Field Dependence of Spin Relaxation in a Dense Rb Vapor

S. Kadlecek, L. W. Anderson, and T. G. Walker

Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706

(Received 5 December 1997; revised manuscript received 18 March 1998)

We observe that the Rb-Rb relaxation rate for spin polarized Rb is reduced by a factor of 3 in magnetic fields of a few kG, even at multiatmosphere buffer gas pressures. This reduction is proportional to the Rb density and is independent of buffer gas pressure between 100 and 3000 Torr. We also report anomalously large relaxation rates below 100 Torr. Both of these observations are inconsistent with the previously held assumption that the Rb-Rb relaxation arises from sudden binary collisions. [S0031-9007(98)06437-0]

PACS numbers: 32.80.Bx, 32.80.Cy, 33.35.+r

Spin-exchange optical pumping warrants study, both for the intrinsic interest in spin-dependent collisional processes, and to maximize the efficiency with which hyperpolarized (highly spin polarized) noble gas nuclei are produced. Large scale, efficient polarization of noble gas nuclei is vital to such applications as polarized ^{3}He targets for nuclear and particle experiments [1], and magnetic resonance imaging [2].

The key collisional processes in spin-exchange optical pumping are spin-exchange collisions between optically pumped alkali atoms and the noble gas atoms, and spin relaxation of the alkali atoms during collisions with each other, the noble gas atoms, or other buffer species present. The ratio of the spin-exchange to spin-relaxation rate determines the maximum efficiency possible for the spin-exchange process [3]. In this Letter, we report that the polarization loss due to Rb-Rb interactions is reduced from its zero- field rate by a factor of 3 in a few kG magnetic field. This field dependence persists even up to multiatmosphere buffer gas pressures. Since Rb-Rb relaxation accounts for a significant fraction of the polarization loss in ^{3}He spin-exchange optical pumping [4], our results suggest a straightforward way to increase optical pumping efficiency, and they require a new interpretation of the relaxation mechanism.

For a variety of technical reasons most current spin-exchange optical pumping experiments use Rb atoms as the alkali spin-exchange agent, so Rb relaxation rates are of particular interest. Previous evidence, obtained through study of the temperature and pressure dependence of the relaxation rates, is consistent with the interpretation that Rb relaxation occurs during sudden binary collisions with other Rb atoms, N_2 molecules (which are present to eliminate depolarization due to radiation trapping), and the noble-gas atoms [4–6]. If the Rb spin relaxation occurs only during binary collisions (as opposed to molecular formation, for example), the average collision time of $\tau \sim 1$ psec implies that laboratory magnetic fields on the order of 1 kG should have no detectable effect on the relaxation. This is because the Larmor frequency of $\Omega = \mu_B B/\hbar = 2\pi \times 2.8$ GHz gives $\Omega\tau \ll 1$, so there is negligible precession of the electron spin about the applied magnetic field during the collision.

Contrary to the above expectations, we observe a reduction of Rb-Rb relaxation rates in kG magnetic fields. In addition, we find that at buffer gas pressures below a few hundred Torr, the zero-field relaxation rate decreases rapidly with increasing buffer gas pressure. This behavior is qualitatively similar to wall relaxation, but the rate is strongly Rb density dependent and is too large to be explained in this way. Both of these observations lead us to conclude that Rb-Rb spin relaxation must be explained by mechanisms other than sudden binary collisions.

To study the magnetic-field dependence of Rb relaxation rates, we prepared a cylindrical stainless-steel chamber ($1\frac{3}{8}$ in. diameter, $2\frac{1}{2}$ in. length) to fit between the pole faces of a 6 kG NMR magnet. Its windows were sealed with copper conflat gaskets recently developed for UHV work [7]. The chamber contained Rb vapor and N_2 gas. The N_2 pressure was adjustable from 100 to 3000 Torr and was measured using a capacitance manometer with the chamber at the operating temperature. We arrived at the Rb number density by measuring the Faraday rotation of linearly polarized, near resonant light in the manner of Ref. [8]. The Rb metal was of high purity (>99.9%) with less than 40 ppm Cs contamination. The chamber was inside an oven with optical access and was heated to produce Rb number densities between 3.5×10^{14} and 2.5×10^{15} cm^{-3}. We used a standing-wave Ti:sapphire laser (500 mW) for optical pumping with $\sim 100\ \mu$W of the laser light used for probing the spin polarization of the alkali atoms. The light was tuned 0.5–1.5 nm off the $5S_{1/2} - 5P_{1/2}$ atomic resonance line to a wavelength where the vapor was optically thin. Care was taken to keep the optical pumping rate much smaller than the relaxation rate so that the Rb spin polarization was always below 10%. The relaxation rates were measured "in the dark," by rapidly shutting off the pump laser with an electronic shutter after 100 msec of optical pumping and then monitoring either the absorption or Faraday rotation of the probe laser beam as a function of time. The combination of large chamber size and approximate matching of the pump laser profile to the lowest diffusion mode of the chamber made the wall relaxation rate $\approx 450\ \mathrm{s}^{-1}/P(\mathrm{Torr})$ which is negligible except at very low pressure. We verified this value by investigating the pressure dependence of the relaxation rate at sufficiently low pressure and Rb number density, and we see no evidence of contamination by higher diffusion modes. At the high temperatures of the cell, the $10^{14}\ \mathrm{cm}^{-3}$ or higher alkali number density gives Rb-Rb spin-exchange rates on the order of $10^5\ \mathrm{s}^{-1}$, ensuring spin-temperature equilibrium for the Rb atoms [9,10]. Under conditions of spin-temperature equilibrium, observed relaxation times are longer than the electron randomization times by the well-known slowing-down factor of 10.8 for Rb [3,11]. The rates reported here are the observed rates and are not corrected for the slowing-down factor.

The measured relaxation rate Γ depends on the N_2 pressure P, the magnetic field B, and the Rb number density [Rb]. The dependence of Γ on these parameters is summarized in Figs. 1 and 2. Figure 1 shows the variation of Γ with B at $P = 969$ Torr and $[\mathrm{Rb}] = 8.5 \times 10^{14}\ \mathrm{cm}^{-3}$. Similar data taken over the entire range of P ($100 < P < 3000$ Torr) and [Rb] are always accurately expressed as a Lorentzian whose width is independent of P and [Rb] (as shown in the inset in Fig. 1). Figures 2a and 2b show that the height of the Lorentzian is independent of P, but is proportional to [Rb].

We have also studied the dependence of Γ on P over the entire range of B and [Rb]. An example is shown in Fig. 2a. For all but the very lowest values of P, we find that the P dependence is well represented by a term proportional to P (due to Rb-N_2 collisions), a term proportional to $1/P$ (due to wall relaxation and the anomalous low pressure relaxation mechanism reported here), and a term that is independent of the N_2 pressure but proportional to [Rb] (Rb-Rb relaxation). We find that only the Rb-Rb relaxation term varies with the application of a magnetic field. Thus, the data are well parametrized by

$$\Gamma(P, B, [\mathrm{Rb}]) = \Gamma_{-1}\frac{P_0}{P} + \left(\kappa_A + \frac{\kappa_B}{1 + (B/B_D)^2}\right)[\mathrm{Rb}] + \Gamma_1 \frac{P}{P_0}\,. \tag{1}$$

This form accurately represents our data with $P_0 = 760$ Torr, $B_D = 1.15 \pm 0.15$ kG, $\kappa_A = 1.50 \pm 0.15 \times 10^{-14}\ \mathrm{cm}^3/\mathrm{s}$, $\kappa_B = 2.88 \pm 0.3 \times 10^{-14}\ \mathrm{cm}^3/\mathrm{s}$, $\Gamma_1 = 21.2 \pm 1\ \mathrm{s}^{-1}$ at 500 K. Γ_{-1} has a more complicated [Rb] dependence which is described later. At zero field, the Rb-Rb relaxation rate is $(\kappa_A + \kappa_B)[\mathrm{Rb}]$. This linear [Rb] dependence has been previously shown [4,5,12] and our value agrees with [5] to within 10%. We find that applying a B field reduces Rb-Rb relaxation by a factor of $1 + \kappa_A/\kappa_B = 2.9 \pm 0.1$. Since κ_A is independent of B, a possible interpretation is that $\kappa_A[\mathrm{Rb}]$ is the relaxation rate due to sudden Rb-Rb collisions. Rb-N_2 collisions have been studied by [4], and Γ_1 agrees with this previous measurement to within 10% as well.

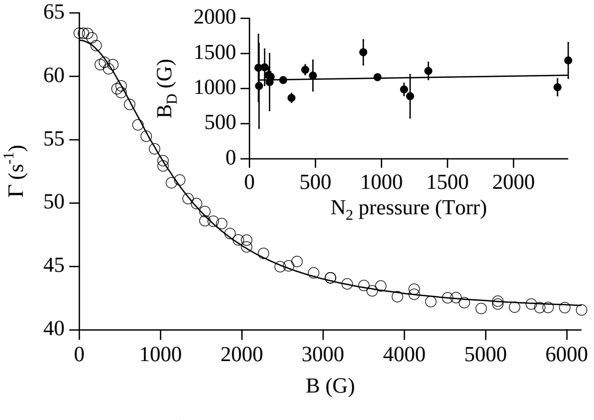

FIG. 1. Magnetic field dependence of Rb spin relaxation at 969 Torr and $[\mathrm{Rb}] = 8.5 \pm 0.9 \times 10^{14}\ \mathrm{cm}^{-3}$. The solid line is a Lorentzian fit, with a half-width of $B_D = 1161 \pm 19$ G. The magnetic-field dependence implies a relaxation mechanism other than binary collisions. Most of the offset is due to Rb-N_2 collisions, which are not affected by the magnetic field. If the N_2 were replaced by 969 Torr of He, the relaxation rate would decrease by nearly a factor of 3 between 0 and 6 kG. The inset shows that B_D is nearly independent of buffer gas pressure.

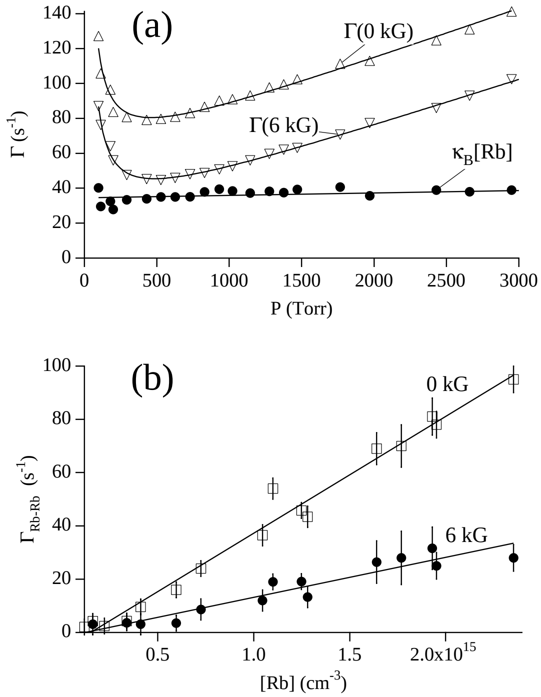

FIG. 2. (a) Relaxation rate at $B = 0$, $B = 6$ kG, and their difference $\kappa_B[\mathrm{Rb}]$ as a function of N_2 pressure P, at a Rb number density of $1.1 \pm 0.1 \times 10^{15}\ \mathrm{cm}^{-3}$. (b) Rb-Rb relaxation rate as a function of Rb number density measured in fields of 0 and 6 kG. Note that the Rb-Rb relaxation rate is reduced by a factor of 2.9 ± 0.1 from the zero-field rate at all Rb densities. Our measurements of [Rb] are reproducible to $\approx 10\%$.

We have made a number of systematic checks. These include measurements to verify that the relaxation rate did not depend on the following: light intensity (of either pump or probe); light frequency; proximity of detector and all electronics to the field region; helicity of pump and probe beams, with respect to B field and also with respect to each other; optical pumping and probing on the $P_{1/2}$ or $P_{3/2}$ transition; switching the oven from ac to dc heating; and whether the relaxation transients were measured by absorption or Faraday rotation. In addition we investigated a 5 amagat $\mathrm{Rb}/\mathrm{N}_2/^3\mathrm{He}$ glass cell [13], and observed that the relaxation rate depended on magnetic field with similar κ_A, κ_B, and B_D to those observed in our N_2 filled stainless steel chamber. This rules out any possible wall effects that might come from the stainless steel.

Two possible noncollisional explanations for the magnetic- field dependence include relaxation due to magnetic-field gradients and a magnetic-field dependent departure of the atoms from spin-temperature equilibrium. In the case of the magnetic- field gradients, our experiment is in the high-pressure regime where the relaxation rate is proportional to the diffusion coefficient [14]. In order to explain our results, a field gradient on the order of 1 kG/cm is needed. This is much larger than the measured field gradient for our setup. In addition, the strong observed temperature dependence, the weak pressure dependence, and the similarity between results obtained in the glass and stainless-steel cells eliminate this possibility. As for the possible field-dependent departure from spin-temperature equilibrium, we note that in a magnetic field, the number of collisions required to establish spin-temperature equilibrium is increased by a factor of roughly $1 + (\Omega/\omega_{hf})^2$ [15,16], where $\omega_{hf}/2\pi$ is the atomic hyperfine splitting frequency. Given the extremely large spin-exchange rates ($>10^5\ \mathrm{s}^{-1}$) at the temperature of this experiment, however, this effect is much too small to explain our observations. In addition, we would not expect a Lorentzian field dependence. Thus all the evidence points to the magnetic-field dependence being a collisional effect.

Since the magnetic-field dependence is collisional in origin, the measured width B_D of 1.15 kG implies that the source of the relaxation has a coherence time $\tau_c > 1/g_S\mu_B B_D \sim 50$ psec. κ_B is independent of N_2 pressure and Rb density over the range of parameters studied, so a natural interpretation might be a magnetic-field dependence of relaxation in Rb-Rb binary collisions. However, the binary collision duration is much too short to explain the relaxation unless the interaction involved in the relaxation has a range of $\sim 50-100$ Å, which seems quite unlikely. We conclude that short duration binary collisions are not responsible for most of the Rb-Rb relaxation.

The next most obvious explanation is that much of the relaxation previously attributed to binary collisions is due to formation of Rb_2 triplet molecules. At the pressures studied here the coherence time for such molecules greatly exceeds the minimum required by the observed field dependence. The interaction that produces the relaxation is likely the anisotropic spin-spin interaction $V_{SS} = \frac{2}{3}\lambda(3\mathbf{S}\cdot\hat{\mathbf{R}}\hat{\mathbf{R}}\cdot\mathbf{S} - \mathbf{S}\cdot\mathbf{S})$ [17], where $\mathbf{R}$ is the internuclear separation. Averaging over the rapid molecular rotation changes this to $V_{SS} = \frac{\lambda}{3}[\mathbf{S}\cdot\mathbf{S} - \mathbf{3}(\mathbf{S}\cdot\hat{\mathbf{N}})^2]$, where $\mathbf{N}$ is the rotational angular momentum of the molecule. As the electronic spin relaxes due to V_{SS}, the hyperfine interaction transfers angular momentum stored in the nucleus back to the electron. The magnetic-field dependence of Γ and the pressure independence of B_D can then be explained as a decoupling of the hyperfine interaction.

The pressure independence of κ_B over such a large range in Fig. 2a is more difficult to understand, however. The relaxation rate due to triplet molecules is given by f/T_F, the product of the formation rate $1/T_F$, and the fraction f of the molecular angular momentum lost in the molecular lifetime τ_M. The formation rate is given by $1/T_F = k[\mathrm{Rb}]/\tau_M$, where $k \sim 450$ Å^3 is the chemical equilibrium coefficient which is weakly temperature dependent for the loosely bound triplet molecules. Thus the triplet relaxation mechanism has the correct Rb density dependence. Since $\tau_M \propto 1/P$, in order for κ_B to be independent of P we require $f \propto 1/P$ or $f \propto \tau_M$, and the data imply that $f/\tau_M = 6.4 \times 10^7\ \mathrm{s}^{-1}$. We obtain a lower limit of 5 Å^2 on the cross section for breakup of the triplet molecules by noting that $f \leq 1$ throughout the N_2 pressure range. This lower limit is reasonable, being somewhat less than the known breakup cross sections for Rb-Xe van der Waals molecules [18,19]. It remains to be seen if a detailed study of the angular momentum evolution in triplet molecules shows that $f \propto \tau_M$ over such a large range in τ_M.

Having described the unusual behavior of Rb-Rb relaxation, we now turn to the fit parameter Γ_{-1}. Figure 3 shows measured zero-field relaxation rates for Rb as a function of P at two different Rb densities, as well as the fits to Eq. (1). At high Rb density, Γ_{-1} rises dramatically, at a rate much too large to be explained by diffusion. This is demonstrated by the dashed lines in the figure which show the expected relaxation rates using previously measured diffusion coefficients [4]. Furthermore, this increase depends strongly on the Rb density (much faster than the weak power law in temperature normally observed for diffusion coefficients), suggesting again a Rb-Rb relaxation mechanism as its origin. This behavior is shown in the inset in Fig. 3. The rapid increase of the relaxation rate with decreasing pressure is suggestive of molecular formation as the origin of the relaxation, in the limit that the relaxation probability is small during the molecular coherence time. In this limit the relaxation rate is proportional to the formation rate $1/T_F \propto P$ per alkali atom times the square of the molecular coherence time $\tau_c^2 \propto 1/P^2$, giving a net relaxation

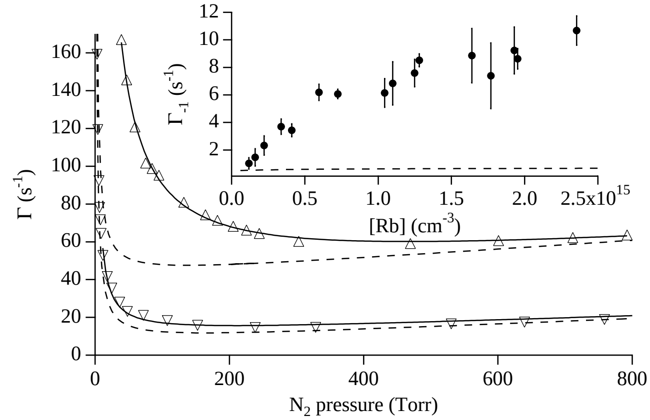

FIG. 3. Zero-field relaxation rates as a function of N_2 pressure P, at Rb densities of $1.2 \pm 0.1 \times 10^{14}$ cm^{-3} and $1.05 \pm 0.1 \times 10^{15}$ cm^{-3}. Solid lines are a fit of the form of Eq. (1). Dashed lines show what is expected assuming diffusion/wall relaxation is responsible for the Γ_{-1}/P term. The inset shows the dependence of Γ_{-1} on the Rb density, with the dashed line again showing the expected value assuming diffusion as the relaxation mechanism.

rate that varies inversely with pressure. This behavior is well known, for example, in alkali-Xe relaxation where van der Waals molecules are known to be important [20], but has never been observed in alkali-alkali relaxation. We believe that the low pressure relaxation, and its Rb density dependence, result from Rb_2 $^1\Sigma_g^+$ molecules [21]. The relaxation rate due to these molecules decreases with increasing buffer gas pressure and lacks a magnetic-field dependence at high pressure. Thus, the results shown in Figs. 1 and 2 must be explained by an additional relaxation mechanism.

In conclusion, we have discovered that magnetic fields of a few kG reduce Rb-Rb relaxation rates by about a factor of 3, even at multiatmosphere pressures. The relaxation mechanism is not yet understood, but the result has important implications for the efficiency of hyperpolarized ^{3}He production. In spin-exchange optical pumping of ^{3}He, with only a small quantity of N_2, a large fraction of the angular momentum loss is through Rb-Rb spin relaxation. We estimate that the application of a few kG magnetic field will allow the polarized ^{3}He production rate to be increased by about a factor of 2 without loss of polarization for a typical large scale pumping apparatus. This makes spin-exchange optical pumping more attractive relative to metastability exchange [22,23] for production of hyperpolarized ^{3}He.

The authors benefited from discussions with and the loan of the high pressure Rb/He/N_2 cell by W. Happer, A. Young, and C. Erickson. This work was supported by the National Science Foundation and the David and Lucile Packard Foundation.

[1] E124 Collaboration, P. Anthony *et al.,* Phys. Rev. Lett. **71**, 959 (1993).

[2] M.S. Albert, G.D. Cates, B. Driehuys, W. Happer, C.S. Springer, Jr., B. Saam, and A. Wishnia, Nature (London) **370**, 199 (1994).

[3] T.G. Walker and W. Happer, Rev. Mod. Phys. **69**, 629 (1997).

[4] M.E. Wagshul and T.E. Chupp, Phys. Rev. A **49**, 3854 (1994).

[5] A. Ben-Amar Baranga, S. Appelt, M.V. Appelt, M.V. Romalis, C.J. Erickson, A.R. Young, G.D. Cates, and W. Happer, Phys. Rev. Lett. **80**, 2801 (1998).

[6] When Xe is present, relaxation has also been observed due to formation of Rb-Xe molecules.

[7] A. Noble and M. Kasevich, Rev. Sci. Instrum. **65**, 3042 (1994).

[8] Z. Wu, M. Kitano, W. Happer, M. Hou, and J. Daniels, Appl. Opt. **25**, 4483 (1986).

[9] L.W. Anderson, F.M. Pipkin, and J.C. Baird, Phys. Rev. **120**, 1279 (1960).

[10] A.R. Young, S. Appelt, A. Ben-Amar Baranga, C. Erickson, and W. Happer, Appl. Phys. Lett. **70**, 3081 (1997).

[11] W. Happer, Rev. Mod. Phys. **44**, 169 (1972).

[12] R.J. Knize, Phys. Rev. A **40**, 6219 (1989).

[13] The cell was one of several studied in Ref. [5]. Using other cells, C. Erickson and W. Happer have independently verified the magnetic-field dependence we report here.

[14] L.D. Schearer and G.K. Walters, Phys. Rev. **139**, A1398 (1965); G.D. Cates, S.R. Schaefer, and W. Happer, Phys. Rev. A **37**, 2877 (1988).

[15] T. Walker and L.W. Anderson, Phys. Rev. Lett. **71**, 2346 (1993); Nucl. Instrum. Methods Phys. Res., Sect. A **334**, 313 (1993).

[16] B. Suleman, Ph.D. thesis, Princeton University (unpublished).

[17] N.D. Bhaskar, J. Pietras, H. Comparo, W. Happer, and J. Kiran, Phys. Rev. Lett. **44**, 930 (1980).

[18] X. Zeng, Z. Wu, T. Call, E. Miron, D. Schreiber, and W. Happer, Phys. Rev. A **31**, 260 (1985).

[19] T. Walker, Phys. Rev. A **40**, 4959 (1989).

[20] W. Happer, E. Miron, S. Schaefer, D. Schreiber, W.A. van Wijngaarden, and X. Zeng, Phys. Rev. A **29**, 3092 (1984).

[21] R. Gupta, W. Happer, G. Moe, and W. Park, Phys. Rev. Lett. **32**, 574 (1974).

[22] M. Ebert, T. Grossman, W. Heil, W.E. Otten, R. Surkau, M. Leduc, P. Bachert, M.V. Knopp, L.R. Schad, and M. Thalen, Lancet **347**, 1297 (1996).

[23] P.J. Nacher and M. Leduc, J. Phys. (Paris) **46**, 2057 (1985).