

²⁰Limits on our available computational time currently prevent us from performing calculations using an appropriately larger basis, e.g., $9s5p/4s$.

²¹See, e.g., S. B. Trickey, A. K. Ray, and J. P. Worth, Phys. Status Solidi (b) **106**, 613 (1981).

²²Results reported in Ref. 16, which were obtained from an analysis of the data of J. J. Ritsko, E. J. Mele, A. J. Heeger, A. G. MacDiarmid, and M. Ozaki, Phys. Rev. Lett. **44**, 1351 (1980).

Slowing Down of Rubidium-Induced Nuclear Spin Relaxation of ^{129}Xe Gas in a Magnetic Field

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The longitudinal relaxation rate of ^{129}Xe nuclear spins slows down substantially in an external magnetic field of about 100 G. From an analysis of the magnetic slowing down and of the dependence of the zero-field relaxation rates on the third-body pressure, the authors have deduced the magnitudes of the spin-rotation and spin-exchange interactions in the Rb^{129}Xe molecule, as well as the formation and breakup rates of RbXe in N_2 gas and the dissociation constant of RbXe . The magnetic slowing down shows directly that binary collisions contribute no more than a few percent to the relaxation rates.

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The nature of the spin interactions in mixtures of ^{129}Xe or ^{131}Xe gas and Rb vapor has attracted much interest lately.¹⁻³ The production of large nuclear polarization in noble gases by optical pumping of a noble-gas-alkali-vapor mixture is simple and effective. Wall-dominated relaxation times of minutes to hours can be obtained. These systems have many potential uses as gyroscopes^{1,2} or magnetometers, in the study of angular correlations of nuclear radiations from radioactive noble-gas nuclei, and in the search for nuclear electric dipole moments.⁴ Thus, it is important to understand the properties of the van der Waals molecules, which mediate the spin exchange, in some detail. Recent experiments of Bhaskar, Happer, and McClelland⁵ have shown that the absolute nuclear spin polarization of ^{129}Xe produced by optical pumping of the RbXe system is much too small to be consistent with the binary exchange cross sections reported in Ref. 2, and that the spin transfer must be completely dominated by interactions in RbXe van der Waals molecules. The estimate of interaction constants and of the molecular formation and breakup rates in Ref. 2 should therefore be revised. However, only ratios of interaction constants and no absolute magnitudes were measured in Ref. 3, and no information about molecular formation and breakup rates was obtained.

We have recently completed extensive studies

of the slowing down of the ^{129}Xe spin relaxation rate in an external magnetic field⁵ for cells with nearly the same composition as those of Ref. 2. These experiments show *directly* that the binary relaxation rates are no larger than a few percent of the molecular-induced relaxation rates. We have used magnetic decoupling data to infer the *magnitude* of the spin-rotation interaction $\gamma\vec{S}\cdot\vec{N}$ between rubidium electron spin \vec{S} and the rotational angular momentum \vec{N} of the RbXe molecule, and have also determined the formation and breakup rates of RbXe molecules in N_2 gas. The measured spin-rotation strength γN is the same, to within experimental uncertainties, as that inferred by Bouchiat and co-workers^{6,7} from an analysis of the complementary phenomenon, the slowing down of the Xe-induced relaxation of Rb electron spins in a magnetic field.

The experimental procedures used in this work are much simpler than those used in Refs. 1 and 2. The basic apparatus used in our work and representative raw data are shown in Fig. 1. We used spherical Pyrex cells, containing 0.5 Torr of Xe (60% ^{129}Xe) at 20 °C, a small droplet of ^{87}Rb metal, and various amounts of N_2 . The ^{129}Xe was spin polarized by pumping the cells with circularly polarized 7947-Å Rb resonance radiation ($5S_{1/2} - 5P_{1/2}$). Representative pumping times, usually with a laser³ but occasionally with a lamp, were about 10 min. In the probe phase of this experi-

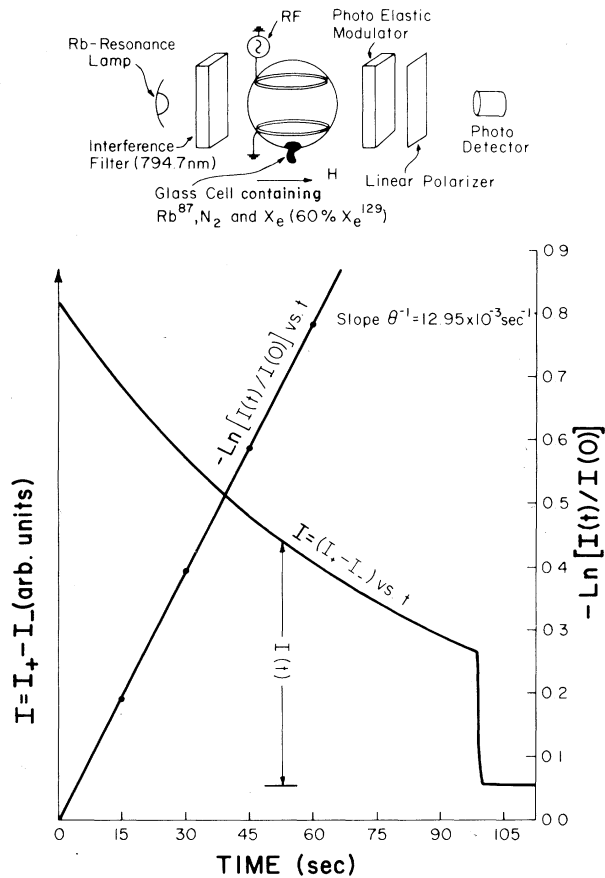


FIG. 1. Basic apparatus and representative decay curve of circular dichroism. The ^{129}Xe polarization is destroyed by applying the 1.178-kHz/G magnetic resonance frequency after 102 sec of decay. The noise is too small to reproduce. The semilogarithmic plot of the spin-dependent circular dichroism shows that the decay is purely exponential.

ment, which is illustrated in Fig. 1, unpolarized 7947-Å radiation from a Rb lamp was passed through the cell and analyzed for circular polarization with a photoelastic modulator (Hinds, Model FS4) and a linear polarizer. The slight excess $I_+ - I_- \approx 5 \times 10^{-3} I_+$ of right circularly polarized transmitted intensity I_+ over left circularly polarized transmitted intensity I_- , i.e., the circular dichroism, is a direct measure^{8,9} of the Rb electronic polarization $\langle S_z \rangle$, which in turn is proportional to the ^{129}Xe polarization $\langle K_z \rangle$ because of spin-exchange collisions.³ The use of circular dichroism is much simpler than the method used in Refs. 1 and 2 which requires operation at nearly zero magnetic field and the use of radio-frequency fields. Circular dichroism can be observed at any magnetic field; no magnetic shielding is needed since the signals are insensitive to

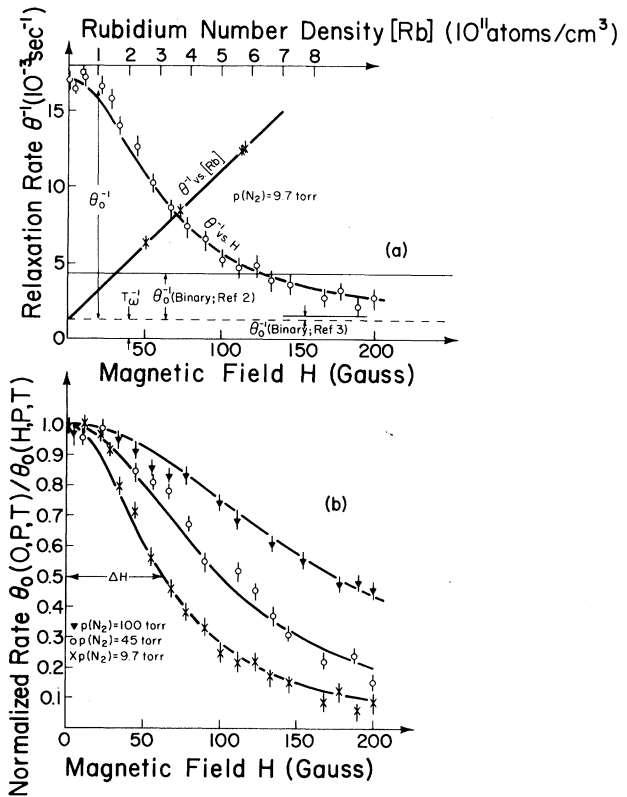


FIG. 2. (a) Dependence of the ^{129}Xe nuclear relaxation rate on the atomic density [Rb] and on the magnetic field H . The binary rate of Ref. 2 is much too large to be consistent with the high-field relaxation rate. (b) Normalized Rb-dependent relaxation rate vs magnetic field H for various nitrogen pressures. The solid lines are fits by functions of the form $\Delta H^2(\Delta H^2 + H^2)^{-1}$.

magnetic noise, and no radio-frequency field is required except to establish the unpolarized baseline by saturating the ^{129}Xe polarization at the end of a relaxation transient, as shown in Fig. 1.

Decay curves like those of Fig. 1 are always well characterized by a single exponential time constant θ . As shown in Fig. 2(a) we find that the measured temperature dependence of the relaxation rate is equivalent to a linear dependence of the rate on the Rb number density [Rb],

$$\theta^{-1} = T_w^{-1} + c[\text{Rb}], \quad (1)$$

where T_w^{-1} and c are temperature-independent constants. The cell-dependent wall relaxation time T_w ranged from 200 to 1200 sec, and the Rb-dependent relaxation rate $\theta_0^{-1} = c[\text{Rb}]$ is a function of the third-body pressure p (nitrogen), and the longitudinal magnetic field H , as is illustrated in Fig. 2(a). For consistency we use the same saturated-vapor-pressure formula¹⁰ as Ref. 2. The cell temperature was determined with cop-

per-Constantan thermocouples.

Because of the short duration of the binary collisions ($\sim 10^{-12}$ sec), the binary relaxation rate cannot be affected by magnetic fields of magnitudes less than some 10^6 G,^{6,7} and we conclude that the binary rate, i.e., the difference between the high-field rate and the wall rate T_w^{-1} , is on the order of the statistical error of the measurements and well below the binary rate assumed in Ref. 2, and indicated in Fig. 2(a). Although the decoupling data are not precise enough to measure the small binary rate, they are consistent with the very small binary rate, also shown in Fig. 2(a), which was estimated in Ref. 3. The normalized magnetic field dependence of Rb-dependent rates θ_0^{-1} is shown in Fig. 2(b) for representative values of the nitrogen pressure. Note that the width ΔH at half maximum of the decoupling curves increases with nitrogen pressure as indicated in Figs. 2(b) and 3(a). The zero-field relaxation rates are plotted in Fig. 3(b) along with the zero-field rates determined by Volk, Kwon, and Mark.² The agreement between the two independent sets of data is excellent.

The simplest spin Hamiltonian which can account for all of the known data^{2,3,6} on the RbXe

system is

$$H = A\vec{S} \cdot \vec{I} + \gamma\vec{S} \cdot \vec{N} + \alpha\vec{S} \cdot \vec{K} + g_S \mu_B \vec{S} \cdot \vec{H}. \quad (2)$$

Reasons for the omission of other spin interactions are discussed in Ref. 3. We may consider the large rotational angular momentum \vec{N} ($N \approx 70$) to be a time-independent classical vector during the lifetime of a particular molecule.⁶ The external magnetic field \vec{H} interacts with \vec{S} through the Zeeman interaction $g_S \mu_B \vec{S} \cdot \vec{H}$, where $g_S \approx 2$ and μ_B is the Bohr magneton. The contact interaction $A\vec{S} \cdot \vec{I}$ is much larger than any other term in (2) and it permits one to use $F = I \pm \frac{1}{2}$ as a good quantum number and to replace (2) with a pair of Breit-Rabi Hamiltonians in practical calculations.

The Rb-dependent decay rate of $\langle K_z \rangle$ is

$$\theta_0^{-1} = T_K^{-1} p_K, \quad (3)$$

where T_K^{-1} is the molecular formation rate (or binary collision rate) per ^{129}Xe atom, and p_K is the probability that $\langle K_z \rangle$ is destroyed during a mean molecular lifetime τ . As in other decoupling phenomenon [cf. Eq. (26) of Gupta, Chang, and Happer¹¹] the fraction $1 - p_K$ of the initial ^{129}Xe polarization remaining after the breakup of a RbXe molecule is

$$1 - p_K = \left\{ \sum_{ij} |\langle i|K_z|j \rangle|^2 (1 + i\omega_{ij}\tau)^{-1} [I]^{-1} \right\}_N, \quad (4)$$

where $[I] = 2I + 1$. The states $|i\rangle$ and $|j\rangle$ are eigenstates of (2) and $\hbar\omega_{ij}$ is the corresponding energy difference between the states. The sum extends over all $16[I]^2$ pairs of states and $\{ \}_N$ denotes an isotropic average over the directions of \vec{N} . For simplicity we assume that the magnitude of \vec{N} is fixed and equal to some most probable value. Physically, (4) describes the mutual rotation of \vec{K} and \vec{S} about each other and about \vec{H} and \vec{N} .

Numerical values of p_K can be evaluated from (4) in a straightforward way with Breit-Rabi¹¹ wave functions and energies. For very high nitrogen pressures where $\gamma N\tau/\hbar \ll 1$, the destruction probability from (4) reduces to

$$p_K = \frac{1}{6} \left(\frac{\alpha\tau}{\hbar} \right)^2 (1 + 2[I]^{-2}) \left[1 + \left(\frac{\omega_0\tau}{[I]} \right)^2 \right]^{-1}, \quad (5)$$

where $\hbar\omega_0 = g_S \mu_B H$. Thus, the molecular breakup rate τ^{-1} is related to the high-pressure half-width ΔH by

$$\tau^{-1} = g_S \mu_B \Delta H \hbar^{-1} [I]^{-1}. \quad (6)$$

From Fig. 3(a) we see that $\Delta H = p \times (1.6 \text{ G Torr}^{-1})$ and we therefore find from (6)

$$p\tau = 1.4 \times 10^{-7} \text{ Torr sec}. \quad (7)$$

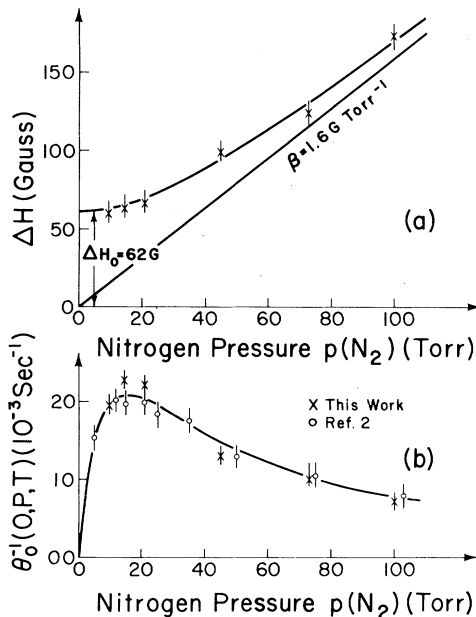


Fig. 3. (a) Dependence of ΔH on nitrogen pressure p . The solid line is a fit by the function $\Delta H^2 = \Delta H_0^2 + \beta^2 p^2$. Also plotted is the asymptote βp . (b) Zero-field relaxation rates for $T = 85.3^\circ\text{C}$ or (Ref. 10) $[\text{Rb}] = 10^{12} \text{ cm}^{-3}$. The solid-line fit is described in the text.

For very low nitrogen pressures where $\gamma N\tau/\hbar \gg 1$, the decoupling curve deduced from (4) resembles, but is not identical to, a Lorentzian curve.⁷ The low-pressure width at half maximum ($\Delta H_0 = 62 \pm 5$ G) is predicted to be related to the spin-rotation interaction by

$$\gamma N/h = n g_S \mu_B \hbar^{-1} \Delta H_0 = 120 \pm 10 \text{ MHz}, \quad (8)$$

where the numerical coefficient n ($n = 0.69$ for $^{87}\text{Rb}^{129}\text{Xe}$) depends weakly on I ($\frac{3}{2}$ for ^{87}Rb) and the ratio³ $x = \gamma N/\alpha$ (4.1 for Rb^{129}Xe). The value of $\gamma N/h$ deduced in (8) is in good agreement with the independent value $g_S \mu_B \hbar^{-1} H_1^* = 106 \pm 4$ MHz deduced by Bouchiat, Brossel, and Pottier.⁶ Combining (8) with the measured³ ratio $\gamma N/\alpha = x = 4.1$ we find

$$\alpha = 29 \pm 3 \text{ MHz}. \quad (9)$$

A simple expression, correct to order x^{-2} , can be derived from (4) for the zero-field spin destruction probability:

$$p_K = \frac{1}{6} \left(1 - \frac{1}{x^2} \right) \frac{(\varphi/2x)^2}{1 + (\varphi/2x)^2} + \frac{1}{3} \left(1 - \frac{3}{2x^2} \right) \frac{(\varphi/4x)^2}{1 + (\varphi/4x)^2} + \frac{2}{x^2} \frac{(\varphi/4)^2}{1 + (\varphi/4)^2}. \quad (10)$$

The solid line in Fig. 3(b) is a fit of (3), with p_K given by (10), to the zero-field relaxation rates. The horizontal scale is adjusted such that

$$\varphi \equiv \gamma N\tau/\hbar = (107 \text{ Torr}) p^{-1}. \quad (11)$$

Combining (11) with (8) we obtain an estimate

$$p\tau = 1.4 \times 10^{-7} \text{ Torr sec} \quad (12)$$

for the pressure-lifetime product, which is in good agreement with the independent estimate (7).

The best fit to the vertical scale in Fig. 3(a) is obtained by setting

$$T_K [\text{Rb}] [\text{N}_2] = 5.3 \times 10^{30} \text{ cm}^{-6} \text{ sec}, \quad (13)$$

a value remarkably close to the value $T_r [\text{Xe}]^2$

$= 5.4 \times 10^{30} \text{ cm}^{-6} \text{ sec}$ reported by Bouchiat, Brossel, and Pottier.⁶

The molecular dissociation constant at the characteristic temperature $T = 70^\circ\text{C}$ of these measurements is then

$$\frac{[\text{RbXe}]}{[\text{Rb}][\text{Xe}]} = \frac{\tau[\text{N}_2]}{T_K [\text{Rb}][\text{N}_2]} = 9.4 \times 10^{-22} \text{ cm}^3, \quad (14)$$

where we have used (12) to evaluate $[\text{N}_2]\tau = 5.0 \times 10^9 \text{ cm}^{-3} \text{ sec}$. This equilibrium constant is some 2 to 4 times larger than one would infer from the parameters given by Bouchiat, Brossel, and Pottier.⁶ However, in this work all the parameters in (13) were obtained from direct measurements, but Bouchiat, Brossel, and Pottier⁶ were forced to use theoretical calculations of the parameter $p\tau$ from imprecisely known RbXe interaction potentials.

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