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Depolarization of nuclear spin polarized ^{129}Xe gas by dark rubidium during spin-exchange optical pumping

M. A. Antonacci^{a,b,*}, Alex Burant^{a,b}, Wolfgang Wagner, and Rosa T. Branca^{a,b,*}

^aDepartment of Physics and Astronomy, University of North Carolina at Chapel Hill, USA

^bBiomedical Research Imaging Center, University of North Carolina at Chapel Hill, USA

Abstract

Continuous-flow spin-exchange optical pumping (SEOP) continues to serve as the most widespread method of polarizing ^{129}Xe for magnetic resonance experiments. Unfortunately, continuous-flow SEOP still suffers from as-yet unidentified inefficiencies that prevent the production of large volumes of xenon with a nuclear spin polarization close to theoretically calculated values. In this work we use a combination of ultra-low field nuclear magnetic resonance spectroscopy and atomic absorption spectroscopy (AAS) measurements to study the effects of dark Rb vapor on hyperpolarized ^{129}Xe in situ during continuous-flow SEOP. We find that dark Rb vapor in the optical cell outlet has negligible impact on the final ^{129}Xe polarization at typical experimental conditions, but can become significant at higher oven temperatures and lower flow rates. Additionally, in the AAS spectra we also look for a signature of paramagnetic Rb clusters, previously identified as a source of xenon depolarization and a cause for SEOP inefficiency, for which we are able to set an upper limit of 8.3×10^{15} Rb dimers per cm^3 .

Keywords

spin-exchange optical pumping; hyperpolarized xenon; low field nuclear magnetic resonance; magnetic resonance imaging

1. Introduction

Nuclear hyperpolarized (HP) noble gases like ^{129}Xe [1,2] continue to find applications in a variety of research fields from material science to biomedical imaging, where the gas is used as a contrast agent in numerous magnetic resonance applications. Thanks to its high solubility in tissues and wide range of chemical shifts, applications of HP ^{129}Xe in magnetic resonance imaging (MRI) have quickly extended from void-space imaging[3–5], to imaging of gas exchange in human lungs[6], to measurements of brain perfusion[7–9], temperature imaging[10], and imaging of metabolically active fatty tissues[11,12]. For biomedical

*Corresponding authors at: Department of Physics and Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC, 27599, USA. michael.antonacci@unc.edu (M.A. Antonacci), rtbranca@unc.edu (R.T. Branca).

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imaging applications, ^{129}Xe is typically polarized via spin-exchange optical pumping (SEOP) in one of two ways: batch-mode or continuous-flow. In both cases, optimization of SEOP efficiency requires monitoring of the nuclear ^{129}Xe polarization in situ, within the optical cell, while optical alignment of the laser beam with the cell is often performed with the use of an optical spectrometer. Despite optimization of experimental parameters and settings that yield maximum in-cell polarization, final polarization values are still far from theoretical maximum values. Although with batch-mode SEOP we recently saw xenon polarization levels close to the theoretical value[13,14], in continuous-flow polarizers final ^{129}Xe polarization levels still fall short of theoretical predictions[15–19].

Even with a mature theoretical framework, the sources of SEOP inefficiencies are not yet fully understood. A number of groups have put significant effort into the study of continuous-flow SEOP inefficiencies over the past decade. Fink et al. made use of finite-element analysis simulations to incorporate the effects of turbulent flow into the standard model of SEOP[20]. These results supported the use of a presaturation region to uniformly distribute Rb vapor throughout the optical cell and increase optical pumping efficiency. Comparison with experimental values for maximum ^{129}Xe polarization under similar conditions was made, but no detailed experimental validation for the simulated results was given.

Schrank et al. examined optical pumping efficiency and total Rb polarization in an effort to explain the discrepancy of standard model ^{129}Xe polarization predictions by up to twice the measured polarization values observed in the lab[21]. Even after adjusting the ^{129}Xe wall relaxation rate and temperature dependence of the Rb-Xe spin-exchange cross section, they found that experimental values for ^{129}Xe polarization were still only qualitatively in agreement with the numerical model. More recently, Freeman et al. sought to account for SEOP inefficiency by proposing depolarization by paramagnetic Rb nanoclusters that could form under continuous-flow polarization conditions [22]. By incorporating the production and depolarizing effects of such nanoclusters into the standard model of SEOP (as presented in Norquay et al.[23]), calculated and observed ^{129}Xe polarization levels were shown to be consistent. Yet, no experimental evidence was provided for the presence of Rb clusters.

In this work we perform combined NMR measurements and atomic spectroscopy measurements to understand some of the possible causes of xenon depolarization during continuous-flow SEOP. Specifically, we first use AAS measurements to assess the presence of the postulated nanoscale Rb clusters inside the optical cell[22]. Since during the formation process of Rb clusters Rb_2 are expected to be formed, AAS could in principle be used to observe the presence of the hypothesized clusters. Then, we evaluate the presence and the impact of optically dark Rb vapor in the outlet of the optical cell on final ^{129}Xe polarization. While seemingly obvious when one compares the better performance of polarizer designs that incorporate cooling regions in the front of the optical cell to condense Rb vapor[15–17,21] with those that do not[18,19,22,24], the effects of dark Rb regions on xenon polarization have never been investigated. In order to perform these measurements, we designed and constructed a LabVIEW-based, ultra-low field NMR spectrometer as well as an optical spectrometer, which are also detailed in this manuscript.

2. Materials and methods

2.1. Continuous-flow spin-exchange optical pumping

All measurements were performed on a commercial polarizer (Model 9800, Polarean, Inc., Durham, NC, USA), whose basic design and operation is common to all continuous-flow SEOP polarizers. Specifically, in order to spin polarize the ^{129}Xe nucleus, we continuously flow a lean mixture of 1% Xe, 10% N_2 , and 89% He (Global Specialty Gases, Bethlehem, PA, USA) through a heated presaturation bulb charged with Rb metal and heated to over 430 K. The presaturation bulb serves to uniformly saturate the gas mixture with Rb vapor. The vapor and gas mixture then flows into the optical pumping cell, placed inside a pair of Helmholtz coils that generate a uniform magnetic field over the volume of the cell. The cell is illuminated by circularly polarized laser light tuned to the D1 transition of Rb (794.7 nm) and, through depopulation pumping, the Rb atoms are continuously forced into the same spin state[15,16,18,20–22]. These polarized Rb atoms then transfer their electronic spin polarization to ^{129}Xe nuclei via a Fermi contact interaction (spin-exchange)[2]. The gas mixture finally flows out of the optical cell and through a cold finger submerged in liquid nitrogen, where the xenon is separated from the gas mixture and stored in the solid state. When collection is completed, the gas flow is stopped and the solid polarized xenon sublimed directly to the gas phase and dispensed into a collection bag for transport and use.

2.2. Theoretical model of xenon polarization used in this work

The temperature dependence of the final xenon polarization is based on SEOP theory. The final xenon polarization depends on laser power, optical cell composition, geometry, temperature, and pressure, as well as xenon concentration and residency time within the optical cell. Since these dependencies are treated in detail in references [1] and [2] they will not be repeated here. The theoretical model used to calculate the expected ^{129}Xe polarization values in this work is given in references [22–25]. Briefly, the final expected ^{129}Xe polarization after cryogenic collection is given by

$$P_{Xe}(t_{res}, t_a, T) = \frac{\gamma_{SE}(T)}{\gamma_{SE}(T) + \Gamma} \langle P_{Rb}(T) \rangle (1 - e^{-(\gamma_{SE}(T) + \Gamma)t_{res}}) \left(\frac{T_1}{t_a} \right) \left(1 - e^{-\frac{t_a}{T_1}} \right) \quad (1)$$

where γ_{SE} is the Rb-Xe spin-exchange rate, Γ is the ^{129}Xe nuclear spin destruction rate, $\langle P_{Rb}(T) \rangle$ is the mean Rb spin polarization throughout the optical cell, t_{res} is the mean xenon residency time in the optical cell, t_a is the total accumulation time, T is absolute temperature, and T_1 is the longitudinal relaxation time of solid xenon. The factor

$\left(\frac{T_1}{t_a} \right) \left(1 - e^{-\frac{t_a}{T_1}} \right)$ accounts for relaxation of solid polarized xenon during progressive cryogenic collection, as described in Ref. [23]. Eq. (1) clearly shows that what ultimately sets the upper bound for the xenon polarization level is the Rb polarization. This can be expressed as a function of position along the cylindrical axis of the cell as

$$P_{Rb}(z, T) = \frac{\gamma_{OP}(z, T)}{\gamma_{OP}(z, T) + \Gamma_{SD}(T)}, \quad (2)$$

where $\Gamma_{SD}(T)$ is the temperature-dependent Rb spin-destruction rate and $\gamma_{OP}(z, T)$ is the temperature- and position-dependent Rb optical pumping rate. The Rb spin-destruction rate is determined by binary collisions between Rb atoms and gases within the cell (Xe, N₂, and He), as well as from the formation and breakup of Rb-Xe van der Waals molecules. If we model the pump laser light as a Gaussian function, with center wavelength λ_l and width λ_b , and the broadened Rb D1 absorption cross section as a Lorentzian function, the optical pumping rate can then be written in terms of photon flux $F = \frac{I \cdot n_p}{A}$ as:

$$\gamma_{OP}(z, T) = \frac{\beta}{[Rb]} F, \quad (3)$$

where I and A are pump laser intensity and cross-sectional area, respectively, n_p is photons per Joule of the pump laser, and $[Rb]$ is the Rb number density. The constant β is given by:

$$\beta = \frac{2 \sqrt{\pi \ln 2} r_e f_{D1} \lambda_l^3 w'(r, s)}{hc \Delta \lambda_1 n_p} [Rb], \quad (4)$$

where r_e is the classical electron radius, f_{D1} is the Rb D1 oscillator strength, h is Planck's constant, c is the speed of light, and $w'(r, s)$ is the real part of the complex overlap function, which depends on r , the ratio of the atomic D1 linewidth to the pump laser linewidth, and s , the relative detuning between the pump laser and D1 cross section[25]. We can then describe the optical pumping rate along the length of the optical cell as:

$$\frac{d\gamma_{OP}(z, T)}{dz} = -\beta \left(1 - s_z \frac{\gamma_{OP}(z, T)}{\Gamma_{SD} + \gamma_{OP}(z, T)} \right) \gamma_{OP}(z, T), \quad (5)$$

where s_z is the fraction of circularly polarized laser photons. Eq. (5) can then be solved by separation of variables and used to calculate the optical pumping rate at discrete positions along the axis of the optical pumping cell[24]. The optical pumping rate at each discrete step is used to find the expected Rb polarization at that position via Eq. (2). By substituting the mean of the Rb polarization values for a given temperature into Eq. (1), we then calculate the expected final xenon polarization. The above equations were all coded and run with Wolfram Mathematica (Wolfram Research, Inc., Champaign, IL, USA) for our particular experimental setup. Specifically, the cell surface temperature was varied from 363 K to 423 K at a pressure of 1.6 atm, flow rate of 1.0 standard liters per minute (SLM), collection time of 20 minutes, incident laser power of 31.4 W, optical cell inner radius of 2.4 cm and cell length of 15 cm. Gas temperatures inside the optical cell were estimated as described in Appendix A.

2.3. Custom-built optical spectrometer

In order to perform absorption spectroscopy measurements, we designed and built a Czerny-Turner optical spectrometer that could be used for both high and low resolution AAS measurements (Fig. 1). The key feature of this spectrometer is the presence of an interchangeable diffraction grating that, unlike most commercially available spectrometers, allows us to easily change bandwidth and center wavelength and perform AAS measurements at any given spectral resolution.

Briefly, light is directed into the spectrometer by a 1000 μm diameter optical fiber and onto a 5 μm mounted slit. A gold-coated parabolic mirror collimates the incoming light onto a blazed reflective diffraction grating. The spectrometer is then fitted with a 300 lines/mm grating for low resolution spectroscopy measurements, and with a 1200 lines/mm grating for high resolution ones. A second gold-coated mirror refocuses the diffracted light onto a 3648 element line CCD camera controlled by a National Instruments LabVIEW interface (National Instruments Corporation, Austin, TX, USA). All components are mounted on an aluminum optical breadboard and enclosed with aluminum rails and black posterboard. The spectrometer is initially aligned by using a HeNe laser. Final component alignment and wavelength calibration is accomplished with an argon calibration source. The resulting pixel resolutions are 0.048 nm/px in low resolution mode and 0.009 nm/px in high resolution mode. The Supplementary Material provides all parts and design details for easy reproduction.

2.4. Custom built ultra-low field NMR spectrometer

In order to monitor the relative polarization of ^{129}Xe inside the optical pumping cell, we designed and constructed an ultra-low field NMR spectrometer similar to those described in previous work[26–31]. The spectrometer is custom-programmed in LabVIEW and run via a National Instruments multifunction data acquisition (DAQ) card (model PCI-6110). A block diagram of the ultra-low field NMR spectrometer, as well as a snapshot of the LabVIEW control interface, is shown in Fig. 2. The multifunction DAQ card produces customizable NMR pulses that are sent through a simple crossed-diode duplexer that also serves as the NMR coil tuning circuit. The NMR surface coil is mounted on the optical pumping cell with Kapton tape. Helmholtz coils with their isocenter located at the center of the optical cell provide the static magnetic field for NMR measurements. Detected NMR signals are then amplified by a Stanford Research SR540 low-noise preamplifier (Stanford Research Systems, Inc., Sunnyvale, CA, USA) and sent back to the DAQ card for digitizing. The spectrometer user interface allows direct control of all pulse and acquisition parameters, channel controls, signal averaging, and optional line broadening. Both time-domain signals and frequency spectra are displayed for convenience and can be saved for post-processing and analysis.

During continuous-flow SEOP, the concentration of polarized ^{129}Xe inside the optical cell is only ~ 1.2 mM, resulting in an induced NMR signal on the order of 1 μV . For a typical NMR coil and load, the associated root-mean-square (RMS) Johnson noise can be calculated by using the following expression:

$$V_{RMSnoise} = \sqrt{4kT \cdot R \cdot BW}, \quad (6)$$

where k is Boltzmann's constant, T is the absolute temperature of the system, BW is the receiver bandwidth, and $R = R_C + R_S$ is the effective resistance of the coil-sample system consisting of R_C , the coil DC resistance, and R_S , the effective resistance due to the sample loading. At our operating frequency of 23.1 kHz, sample noise is negligible, leaving the coil DC resistance as the dominant noise contributor. For NMR measurements taken during SEOP at an oven temperature of 408 K, with a coil resistance 20.95 Ω , and an acquisition bandwidth of 20 kHz, the expected RMS thermal noise according to Eq. (6) is $\sim 0.1 \mu V$. The result is a low intrinsic signal to noise ratio (SNR) that is further degraded by the presence of electronic noise generated by other necessary components of the polarizer such as the power supplies, the digital sensors, and the heating tape.

As a result, specific design measures had to be implemented in order to detect this low NMR signal. First, the NMR surface coil was wound with 550 turns of 32 AWG 15/44 Litz wire, in order to minimize the coil DC resistance. Second, the coil was remotely tuned so that the duplexer and tuning circuit could be mounted inside an aluminum box that shielded the circuit from electromagnetic and RF interference. The duplexer circuit was PCB printed and used only ultra-high Q components to further reduce thermal noise. Finally, signal averaging was absolutely necessary in order to extract a measurable signal out of the background noise. Consecutive averages could be added coherently by precisely timing each acquisition relative to the RF excitation pulse. Since the NI DAQ card (PCI-6110) used in this study does not support hardware-timed digital output, all acquisitions were timed using an SE555P integrated circuit timer running in monostable mode. One could avoid these extra electronics by using a different NI DAQ card that does support hardware timing on the digital channels (e.g. PCI-6251, PCIe-6351, USB-6351, etc.). See Supplementary Material for more design details, including a bill of materials.

2.5. Low-resolution broadband Rb absorption spectroscopy on a sealed optical cell

In an attempt to observe Rb clusters during SEOP, AAS measurements were the first to be made. Before performing AAS directly on the optical cell, measurements were made on a sealed Rb cell, where temperature could be tightly controlled and Rb and Rb₂ number densities could be easily calculated [32]. The sealed Pyrex cell, 7.5 cm long and with a 2.5 cm outer diameter, was evacuated to about 10^{-6} torr and charged with ~ 20 mg of molten Rb (Ophos Instruments, Inc., part D7). Initial observations were performed in low resolution mode to observe the $1(X)^1\Sigma_g^+ \rightarrow 1(B)^1\Pi_u$ Rb₂ absorption band due to its large absorption cross-section [33,34] and the availability of a diffraction grating with high efficiency in this wavelength range. A resistive temperature detector (RTD) was taped to the center of the cell with Kapton tape and the entire cell wrapped in heating tape and placed within an insulated aluminum box mounted on an optical quality aluminum breadboard (model MB4545/M, Thorlabs, Newton, NJ, USA). The temperature of the cell was regulated by a microcontroller (iTRON 702040, Jumo Process Control, Inc., East Syracuse, NY, USA). Absorption measurements were made by shining a broadband halogen light source (Thorlabs

QTH10/M) through the absorption cell and collecting the transmitted light with a fiber collimator (Thorlabs F220SMA-780) for cell temperatures from 673 to 853 K.

2.6. Low-resolution broadband Rb absorption spectroscopy during SEOP

Similar measurements were made on the optical cell during continuous-flow SEOP. For these measurements, the original oven enclosure on the commercial polarizer was duplicated and modified to allow spectroscopy measurements to be performed in a direction perpendicular to the direction of the optical pumping laser (see Fig. 3). The halogen light source was mounted to shine within the polarizer oven and allowed to equilibrate for at least 12 hours prior to polarizer warm-up. The fiber collimator was mounted opposite the light source and both were aligned for maximum transmission into the custom spectrometer.

We collected AAS spectra during SEOP with flow rates of 0.1 SLM (typical rate for standby operation) and 1.5 SLM (typical rate for collection of clinical-scale volumes). We also collected AAS spectra immediately after flow began since dense Rb vapor was always observed at the beginning of the gas flow with a digital camera (see discussion section below). Standard parameters for HP ^{129}Xe production for these experiments were an optical cell pressure of 4.1 atm, cell temperature of 358 K, and presaturation bulb temperature of 438 K. Integration time for each spectrum was 10 ms with 4599 averages. Baseline spectra were also collected during polarizer cool-down once the Rb D1 and D2 absorption lines receded below noise level. This ensured maximum transmission of the broadband light through the optical cell. Baseline spectra were then used in postprocessing as described below.

2.7. High-resolution broadband Rb absorption spectroscopy during SEOP

In order to study the presence of dark Rb in the optical cell outlet and its effect on xenon polarization, the AAS setup described above was mounted within the polarizer oven such that the optical cell outlet sat between the halogen lamp and the collimation lens. The same stabilization procedure was used to allow the lamp to reach thermal equilibrium. Outlet absorption spectra were collected during SEOP at a flow rate of 1.0 SLM, optical cell pressure of 1.8 atm, and presaturation bulb temperature of 438 K, for a variety of oven temperatures between 363 and 423 K. Collection time was 20 minutes for each batch of HP ^{129}Xe and absorption spectra were obtained 8–10 minutes into the collection time, with 10 ms integration time and 4599 averages.

The NMR surface coil was placed in the center of the optical pumping cell in order to monitor the in-cell ^{129}Xe polarization throughout the SEOP process. NMR spectra were collected using a hard pulse of frequency 23.1 kHz, pulse length 0.325 ms, repetition time 524 ms, 50 averages, sampling frequency 200 kHz, and 4096 points. NMR measurements were made immediately following the outlet absorption measurement. The pump laser transmission was monitored by an on-board photodiode located behind the optical cell. This value was recorded concurrently with the NMR measurement. At the end of the collection time, the frozen xenon was sublimated into a 150 ml Tedlar bag (Jensen Inert Products, Coral Springs, FL, USA) and the polarization was measured with a calibrated polarization measurement station (Model 2881, Polarean, Inc., Durham, NC, USA).

2.8. Analysis of spectra

All absorption spectra were processed by first dividing by the scaled baseline spectrum from the halogen lamp. The D2 peaks were then fitted with a normalized Lorentzian lineshape function with area uncertainty given by the 95% confidence interval of the line area parameter. NMR spectra were likewise fit with a normalized Lorentzian lineshape and the line area used as a measure of the signal intensity.

3. Results

The theoretical final ^{129}Xe polarization vs. cell temperature as predicted by the standard model above is plotted in Fig. 4, along with experimental measurements made on our commercial polarizer. The maximum expected xenon polarization should be on the order of 44% for these parameters, whereas the maximum final xenon polarization obtained experimentally was only 25%. While slight mismatches between the calculated and observed temperature for maximum ^{129}Xe polarization can be easily explained by uneven laser light heating of the gas inside the optical cell, as previously reported in the literature [35–38], the decrease in polarization observed at higher temperatures is clearly faster than what is predicted by the standard model.

3.1. Rb dimers

Fig. 5 shows spectra acquired from the sealed Rb cell. The $1(\text{X})^1\Sigma_g^+ \rightarrow 1(\text{B})^1\Pi_u$ molecular transitions between 640–740 nm begin to appear clearly around 773 K, becoming stronger at higher temperatures, as expected. The Rb D2 absorption line is also clearly visible in the observed bandwidth. Based on known vapor curves [32], at 773 K the density of atomic Rb is $8.6 \times 10^{19} \text{ cm}^{-3}$ and of Rb_2 is $2.3 \times 10^{16} \text{ cm}^{-3}$.

Fig. 6 shows absorption spectra collected during SEOP, both during continuous-flow SEOP and at the start of flow. The Rb D2 absorption line is clearly visible. Within the observed bandwidth, we would expect to see a broad absorption band from the X-B molecular transitions if a sufficient density of dimers were present in the optical cell [34]. In neither the case of continuous-flow SEOP at 0.1 and 1.5 SLM, nor at the time of the cell opening, did we observe this absorption band.

Based on the Rb absorption spectra collected from the closed Rb cell, we estimated a sensitivity of $8.3 \times 10^{15} \text{ per cm}^3$ for Rb_2 and a similar upper-limit value for Rb_2 present during our continuous-flow SEOP experiments.

3.2. Depolarization in the optical cell outlet by dark Rb

Fig. 7 reports both NMR spectroscopy and AAS measurements performed on the optical cell during SEOP as a function of cell temperature, as well as the pump laser transmission along the optical cell. Despite the two measurements being performed more than a month apart, during which the polarizer was used to produce HP ^{129}Xe for human use, results were very consistent. As expected, the increased Rb density at high temperature leads to an increase in absorption and to a reduction of the transmitted light. Over the range of temperatures measured, the NMR signal from polarized ^{129}Xe remained basically constant (Fig. 7b).

However, as can be seen in Fig. 7c, the final xenon polarization reached a maximum at 419 K and at 423 K for the earlier and later trials, respectively. Clearly, some depolarization mechanism overtook the positive spin-exchange at higher temperatures, damaging the final polarization. Fig. 7d shows the absorption intensity of the Rb D2 transition across the optical cell outlet vs. cell temperature, indicating an increase in the Rb vapor density in the cell outlet at higher temperatures.

4. Discussion and conclusions

As far as we know, this is the first experimental attempt to observe Rb_2 during SEOP using broadband absorption. Some attempts have been made to observe Rb clusters through Mie scattering of broadband light, but none have succeeded[39].

Although we were not able to directly observe Rb_2 during continuous-flow SEOP, we were able to set an upper limit for the observable density of Rb_2 present in the optical pumping cell during SEOP to less than 8.3×10^{15} dimers per cm^3 , which is what could be directly detect by our spectrometer. Since for our polarization setup Freeman et al.'s model predicts a cluster density on the order of 10^9 per cm^3 , an improvement in sensitivity of 6 orders of magnitude would be necessary in order to directly detect Rb dimers during SEOP with our current spectrometer. Although the sensitivity could be improved by extending the absorption path via multiple reflections through the optical cell and/or by increasing the integration time and number of averages, it is highly unlikely that we could achieve an improvement in sensitivity of 6 orders of magnitude. Taken together, our results indicate that absorption spectroscopy, unlike what was originally proposed by Freeman et al., is not sensitive enough to detect the presence of Rb dimers during continuous-flow SEOP and other techniques should be investigated in order to experimentally validate the cluster model.

Interestingly, when gas flow was first turned on, we did observe through a digital video camera (model HMC-40, Panasonic, Chesapeake, VA, USA. See Supplementary Material for video) a dense Rb vapor that was quickly dispersed throughout the optical cell. However, when AAS measurements were performed to detect the possible presence of Rb dimers in this dense vapor, no significant differences were seen with respect to spectra acquired during steady-state flow (see Fig. 6). Therefore, at this point, it is unclear whether this vapor is simply atomic Rb that has condensed at the optical cell inlet and is disturbed at the start of flow, or whether it is the result of some more complex process.

Combined NMR measurements of in-cell polarization and final polarization suggest that, at high temperature, part of the xenon polarization is lost outside the optical cell. Since AAS measurements show an increase in Rb density in the outlet of the cell when temperature is increased, it is reasonable to think that HP ^{129}Xe interaction with dark Rb vapor present in the outlet of the cell is responsible for at least part of the observed xenon depolarization at higher temperatures. This temperature-dependent spin-exchange depolarization effect from dark Rb in the optical cell outlet can be included in the SEOP theory in the form of a correction factor

$$\Delta_{\text{darkRb}}(t_{\text{outlet}}, T) = e^{-\gamma_{SE}(T)t_{\text{outlet}}}, \quad (7)$$

where T is the absolute cell temperature and t_{outlet} is the residency time of polarized ^{129}Xe in the optical cell outlet. The final xenon polarization will then be given by

$$P_{Xe}(t_{\text{res}}, t_a, t_{\text{outlet}}, T) = P_{Xe}(t_{\text{res}}, t_a, T) \Delta_{\text{darkRb}}(t_{\text{outlet}}, T). \quad (8)$$

For our polarizing parameters, Fig. 8 shows the predicted ^{129}Xe polarization vs. cell temperature curve as modeled in Eq. (8). In the absence of turbulence in the cell outlet, the estimated residency time of HP ^{129}Xe in our cell outlet at a flow rate of 1.0 SLM is about 0.8 s. Under this condition, and at the maximum cell temperature studied here (432 K), a reduction of the final polarization of ~8% is expected by dark Rb in the outlet of the cell. While the depolarizing effect of dark Rb is not more than a few percent at our typical running parameters, this could be a significant effect for polarizers running in a higher temperature regime and/or at lower flow rates[19,22,23,36]. In the presence of turbulence in the cell outlet, such values could be considerably higher. Interestingly, despite when we assume absence of turbulence the reduction of the final xenon polarization is only ~8%, the rate at which the final xenon polarization is expected to decrease with temperature due to dark Rb nicely followed the experimental values.

In conclusion, we have attempted to observe Rb_2 during SEOP using broadband AAS. Comparison with measurements performed on a sealed Rb absorption cell indicated that broadband AAS is not sensitive enough to observe the density of paramagnetic Rb clusters postulated by Freeman et al., even if that population were composed entirely of dimers. We also studied the depolarizing effect of dark Rb vapor in the optical cell outlet on the final ^{129}Xe polarization. While wall relaxation is typically assumed to be the primary source of relaxation for xenon polarization[15,16,18,40,41], our results show that dark Rb vapor can make a sizable contribution to SEOP inefficiency at higher temperatures and lower flow rates, and should be considered carefully in polarizer design. Although References [15] and [16] mention the need for cooling regions to prevent the presence of unpumped Rb vapor, no one, to our knowledge, has measured the effects of this vapor on the final xenon polarization. Furthermore, this study also shows that an optimized in-cell xenon polarization does not necessarily entail an optimized final HP ^{129}Xe polarization.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Appendix A: Optical cell temperature corrections

To experimentally determine the temperature of the gas mixture flowing through an optical cell during SEOP is a notoriously difficult task. Turbulent fluid flow patterns[20], temperature gradients and laser heating make the RTD temperature measurement from the cell surface suspect, at best. Newton, et al succeeded in using Raman spectroscopy to measure temperature at specific points in an optical cell during batch-mode SEOP[35], but no such measurements for continuous-flow SEOP have been reported in the literature. In an effort to obtain more accurate temperature measurements for the gas mixture in our optical cell, we developed a method to estimate the actual gas temperatures from the external RTD measurements.

First, we used the RTD temperature measurements on our cell, without flow or laser illumination, to calibrate transverse AAS measurements through the center of the optical cell. We expect the buffer-gas broadened D2 absorption line of Rb to be well-approximated by a Lorentzian lineshape. Following Zheng et al.[42], we first calculate $f(\nu)=\log\left(\frac{I}{I_0}\right)$, the natural log of the ratio of our absorption spectrum I to our baseline spectrum I_0 . Then we fit this result according to:

$$f(\nu)=\frac{a+b(\nu-\nu_o)}{(\nu-\nu_o)^2+(\Delta\nu/2)^2}+d, \quad (\text{A1})$$

where a is the peak amplitude, b is a dispersive correction resulting from buffer gas interactions, ν_o is the center frequency of the D2 line, ν is the D2 linewidth, and d is a constant offset. From the peak amplitude, linewidth, and absorption path length l we calculate the average Rb density over the optical path:

$$[\text{Rb}]=\frac{2a}{r_e c f_{D2} \cdot l \cdot \Delta\nu}, \quad (\text{A2})$$

where f_{D2} is the Rb D2 oscillator strength. With a Rb vapor pressure curve[43], this number density can then be used to extract an average temperature for the vapor along the absorption path inside the optical cell.

We found that this method systematically results in measured temperatures 7–26 K lower than what was measured by the RTD, even though there was no gas flow through the cell. Thereafter, we fitted a correction function that appropriately scaled the AAS temperature measurement to match the RTD measurement, and hence calibrated our AAS measurements within the temperature range of interest (Fig. A1 below). This allowed us to make AAS temperature measurements during SEOP with the same setup, obtain reliable temperature measurements of the gas at the center of the cell, and correlate them with the RTD temperature measurements.

Fig. A1. (single column) Plot of the correction function used to calibrate AAS temperature measurements within the optical cell. Data were acquired with no gas flow or pump laser illumination.

Appendix B: Supplementary Material

The optical cell video as well as more details regarding the custom optical spectrometer and ultra-low field NMR spectrometer designs can be found at [URL].

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Highlights

- Home-built, LabVIEW-run optical & NMR spectrometers to study SEOP fully described
- Atomic absorption spectroscopy can't detect Rb clusters in standard SEOP conditions
- Max ^{129}Xe polarization in optical cell does not assure max final ^{129}Xe polarization
- Dark Rb can contribute to ^{129}Xe depolarization at high cell temperatures.

Fig. 1.
(single-column, color online) Three-dimensional rendering of the optical spectrometer assembly.

Fig. 2.
(2-column, color online) Block diagram of the ultra-low field NMR spectrometer (left).
Screen shot of the LabVIEW user interface for the ultra-low field NMR spectrometer (right).

Fig. 3. (single column) Simplified schematic of the broadband atomic absorption spectroscopy setup around the optical cell on the commercial polarizer. Note that the gas mixture would flow out of the page and the optical pumping laser would shine into the page along the axis of the cylindrical optical cell. The observed absorption column is indicated by fine dashed lines through the optical cell. Light collected by the collimator is passed to the spectrometer via optical fiber.

Fig. 4. (single column, color online) Experimental and theoretical final ^{129}Xe polarization as a function of cell temperature. (blue) Experimental final ^{129}Xe polarization vs. cell temperature at a gas flow rate of 1.0 SLM and collection time of 20 min. Dashed connecting lines are drawn only to guide the eye. (red) Theoretical ^{129}Xe polarization vs. cell temperature for the same operating parameters as in (a), calculated using Eq. (1).

Fig. 5. (single column, color online) Rb_2 absorption bands in closed Rb cell. The sharp absorption line at 780 nm is the atomic Rb D2 line. The weakest Rb_2 band was observed at a cell temperature of 773 K, and the strongest at 853 K.

Fig. 6. (single column, color online) Rb absorption spectra obtained during SEOP at 0.1 and 1.5 SLM, as well as at the start of flow through the optical cell. Notice the clear D2 atomic absorption line at 780 nm. The inset shows a zoomed-in view of wavelengths where the Rb₂ X-B absorption band would be expected. No absorption band is discernable above background.

Fig. 7.

(2-column) Results from the cell outlet depolarization measurements taken at a flow rate of 1.0 SLM. The temperature of the presaturation bulb was kept constant at 438 K, while cell pressure was 1.8 atm. The measurements were made twice on the same cell, over a month apart, for validation. (a) Transmitted photons as measured by a photodiode located on the back of the cell vs. optical cell temperature; (b) NMR signal from the optical cell vs. cell temperature; (c) Final xenon polarization vs. cell temperature; (d) Rb D2 absorption intensity at the cell outlet vs. cell temperature. Connecting lines are drawn to guide the eye.

Fig. 8. (single column, color online) Final ^{129}Xe polarization vs. cell temperature with the same polarizing parameters as the experimental data shown in Fig. 4, (red line) without outlet depolarization and (blue dashed line) calculated using Eq. (8).