Breakdown of Angular Momentum Selection Rules in High Pressure Optical Pumping Experiments

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We present measurements, using two complementary methods, of the breakdown of atomic angular momentum selection rules in He-broadened Rb vapor. Atomic dark states are rendered weakly absorbing due to fine-structure mixing during Rb-He collisions. The effect substantially increases the photon demand for optical pumping of dense vapors.

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Optical pumping [1] of alkali-metal atoms at high temperatures and high buffer gas pressures is a powerful technique for precision spectroscopies (clocks, magnetometers, masers) [2], and for production of hyperpolarized noble gas nuclei by spin-exchange collisions [3]. Hyperpolarized noble-gas nuclei are extensively used as neutron spin-filters [4], targets for electron scattering [5], for magnetic resonance imaging [6], nuclear magnetic resonance [7], and for fundamental studies [8]. For spin-exchange optical pumping, the small cross-sections for spin exchange [3] are compensated for by operating at high alkali densities, producing optical depths of $D \sim 100$. Such extreme opacities are managed by pumping the atoms into “dark” Zeeman levels that do not absorb the pumping light. Ideally, the vapor would become completely transparent to the pumping light, except for a small unpolarized layer near the cell walls. Including collisional spin-relaxation losses would lead to a modest linear attenuation of the pumping light as it propagates through the cell [3].

Under these extreme conditions the quality of the dark state becomes of great importance. In order to maintain high population of the dark state throughout the cell, the rate $R$ at which unpolarized atoms at the entrance to the cell absorb pumping light must be $\sim D\Gamma$, where $\Gamma$ is the spin-relaxation rate. Now suppose the dark state atoms absorb the light at a small rate $R_d$. This directly increases the light absorption and also causes a small fraction of the atoms to populate strongly absorbing states. Under these conditions, the laser power required to optically pump the entire cell (the photon demand) increases by a factor

$$\Upsilon = 1 + 2R_d/\Gamma = 1 + 2DR_d/R. \quad (1)$$

For typical $D = 100$, a dark state absorption rate of only 1/200 of the unpolarized absorption rate doubles the photon demand.

In this Letter we present the first observations of dark-state absorption due to fine-structure mixing in alkali-metal He collisions. We show that this light-induced spin-relaxation mechanism limits the attainable alkali polarization and substantially increases the photon demand for optical pumping. While these collisions are well-studied in the context of line-broadening [9] and fine-structure population transfer [10], prior line-shape studies were insensitive to how the collisions alter the angular momentum selection rules for light absorption [11].

The dark state for optical pumping of alkali-metal atoms with light of photon spin projection $p = 1$ tuned to the first excited $^2P_{1/2}$ level is a fully nuclear ($I$) and electron ($S$) spin-polarized state with projection $m = S + I$. It follows from angular momentum conservation and the lack of an excited Zeeman sublevel of projection $m' = S + I + 1$ that excitation from the dark state is forbidden. In contrast, the increased angular momentum of a $^2P_{3/2}$ level allows no such dark state when pumping to that excited level [12].

To the extent that collisions of excited alkali-metal atoms with the buffer-gas atoms do not mix states of different electronic angular momentum, the above arguments are unchanged in a buffer gas. However, interactions with He substantially mix the $^2P_{1/2}$ and $^2P_{3/2}$ states even for Rb and Cs atoms with large fine-structure splitting [9]. This mixing appears in Fig. 1 as a divergence of the $|\Omega| = 1/2$ adiabatic potentials, $\Omega$ being the projection of the electronic angular momentum along the interatomic axis. In addition, the strong repulsion between $^2S_{1/2}$ atoms and He produces a transient

![FIG. 1. Adiabatic energy curves for RbHe molecules [13] adapted to include fine-structure [9]. The projection $|\Omega|$ of the total electronic angular momentum along the interatomic axis is given in brackets. The curve crossings between the photon-dressed $5s\sigma$ state and the two excited-state curves mean that photon absorption is allowed during a collision. These absorption processes are not subject to the free-atom dipole selection rules, allowing normally angular momentum forbidden transitions to occur.](image-url)
absorption to the \( \Omega = 3/2 \) state of purely \( ^2P_{3/2} \) character at an interatomic distance of \( 8a_0 \). Both of these effects lead to substantial absorption of the pumping light from the dark state in the atmospheric pressure cells typically used for these experiments. Thus the usual atomic angular momentum selection rules are violated in Rb-He collisions.

As described below, we have measured the dark-state absorption cross section for Rb in the presence of \(^3\)He gas of density \([\text{He}]\) to be \( \sigma_d = [\text{He}] \times 1.21 \pm 0.12 \times 10^{-17} \text{cm}^2/\text{amg} \) [14] for light near the \(^2S_{1/2} \rightarrow ^2P_{1/2} \) resonance at a wavelength of 795 nm. The consequences of this number can be understood by calculating the photon demand for a detuned monochromatic pump laser. With a pressure-broadened atomic lineshape of width \( B'[\text{He}] \), the photon demand doubles for light detunings of

\[
\Delta = \sqrt{\frac{r_c f B'}{4D\sigma_d}} = 104 \text{ GHz} \sqrt{\frac{100}{D}},
\]

where we have assumed \( \Delta \gg B'[\text{He}] \), and \( B' = 18.7 \text{ GHz/amu} \) [11]. The oscillator strength is \( f \) and \( r_c \) is the classical electron radius. Thus light sources with widths exceeding 100 GHz will be very inefficient, at least partially explaining why the narrowing of commercial high power diode lasers has produced substantial improvements in spin-exchange optical pumping [15]. When light of broader bandwidth is used, the on-resonant part of the pumping spectrum is rapidly depleted near the cell entrance, causing the pumping spectrum to become increasingly off-resonant and therefore inefficient as the light propagates through the cell.

Fig. 2 illustrates the dark state absorption effect, simulating the alkali polarization and laser power as a function of position in the cell, both with and without the dark state absorption. We assume 100 W of pumping light with a 1000 GHz FWHM spectral profile, a 10 cm diameter, 7 cm long cell with 8 amg of \(^3\)He and 0.066 amg of \( \text{N}_2 \), and \([\text{Rb}]=4 \times 10^{14} \text{ cm}^{-3} \). Under these conditions we estimate a spin-relaxation rate of 630/s [15]. Without dark-state absorption the light is attenuated only due to ground-state spin-relaxation and only 35 W would be dissipated in the cell, maintaining a very high Rb polarization. When the dark-state absorption is taken into account, several changes occur. The power dissipation per unit length is substantially increased, as seen in Fig. 2, even at the entrance to the cell before the spectral hole is burned.

The average power dissipation is much greater than in the ideal case, now 65 W. The polarization drop is now quite substantial, reducing to 75% at the back of the cell. This is due to two effects: 1) the pumping rate is lower due to the greater power dissipation and the production of a complete hole in the spectral profile, and 2) the remaining light is in the spectral region with low efficiency, further reducing the maximum attainable polarization.

We deduced the dark-state absorption cross sections using the change in transmission of circularly polarized light through an optically pumped vapor as the atomic spin-polarization is reversed. This is effectively a measurement of the circular dichroism of the vapor. Combining this with previous measurements of the absorption cross sections for unpolarized atoms [11] allows us to avoid a measurement of the Rb vapor pressure.

As shown in Fig. 3, a Rb vapor cell was optically pumped by a circularly polarized frequency narrowed diode array bar [16]. A magnetic field of 50 G was applied in the pump propagation direction. A tunable probe external-cavity diode laser was attenuated to \( P < 50 \mu \text{W} \), sent through a mechanical chop-
per operating at 485 Hz, and linearly polarized with a polarizing beam splitter cube. A portion was split off by a non-polarizing beam splitter plate to provide a measure of the incident intensity, and the remainder was circularly polarized with a quarter wave plate. The probe beam propagated through the cell at an angle $\theta = 17.6^\circ$ with respect to the magnetic field. The incident and transmitted intensities were sent to lock-in amplifiers referenced to the chopper frequency. To change the direction of the atomic spin polarization, the pump $\lambda/4$ plate was rotated $90^\circ$. To obtain the relation between the incident and transmitted intensities in the absence of Rb (thus accounting for loss in the windows of the oven and cell), a measurement was taken at room temperature.

Two natural abundance Rb cells were used in this experiment. The low pressure cell is a closed 4.9 cm long cylinder, with 0.80 amg $^3$He and 0.07 amg of $N_2$. The high pressure cell is a blown GE180 sphere of diameter 3.5 cm, filled with 3.27 amg of $^3$He and 0.13 amg $N_2$. The cell being studied was placed in temperature-controlled flowing hot air oven. Temperatures ranging from ~60 °C to ~180 °C, corresponding to [Rb] = 1-200 $\times$ 10$^{12}$ cm$^{-3}$, were used to produce appropriate optical thickness for transmission measurements at a range of frequencies.

The Rb spin polarization was measured with transverse electron paramagnetic resonance (EPR) spectroscopy [17, 18]. A 26.4 MHz RF field was applied perpendicular to the holding field by driving a pair of 9 cm diameter coils, separated by 7 cm, with a synthesized function generator. As the holding field was swept through the EPR resonances, the resulting polarization modulation of the probe beam was measured by a polarizer and a fast photodetector, which was demodulated to 100 KHz by mixing it with a 26.5 MHz signal from a second synthesized function generator. This 100 KHz signal was then sent to a lock-in amplifier referenced to a signal generated by mixing the outputs of the two function generators. The phase of the lock-in was chosen to produce Lorentzian EPR spectra. The spin-polarization was deduced using the area ratio method [17].

The basic parameters observed by the experiment are the transmissions $I_{\pm}$ for circularly polarized light propagating at angle $\theta$ to the spin polarization $\pm P$. The absorption cross section for the probe light is

$$\sigma(\pm) = \sigma_0(1 \mp P_\infty P \cos \theta)$$

where $P_\infty$, the normalized circular dichroism of the vapor, would be 1 in the absence of the dark state absorption. We extract $P_\infty$ from the transmitted intensities $I_{\pm} = I_0 \exp(-[\text{Rb}] l \sigma(\pm))$ by finding

$$\frac{-\ln(I_-/I_0) + \ln(I_+/I_0)}{-\ln(I_-/I_0) - \ln(I_+/I_0)} = PP_\infty \cos \theta.$$  \hspace{1cm} (4)

Note that in forming this ratio the optical thickness $[\text{Rb}] l$ and instrumental gains cancel. We then use the previously measured pressure-broadened lineshape [11] $\sigma_0$ to obtain

$$\sigma_d = \sigma_0(1 - P_\infty)$$

Thus by measuring $P(\nu)$, pumping rate $R(\nu)$, and spin-relaxation rate $\Gamma$, we deduce $P_\infty$.

We chopped the pumping laser with a mechanical shutter and measured the spin-polarization as a function of time, as illustrated in Fig. 5, using Faraday rotation. For small polarizations, the rising transient builds up polarization to the steady state value (6) at a rate $(R(\nu) + \Gamma)/\eta$, and the falling transient decays at the rate $\Gamma/\eta$, where the slowing-down factor $\eta = 10.8$ for natural abundance Rb takes into account the spin inertia due to the alkali-metal nuclei at low polarizations [18]. The Faraday rotation was calibrated by EPR spectroscopy.

![FIG. 4. Normalized circular dichroism results near the 5S$_{1/2}$-5P$_{1/2}$ resonance line of Rb. The agreement between cells of different He pressure verifies that the effect originates from absorption in Rb-He collisions. The solid line shows the frequency dependence of the dichroism due to the dark state absorption.](image-url)
FIG. 5. Pumping/decay transients used to measure $P_\infty$. Pumping light is turned on at $t = 0$, and the polarization builds up to the steady-state value of Eq. 6. The exponential build-up and decay constants allow the pumping rate $R$ and the relaxation rate $\Gamma$ to be measured. Note that the sign of the polarization is opposite for 785 nm pumping as compared to 793 nm pumping, due to the dichroism of the vapor being negative for the former case.

The deduced values of $P_\infty$ using this optical pumping (OP) method are shown in Fig. 6 and agree with the results of the direct dichroism measurements. With the OP method, the zero crossing of the dichroism is particularly dramatic as the signal of Fig. 5 reverses sign near 790 nm. We note that a naive pressure broadening model that neglects the angular momentum altering properties of RbHe collisions would predict the zero crossing to occur at 787.5 nm.

In summary, we used two distinct methods to demonstrate the breakdown of atomic angular momentum selection rules due to buffer gas collisions. This breakdown compromises the atomic dark state and has dramatic effects on the performance of optical pumping experiments with dense vapors. To mitigate this effect, it is clearly important to perform the optical pumping with narrowband light tuned close to the atomic resonance.

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