Efficiency of Spin Exchange between Rubidium Spins and ^{129}Xe Nuclei in a Gas

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By directly observing the nuclear polarization of ^{129}Xe, the efficiency η of spin exchange between optically pumped Rb spins and ^{129}Xe nuclei has been measured. It is found that $1/\eta = 23 \pm 4$ rubidium D_1 resonance-line photons are required to polarize a ^{129}Xe nucleus when long-lived van der Waals molecules are unimportant. The binary spin-exchange cross section deduced from our measurements is $\sigma_{ex} = (7.3 \pm 1.1) \times 10^{-21}$ cm^2.

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Recent experiments by Grover[1] and by Volk, Kwon, and Mark[2] have suggested that large nuclear-spin polarization can be produced in ^{129}Xe nuclei by spin polarization with optically pumped rubidium atoms. However, no direct measurements of the xenon spin polarization have been reported. In this Letter we report on the results of extensive experimental studies of the absolute nuclear spin polarization of ^{129}Xe. These measurements show that the binary spin-exchange cross sections cited by Volk, Kwon, and Mark[2] are more than an order of magnitude too large.

The apparatus used in this work is sketched in Fig. 1. Spherical Pyrex cells, 29 mm in diameter, were filled with a small amount of ^{87}Rb metal and various amounts of xenon (isotopically enriched to 60% ^{129}Xe), nitrogen, and helium gas. The cells were maintained at temperatures between 50 and 100 °C in a nonmagnetic oven. A solenoid, corrected to sixth order, provided a magnetic field of 220 G which was homogeneous to a few milligauss over the cell volume. The cells were pumped with circularly polarized, 7947-Å D_1 resonance light from a Spectra Physics Model 375 dye laser operating with Oxazine 750 dye. The multimode linewidth of the dye laser was about 40 GHz and output power was as high as 400 mW. The dye laser was pumped by the red lines of a 5-W Spectra Physics Model 171 krypton ion laser.

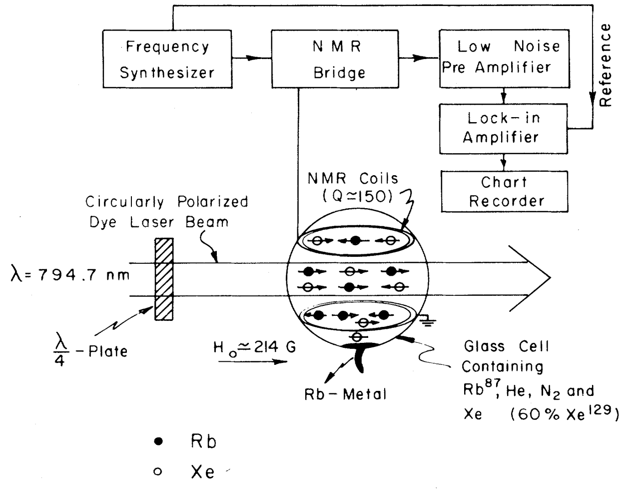

FIG. 1. NMR apparatus for measuring the absolute nuclear polarization in ^{129}Xe.

The ^{129}Xe polarization was detected by classical nuclear magnetic resonance. The cell was contained in an NMR coil of Helmholtz configuration with a Q of about 150. An Anderson bridge, similar to that described by Gamblin and Carrer,[3] was used in conjunction with a PAR Model 113 preamplifier, and a PAR Model 5202 lock-in amplifier operating at 251 kHz to detect the NMR signal. In agreement with the results of Refs. 1 and 2, we found that the ^{129}Xe relaxation rate varied linearly with Rb number density.

We have interpreted our measurements by assuming that the major spin interactions in the Rb-Xe pair are described by the Hamiltonian

$$H = A\vec{S}\cdot\vec{I} + \gamma\vec{S}\cdot\vec{N} + \alpha\vec{S}\cdot\vec{K}. \qquad (1)$$

The angular momenta in (1) are illustrated in Fig. 2. All three coupling coefficients A, γ, and α depend on the internuclear separation of the Rb-Xe pair. The large contact interaction $A\vec{S}\cdot\vec{I}$ ensures that the electronic spin $\vec{S}$ and the nuclear spin $\vec{I}$ of the Rb atom will remain coupled in all but the shortest-lived van der Waals molecules. The spin rotation interaction $\gamma\vec{S}\cdot\vec{N}$ between $\vec{S}$ and

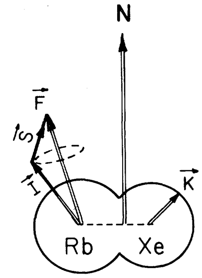

FIG. 2. Rb-Xe molecule and the various angular momenta. Typically $|\vec{\mathrm{N}}| \simeq 70\hbar$. For ^{87}Rb $I/\hbar = \frac{3}{2}$, $S/\hbar = \frac{1}{2}$, and for ^{129}Xe $K/\hbar = \frac{1}{2}$.

the tumbling angular momentum $\vec{\mathrm{N}}$ of the Rb-Xe pair was extensively studied by Bouchiat and coworkers.[4,5] The exchange interaction $\alpha\vec{\mathrm{S}}\cdot\vec{\mathrm{K}}$ between $\vec{\mathrm{S}}$ and the nuclear spin $\vec{\mathrm{K}}$ of the ^{129}Xe atom was introduced by Gamblin and Carver[3] to account for the spin polarization of ^{3}He in their pioneering studies of alkali-noble-gas spin exchange. Theoretical estimates by Herman[6] indicate that the anisotropic hyperfine couplings are negligible, and experimental studies of alkali relaxation[3,4] and alkali-^{3}He spin exchange support the idea that the anisotropic hyperfine couplings are small.

To simplify the interpretation of our data we used cells with several hundred Torr of total gas pressure and at least 10 Torr of N_2. This ensured that the lifetime τ of the van der Waals molecules was much shorter than the characteristic evolution times h/γ, h/α, and $1/\nu_L$, the Larmor period of the Rb atoms in the NMR field. The gas also ensured that the Rb nuclear spin did not have enough time to relax during the lifetime of an excited atom,[7] while the electronic polarization of the excited state was completely randomized by collisions. These conditions imply that each of the circularly polarized D_1 photons absorbed by a rubidium atom deposits $\hbar/2$ units of angular momentum in the Rb spin system. Independent experimental studies by Tran[8] show that the nuclear spin is conserved during the optical pumping cycle for cells similar to those described above. Then the evolution of $\langle F_z\rangle$ due to the combined effect of optical pumping and the interaction (1) is described by

$$\frac{\partial}{\partial t}\langle F_z\rangle = \frac{\langle\delta\Gamma\rangle}{2} - \frac{1}{T_R}\frac{2}{3}\left\langle\left(\frac{\gamma\tau N}{[I]\hbar}\right)^2\right\rangle\langle F_z\rangle + \frac{f}{T_R}\frac{1}{2}\left\langle\left(\frac{\alpha\tau}{[I]\hbar}\right)^2\right\rangle\{2\langle F^2 - F_z{}^2\rangle\langle K_z\rangle - \langle F_z\rangle\}, \tag{2}$$

where $\langle\delta\Gamma\rangle$ is the mean photon absorption rate per Rb atom, $(T_R)^{-1}$ is the molecular formation rate per Rb atom, $[I] = 2I+1$, and f is the fraction of ^{129}Xe in the isotopically enriched sample. We neglect the small additional relaxation due to the nuclei of ^{131}Xe. All other relaxation mechanisms (e.g., diffusion of the Rb atoms to the cell walls) are negligible. The corresponding evolution of $\langle K_z\rangle$ is

$$\frac{\partial}{\partial t}\langle K_z\rangle = \frac{1}{T_k}\frac{1}{2}\left\langle\left(\frac{\alpha\tau}{[I]\hbar}\right)^2\right\rangle\{\langle F_z\rangle - 2\langle F^2 - F_z{}^2\rangle\langle K_z\rangle\} + D\nabla^2\langle K_z\rangle, \tag{3}$$

where D is the diffusion constant of xenon in the cell, and $(T_k)^{-1}$ is the molecular formation rate per Xe atom. We pump the cells with the laser until steady state is attained (representative times are about 10 min) before measuring the xenon polarization. To describe this initial state theoretically, we integrate the right-hand sides of (2) and (3) over the cell volume V, set the left-hand sides equal to zero, and define the wall relaxation time T_w in terms of the diffusional flux of $\langle K_z\rangle$ through the surface elements $d\vec{\mathrm{S}}$ of the cell

$$-\frac{1}{T_w}\langle K_z\rangle V = \oint D\nabla\langle K_z\rangle\cdot d\vec{\mathrm{S}}. \tag{4}$$

Eliminating $\int\langle F_z\rangle dV$ from the resulting pair of equations, we find

$$\frac{2\langle K_z\rangle[\mathrm{Xe}]V}{\Delta I T_1} = \eta = \frac{\frac{1}{2}\langle\alpha^2\rangle}{\frac{2}{3}\langle(\gamma N)^2\rangle + f/2\langle\alpha^2\rangle} \doteq \frac{\sigma_{\mathrm{ex}}}{\sigma_{\mathrm{sr}} + f\sigma_{\mathrm{ex}}}. \tag{5}$$

Here T_1 is the longitudinal relaxation time of ^{129}Xe spins in the illuminated cell, and the small spatial nonuniformity of $\langle K_z\rangle$ has been ignored. We neglect the very slight differences of $\langle F^2 - F_z{}^2\rangle$ in the illuminated and darkened cell. The photon current deposited in the cell is

$$\Delta I = \int[\mathrm{Rb}]\langle\delta\Gamma\rangle dV. \tag{6}$$

Physically the very basic equation (5) states that the current of angular momentum $\Delta I h/2$ deposited by the pump beam in the Rb spin system is partitioned into a fraction $f\eta\Delta I h/2$ which flows to the ^{129}Xe nuclear spins; the rest is lost to the tumbling angular momentum $\vec{\mathrm{N}}$. The influx to the ^{129}Xe spin system is balanced by an efflux $f\langle K_z\rangle h[\mathrm{Xe}]V/T_1$ to the walls and back to the Rb atoms. We may therefore call η the spin-transfer efficiency.

We determine η experimentally by measuring the parameters on the left of Eq. (5) after steady state has been attained. The laser illuminates about 10% of the total volume of the cell. The Rb polarization in the laser-illuminated region is usually 60%–95%. We measure the Xe nuclear polarization averaged over the volume of the cell. Typically, the Xe nuclear polarization is ~5%–10%. The determination of $f\langle K_z\rangle[\mathrm{Xe}]$ and T_1 is illustrated in Fig. 3 where we show the adiabatic spin-reversal signals of ^{129}Xe and a calibration adiabatic reversal signal from the protons in a distilled water cell of identical dimensions in the same NMR coils and at the same frequency but at a smaller static field. We may measure the slight nonadiabaticity of the spin reversal from the different amplitudes of the spin-reversal signals spaced a few seconds apart. The longitudinal relaxation time T_1 is determined by noting the decay of the NMR signal amplitudes when a second pair of spin reversals is executed some 60 sec later. The values of T_1 deduced from data like those in Fig. 3 were confirmed by independent measurements of the decay of the circular dichroism of the cells for 794-Å light.[9] The photon current ΔI is determined by measuring the incident dye laser flux with a power meter (Coherent Model 210), correcting for reflection losses at the oven window and cell wall, and determining the fraction of photons stopped by the vapor by tuning on and off the 7947-Å resonance line.

The quantities $\langle K_z\rangle[\mathrm{Xe}]f$, T_1, and ΔI vary substantially with temperature in a given cell; T_1 becomes much shorter, $\langle K_z\rangle[\mathrm{Xe}]f$ becomes smaller, and ΔI increases as the cell temperature increases. However, we have verified that the ratio η of Eq. (5) is independent of cell temperature or laser power for a given cell. The ratio η is also the same, within experimental error, for cells with very different gas compositions, as shown in Table I. The weighted mean for three cells is

$$\eta = 0.043 \pm 0.006 \tag{7}$$

with an error estimate which includes uncertainties in NMR calibration, power meter calibration, etc. Combining (7) with (5) we find the ratio of the root-mean-square coupling coefficients of Eq. (1) to be

$$\gamma N/\alpha = 4.1. \tag{8}$$

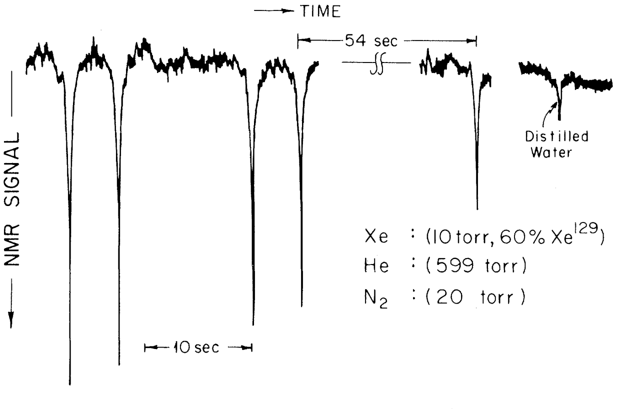

FIG. 3. NMR signals from polarized ^{129}Xe. Distilled water is used for calibration. The decay constant for this run is $T_1 = 104.5$ sec.

We have used the measured coupling-constant ratio of Eq. (8) in combination with the spin-disorientation cross section $\sigma_{\mathrm{sr}} = 1.64\times10^{-19}$ cm^2 measured by Bouchiat, Brossel, and Pottier[4] to deduce the binary spin-exchange cross section for Rb-^{129}Xe

$$\sigma_{\mathrm{ex}} = \frac{3}{4}\frac{\langle\alpha^2\rangle}{\langle\gamma^2N^2\rangle}\sigma_{\mathrm{sr}} = (7.3\pm 1.1)\times 10^{-21}\ \mathrm{cm}^2. \tag{9}$$

We believe that the binary spin-exchange cross section 110×10^{-21} cm^2 cited by Volk, Kwon, and Mark[2] is too large because of the oversimplified model used to interpret the data of Fig. 6 in their paper. Their model ignores the spin-rotation interaction in the low-pressure regime where it can influence the relaxation of ^{129}Xe. They also ignore the nuclear spin I of the rubidium atom. By including both of these effects we can fit the data of Volk, Kwon, and Mark[2] with negligible contributions from binary collisions. The small exchange cross section implied by our work would have had negligible influence on the rubidium spin relaxation rates measured by Bouchiat, Brossel, and Pottier.[4]

We note that in Refs. 1 and 2 the basic measurement is of a transverse relaxation time, T_2. Recently Kwon[10] has shown that the inhomogen-

TABLE I. Measured values of η for cells with different gas compositions.

Xenon[a,b] (Torr)	Helium (Torr)[b]	Nitrogen (Torr)[b]	η
9.98	599	20	0.0435(15)
19.8[c]	200	21	0.0393(67)
338.0	0	14	0.0452(50)

[a] Enriched to 60% ^{129}Xe.

[b] Partial pressures measured at 20 °C.

[c] Drift of laser frequency contributes to scatter.

eous polarization of the optically pumped rubidium can substantially influence the relaxation time T_2. We measure T_1, the longitudinal relaxation time, and our system is not sensitive to field inhomogeneities, wall shifts, or alkali polarization inhomogeneities. Our measurements are also independent of the number density of Rb or Xe atoms.

Although the spin transfer efficiency η of (7) is much less favorable than one would infer from the numbers cited by Volk, Kwon, and Mark,[2] it still seems certain that large and highly polarized samples of ^{129}Xe can be prepared by spin exchange with optically pumped alkali atoms. For example, the photon current corresponding to 1 W of absorbed dye laser power and a wall-dominated relaxation rate of 1 h will allow one to polarize 3×10^{20} ^{129}Xe spins, according to Eqs. (5) and (7). This is 11 cm^3 of 100% polarized ^{129}Xe at STP. Such a sample would be of considerable interest as a target for nuclear scattering experiments.

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Observation of Rydberg($C^2\Pi$)-valence($B^2\Pi$) Interactions in NO by Multiphoton Photoelectron Spectroscopy

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Photoelectron spectra for the three-photon resonant, five-photon ionization of NO via the $v''=0$ level of the $C^2\Pi(3p\pi)$ Rydberg state show that NO$^+$ $(X^1\Sigma^+)$ is formed primarily in $v'=0$ and $v'\geqslant3$. The relative populations of the $v'=0$ to $v'\geqslant3$ levels are strongly dependent on the excited rotational level of the C state. These data are consistent with known perturbations between the nearly degenerate $C^2\Pi$, $v''=0$ Rydberg and $B^2\Pi$, $v=7$ valence levels.

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Multiphoton ionization (MPI) has become an increasingly important tool in high-resolution spectroscopy because of its sensitivity and ability to detect excited states which do not fluoresce. For the most part, MPI experiments have used the total ion (or photoelectron) yield as a measure of the absorption strength. Such data have provided a great deal of spectroscopic information on the resonant, intermediate excited states.[1] Analysis of the ejected photoelectrons (energy and angular distribution) adds a new dimension to the MPI technique, since photoelectron spectroscopy can provide information on the final-state (internal energy) distribution of the ion and the dynamics of the photoejection process. Several groups have recently applied multiphoton photoelectron spectroscopy (MP-PES) to the study of nonresonant and resonant ionization of