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A Semi-empirical Model to Optimize Continuous-Flow Hyperpolarized ^{129}Xe Production under Practical Cryogenic-Accumulation Conditions.

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Abstract

Continuous-flow spin exchange optical pumping (SEOP) with cryogenic accumulation is a powerful technique to generate multiple, large volumes of hyperpolarized (HP) ^{129}Xe in rapid succession. It enables a range of studies, from dark matter tracking to preclinical and clinical MRI. Multiple analytical models based on first principles atomic physics and device-specific design features have been proposed for individual processes within HP ^{129}Xe production. However, the modelling efforts have not yet integrated all the steps involved in practical, large volume HP ^{129}Xe production process (e.g., alkali vapor generation, continuous-flow SEOP, and cryogenic accumulation). Here, we use a simplified analytical model that couples both SEOP and cryogenic accumulation, incorporating only two system-specific empirical parameters: the longitudinal relaxation time of the polycrystalline ^{129}Xe “snow”, T_1^{snow} , generated during cryogenic accumulation, and 2) the average Rb density during active, continuous-flow polarization. By fitting the model to polarization data collected from >140 L of ^{129}Xe polarized across a range of flow and volume conditions, the estimates for Rb density and T_1^{snow} were $1.6 \pm 0.1 \times 10^{13} \text{ cm}^{-3}$ and 84 ± 5 minutes, respectively — each notably less than expected based on previous literature. Together, these findings indicate that 1) earlier polarization predictions were hindered by miscalculated Rb densities, and 2) polarization is not optimized by maximizing SEOP efficiency with a low concentration ^{129}Xe , but rather by using richer ^{129}Xe -buffer gas blends that enable faster accumulation. Accordingly, modeling and experimentation revealed the optimal fraction of

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Data Availability Statement:

The data that support the findings of this study are available from the corresponding author upon reasonable request.

^{129}Xe , f , in the ^{129}Xe -buffer gas blend was ~2%. Further, if coupled with modest increases in laser power, the model predicts liter volumes of HP ^{129}Xe with polarizations exceeding 60% could be generated routinely in only tens of minutes.

Graphical Abstract

Keywords

Continuous-flow Spin-exchange Optical Pumping; hyperpolarized ^{129}Xe ; Rb density; solid T_1 relaxation; polarization model; parameter optimization; ^{129}Xe -buffer gas blend; laser power

Introduction:

Spin Exchange Optical Pumping (SEOP) is the process by which angular momentum is transferred first from circularly-polarized laser light to the valence electrons of an alkali metal vapor (usually rubidium) and then exchanged onward to noble-gas nuclei to generate a highly non-equilibrium or hyperpolarized (HP) spin state in the noble gas [1, 2]. Steady improvements to SEOP technology such as the development of high-power, ultra-narrowed and tunable laser diode arrays, improved cell designs, and optimized cryogenic-collection chambers have enabled large volumes of polarized gas to be generated quickly, thus allowing hyperpolarized (HP) ^{129}Xe to emerge as a powerful magnetic-resonance tool. Consequently, this has enabled studies spanning fundamental atomic physics; nuclear magnetic resonance (NMR) spectroscopy [3]; highly sensitive biosensors [4–7]; dark matter research [8]; and magnetic resonance imaging (MRI) in animals and human subjects [9–12]. Such studies often demand that multiple doses of large volumes of highly-polarized ^{129}Xe gas be generated in a short time period (for example, in the case of *in vivo* MRI, this ranges from several hundreds of milliliters in preclinical and pediatric studies to several liters for adult studies, all within a human MRI scanning session of < 60 minutes). As the translational applications of HP ^{129}Xe grow, there is an ever-increasing demand for higher polarization levels and more rapid HP ^{129}Xe production. While the fundamental atomic physics underlying SEOP has been elucidated in detail over the last few decades, there is a pressing need to revise and apply these basic insights to maximize HP ^{129}Xe generation efficiency under the demanding conditions required for practical applications.

Broadly, there are two types of HP ^{129}Xe SEOP devices. The conceptually simplest design is the stopped-flow polarizers, where the SEOP cell is filled with ^{129}Xe and buffer gases (typically N_2 and He). The cell is then illuminated with circularly polarized laser light resonant with the D_1 transition of Rb for extended periods (tens of minutes to hours). The

cell is then cooled, and HP ^{129}Xe is then dispensed, most typically as a single batch of ^{129}Xe per SEOP cycle in a buffer-gas blend. While ^{129}Xe polarization, P_{Xe} , values as high as 90% have been reported for stopped-flow SEOP devices [13, 14], this came at the cost of a reduced ^{129}Xe concentration ($P_{Xe} = 90\%$ was achieved in a 300:1700 $^{129}\text{Xe}:\text{N}_2$ blend [13]; $P_{Xe} = 74\%$ was achieved in a 1000:1000 $^{129}\text{Xe}:\text{N}_2$ blend [15], at ~85% and ~26% abundance respectively). Because the signal from HP ^{129}Xe is proportional to the product of polarization and concentration, the signal available from these dilute SEOP mixtures are often too low for practical applications such as high-resolution, *in vivo* MRI. Furthermore, the single batch-mode generation may be unattractive to research studies requiring multiple, large doses in rapid succession.

Alternatively, HP ^{129}Xe can be produced in continuous-flow polarizers, where ^{129}Xe constantly flows through the SEOP cell. Continuous-flow SEOP is usually performed using a lean ^{129}Xe gas mixture (typically comprising 1% to 3% ^{129}Xe balanced by buffer gases). HP ^{129}Xe is then used directly [16, 17], or more commonly separated from the buffer gases. While some buffer gases can be separated directly from gaseous HP ^{129}Xe —e.g., isobutene by condensation [18] or H_2 by combustion [19]—the most commonly used buffer gases (N_2 and He) are removed by freezing out within a cryogenic trap submerged in liquid nitrogen [20]. HP ^{129}Xe is then deposited as polycrystalline ‘snow’, and the polarization is preserved, because the T_1 relaxation times of solid ^{129}Xe (150 minutes in snow-phase ^{129}Xe at 77 K in 2.08 T [21]) are longer than typical HP ^{129}Xe accumulation times of < 60 minutes. Gas flow rates and accumulation times are adjusted to cryogenically collect the desired volume of HP ^{129}Xe , and the xenon snow is sublimated to dispense the concentrated HP ^{129}Xe gas. This technique also ensures the dispensed gas is at room temperature and rubidium-free, meaning that concentrated HP ^{129}Xe can be safely delivered to the sample of interest or inhaled for *in vivo* experiments.

Unfortunately, continuous-flow SEOP suffers from conflicting demands. Spin-exchange efficiency, and thus P_{Xe} , is maximized in the SEOP cell using ^{129}Xe -lean gas mixtures and slow gas-flow rates, whereas T_1 -induced polarization losses in the solid ^{129}Xe snow during cryogenic accumulation are minimized at the *high* flow rates that enable rapid accumulation. Particularly for clinical applications, there are additional considerations such as the ^{129}Xe volume or dose to be produced, how many doses must be delivered, and timing constraints resulting from MRI scanner availability. However, the relevant experimental parameter-space (e.g., ^{129}Xe accumulation volume, gas flow rates, and ^{129}Xe -buffer gas composition) has never been investigated rigorously. Here, first principles spin-exchange-physics are combined with the best available empirical SEOP parameters from the atomic physics literature, and detailed ^{129}Xe polarization data acquired during continuous-flow SEOP with cryogenic accumulation of over > 140 L of HP ^{129}Xe gas in a 10% N_2 , 89% He, 1% Xe blend. Dose volumes and accumulation times were varied from 200 mL to 1000 mL and 5 minutes to 60 minutes. Data from this broad parameter space were fit to an analytical model incorporating both SEOP and solid-state ^{129}Xe relaxation using only two free fitting parameters: Rb density in the SEOP cell, and the solid ^{129}Xe snow T_1 relaxation time. These resulting data were used to develop a semi-empirical model to predict ^{129}Xe polarization following continuous-flow production and cryogenic accumulation. The model was validated by comparing predicted polarization with empirical results obtained using a 2% Xe

blend. In doing so, we show that ^{129}Xe polarization in 1000 mL batches can be increased beyond 30%, with accumulation times reduced to as little as 15 minutes - almost doubling the current HP ^{129}Xe generation efficiency.

Theory:

Overview:

Continuous-flow ^{129}Xe SEOP involves three processes: (i) optical pumping of an alkali-metal vapor valence electrons (typically Rb); (ii) spin-exchange between the polarized Rb vapor and gaseous ^{129}Xe nuclei; and (iii) cryogenic collection of the HP ^{129}Xe from the ^{129}Xe -buffer gas blend.

In the presence of a magnetic field, Zeeman splitting generates two non-degenerate sublevels in the ground state of the Rb valence electron, $m_s = \pm 1/2$ levels [22]. Left-circularly polarized light resonant with the Rb- D_1 transition line (794.77nm) selectively excites Rb valence electrons from the $m_s = -1/2$ level in the ground state ($5^2S_{1/2}$) to the $m_s = +1/2$ level in the excited state ($5^2P_{1/2}$) [23, 24]. Collisional mixing with ^{129}Xe /buffer gases equalize the spin populations in the excited-state sublevels before relaxing into the $m_s = \pm 1/2$ levels of the ground state. Rb electrons that return to the $m_s = -1/2$ sublevel are re-excited by the continuous-wave laser, ultimately resulting in near-unity polarization in the $m_s = +1/2$ ground state.

For practical SEOP, the buffer-gas usually comprises a combination of N_2 and He. N_2 has higher energy rotational and vibrational states that help quench the excited Rb electron energy, reducing the chance of highly-depolarizing fluorescence [13, 25–27]. He is also typically added, because it displays a low Rb spin-destruction rate and widens the Lorentzian profile of the Rb D_1 line, thus improving optical absorption of laser light [28] (typically with powers of 10s to 100s of Watts).

In spin exchange, polarized Rb electrons act as intermediary agents to transfer spin-polarization via Fermi-Contact hyperfine interaction to the target ^{129}Xe nuclei [29]. Polarization transfer occurs through binary collisions between Rb and ^{129}Xe and relatively long-lived Xe-Rb van der Waals molecules generated via three-body collisions between Rb, ^{129}Xe and another gas atom or molecule. A variety of experimental parameters impact spin-exchange efficiency, including optical cell pressure, temperature, Rb density, ^{129}Xe density, buffer-gas composition and in-cell residence time. For continuous-flow SEOP, the in-cell residence time is controlled by the flow rate of the ^{129}Xe -buffer gas blend through the cell, which must be adjusted to achieve the desired production time and volume. Most documented continuous-flow polarizers generate volumes up to 3.5 liters using lean ^{129}Xe -buffer gas blends containing 1% to 3% ^{129}Xe and flows of 0.1 – 4.5 standard liters per minute (SLPM) through the SEOP cell. This parameter space ensures sufficiently long residence times to enable reasonably efficient Rb ^{129}Xe spin-exchange, with in-cell ^{129}Xe polarizations thought to be as high as 70% [30, 31].

Following hyperpolarization, the ^{129}Xe -buffer gas blend flows into the 77 K liquid N_2 (LN_2) cooled cryogenic chamber (*short*: cryotrap) for extraction and concentration. This process is

shown in Figure 1, where the long axis of the cell is aligned with the direction of the pumping laser (i.e., along the z -axis) and gas flows in the direction opposite that of the incident light before exiting the cell. Over time, the HP ^{129}Xe freezes and accumulates inside the cryotrap, while the remaining buffer gases continue to flow out of the polarizer. In this paper, ‘active-flow’ is defined as the flow mode when the hot, hyperpolarized ^{129}Xe -buffer gas mixture flows through the cryotrap to be collected (i.e., active accumulation of HP ^{129}Xe gas). In contrast, ‘static-hold’ is defined as a period in which no gas flows through the cryotrap, and ^{129}Xe snow is held in its frozen state under LN_2 .

Although ^3He SEOP was reported by Bouchiat *et al.* in 1960 [32], it was not until 1987 that Chupp *et al.* attempted to model SEOP [1] under relatively simple conditions, involving a static cell with low laser power, and low Rb density.. However, underconditions needed for modern, practical continuous-flow SEOP, additional factors come into play [20]. These include depolarization caused by aerosolized radiation trapping [33], skew light optical pumping [34], (hypothesized) Rb nanoclusters generated under high power illumination [35], and complex in-cell fluid dynamics (such as convection rotations and turbulent flow) [36, 37]. However, many of these complexities are difficult to incorporate into analytically useful models that allow for the overall process to be meaningfully optimized. To provide practical insights, Norquay *et al.* [38, 39] outlined a simplified, semi-empirical model to explain the behavior of their continuous-flow polarizer, in which mass transport is described according to plug flow (i.e. constant fluid velocity in the z dimension across the cell), the rubidium density in the SEOP cell was estimated using empirical equilibrium vapor pressure equations of Killian [40], and the optical-pumping spectral profile is calculated for discrete spatial elements along z .

In this work, we extend the model of Norquay *et al.* with slight modifications to van der Waals and binary collision-induced spin-destruction calculations. Furthermore, instead of using Killian’s formula to estimate the Rb vapor density inside the cell [40] (provided in Table 1), $[\text{Rb}]$ is set as a free-fitting parameter. Simplifying assumptions in the model include (ordered from most to least significant): P_{Xe} loss during the solid-to-gas phase change is negligible; cell temperature, magnetic field, Rb density and wall relaxation can be characterized as single steady-state values across the SEOP cell; ^{129}Xe snow T_1 relaxation can be treated as a single mono-exponential decay; gases can be treated as ideal, except for the Van der Waals molecule formation and breakup during the SEOP; any hypothesized contributions due to Rb nanoclusters are neglected; P_{Xe} loss caused by condensed Rb in the cell outlet is negligible; P_{Xe} losses occurring during transport of the dispensed Xe gas to the polarimetry station are negligible; and sufficient N_2 has been added to ensure that radiation trapping is negligible.

Rubidium Optical Pumping:

In a well-designed optical cell illuminated with uniform, circularly polarized laser light, the Rb polarization P_{Rb} as a function of position along the length of the cell, z can be expressed as

$$P_{Rb}(z) = \left(\frac{\gamma_{opt}(z)}{\gamma_{opt}(z) + \Gamma_{SD}} \right), \quad (1)$$

where $\gamma_{opt}(z)$ is the position-dependent optical pumping rate, and Γ_{SD} is the Rb electron spin-destruction rate [1]. (Note, variable symbols and names, as well as values and literature citations if applicable are provided in Table 1.) The value of $\gamma_{opt}(z)$ can be quantified by first evaluating the optical pumping rate at the front of the cell, $\gamma_{opt}(0)$ [41], which depends on laser power, P_l ; relative atomic linewidth, r ; relative detuning, s ; Rb density, $[Rb]$; and known physical parameters. This is given by

$$\gamma_{opt}(0) = \frac{2\sqrt{\pi \ln(2)} r_e f_{D1} \lambda_l^3 w'(r, s) p_l n_p}{hc \Delta \lambda_l n_p} = \alpha \frac{P_l n_p}{A}. \quad (2)$$

Here, r_e is the classical electron radius, f_{D1} is the oscillator strength at the Rb D_1 transition, is c the speed of light, and λ_l is the laser beam linewidth. The real part of the complex error function, $w'(r, s)$ [42], is defined by $w = w' + jw'' = e^{\left[\ln 2(r + js)^2 \right]} \text{erfc}[\sqrt{\ln 2}(r + js)]$, with $r = v_d / v_b$ and $s = 2(v_l - v_a) / v_b$. Further, $\Delta v_l = c \Delta \lambda_l / \lambda_l^2$; v_a is the center frequency, and v_b is the linewidth of Rb- D_1 absorption line. To avoid ambiguity later with the index i, j here represents the imaginary number.

The solution to the nonlinear differential equation describing $\gamma_{opt}(z)$ [41] takes the form of a Lambert-W function [42] (i.e. satisfies $W(f(x)) = x$ for $f(x) = xe^x$), and is given by

$$\gamma_{opt}(z) = \Gamma_{SD} W \left(\frac{\gamma_{opt}(0)}{\Gamma_{SD}} \exp \left(\frac{\gamma_{opt}(0)}{\Gamma_{SD}} - [Rb] \sigma(v) z \right) \right), \quad (3)$$

where $\sigma(v)$ is the photon absorption cross-section at frequency, v .

The Rb spin-destruction rate, $\Gamma_{SD} = \Gamma_{SD}^{vdW} + \Gamma_{SD}^{BC}$ is determined by: 1) the relaxation rates due to formation and breakup of short-lived Rb-Xe van der Waals molecules, Γ_{SD}^{vdW} ; and 2) binary collisions of Rb with components of the buffer gas mixture (i.e. He and N_2), Γ_{SD}^{BC} . Γ_{SD}^{BC} depends on the density of the i buffer gas components, $[G_i]$, and the binary collision spin-destruction cross section of Rb, κ_{SD}^{Rb-i} , according to

$$\Gamma_{SD}^{BC} = \sum_i [G_i] \kappa_{SD}^{Rb-i}. \quad (4)$$

It is not possible to accurately account for spin-destruction in Rb-Xe van der Waals molecules, Γ_{SD}^{vdW} , via simple cross section calculation because of turbulent flow conditions [43]. However, Nelson and Walker previously measured Γ_{SD}^{vdW} in a similar cell with a [1:1:98 Xe: N_2 :He] 150 °C blend, yielding $\Gamma_{SD}^{vdW} = 2049 \text{ s}^{-1}$ [44]. A $T^{-2.5}$ dependence was also observed, where T is the operating temperature. By using a technique similar to

methods by Schaefer, Cates and Happer [45], a $^1(1 + b_1r_1 + b_2r_2)$ correction factor (see Table 1) can be used to normalize Nelson and Walker's value to our own system parameters, ultimately giving:

$$\Gamma_{SD}^{vdW} = \left(\frac{65705}{1 + 0.92 \frac{[N_2]}{[Xe]} + 0.31 \frac{[He]}{[Xe]}} \right) \left(\frac{T}{423} \right)^{-2.5}. \quad (5)$$

To minimize the number of free-fitting parameters, we will assume the SEOP can be described with a volume-averaged Rb polarization across the cell [20]. This average is obtained by integrating $P_{Rb}(z)$ along the z dimension according to

$$\langle P_{Rb} \rangle = \frac{1}{Z} \int_0^Z \frac{\gamma_{opt}(z)}{\gamma_{opt}(z) + \Gamma_{SD}} dz, \quad (6)$$

where, Z , is the total length of the spin exchange cell.

Rb- ^{129}Xe Spin Exchange:

Overall spin-exchange to ^{129}Xe is determined by the spin-exchange rate, γ_{SE} , ^{129}Xe spin relaxation rate, Γ , and the Rb density, $[Rb]$, according to:

$$\gamma_{SE} = \left(\sum_i \frac{1}{\left(\frac{[G_i]}{\xi_i} \right)} + \kappa_{SE}^{Rb-Xe} \right) [Rb], \quad (7)$$

where κ_{SE}^{Rb-Xe} is the binary spin-exchange cross section between Rb and Xe, and ξ_i is the i -specific constant that describes the rate of spin-exchange within Rb-Xe van der Waals complexes [43]. The relaxation processes that contribute to Γ include binary collisions, Γ^{BC} , the formation and breakup of gas-phase xenon-xenon van der Waals molecules, Γ^{vdW} , and wall collisions, Γ^w , with Γ given by

$$\Gamma = \Gamma^{BC} + \Gamma^{vdW} + \Gamma^w, \quad (8)$$

Under a magnetic field of 3 mT, the reported T_1 relaxation times due to binary collisions is expected to be ~56 hours [46], and the relaxation time due to van der Waals molecules is ~4.1 hours [47]. Then, by relating the surface relaxivity, k_r , and the surface to volume ratio, S_{cell}/V_{cell} , T_1^w can be $1/(\kappa_r S_{cell}/V_{cell})$, giving $T_1^w \sim 30$ minutes for untreated walls. The relatively short T_1 estimated by (k_r indicates that ^{129}Xe wall collisions dominate the relaxation processes [48], enabling the approximation $\Gamma \approx \Gamma^w$.

The likelihood of spin-exchange is determined by the degree to which the mean in-cell ^{129}Xe residence time, t_{res} , is greater than the spin-up time constant, τ_{SU} , defined as $\tau_{SU} = 1/(\lambda_{SE} + \Gamma)$. In-cell residence time can be calculated using $t_{res} = V_{cell}[G]/F$, where V_{cell} is the cell volume, $[G]$ is the total gas number density (amagats) and F is the total gas flow rate. P_{Xe}

can be maximized if the system performs SEOP with $t_{res} \gg \tau_{SU}$ [35], as it allows ample time for spin-exchange to occur within the gases before they exit the cell. Thus, the polarization of hot ^{129}Xe gas exiting the SEOP cell, $P_{Xe}(0)$, is given by

$$P_{Xe}(0) = \left\langle P_{Rb} \right\rangle \left(\frac{\gamma_{SE}}{\gamma_{SE} + \Gamma} \right) \left(1 - e^{-\frac{[G]V_{cell}(\gamma_{SE} + \Gamma)}{F}} \right). \quad (9)$$

Cryogenic Accumulation:

Additional polarization losses occur after the ‘hot’ gaseous HP ^{129}Xe -buffer gas blend flows out of the SEOP cell. Specifically, ^{129}Xe snow deposited in the cryotrap experiences T_1 relaxation, denoted T_1^{snow} , during accumulation time, t_a , allowing the final polarization after thaw to be written as

$$P_{Xe}(t_a) = P_{Xe}(0) (T_1^{snow}/t_a) \left(1 - e^{-t_a/T_1^{snow}} \right), \quad (10)$$

and t_a can be written as

$$t_a = \frac{V}{F_{Xe}} = \frac{V}{fF}, \quad (11)$$

where V is the accumulated volume in liters of HP ^{129}Xe at STP, F_{Xe} is the ^{129}Xe specific flow rate, and f is the fraction of ^{129}Xe in the gas blend. Substituting Equations 6, 9, and 11 into Equation 10 yields a final expression for the overall $P_{Xe}(t_a)$:

$$P_{Xe}(t_a) = \left\langle P_{Rb} \right\rangle \left(\frac{\gamma_{SE}}{\gamma_{SE} + \Gamma} \right) \left(1 - e^{-\frac{[G]V_{cell}(\gamma_{SE} + \Gamma)}{F}} \right) (T_1^{snow}/t_a) \left(1 - e^{-t_a/T_1^{snow}} \right). \quad (12)$$

Methods and Equipment:

Polarizer Details

Experiments were performed using the continuous-flow polarizer depicted in Figure 1 (Polarean 9820-A, Durham, NC), and a ^{129}Xe -buffer gas blend (Linde Gas, Stewartville, NJ) consisting 2 different isotopically-enriched (>85%) ^{129}Xe concentrations: $f = 1\%$ and 2% , mixed with $10\% \text{ N}_2$ and balanced by He. An external dual-stage regulator was used to ensure a constant 30 psig total pressure inside the cell. The system utilizes an internal mass flow meter and a pressure transducer, each with $\pm 5\%$ accuracy, to control the flow rate during warm up and active accumulation. An internal and external (SAES Pure Gas, Micro-Torr FT400–902F) 3L $\text{Xe}/\text{N}_2/\text{He}$ purifier was used to prevent chemical contamination of the Rb (e.g. by O_2 , H_2O and hydrocarbons) with the SEOP cell.

An air dryer and internal heater, controlled by a proportional integral differential (PID), were used to warm up the oven containing the SEOP cell to 120°C . Two thermocouples were attached to outside of the cell, one at the front and one at the middle (Figure 1 (a)). By ensuring the temperature was equal at both points, a steady-state temperature of 120°C

could be assumed along the cell. Newton, *et al.* [49] showed that in geometrically similar cells under static-hold (zero flow), the temperature of the internal contents approximately matched the oven temperature outside the cell. Thus it is assumed that thermal transfer through cell walls does not produce a variable temperature profile. The SEOP cell also includes a Rb vapor saturating region in line before the illuminated cell body that contains 2 g of Rb. By wrapping the saturation region in 400 W electrical heating tape, the internal volume was heated to 180 °C to generate and introduce Rb vapor into the xenon flow stream. This pre-saturation region functions to maintain a consistent uniform Rb density profile over time [36]. While this process heats the gas to > 120 °C before entrance to the cell, PID controllers for the internal heater ensure the average cell temperature remains set at 120 °C.

To generate Zeeman splitting, four electromagnetic field coils in series are run by the same power supply at a fixed current of 3 Amps, to provide a homogenous 2 mT magnetic field, B_0 , over the entire cell. A 170 Watt line-narrowed, circularly polarized laser (QPC, Sylmar, CA) with left helicity and centered on 794.80 nm with a full-width half-maximum (FWHM) of 0.15 nm, was used to optically pump the Rb inside the cell. The transmittance and voltage readings through the back of the cell were monitored remotely alongside an OceanOptics (Largo, FL) spectrometer reading to ensure a relatively constant Rb polarization. The cylindrical cell (Figure 1(a), 80 mm × 330 mm ID) was made of non-ferrous borosilicate glass (worked-Pyrex – Pyrex, Corning, PA), and is thermally resistant to a running temperature of 200 °C and a pressure of 4 atm. To collect HP ^{129}Xe , a squared-helical borosilicate glass cryotrap (Figure 1(c)) located immediately after the cell was submerged in 77 K LN_2 , within a 0.3 T field.

Delivering HP ^{129}Xe and Measuring Polarization

Following cryogenic collection, the frozen ^{129}Xe was rapidly sublimated into a Tedlar bag (Jensen Inert, Coral Springs, FL) by submerging the cryotrap in room-temperature distilled water. The individual Tedlar bag volumes were 300 mL, 600 mL and 1000 mL, with the bag selected based on the required dosage (200 mL to 1000 mL). The filled Tedlar bags were immediately transferred to a polarimetry NMR station (Model 42881, Polarean, Durham, NC), where a calibrated radio frequency pulse is applied to the HP ^{129}Xe sample and the amplitude of the resulting free induction decay is used to estimate P_{Xe} for each bag. To ensure accuracy, the bag was centered directly over the coil, and P_{Xe} was measured three times, with the highest value retained for subsequent analysis. The resulting experimental error was within ± 1 absolute percent points.

Generating a Computational Model

Polarization, flow and volume data were collected during the accumulation of HP ^{129}Xe gas used for 110 human imaging studies, corresponding to > 15,000 L of $f = 1\%$ isotopically-enriched (85% abundance) ^{129}Xe . Using the MATLAB Curve Fitting Toolbox (Mathworks, Natick, MA), the data were fit to Equation 12 following use of the literature values in Table 1. Time and equipment limitations inhibited *in situ* measurements of the longitudinal relaxation rate of the polycrystalline ‘snow’ ^{129}Xe , T_1^{snow} , and the Rb vapor density, $[\text{Rb}]$, during active accumulation, so each were set as free-fitting parameters. Upon successful

fitting of Equation 12, $P_{Xe}(t_a)$, the ^{129}Xe polarization for a given accumulation time, was modeled in MATLAB under various conditions, including input concentrations of ^{129}Xe ($f=0.5\%$ to $f=4\%$); flow (1.0 to 4.0 SLPM); volume (500 mL and 1000 mL); T_1^{snow} relaxation time (our empirically fitted value against longer literature value); and laser power (0 – 600 Watts).

To validate the model, 18x $f=1\%$ and 25x $f=2\%$ Xe blends for 1000 mL accumulations were run through the polarizer, and $P_{Xe}(t_a)$ was recorded. A volume of 1000 mL accumulation was chosen for testing, because it is the most commonly used adult inhalation dose [50, 51] as set out by our clinical protocol.

Results:

Figure 2 shows P_{Xe} following $f=1\%$ blend ^{129}Xe accumulations as a function of dispensed ^{129}Xe volume and gas flow during accumulation, fit to Equation 12 ($R^2 = 0.725$, 163 experimental data points). The free-fitting parameters, $[Rb]$ and T_1^{snow} , were found to be $1.6 \pm 0.1 \times 10^{13} \text{ cm}^{-3}$ and 84 ± 5 minutes, respectively. This $[Rb]$ value is approximately half the value estimated by the Killian formula (see Table 1), at $\sim 3.0 \times 10^{13} \text{ cm}^{-3}$ [40]. Generally, the highest polarizations ($P_{Xe} \sim 50\%$) were achieved for small accumulation volumes ($< 400 \text{ mL}$) at low flow rates (< 2 standard liters of total gas per minute, SLPM). Larger accumulation volumes and flows (e.g. 1000 mL and 3.6 SLPM, respectively) yielded P_{Xe} of $\sim 30\%$.

Importantly, the Equations 4, 5, 7 and 11 within Equation 12 indicate that, for a given accumulation volume and time, there is an optimal ^{129}Xe concentration in the input gas blend that maximizes $P_{Xe}(t_a)$. Figure 3 shows the results from a simulation based on Equation 12 and the extracted free-fitting parameters from Figure 2, $[Rb]$ and T_1^{snow} . Specifically, the simulation parameter space explored included HP ^{129}Xe accumulation volumes ranging from 500 to 1000 mL, accumulation times ranging from 5 to 60 minutes, and ^{129}Xe -buffer gas blends ranging from $f=0.5\%$ to 4.0% . Dotted lines in Figure 3 delineate the range of peak polarizations, showing that for the given accumulation conditions, the optimal input ^{129}Xe fraction lies between $f=2.0\%$ and $f=2.4\%$.

To assess the model's predictive accuracy, 1000 mL batches of HP ^{129}Xe were polarized using $f=1\%$ and $f=2\%$ ^{129}Xe blends, and P_{Xe} was recorded as a function of t_a in the range from 14 to 60 minutes. These empirical data are overlaid with the model-based predictions for P_{Xe} in Figure 4(a), which demonstrated good qualitative agreement between measurement and prediction. Of most significance, empirical data confirm that, relative to the 1% ^{129}Xe blend, the $f=2\%$ blend yields substantially improved polarization—up to 15 absolute percent—for each given t_a . As such, these results clearly demonstrate that higher polarizations can be achieved for a given volume of HP ^{129}Xe by exploiting the reduced accumulation times made possible by the richer gas mixture.

Agreement between modeled and experimental polarization was examined via a Bland-Altman plot in Figure 4(b & c) for both $f=1\%$ and 2% blends, respectively. For both gas compositions, the difference between the modeled and experimental values was near zero

(absolute percent differences of +0.67% for $f=1\%$ and -0.43% for $f=2\%$), and all but two data points (one for each blend) were within their respective 95% confidence intervals. However, the width of the 95% confidence interval for the $f=2\%$ blend was more than 2-fold larger than the $f=1\%$ blend, likely reflecting greater instabilities in the fluid dynamics and overall polarization process at the lower flow rates used for the richer ^{129}Xe blend.

The improved accumulation rates and absolute polarization achieved with the richer ^{129}Xe blend highlight the importance of solid-state T_1 relaxation in the ^{129}Xe snow as demonstrated in Figure 5, where 1000 mL accumulations were simulated for ^{129}Xe blends of $f=1\%$, 2% and 3% as a function of accumulation time. Here, two T_1^{snow} times are considered: 150 minutes, reported by M. E. Limes *et al.* [21] for ^{129}Xe in 77 K polycrystalline snow, and the shorter 84 minutes in ^{129}Xe snow extracted from the experimental data in this work. Unsurprisingly, deviations in the behavior predicted for the two relaxation times are minimal for all three gas blends at low accumulation times (20 minutes or less). However, at accumulation times beyond 40 minutes, the effects of relaxation become more pronounced, with the model predicting polarization differences of >5 absolute percent points between the two T_1^{snow} times. For a 1000 mL accumulation with $T_1^{\text{snow}} = 84$ minutes, the $f=2\%$ blend is preferable to the 1% blend for all accumulation times in the simulation, despite the superior SEOP efficiency of the leaner ^{129}Xe mixture. Indeed, even the 3% blend is expected to yield superior polarization, relative to the leaner 1% blend at accumulation times less than 60 minutes.

Advances in laser technology in recent decades have enabled polarizers to generate ever-higher P_{Xe} , so the impact of increased laser power, P_l , were also considered via model-based simulation. In Figure 6, P_{Xe} following (a) 500 mL and (b) 1000 mL accumulations were simulated for gas blends varying from $f=1\%$ to 5% , at P_l ranging from 0 to 600 W. Across all blends and volumes, there is a monotonically increasing dependence of P_{Xe} and P_l that is nearly linear for sufficiently low laser powers. At higher P_l levels, P_{Xe} asymptotically approaches a polarization maximum, but the magnitude of this maximum depends on the ^{129}Xe content of gas blend. Leaner ^{129}Xe blends display lower maximal polarization at lower laser powers, indicating minimal polarization gains will be achieved using higher power lasers. That is, for a fixed accumulation volume and SEOP cell size, high flows are required for low xenon fraction blends. As a result, higher Rb polarizations generated from the increased laser power cannot overcome the reduced in-cell residence times produced by the high flow. Despite the competing demands, the simulation predicts polarization maxima in excess of 60% can be achieved for 1000 mL accumulations and in excess of 70% for 500 mL accumulations. Together, these results indicate that significantly improved gas polarization and production rates are achievable by combining richer ^{129}Xe blends with improved laser technology.

Discussion:

While obtaining the highest possible ^{129}Xe polarization is always desirable, the demands of real-world applications (e.g., those needed for spectroscopy and imaging of human lungs) often require that maximal P_{Xe} be forfeited to decrease accumulation time or generate larger

volumes of HP ^{129}Xe . However, quantitatively predicting the conditions needed to achieve the optimal tradeoff between the often-conflicting demands of continuous flow SEOP is challenging, because of the extensive operational-parameter space (flow, cell pressure, cell volume, [Rb], gas composition, accumulation time, etc.). Thus, the goal of this work was to develop a semi-empirical model of combined continuous-flow ^{129}Xe SEOP and cryogenic accumulation, specifically to predict P_{Xe} across the parameter-space applicable to practical HP ^{129}Xe production using well-validated atomic physics, published physical parameters, and two system-specific empirical parameters: [Rb] and T_1^{snow} .

To adequately predict polarization with only two system-specific parameters, several assumptions and simplifications were required. For instance, instead of mass-transport following a winding path between the front and back of the cell (well described by Fink, *et al.* [36]), the model assumed plug flow, greatly simplifying the gas density and spin-exchange calculations. In addition, cell temperature, pressure and [Rb], were assumed to be single, steady-state values throughout the cell, rather than being time and position dependent variables. As [Rb] is a parameter in the expressions for $\gamma_{op}(z)$, Γ_{SD} and γ_{SE} (Equations 1–7), the assumption of steady state [Rb] had implications for both $P_{Rb}(z)$ and the spin-exchange efficiency. Despite these simplifications, the analytical model combined with only two extracted fitting-parameters provides sufficient accuracy to plan accumulation timings that meet practical experimental demands, and to assess the potential utility of future polarizer modifications (e.g., SEOP cell length or changes to Rb presaturation).

One major motivation for cryogenic accumulation stemmed from Driehuys, *et al.* [20], where the T_1 relaxation time in crystalline ‘ice’ ^{129}Xe was thought to be very long (180 minutes) at liquid N_2 temp (77 K) [52, 53]. However, M. E. Limes *et al.* [21] showed that the T_1 relaxation time in polycrystalline ‘snow’ at 2.0 T is 30 minutes shorter than in crystalline ice, suggesting that losses during cryogenic accumulation may be non-trivial. Norquay, *et al.* further showed that for a lower field of 0.3 T, and in helical cryogenic glassware to approximate active accumulation, the T_1^{snow} was shorted to 87 minutes [38]. In addition, constant bombardment with hot, 120 °C gas during active ^{129}Xe accumulation make direct *in situ* measurements of T_1^{snow} impractical. However, by fitting a parameter space comprising > 140 L of flow, volume and polarization data, we measured a T_1^{snow} very near that of Norquay, *et al.* at the same field strength [38]. This result suggests two things: 1) increasing T_1^{snow} , for example by accumulating at higher field strength or adjusting the surface properties of the cryotrap, would boost polarization; and 2) the optimal conditions for polarization production are not those that favor the most efficient SEOP.

The most striking improvements to P_{Xe} were found by examining the ^{129}Xe fraction in the input gas blend, (f). Because the T_1^{snow} relaxation is more deleterious to the final P_{Xe} than generally expected, the leanest ^{129}Xe blend ($f=1\%$), the gas composition historically used for human MRI, is suboptimal. Instead, shorter accumulation times made possible with a richer $f=2\%$ ^{129}Xe blend significantly reduce the amount of P_{Xe} loss in the ^{129}Xe snow, thereby outweighing the polarization inefficiency driven by increases in Rb binary collision and van der Waals-induced spin-destruction. As described by Equations 4 and 5, these spin-

destruction effects again become more deleterious than T_1^{snow} relaxation when f is increased further. Thus, as shown in Figure 3, the optimal range of f lies between 2% and 2.4% for this polarizer design, while blends outside this range suffer increasingly larger losses to P_{Xe} . This was supported experimentally in Figure 4(a), where P_{Xe} gains of nearly 15% (absolute percent points) were achieved by increasing f from the historical 1%, to 2%, for a given time and accumulation volume. In the case of a 1000 mL accumulation, $P_{Xe} = 30\%$ was generated within 30 minutes with a 1% blend, while this same polarization was generated in only 15 minutes using a 2% blend. In Figure 4(b & c), a greater spread was observed between the experimental and modeled data in the $f = 2\%$ blend than with the $f = 1\%$ blend, perhaps due to plug flow approximations being less accurate at lower flow rates used with richer f . However, these effects are ultimately mitigated by the time savings achieved by running the richer ^{129}Xe mixture.

Furthermore, it is still more effective to switch to a $f = 2\%$ blend than to lengthen the T_1^{snow} relaxation time via cryotrap redesign. This is evident in Figure 5, where it is shown that the result of switching to a 2% blend side-steps the effects of T_1^{snow} relaxation, regardless of whether the previously-reported relaxation times have been achieved. Although lengthening the T_1^{snow} relaxation time would be useful, it does not have as profound an effect as adjusting f in accumulation times under 70 minutes. Finally, while the quantitative details will vary depending on continuous-flow polarizer design, the overall predicted trends are likely to be universal for large-scale HP ^{129}Xe production.

One major difference between this model, and previously published models (e.g., by Norquay, *et al.* [38, 39], and by Freeman, *et al.* before the addition of Rb nanoclusters [30, 31]), is that the predicted polarization in each of these works exceeded the observed P_{Xe} values by up to ~20% absolute percent. However, in those studies, [Rb] was estimated from historic vapor-pressure curves (Norquay, *et al.* used a formula generated by Killian [38–40], while Freeman, *et al.* used a similar rescaling [31, 54]). Because these formula assume equilibrium Rb vapor pressure, and the dynamically flowing SEOP is an intrinsically non-equilibrium system, we reasoned that [Rb] is overestimated when based upon such curves. This reasoning motivated our decision to extract [Rb] as a fitting parameter across a broad range of practical accumulation conditions. To test the validity of this reasoning, we re-examined previously published SEOP models, but incorporated a [Rb] value that was half that predicted by the Killian formula (i.e., matching the [Rb] difference observed in this work). For Norquay, *et al.* [39], where a $f = 3\%$ blend was used in an 80 cm depth SEOP cell, the predicted P_{Xe} was narrowed to $\pm 4\%$ absolute percent of their experimental results. Similarly, by rescaling [Rb] by 50% in the model by Freeman, *et al.* [30, 31], where a $f = 1\%$ blend was used in a 300 ccm SEOP cell, the predicted P_{Xe} dropped to within $\pm 7\%$ absolute percent of their experimental results. While additional mechanisms such as temperature-dependent spin-destruction [38] or hypothesized Rb nanocluster formation [31, 35] are well documented to reduce SEOP efficiency, many of these effects can be mitigated through improved engineering, such as using a pre-saturated Rb chamber to decouple Rb saturation from laser illumination. Thus, these results suggest overestimating [Rb] will have a much greater impact on polarization prediction in current and future polarization designs.

It is also worth noting that richer ^{129}Xe blends could also cause a discrepancy between localized temperature, and thus $[\text{Rb}]$, across the length of the cell. This was observed by monitoring the exterior cell temperature at the front and middle of the cell and the laser transmittance from the back of the cell. For $f = 1\%$ blends, the temperatures at both locations were equal to within 1°C . For $f = 2\%$ blends, the temperatures were equal during active-flow, but the frontal temperature increased by up to 10°C while under extended static-hold periods. Furthermore, the transmittance almost halved when switching to the $f = 2\%$ blend. One possible explanation is that the richer ^{129}Xe blend increases the rate of Rb spin destruction (evident by Equations 4 and 5). As a result, more of the incident infrared light is absorbed and ultimately transformed to thermal energy—a process that would preferentially occur at the front of the cell upon entry of the laser. Such observations are consistent with those of Witte *et al.*, where switching from 2% to 5% ^{129}Xe -blends at static-hold led to Rb runaway (and Rb spin-destruction) following the large rise in localized temperature (and thus heat dissipation) at the front of the cell [5]. An interesting future experiment would be to monitor whether mechanisms such as Rb pre-saturation or increased oven air flow help reduce these effects during accumulations with richer f blends.

Ignoring these minor thermal variations, it was possible to examine P_{Xe} simulations for higher laser powers against various ^{129}Xe blends - a useful design consideration as laser power, P_l in clinical-scale SEOP polarizers currently ranges from 29 W [55] to 1.5 kW (XeBox-E10, XeMed LLC, Durham, NH). While higher P_l is expected to generate higher P_{Xe} , Figure 6 demonstrates that for each gas blend there is a point at which increasing P_l delivers no significant enhancement in polarization. For example, increasing P_l beyond 100 W in a $f = 1\%$ blend yields minimal improvement to P_{Xe} , and increasing P_l beyond 300 W in a $f = 5\%$ blend again yields minimal polarization gains. This P_{Xe} plateau occurs, because for a given, there is a laser power at which the Rb polarization, fP_{Rb} , approaches unity along the entire cell length, with greater laser power being required to reach the asymptotic approach to polarization maximum for richer, more depolarizing ^{129}Xe blends. Such qualitative trends are independent of ^{129}Xe accumulation time or volume, as demonstrated in Figure 6, because P_{Rb} is independent of t_d and V ; rather it is only affected by changes to P_l and cell constituents/dimensions.

It is worth noting that under substantially different input conditions such as longer cell lengths, larger cell windows, higher or non-steady state cell temperatures, very rich f , or extremely-high P_l (which could assist formation of large, unstable, and highly depolarizing Rb nanoclusters [5, 30, 56]), the model's ability to accurately predict P_{Xe} will be reduced. However, the results highlight that for geometrically similar continuous-flow polarizers, extremely high-power lasers are not required to achieve maximal performance for a given gas composition. In fact, substantial gains in both production rate and P_{Xe} can be achieved without any complicated or expensive engineering upgrades, simply by adjusting the SEOP gas composition to match practical experimental demands. Finally, though beyond the scope of this investigation, there are additional areas continuous-flow parameter optimization that also warrant investigation and could readily build up the results reported here, including cell/pre-saturator temperature for varying ^{129}Xe blends, cell dimensions and gas pressures. Moreover, the model could be expanded to allow xenon blend-specific $[\text{Rb}]$, which would likely lead to improved predictive accuracy.

Conclusion:

It is possible to systematically explore the ^{129}Xe SEOP parameter space (e.g., ^{129}Xe -buffer gas blend, gas flow, and laser power) under routine operating conditions. These experimental results (e.g. fitted T_1^{snow}) can be incorporated into a semi-empirical model of ^{129}Xe hyperpolarization to optimize both accumulation time and polarization efficiency of continuous-flow polarizers. Of note, the most substantial improvements in this work were achieved through trivial changes such as employing a richer ^{129}Xe -buffer gas composition. However, further gains are expected if T_1^{snow} can be increased—possibly by improving the shape or surface chemistry of the cryotrap or performing cryogenic accumulation at higher magnetic field strengths. Further, the model suggests that if these improvements are implemented along with modest increases laser power, liter-volumes of HP ^{129}Xe with polarizations exceeding 60% can be routinely generated in only tens of minutes.

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- Optimal parameters for continuous-flow ^{129}Xe SEOP are generally unexplored
- Solid ^{129}Xe T_1 relaxation, Rb density, input gas blend and laser power are examined
- A semi-empirical model is developed to accurately predict ^{129}Xe hyperpolarization
- Experiments reveal optimal ^{129}Xe hyperpolarization is achieved with richer gas blends
- Modest device improvements enable rapid production of ^{129}Xe polarized to >60%

Figure 1:

(a) Polarean 9820-A SEOP cell featuring a gas flow path through a pre-saturated Rb chamber. Two thermocouples are attached externally to the cell to measure the local temperature. 795nm pumping beam aligns in +z direction. The laser polarizes Rb valence electrons inside the cell, while Rb-Xe spin exchange to occurs. The HP ^{129}Xe buffer-gas blend exits out the top of the cell into the cryotrap. (b) Polarean 9820-A Polarizer device. (c) Polarean borosilicate cryotrap.

Figure 2:

Fitted surface of Equation 12 expanded with literature values in Table 1 across clinically-relevant ^{129}Xe flow rates and accumulation volumes (at STP) for a $f = 1\%$ ^{129}Xe -buffer gas blend. Data points are individual $P_{\text{Xe}}(V, F)$ experimental measurements from 163 batches of ^{129}Xe accumulated for use in clinical-research studies. The data are well fit by the model ($R^2 = 0.725$). Free parameters extracted by fitting the data to Equation 12 were $[\text{Rb}] = 1.6 \pm 0.1 \times 10^{13} \text{ cm}^{-3}$ and $T_1^{\text{slow}} = 84 \pm 5$ minutes.

Figure 3:

P_{Xe} modeled for (a) 500 mL and (b) 1000 mL Xe volumes as a function of ^{129}Xe -buffer gas concentration, f , at varying accumulation times using the estimated fitting parameters: $[\text{Rb}] = 1.6 \times 10^{13} \text{ cm}^{-13}$ and $T_1^{\text{snow}} = 84$ minutes from the 1% ^{129}Xe -buffer gas data fitting in Figure 2. Vertical dotted lines indicate the range of ^{129}Xe blends that deliver optimal P_{Xe} . Longer accumulation times correspond to slower flow rates (and thus greater in-cell residence times) for a given HP ^{129}Xe volume.

Figure 4:

(a) Solid lines are predicted 1000 mL P_{Xe} curves for 1% and 2% input blends against accumulation time, using the estimated fitting parameters: $[Rb] = 1.6 \times 10^{13} \text{ cm}^{-13}$ and T_1^{snow} minutes from the 1% ^{129}Xe -buffer gas data in Figure 2. Overlaid are 18 (1%, red) and 25 (2%, blue) experimental P_{Xe} data points. (b) & (c) Bland-Altman plots show good agreement between experimental and modeled P_{Xe} data in 1% (b) and 2% (c) gas blends. Solid lines (central) show the mean difference between experimental and modeled P_{Xe} . Dashed lines show the upper and lower 95% confidence intervals of the P_{Xe} difference.

Figure 5:

P_{Xe} changes between models based on the empirical model determined T_1^{snow} time of 84 minutes (solid lines), compared to the longer T_1^{snow} time of 150 minutes (dashed lines), reported by M. E. Limes, et al.[13]. Across input blends: $f = 1\%$, 2% , and 3% , the effects of a longer T_1^{snow} time become notable for accumulation times greater than ~ 40 minutes.

Figure 6:

P_{Xe} vs laser power for (a) 500mL, and (b) 1000mL, 30 minute accumulations, for ^{129}Xe input blends ranging from 1% to 5%, with a T_1^{snow} time of 84 minutes, on the Polarean 9820 polarizer. The laser power at which different input blends hit maximal P_{Xe} (due to fully polarized Rb vapor) increases as input blend increases. This model is based on a line-narrowed, circularly polarized Rb-794.80 nm laser with linewidth, $\lambda_1 = 0.15$ nm.

Table 1:

Alphabetized Symbols and Physical Parameters

Symbol	Definition	Value/Formula	Ref. #
A	Laser beam cross sectional area	$5.7 \times 10^{-3} \text{ m}^2$	*
b_1	vdW-specific spin exchange coefficient ratio Xe:N ₂	ξ_{Xe}/ξ_{N_2}	[45]
b_2	vdW-specific spin exchange coefficient ratio Xe:He	ξ_{Xe}/ξ_{He}	[45]
Γ_{SD}	Total Rb spin destruction rate (s ⁻¹)	$\Gamma_{SD}^{BC} + \Gamma_{SD}^{vdW}$	–
Γ_{SD}^{BC}	Binary collision (BC) Rb spin destruction rate (s ⁻¹)	Eq (4)	–
Γ_{SD}^{vdW}	Van der Waals (vdW) Rb spin destruction rate (s ⁻¹)	Eq (5)	–
Γ	Total Xe spin relaxation rate inside cell (s ⁻¹)	Eq (8)	–
Γ_w	Wall-induced Xe spin relaxation rate (s ⁻¹)	$\kappa_r S_{cell} / V_{cell}$	–
$\gamma_{op}(z)$	Rb optical pumping rate at position z (s ⁻¹)	Eq (2)	[27]
γ_{SE}	Rb-Xe spin exchange rate (s ⁻¹)	Eq (7)	[27]
c	Speed of light	$3.00 \times 10^8 \text{ m s}^{-1}$	[57]
ξ_{Xe}	Xe vdW-specific spin exchange coefficient	$5.23 \times 10^3 \text{ Hz}$	[58]
ξ_{N_2}	N ₂ vdW-specific spin exchange coefficient	$5.7 \times 10^3 \text{ Hz}$	[59]
ξ_{He}	He vdW-specific spin exchange coefficient	$1.7 \times 10^4 \text{ Hz}$	[58]
f_{D_1}	Electron oscillator strength at D ₁ transition	0.337	[60]
f	Fraction of Xe in Xe:N ₂ :He blend	-	–
F	Total gas flow rate	-	–
$[G_i]$	Gas concentration for isotope i	-	–
H	Planck's constant	$6.63 \times 10^{-34} \text{ m}^2 \text{ kg s}^{-1}$	[57]
κ_{SD}^{Rb-Xe}	Binary collision spin destruction cross section Rb-Xe (cm ³ s ⁻¹)	$6.02 \times 10^{-15} (T/298)^{1.17}$	[44]
$\kappa_{SD}^{Rb-N_2}$	Binary collision spin destruction cross section Rb-N ₂ (cm ³ s ⁻¹)	$3.44 \times 10^{-18} (T/298)^3$	[61]
κ_{SD}^{Rb-He}	Binary collision spin destruction cross section Rb-He (cm ³ s ⁻¹)	$3.45 \times 10^{-19} (T/298)^{4.26}$	[27]
κ_{SD}^{Rb-Rb}	Binary collision spin destruction cross section Rb-N ₂ (cm ³ s ⁻¹)	4.2×10^{-13}	[27]
κ_{SE}^{BC}	Binary collision spin exchange cross section	$2.17 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$	[62]
κ_{SE}^{vdW}	Van der Waals spin exchange cross section (cm ³ s ⁻¹)	Eq (6)	[58]
κ_{SE}^{Rb-Xe}	Binary collision spin exchange cross section Rb-Xe (cm ³ s ⁻¹)	κ_{SE}^{BC}	[38]
κ_r	Worked Pyrex Surface Relaxivity	$1.14 \times 10^{-3} \text{ cm s}^{-1}$	[63]
λ_l	Laser wavelength	794.8 nm	*
λ_l	Laser beam linewidth	0.15 nm	*
ν_l	Laser frequency	$3.77 \times 10^{14} \text{ Hz}$	*

Symbol	Definition	Value/Formula	Ref. #
ν_a	Center frequency	3.77×10^{14} Hz	*
ν_a	Center frequency of D ₁ absorption line	3.80×10^{10} Hz	[28]
ν_l	Pump beam linewidth (frequency)	7.12×10^{10} Hz	*
n_p	Number of photons per Joule	$1/h\nu_l$	–
P_l	Laser power	170 Watts	*
P_{Rb}	Rb polarization	Eq (1)	–
P_{Xe}	Xe polarization	Eq (12)	–
r	Relative atomic linewidth	ν_d / ν_l	[27]
r_e	Electron radius	2.82×10^{-15} m	[57]
r_1	N ₂ :Xe ratio	$[N_2]/[Xe]$	–
r_2	He:Xe ratio	$[He]/[Xe]$	–
$[Rb]$	Rubidium vapor density	1.6×10^{13} cm ⁻³	Fitting
$[Rb], ^+$	Rubidium vapor density by Killian Formula (m ⁻³)	$10^{10.55 - 4132/T(1/10k_B\theta)}$	[40], ⁺
$\sigma(\nu)$	Total optical absorption cross section (cm ²)	α in Eq (2)	[41]
s	Relative detuning	$2(\nu_l - \nu_a) / \nu_l$	[27]
S_{cell}	SEOP cell surface area	9.95×10^{-2} m ²	**
t_a	Accumulation time	Eq (11)	–
t_{res}	Residence time in cell	$V_{cell} / G / F$	–
T	Cell temperature	120 K	**
T_1^{snow}	Longitudinal relaxation in snow-phase Xe	84 minutes	Fitting
V	Volume of Xe accumulated	–	–
V_{cell}	SEOP cell volume	1.87×10^{-3} m ³	**
$w'(r,s)$	Real part of complex overlap function, w	–	[42]
$W()$	Lambert-W function (“product logarithm”)	–	[42]
Z	Length of cell	0.33 m	**

* QPC, Sylmar, CA

** Polarean 49820, Polarean Imaging PLC, Durham, NC

– No reference available

⁺ Not used in this model