The origin of these fluctuations is unknown.

The spin-relaxation rates, as predicted, decrease with increasing buffer gas density ratio. Thanks to the long wall relaxation time for this cell, we were able to reduce the relaxation rate by nearly a factor of 2 at high buffer gas ratios. The longest relaxation time observed was 2.6 h, corresponding to 3.0 h from the wall and 22 h from the Xe-Xe relaxation. The data were fit to the functional form $\Gamma = \Gamma_w + \Gamma_{vdW}^{Xe}/(1 + r[B]/[Xe])$, with Γ_w the wall relaxation rate. The fit results for each of the three buffer gases are given in Table I. The errors shown are statistical.

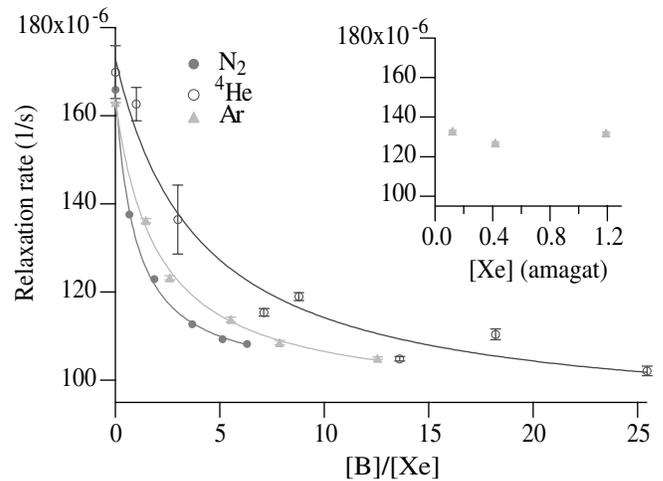


FIG. 1. Xe spin-relaxation rate as a function of composition, for various buffer gases, at a fixed Xe density of 0.15 amagat. Inset: Relaxation rate for [Ar]/[Xe] = 1.75 as a function of Xe density.

The weighted mean for the pure Xe relaxation rate is

$$\Gamma_{vdW}^{Xe} = 6.72 \pm 0.1 \times 10^{-5} \text{ s}^{-1}, \quad (5)$$

corresponding to a relaxation time of 4.1 h. The results for r suggest that He has the smallest breakup rate coefficient for Xe₂ molecules. Ar is next, being larger than He by a factor of 2, and N₂ breaks up Xe-Xe molecules as efficiently as does Xe.

The inset to Fig. 1 shows that, for fixed gas composition, the relaxation rate is independent of gas density, as expected.

We now compare these results to the prediction of Eq. (2). We used a Fourier grid method [25] to find the rovibrational wave functions $|i\rangle$ and energies E_i , and from them the chemical equilibrium coefficient at 297 K of

$$\mathcal{K} = \frac{1}{2} \left(\frac{h^2}{2\pi\mu kT} \right)^{3/2} Z = 230 \text{ \AA}^3, \quad (6)$$

where $Z = \sum_i (2N_i + 1) e^{-E_i/kT}$ is the partition function for the internal states of the Xe₂ molecule, and μ its reduced mass.

The mean value of the spin-rotation coupling is properly also a weighted sum over states:

$$\langle c_K^2 N^2 \rangle = \frac{1}{Z} \sum_i N_i^2 (2N_i + 1) \langle i | c_K(R) | i \rangle^2 e^{-E_i/kT}. \quad (7)$$

TABLE I. The Xe-Xe molecular spin-relaxation rates Γ_{vdW}^{Xe} and the relative breakup rate coefficients r as deduced from the relative density dependence of Xe spin-relaxation in a quartz cell of wall relaxation rate Γ_w .

Buffer gas	Γ_{vdW}^{Xe} (10^{-5} s^{-1})	r	Γ_w (10^{-5} s^{-1})
He	8.23 ± 0.6	0.25 ± 0.08	9.05 ± 0.6
Ar	6.81 ± 0.2	0.49 ± 0.06	9.5 ± 0.2
N ₂	6.63 ± 0.1	1.05 ± 0.08	9.9 ± 0.1

The matrix elements $\langle i|c_K(R)|i\rangle$ require a knowledge of $c_K(R)$, which can be deduced from other experiments. In particular, the Xe-Xe NMR chemical shift is known to be $\sigma_1 = -553$ ppb/amagat at room temperature [26]. Assuming the R dependence has the form $\sigma_1(R) = \sigma_1(R_0)(R_0/R)^6$ [27] gives

$$\sigma_1(T) = \int dR 4\pi R^2 \sigma_1(R) e^{-V(R)/kT} = -553 \frac{\text{ppb}}{\text{amagat}} \quad (8)$$

if $\sigma_1(R_0) = 2.3 \times 10^{-5}$. The chemical shift is related to the spin-rotation coupling via [17]

$$\frac{c_K(R)}{h} = \frac{\mu_K}{K\mu_B} \frac{3\hbar}{4\pi\mu R^2} \sigma_1(R) = \frac{c_K(R_0)}{h} \left(\frac{R_0}{R}\right)^8, \quad (9)$$

where μ_B is the Bohr magneton, and $c_K(R_0) = -24$ Hz. This value is very close to the -27 Hz obtained by Fitzgerald *et al.* [11] from chemical shifts in solid Xe. Using this $c_K(R_0)$, we find

$$\sqrt{\langle c_K^2 N^2 \rangle} = h \times 820 \text{ Hz}. \quad (10)$$

Combining Eqs. (2), (3), and (10) along with our measured value for $\Gamma_{\text{vdW}}^{\text{Xe}}$ allows us to deduce the breakup rate coefficient

$$k_{\text{Xe}} = 1.2 \times 10^{-10} \text{ cm}^3/\text{s} \quad (11)$$

corresponding to a breakup cross section of $4.4 \times 10^{-15} \text{ cm}^2$, a quite reasonable value. Our experimental result is therefore in good agreement with expectations.

We can obtain another estimate of c_K by scaling to the recently remeasured binary spin-relaxation rate [14]. An energy dependent binary spin-relaxation cross section can be defined as

$$\sigma(E) = \frac{8\pi\mu^2}{3\hbar^4} \int_0^\infty b^3 db \times \left| \int_{r_0}^\infty dR \frac{c_K(R)}{\sqrt{1 - b^2/R^2 - V(R)/E}} \right|^2, \quad (12)$$

where r_0 is the classical turning point for the collision with impact parameter b . At a given temperature T , the binary cross section is found by the thermal average

$$\sigma(T) = \frac{1}{(kT)^2} \int_0^\infty dE \sigma(E) E e^{-E/kT}. \quad (13)$$

These formulas agree with those of Ref. [28]. The resulting cross section at 25°C agrees with the binary result of $5.9 \times 10^{-30} \text{ cm}^2$ if

$$|c_K(R)|/h = 41 \text{ Hz} \times \left(\frac{R_0}{R}\right)^8, \quad (14)$$

in fair agreement with the estimate using the frequency shift.

In addition to Xe-Xe molecules, there is also the potential for relaxation from Xe-Ar [29] or Xe-N₂ [30] molecules, which have binding energies of 15–20 meV.

The relaxation produced by these molecules will be, in analogy to Eq. (2),

$$\Gamma'_{\text{vdW}} = \frac{2\mathcal{K}'[\text{B}]\langle c_K^2 N^2 \rangle \tau_B'}{3\hbar^2(1 + \Omega^2 \tau_B'^2)}. \quad (15)$$

This predicts a linear dependence at small density, saturating at high density. From experimental frequency shifts [27] and the potential curves we estimate $\mathcal{K}' = 185 \text{ \AA}^3$ and $\sqrt{\langle c_K^2 N^2 \rangle} = h \times 765 \text{ Hz}$ for Xe-Ar. Assuming these more weakly bound molecules are more readily broken up as compared to Xe-Xe then implies that $\Gamma'_{\text{vdW}}(\text{max}) < 0.35\Gamma_{\text{vdW}}^{\text{Xe}}$. Thus it is possible that in the data of Fig. 1 there is an undifferentiated background rate, increasing with pressure, that is responsible for as much as 1/3 of $\Gamma_{\text{vdW}}^{\text{Xe}}$. However, the observation of nearly the same Γ_w for each of the three buffer gases puts an experimental upper limit $\Gamma'_{\text{vdW}} < 1 \pm 0.6 \times 10^{-5}/\text{s}$. In particular, the 2.5 meV binding of Xe-He [31] makes Γ'_{vdW} extremely small for He and so the observation of nearly the same wall rate for He as for the other buffer gases leads us to conclude that Xe-Ar and Xe-N₂ molecules are not substantially affecting this experiment.

Combining the molecular and binary relaxation mechanisms gives a gas phase relaxation rate in pure Xe of

$$\Gamma = 6.7 \times 10^{-5} \text{ s}^{-1} + 5.0 \times 10^{-6} \text{ s}^{-1} \frac{[\text{Xe}]}{1 \text{ amagat}}, \quad (16)$$

which shows that for pure Xe molecular relaxation exceeds binary relaxation at densities below about 14 amagat.

The Xe-Xe molecular relaxation can be decoupled by a large magnetic field. The magnetic field at which the relaxation rate is reduced by a factor of 2 is

$$B_{1/2} = \frac{\hbar k_{\text{Xe}}[\text{G}]}{\mu_K/K} \sim \frac{44 \text{ T}}{\text{amagat}} [\text{G}]. \quad (17)$$

It will be essential to go to lower densities for this magnetic field to effectively reduce the relaxation rate.

It is interesting to consider what wall characteristics would be required to produce a T_1 of about 1 day for a liter of Xe gas at NTP, a time that would allow polarized Xe to be conveniently transported from place to place. Assuming a 1:10 Xe:N₂ mixture gives a relaxation time of 41 h. The volume of the storage chamber would be 10 l, and assuming a spherical chamber the relaxivity would need to be less than $2 \times 10^{-5} \text{ cm/s}$, a value that is within the range of known materials.

In conclusion, we have identified the formation of Xe-Xe van der Waals molecules as the primary fundamental relaxation process at gas densities below a few amagat. By studying the relaxation rate with different buffer gases, we have extracted the Xe-Xe molecular relaxation rate and shown that it is consistent with spin-rotation coupling strengths that have been previously deduced from other solid and gas-phase Xe relaxation measurements.

We acknowledge helpful discussions with S. Kadlecěk, W. Happer, and L. Bruch. Support was provided by the National Science Foundation.

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