Polarization of ^{3}He by Spin Exchange with Optically Pumped Rb and K Vapors

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We report on extensive experimental measurements of the key rates that determine the efficiency for polarizing the nuclei of ^{3}He by spin exchange with optically pumped Rb vapor. In agreement with recent theoretical predictions, we find a strong temperature dependence of the electron-spin loss rates due to ^{3}HeRb collisions. We also find that the maximum possible efficiency for spin-exchange polarization of ^{3}He by K is 10 times greater than for Rb. [S0031-9007(98)05659-2]

Applications of hyperpolarized ^{3}He (where the nuclear spin polarization is many tens of percent) include targets for nuclear scattering experiments [1], neutron beam polarizers and analyzers [2], masers for tests of fundamental symmetries [3], and medical magnetic resonance imaging [4–7]. These applications have encouraged the optimization of hyperpolarization methods, the most successful of which are metastability-exchange optical pumping [5,8] and spin-exchange optical pumping [9], the subject of this Letter. Literature values for the key spin-exchange and spin-loss rates are sufficiently inconsistent with each other that reliable modeling of polarization systems is not possible. We have therefore made extensive experimental studies to determine key rates for ^{3}HeRb. An effective new method was used to measure the spin-exchange efficiencies for ^{3}HeRb and ^{3}HeK. Important new results of these studies are as follows: the spin depolarization rate of Rb atoms due to collisions with ^{3}He increases very rapidly with the absolute temperature T—approximately as T^4; the temperature dependence of the other key relaxation rates is too small to measure; the maximum possible spin-exchange efficiency η for ^{3}HeK is 10 times greater than that of ^{3}HeRb at representative temperatures for spin-exchange optical pumping.

The spin destruction rates were determined as a function of temperature by measurements of Rb spin relaxation "in the dark" [10,11]. A Ti:sapphire laser with a 500 kHz linewidth provided tunable laser radiation near 794.8 nm (the Rb $5S_{1/2} \rightarrow 5P_{1/2}$ D_1 transition) for both pump and probe beams. A 1 W, circularly polarized pump beam, mechanically chopped at a rate of 2–30 Hz, was used to periodically polarize the Rb vapor, as sketched in Fig. 1(a). The dark interval was 20 times the light interval. The pump beam was expanded to entirely cover the sample cell with collimated light, directed along a 31 G uniform magnetic field produced by Helmholtz coils, 1.5 m in diameter. The spherical cells, with radii $r \approx 10$ mm, were blown from Corning 1720 glass. They were filled at room temperature with 3 to 14 amagat of ^{3}He (1 amagat = 2.69×10^{19} molecules cm^{-3}), approximately 0.08 amagat of N_2 for quenching, and a few mg of Rb metal of natural isotopic abundance. The cells were maintained at temperatures of 90 to 190 °C, by hot air, flowing in an oven

with glass windows. A circularly polarized probe beam with a power of a few mW crossed the cell at a small angle $<5°$) with respect to the magnetic field and was directed onto the face of a photodetector. The transient decay signal, resulting from the depolarization of the Rb when the pump radiation was blocked by the chopping wheel, was recorded by a digital oscilloscope. In the analysis of our data, we used only the slowest (late-time) exponential time constant, which we denote by T_1.

A number of precautions were taken to minimize systematic errors. To limit diffusion losses of polarized Rb to the cell walls [9,12], and to ensure homogeneous pumping and detection over the entire cell, the Ti:sapphire laser was normally detuned from resonance by a few tenths of a nm. Although the probe laser was low power, it did increase the transient relaxation rates, so we measured $1/T_1$ for a series of low probe-laser powers (from 5 to 0.5 mW) and extrapolated to the zero-power limit. The extrapolation gave the same limiting rate $1/T_1$ for various values of the detuning.

Because of the high gas pressure of these experiments, it is not practical to account for diffusion by a normal
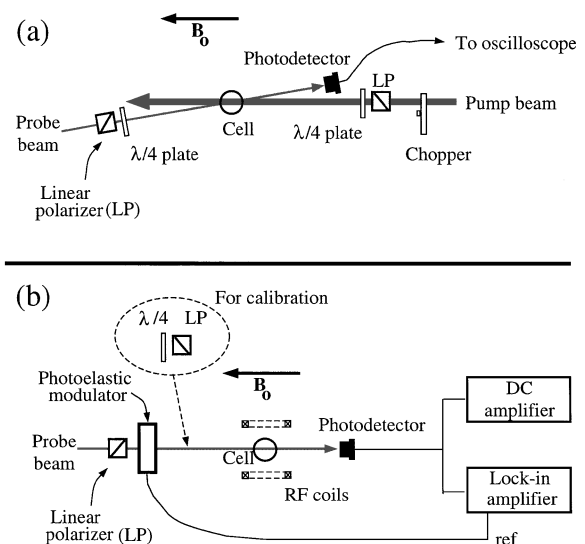

FIG. 1. (a) Apparatus for measuring Rb spin relaxation in the dark. (b) Apparatus for measuring spin-exchange efficiency.

mode expansion, which would involve many modes of comparable weights. In complete analogy to the temperature distribution of a classical "heat pole" at one end of a thermally conducting rod [13], at a time t after termination of the pumping light, diffusion produces a surface layer of Rb atoms with a polarization which varies with distance z from the cell walls as $\mathrm{erf}(z/\sqrt{4Dt})$, where erf denotes the error function, and D is the diffusion coefficient of Rb atoms in the gas. Diffusion increases the spin-relaxation rate due to gas-phase collisions by $\sim\sqrt{D/(\pi r^2 T_1)}$, which can amount to as much as 5% of $1/T_1$ in our lowest-pressure cells. The gas-induced relaxation rate, corrected for diffusion to the walls, can therefore be estimated to be $\gamma = 1/T_1 - \sqrt{D/(\pi r^2 T_1)}$.

We measured the dependence of γ on the ^{3}He and Rb number densities ([He] and [Rb]) and the absolute gas temperature T. We determined [He] in two ways: from the measured pressures at the time the cell was manufactured, and from the pressure-broadened absorption profile of D_1 light, from which [He] can be extracted with better than 3% accuracy [14]. We determined [Rb] by measuring the cells' temperature (using a sensor attached directly to the cell) and by applying the Killian formula [15]. We independently determined [Rb] in each cell from the integrated absorption profile of laser light for temperatures between 90 and 160 °C. The Killian formula was in excellent agreement with these measurements. The discrepancies were at the 6% level or below, and can be attributed to the ±1 K uncertainty in our temperature measurements. To avoid optical pumping, low-power linearly polarized light was used in the spectroscopic determinations of [Rb] and [He].

Figure 2(a) displays representative values of γ measured in four different pumping cells and plotted as a function of [Rb] (the bottom scale). The temperature scale across the top of Fig. 2(a) is related to the bottom scale by the Killian formula [15]. The two scales are equivalent, except for data from a cell containing a RbNa alloy (labeled RbNa) which is plotted versus spectroscopically measured values of [Rb], which are smaller than the Killian value. The experimental signal-to-noise ratio varied with temperature, and was optimal near 150 °C. The 1σ statistical uncertainty in the fitted value of γ, extrapolated to zero probe power, was approximately 4% near 150 °C, increasing to 10% at the limits of our temperature range. Analysis of our extensive data shows that the late-time rate γ is well described by

$$\gamma = \kappa'_{\mathrm{sd}}[\mathrm{Rb}] + \kappa''_{\mathrm{sd}}[\mathrm{N_2}] + (\kappa_{\mathrm{sd}} + \kappa_{\mathrm{se}})[\mathrm{He}]. \quad (1)$$

That is, the gas-induced relaxation is the sum of contributions from RbRb, N_2Rb, and ^{3}HeRb interactions (with rate coefficients κ'_{sd}, κ''_{sd}, and κ_{sd}) and from ^{3}HeRb spin exchange with a rate coefficient κ_{se}. The solid lines of Fig. 2(a) were obtained from Eq. (1), with temperature-dependent late-time rate coefficients κ determined as outlined below.
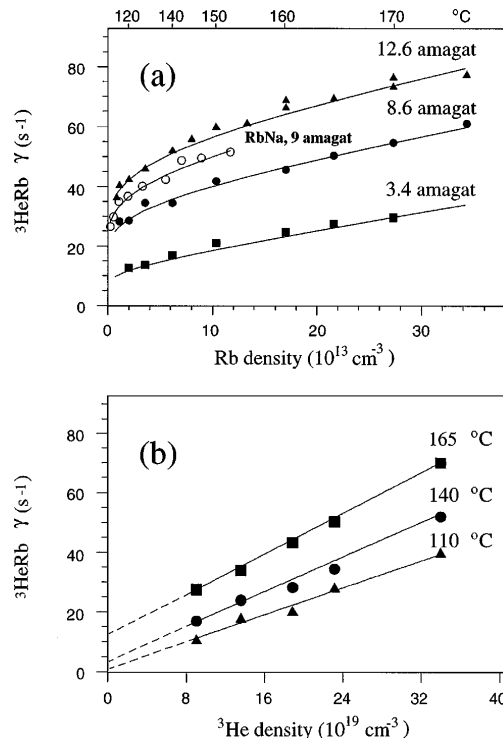
FIG. 2. (a) Representative data for gas-induced spin relaxation rate γ of Rb versus Rb number density. The upper scale gives the temperature of the saturated Rb vapor, except for the RbNa alloy, where the temperature was higher. (b) Representative data for γ versus [He] for fixed T and [Rb]. The data points γ are the difference between the late-time decay rates, $1/T_1$, and a small (few per cent) diffusional correction $\sqrt{D/(\pi r^2 T_1)}$ (see text). The solid lines are from Eq. (1), with the coefficients of Eqs. (2) and (3).

Representative data, plotted as a function of [He], are shown in Fig. 2(b). The rates depend linearly on [He] with no evidence for a dependence on $[\mathrm{He}]^2$ as reported by Larson et al. [16]. In accordance with Eq. (1), the slopes give the late-time rate coefficients $\kappa_{\mathrm{sd}} + \kappa_{\mathrm{se}}$, which increase with temperature, and can be well represented by the empirical function

$$\kappa_{\mathrm{sd}} + \kappa_{\mathrm{se}} = 9.29 \times 10^{-31} T^{4.259} \mathrm{\ cm^3\,s^{-1}}, \quad (2)$$

with T in K. Recent calculations of Walker et al. [17] for relaxation via the spin-rotation interaction exhibit a comparable magnitude and strong temperature dependence, provided that the late-time rate coefficient of Eq. (2) is multiplied by a nuclear slowing-down factor of $s = 10.8$, appropriate for sudden binary collisions and a spin temperature [12,18]. The resulting electron spin-destruction coefficient for ^{3}HeRb collisions is $s(\kappa_{\mathrm{sd}} + \kappa_{\mathrm{se}}) = 1.0 \times 10^{-29} T^{4.259} \mathrm{\ cm^3\,s^{-1}}$.

The intercepts of the straight-line fits of Fig. 2(b) give $\kappa'_{\mathrm{sd}}[\mathrm{Rb}] + \kappa''_{\mathrm{sd}}[\mathrm{N_2}]$ of Eq. (1). The intercepts show a linear dependence on [Rb], with a slope

$$\kappa'_{\mathrm{sd}} = (3.9 \pm 0.4) \times 10^{-14} \mathrm{\ cm^3\,s^{-1}}, \quad (3)$$

which is independent of temperature. The error estimate is dominated by the statistical spread of the measurements and by the uncertainties of the Rb densities.

For comparison with previous measurements at low magnetic field, where the rate coefficients for late-time exponential decay were multiplied by the slowing-down factor $s = 10.8$, our value of $s\kappa'_{sd}$ from Eq. (3) is smaller by a factor of 2 than published values [12,16,19], perhaps because of the previously unrecognized strong temperature dependence of κ_{sd}. Walker [20] has kindly informed us that he and his colleagues at the University of Wisconsin have found that the Rb-induced rate decreases by a factor of 2 or more at magnetic fields of a few kilogauss. This field dependence, which we have confirmed in our laboratory, is incompatible with the assumption of sudden Rb–Rb collisions, the rationale for the slowing-down factor s.

As indicated in Fig. 2(a), we were able to check the validity of Eq. (1) with a cell containing an alloy of Rb and Na metal, 9 amagats of ^{3}He and 0.08 amagats of N_2. The Rb vapor pressure over the Rb/Na alloy was reduced by a factor of 3 (as determined by the spectroscopic methods mentioned above) relative to pure Rb at the same temperature. The Na had negligible effect on the relaxation rate, due to its small partial pressure at these temperatures. The solid line, which is in excellent agreement with the data points labeled RbNa, was calculated versus measured values of [Rb] and T with Eq. (1) and the late-time rate coefficients discussed above.

We also performed a direct measurement of the maximum possible photon efficiency η of spin exchange optical pumping, where $1/\eta$ is the minimum number of photons needed to provide $\hbar/2$ units of spin to an initially unpolarized ^{3}He nucleus and fully polarize it [9,21]. The Rb spin polarization P_{Rb} induced in the absence of optical pumping by spin exchange with ^{3}He of nuclear polarization P_{He} is

$$P_{Rb} = \kappa_{se}[He]P_{He}/\gamma = \eta P_{He}. \qquad (4)$$

From the measurements of γ, discussed above, and from independent measurements of P_{Rb}, P_{He}, we determine the efficiency η and the ^{3}He spin-exchange rate κ_{se}. Unlike previous experimental methods for measuring κ_{se} [16,24], this new, polarization-ratio method requires no precise knowledge of the Rb number density or of the wall-induced relaxation rate of ^{3}He.

We optically pumped a ^{3}HeRb cell containing 7.0 amagat of ^{3}He and 0.07 amagat of N_2 until the ^{3}He polarization was (20–50)%. After the pumping laser was turned off, the Rb vapor remained partially polarized by spin exchange with ^{3}He. Since the ^{3}He remained polarized for many hours, we could carry out a number of measurements before the ^{3}He polarization was too small for use.

To measure the Rb polarization [see Fig. 1(b)] we let a weak, linearly polarized probe beam from the Ti-sapphire laser pass through a photoelastic modulator (PEM), with its fast and slow optical axes oriented at 45° to the linear polarization. The PEM produced a time-varying phase retardation between the fast and slow axes $\phi(t) = \phi_0 \sin \omega t$. The light emerging from the PEM had circular polarization

$s_z(t) = \sin \phi(t)$ with components oscillating at the frequencies $n\omega$ ($n = 1, 3, \ldots$) with amplitudes proportional to the Bessel functions $J_n(\phi_0)$. The probe beam, tuned close to resonance for the Rb atoms, passed through the cell to a photodetector, where V_{dc} and V_{ac}, the dc and ac components of the photodetector voltage, were measured with a dc voltmeter and a lock-in amplifier, referenced to the PEM drive frequency $\omega = 2\pi \times 50$ kHz. To calibrate the detectors and the PEM, the probe laser was detuned from the Rb absorption line and a circular analyzer (a quarter-wave plate followed by a polarizing beam-splitter cube) was inserted in the path of the beam. The calibrating voltages v_{dc} and v_{ac} were measured with the same procedure outlined above. Finally, the circular analyzer was removed and the dc voltage V_0 was measured for the detuned probe beam. Since Rb atoms absorb D_1 photons of mean polarization s_z with an effective cross section $\sigma_0(1 - P_{Rb}s_z)$, and since the polarization-induced increment to the optical depth is very small $r[Rb]\sigma_0 P_{Rb} \ll 1$), one can readily show that the Rb polarization, averaged along the probe beam, is

$$P_{Rb} = \frac{v_{dc}V_{ac}}{v_{ac}V_{dc} \ln(V_0/V_{dc})}. \qquad (5)$$

All voltages were normalized to constant probe-laser intensity. We verified that the measured value of P_{Rb} (typically a few percent or less) was independent of the amount of probe detuning.

For the measurement of the ^{3}He polarization we used the polarization-dependent shift of the Rb Zeeman frequency [22]. We measured the Zeeman resonance frequency of the Rb atoms by scanning a radio frequency (RF) field through a small frequency interval centered at about $\sim$14.4 MHz where Zeeman resonances of ^{85}Rb occur for a 31 G field. The RF transitions diminished the Rb polarization and therefore V_{ac}. The center frequency ν_1 of the resulting resonance line could be determined to ± 0.5 kHz. We reversed the direction of ^{3}He spins by adiabatic fast passage to measure the shifted Rb resonance frequency ν_2. The ^{3}He polarization is

$$P_{He} = \frac{3(\nu_1 - \nu_2)}{16\pi\mu_K[He]\kappa_0(d\nu/dB)}, \qquad (6)$$

where μ_K is the magnetic moment of the ^{3}He nucleus, $d\nu/dB$ is the rate of change of the Rb resonance frequency with magnetic field, and the frequency-shift coefficient [$\kappa_0(T) \approx 1.97 + 0.00934T$ with T in K] for the ^{3}HeRb system [22] has been measured as a function of temperature [23] with an accuracy of 1.5%.

For ^{3}HeK, the value of κ_0 was determined by measurements in a ^{3}He cell containing both K and Rb. Thus, the Rb frequency shift served to determine the ^{3}He polarization, permitting a precise measurement of κ_0 for K. We find that $\kappa_{0,K} = (0.94 \pm 0.01)\kappa_{0,Rb}$ over the entire temperature range of interest. Then η was measured in a ^{3}He optical pumping cell containing only K metal, 6.9 amagat of ^{3}He, and 0.09 amagat of N_2.

Our results for the spin-exchange efficiencies for ^{3}HeRb and ^{3}HeK are shown as a function of temperature in Fig. 3(a). For K, the measured efficiency is well described by $\eta(T) = 0.756 - 0.001\,09T$ with T in K. Before insertion into Eq. (4), the average polarizations of Eq. (5) were increased by 5% for Rb and 13% for K to compensate for the effect of the depolarized diffusion layer near the walls [9]. The errors of our measurements, 8% for Rb and 20% for K, are dominated by the statistical uncertainty and the systematic error due to the diffusion correction. This large measured value of η for ^{3}HeK compared to that for ^{3}HeRb was foreseen in the theoretical estimates of Walker et al. [17], who also predict efficiencies of nearly 100% for Na. Under appropriate conditions, lasers pumping K or Na atoms could provide the same polarization rates as those used today in the ^{3}HeRb system but with one or two orders of magnitude less laser power.

In accord with Eqs. (1) and (5), κ_{se} was found from the measured values of η and the late-time rate γ to be

$$\kappa_{se} = \eta\gamma/[\text{He}] = (6.2 \pm 0.6) \times 10^{-21} \text{ cm}^3 \text{ s}^{-1}, \quad (7)$$

with no measurable temperature dependence. The error is dominated by the statistical uncertainty in the measurement of the Rb and He polarizations and the late-time rate γ. Since the measurements of η and γ were performed under similar conditions on the same cell, certain sources of error cancel in the calculation of κ_{se}. Multiplying the coefficient κ_{se} of Eq. (7) by the nuclear slowing-down factor $s = 10.8$, we infer a coefficient $(6.7 \pm 0.6) \times 10^{-20}$ cm^3 s^{-1} for polarizing ^{3}He by spin exchange with optically pumped Rb. This value agrees well with a measurement of Larson et al. [16]: $\kappa_{se} = (6.2 \pm 0.2) \times 10^{-20}$ cm^{-3} s^{-1}, but is about a factor of 2 smaller than the result of Coulter et al. [24]. A summary of the late-time rate coefficients for ^{3}HeRb is shown in Fig. 3(b).

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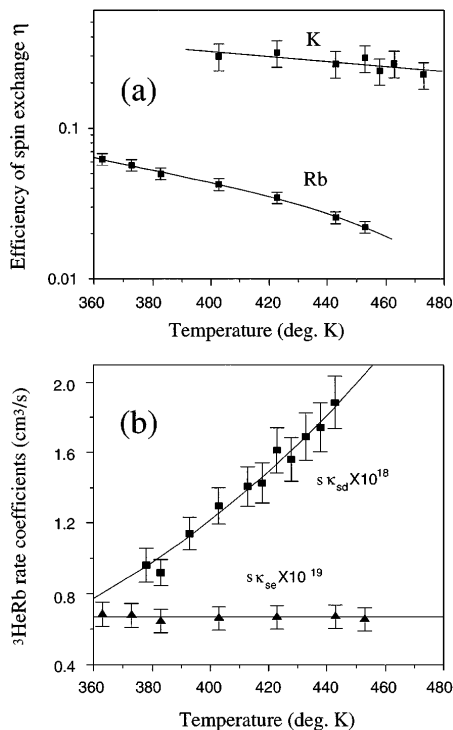
FIG. 3. (a) Spin-exchange efficiencies (note logarithmic scale) for ^{3}HeRb (7.0 amagat of ^{3}He) and ^{3}HeK (6.9 amagat of ^{3}He) versus temperature. (b) Summary of temperature dependences of key spin-relaxation rate coefficients: $s\kappa_{sd}$ for ^{3}HeRb spin destruction and $s\kappa_{se}$ for ^{3}HeRb spin exchange. The slowing-down factor $s = 10.8$ converts the rate coefficients for late-time transients of Rb vapor with natural isotopic composition to rate coefficients for a hypothetical Rb atom with no nuclear spin.